Monitoring Cement Hydration with Embedded NMR Probes

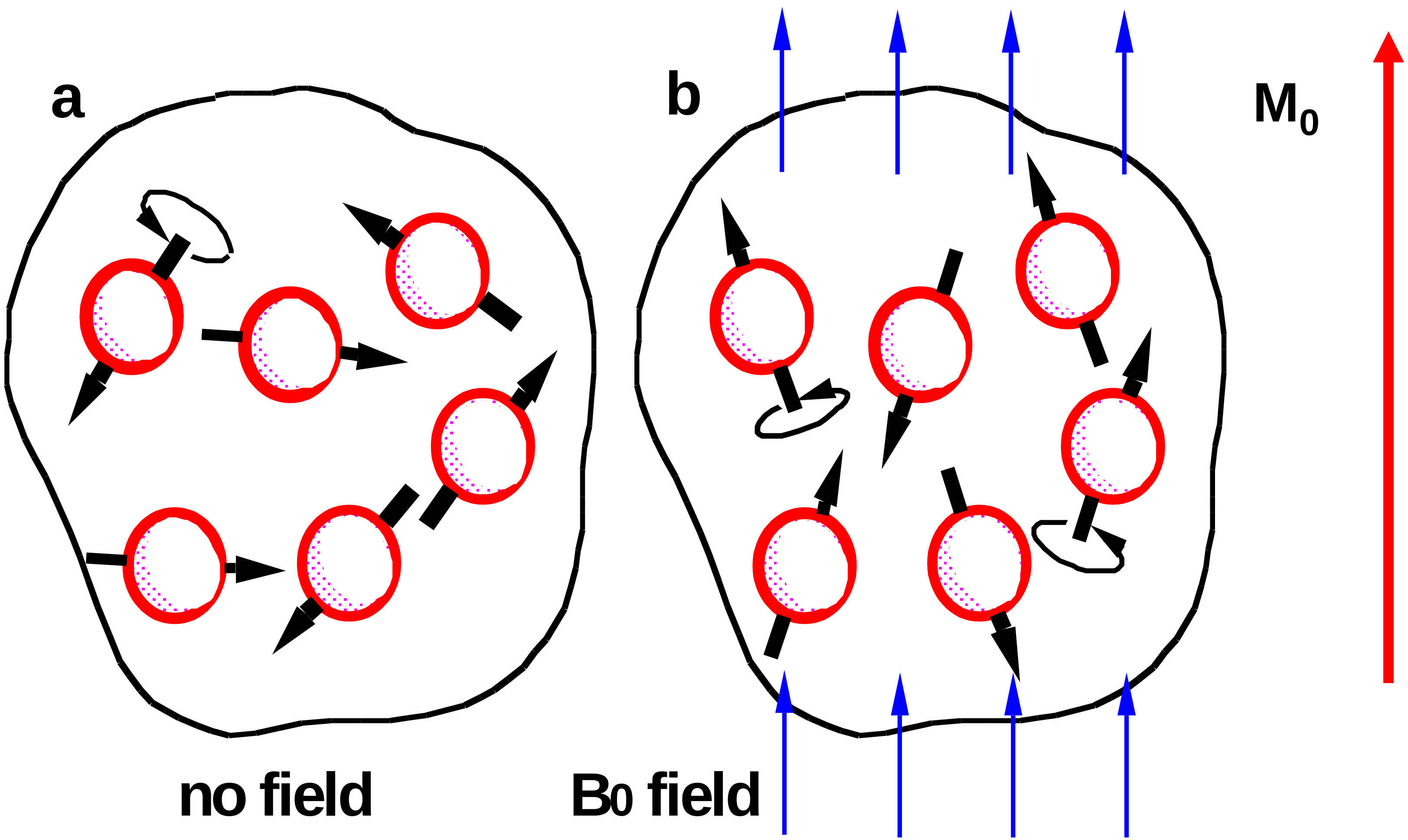
B. J. Balcom

UNB MRI Centre, Department of Physics, University of New Brunswick

Outline

- Magnetic Resonance
- Spin Spin relaxation, pore structure
- Portable Magnetic Resonance
- Embedded magnets, in situ measure
- Hydration measurements

Magnetic Moment of Nuclei in a Static Magnetic Field

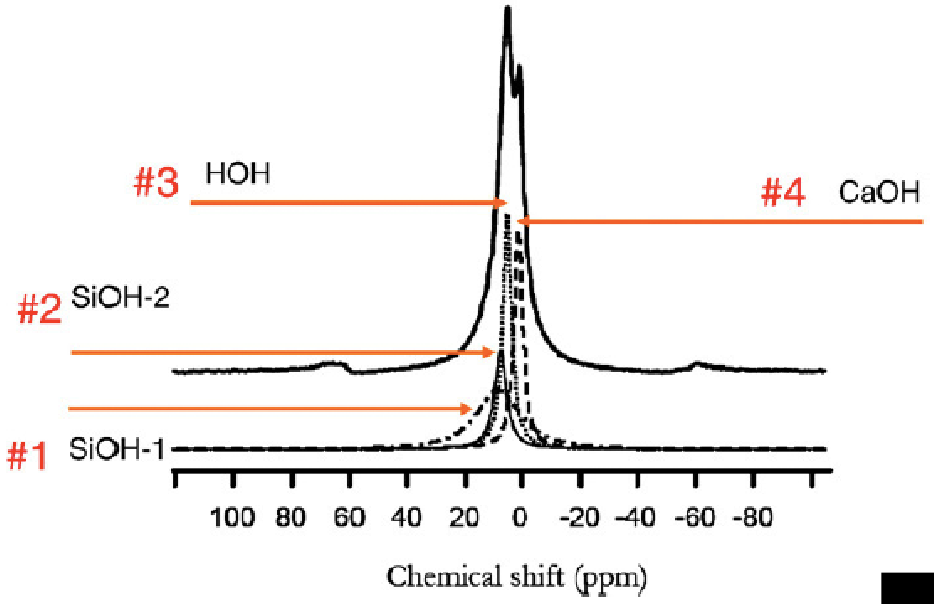


7.0 Tesla UNB MRI Magnet

- **20 cm horizontal bore.**
- **Optimized for materials imaging.**
- **Laboratory technique.**

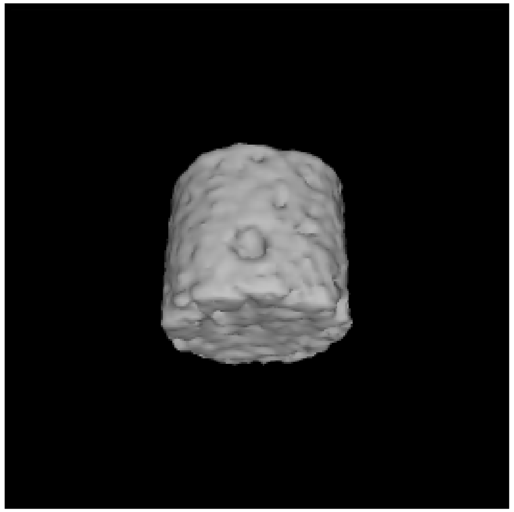
$$M_0 = \frac{N\gamma^2 h^2 I(I+1)B_0}{3kT}$$

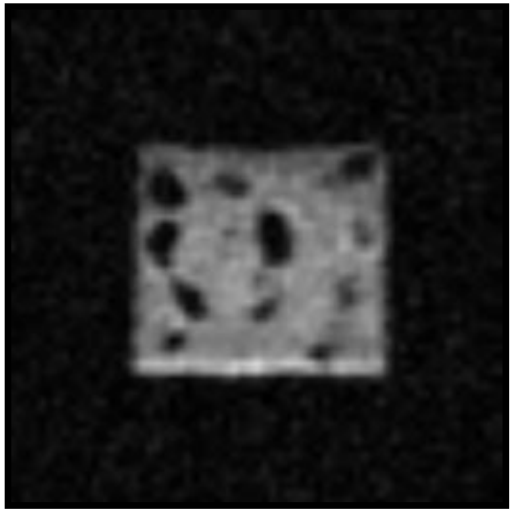
^{1}H Magnetic Resonance of Cementitious Materials



Magic Angle Spinning Spectroscopy. C_3S hydrated one year. Korb, Current Opinion Colloid Interface Science, 2009.

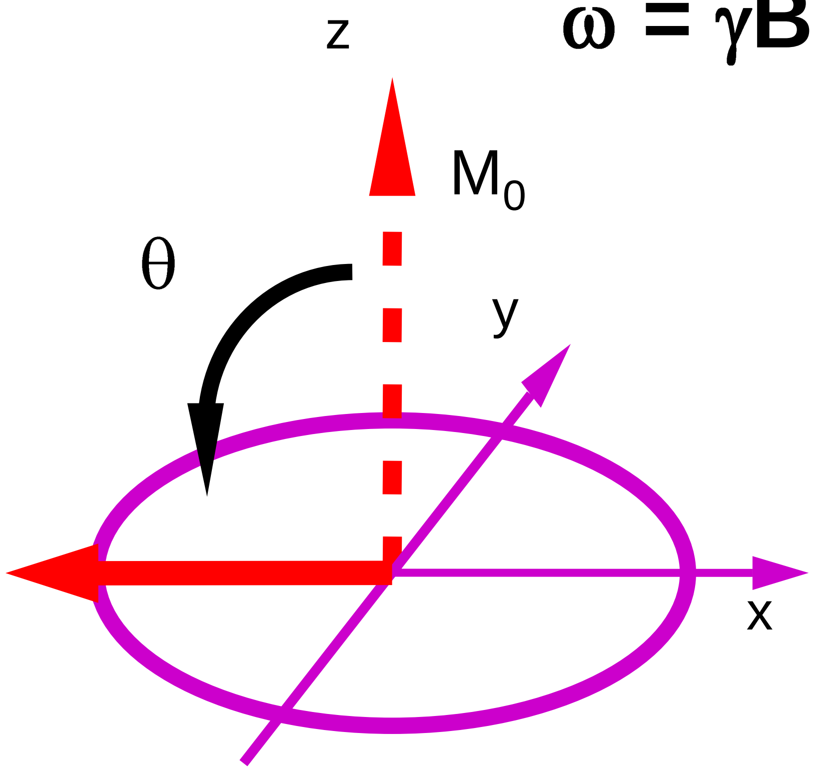
SPRITE MRI of water content distribution. White Portland cement based concrete, isotropic FOV 6 cm,150 sec acq. Balcom et al JMR 2004.

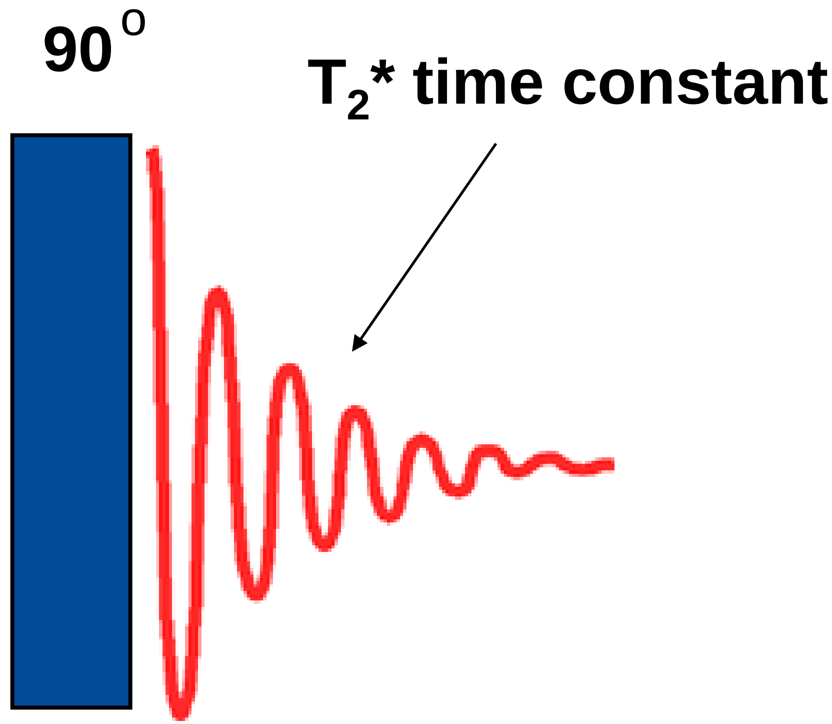




Time Domain Magnetic Resonance, TD-NMR

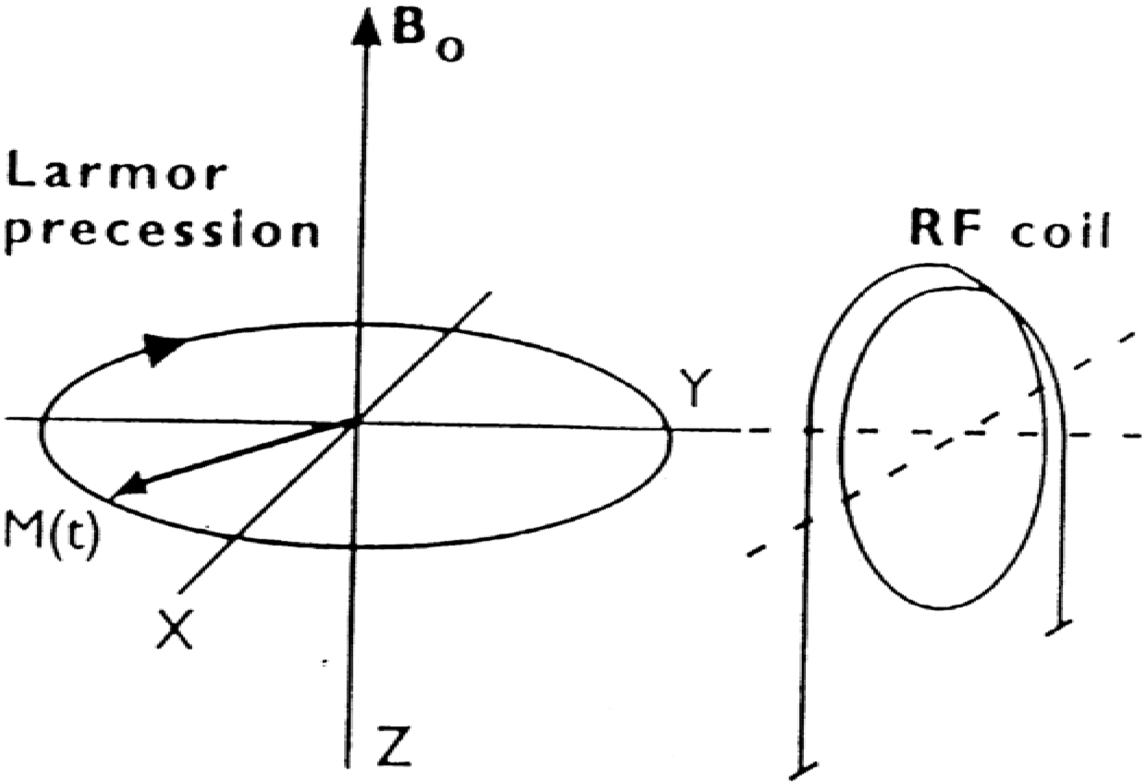
$$\omega = \gamma B_o$$





B_o 2.4 Tesla, RF signal 100 MHz

Sample and RF Probe



Voltage induced in RF coil by precession of sample magnetization - Faraday's law.

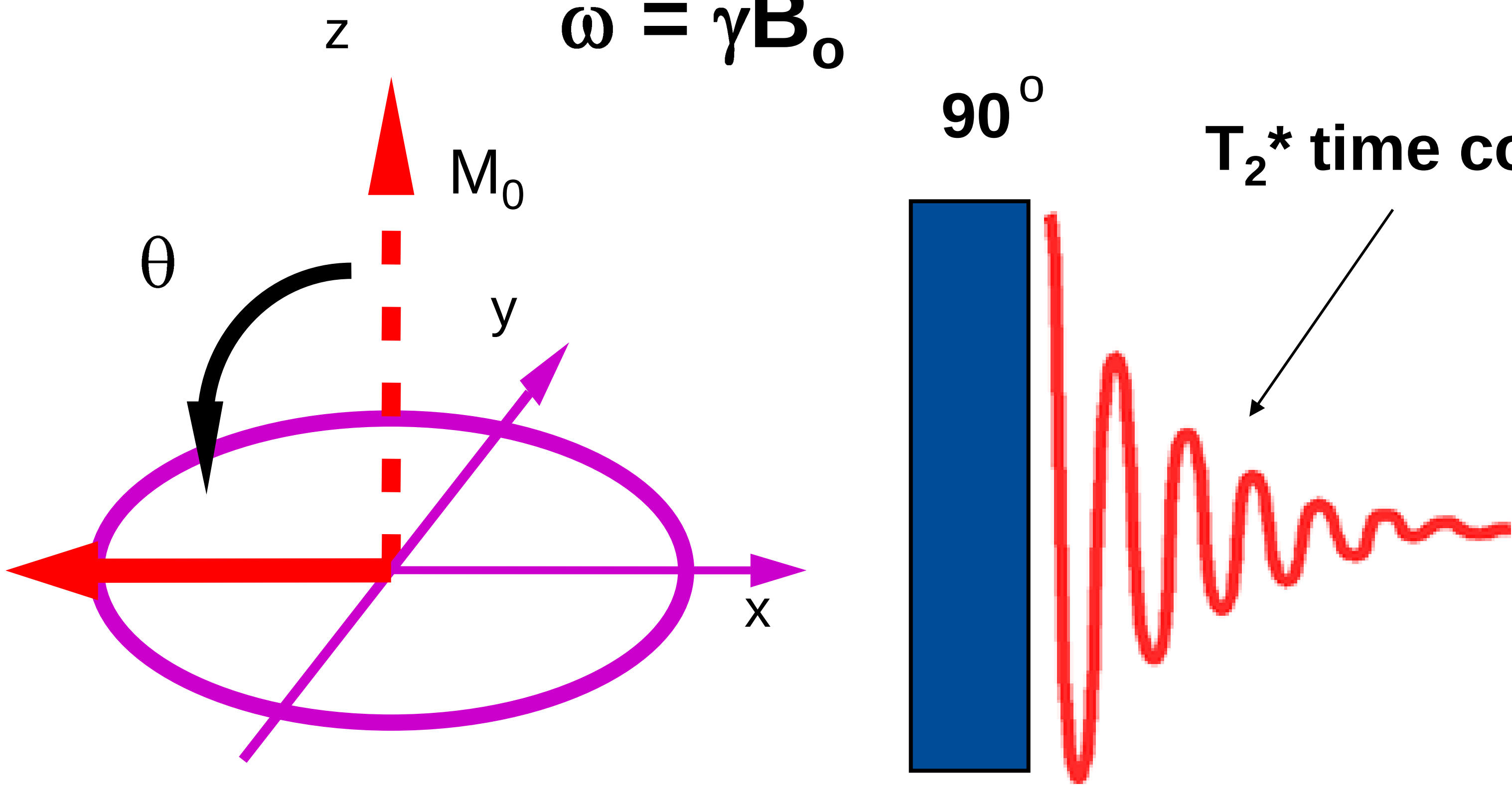
Faster precession yields higher voltage (signal) for same M_0.

voltage $\alpha\ \gamma\ M_0(\gamma^2)$

Signal varies as γ^3 , ^{1}H has the largest γ and the highest concentration, ^{1}H is the most sensitive measure.

Time Domain Magnetic Resonance, TD-NMR

$$\omega = \gamma B_o$$



B_o 2.4 Tesla, RF signal 100 MHz

MR Signal Lifetimes

- **T_1 spin lattice relaxation time, governs recovery of M_z after RF perturbation.**
- **T_2* effective spin spin relaxation time, decay of observable transverse magnetization M_{xy} after RF pulse.**
- **T_2 spin spin relaxation time more fundamental decay of observable transverse magnetization.**

$$1/T_2^* = 1/T_2 + \gamma \Delta B_0$$

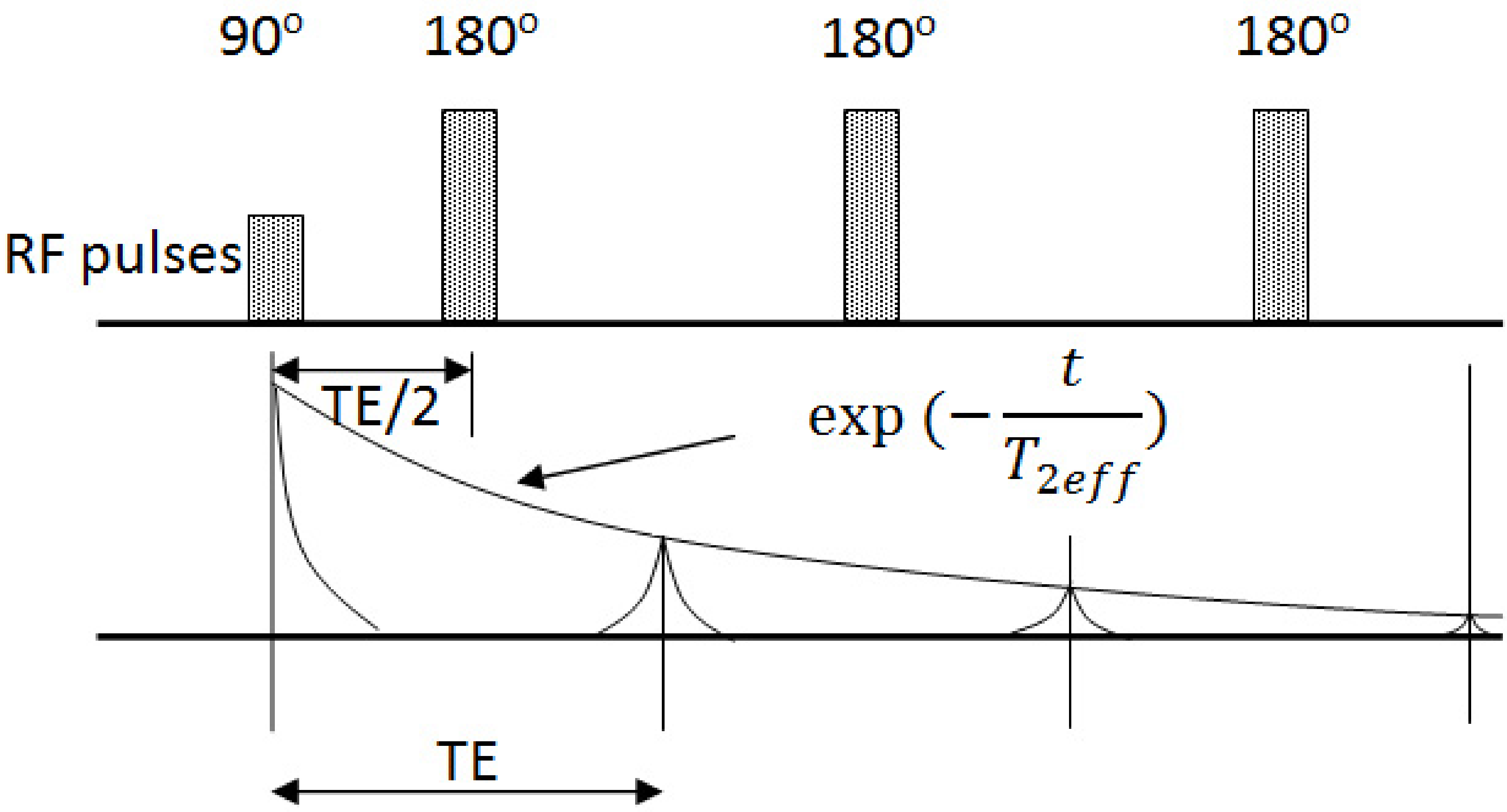
Time Domain Magnetic Resonance, TD-NMR

‘NMR studies of hydrating cement: a spin-spin relaxation study of the early hydration stage’ Lasic, Pintar et al, Cement and Concrete Research 18, 951-956 (1988).

‘Microstructure determination of cement pastes by NMR and conventional techniques’ Bhattacharja, Halperin et al, Advanced Cement Based Materials 1, 67-76, (1993).

‘NMR and nuclear spin relaxation of cement and concrete materials’ Korb, Current Opinion in Colloid and Interface Science 14, 192-202 (2009).

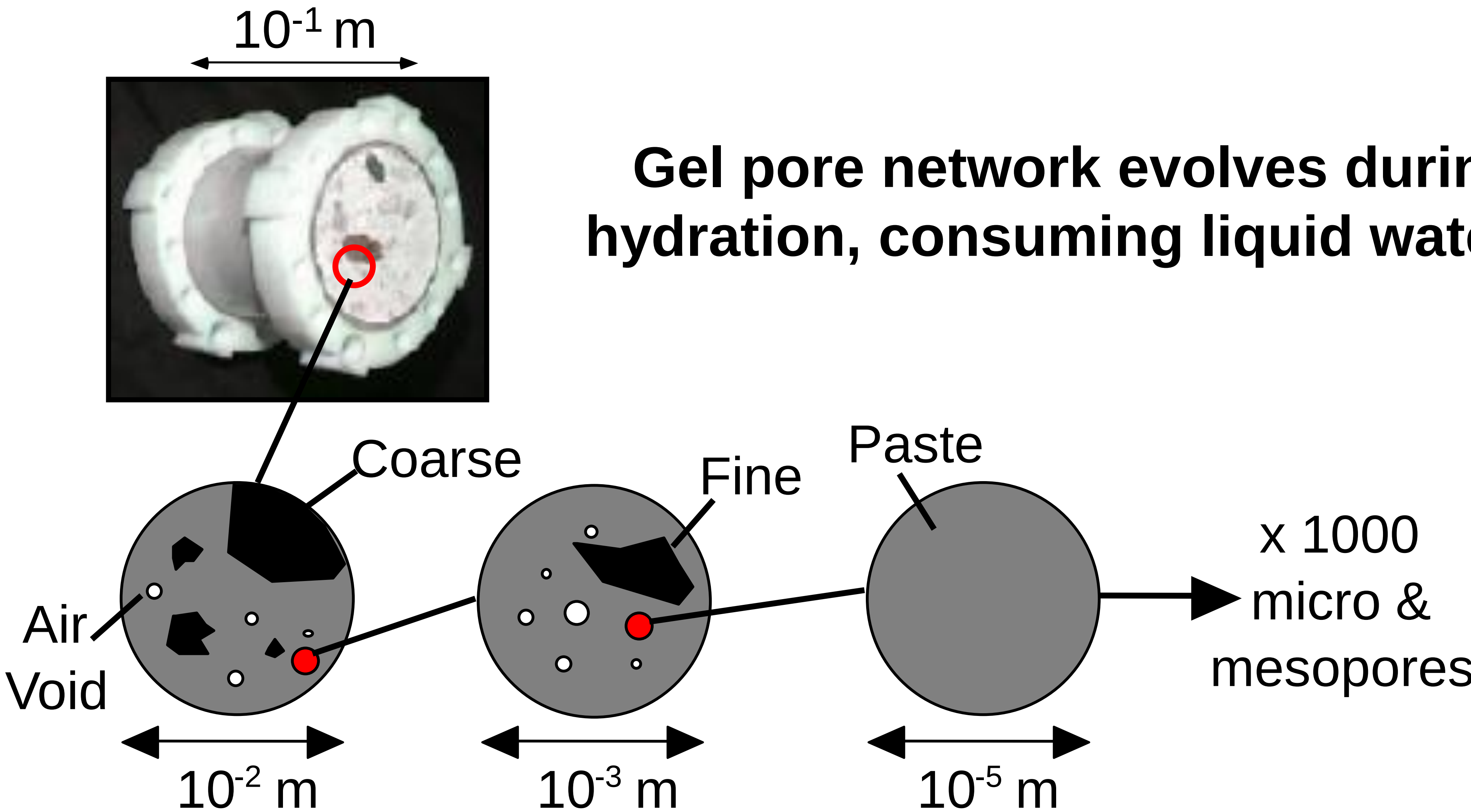
TD-NMR T_2 Measurement



Initial amplitude is M_o, quantity.

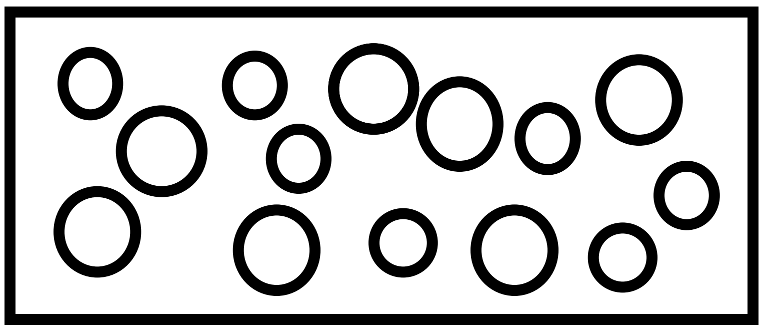
Pore Size Distribution in Cement Based Materials

Gel pore network evolves during hydration, consuming liquid water.



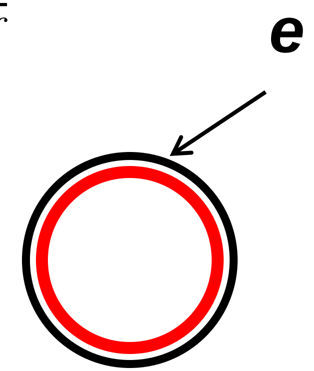
Surface Relaxation

MR relaxation times T_{2i} are determined by the size of the water-containing pores.



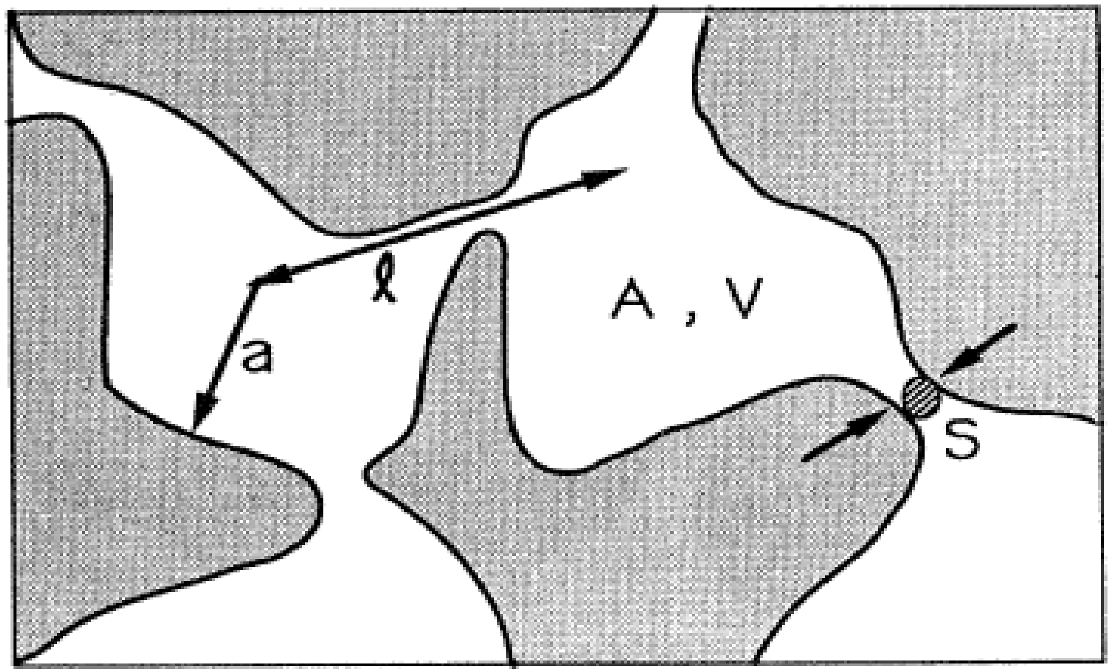
$$\frac{1}{T_{2i}} = \frac{f_{bulk}}{T_{2i}^{bulk}} + \frac{f_{surf}}{T_{2i}^{surf}}$$

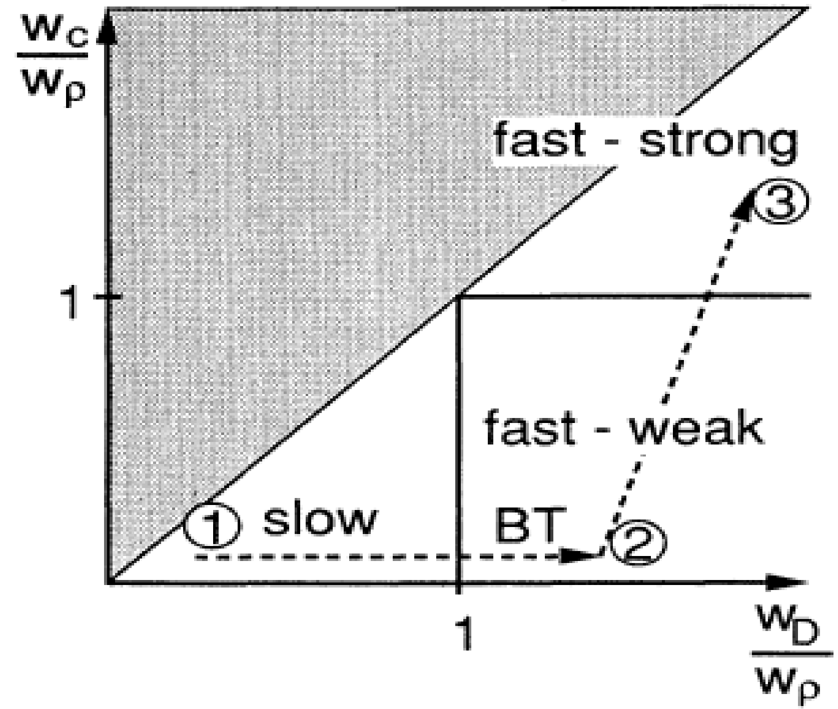
$$\frac{1}{T_{2i}} = \frac{eS}{V}\frac{1}{T_{2i}^{surf}}$$



Assumes rapid exchange of bound water surface layer and bulk water in pore centre. S/V is pore size. 'Solid' ^{1}H not observed.

MR Fluid Dynamics in Porous Media



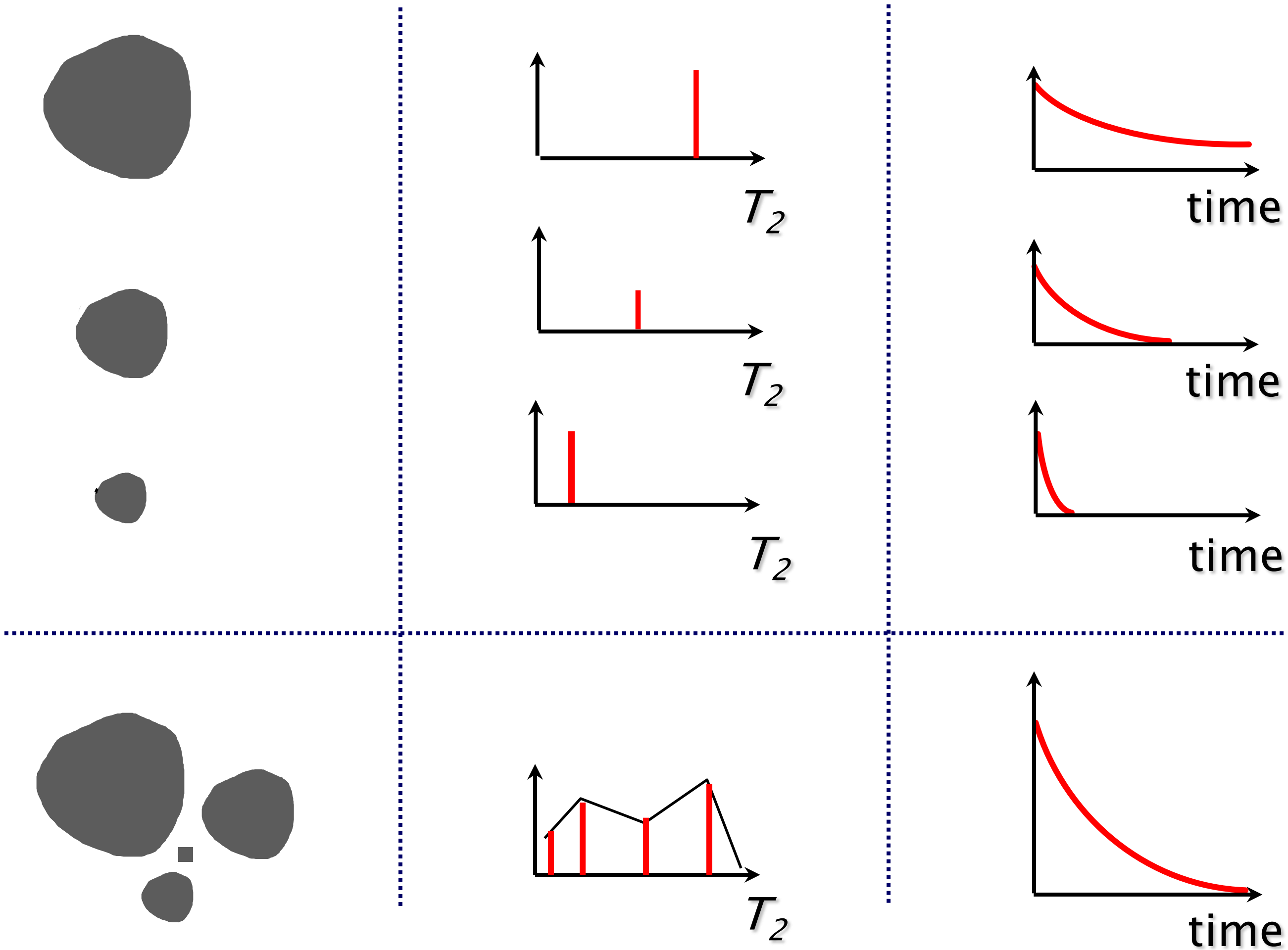


$\omega_D = D/a^2$, $\omega_C = SD/VL$, $\omega_\rho = \rho A/V$

Common regime, rapid diffusional averaging within pores, no exchange.

McCall et al Phys Rev B (1991) 44, 7344-7355.

Pore Size Distribution - T_2 Distribution



$$S(t) = \sum_i \rho_i e^{-t/T_{2i}}$$

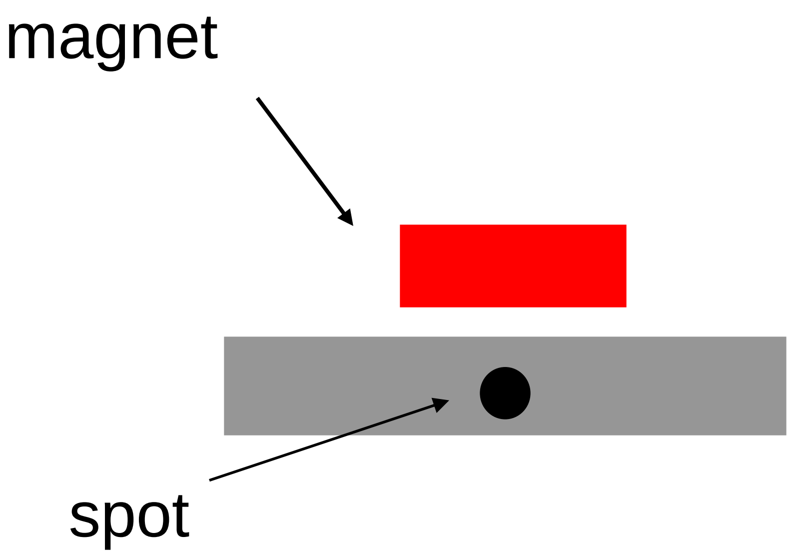
Inverse Laplace transform recovers T_2 distribution.

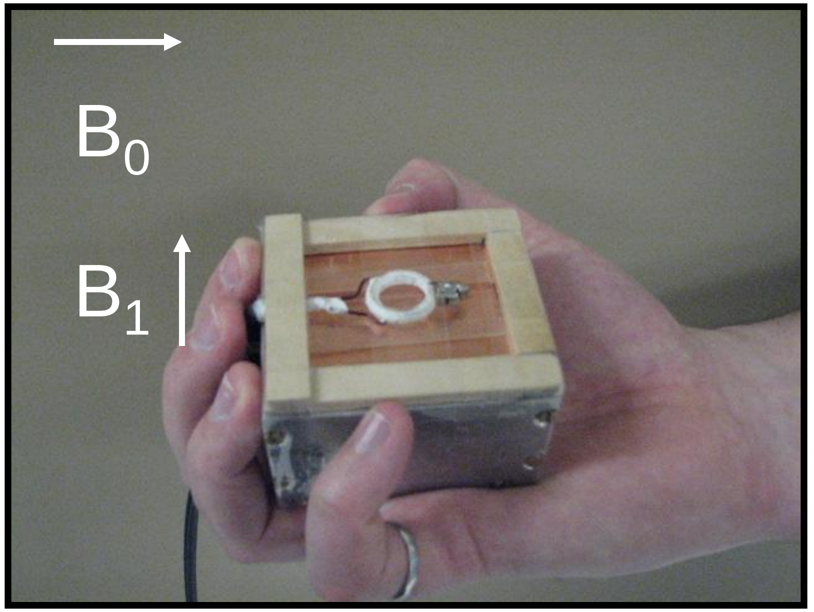
Unilateral Magnetic Resonance

Magritek

Simple mobile instrumentation. Sample is removed from the main field magnet.

Unilateral Magnetic Resonance





~ 1 cm^3 spot displaced 0.8 cm from surface, 0.9 kg magnet.

Experimental measurement is taken from a sensitive spot inside the sample of interest. The 'spot' is defined by the intersection of the B_o and B_1 fields, which are at right angles.

The Big Idea - Embedded Magnets

- Avoid near surface measure with a sensor that is positioned ’deep’ in a cement paste/mortar/concrete sample at the time of placing.
- A simple sensor which is cheap can be ‘sacrifical’.
- An array of such point sensors can provide depth and lateral spatial resolution.

Cano-Barrita, Balcom et al Cem. Concr. Res. (2009) 39, 324-328.

The Big Idea - Embedded Magnets

- T_2 measurements will yield evaporable water content, and pore size distribution, as a function of hydration or wetting/drying over short (hours, days) or long (weeks, months) time scales.

- Such sensors will bridge laboratory and field measurement.

Cano-Barrita, Balcom et al Cem. Concr. Res. (2009) 39, 324-328.

Embedded Magnet Unilateral MR

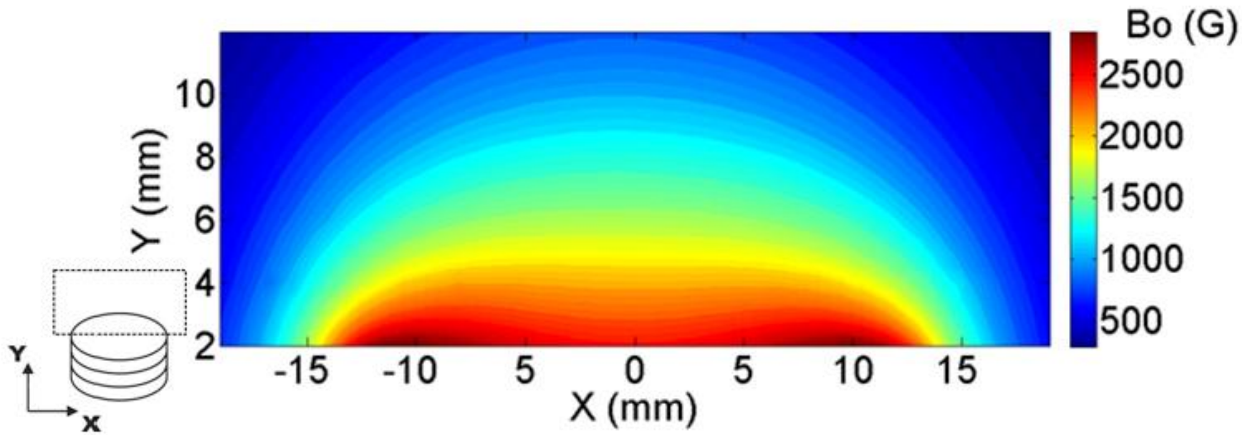
- Materials < $50, a disposable single sided sensor.
- Lee Valley Tools, Nickel plated NdFeB, $8 each.
- Immersed or embedded in sample.

Cano-Barrita, Balcom et al Cem. Concr. Res. (2009) 39, 324-328.

Embedded Magnet Unilateral MR

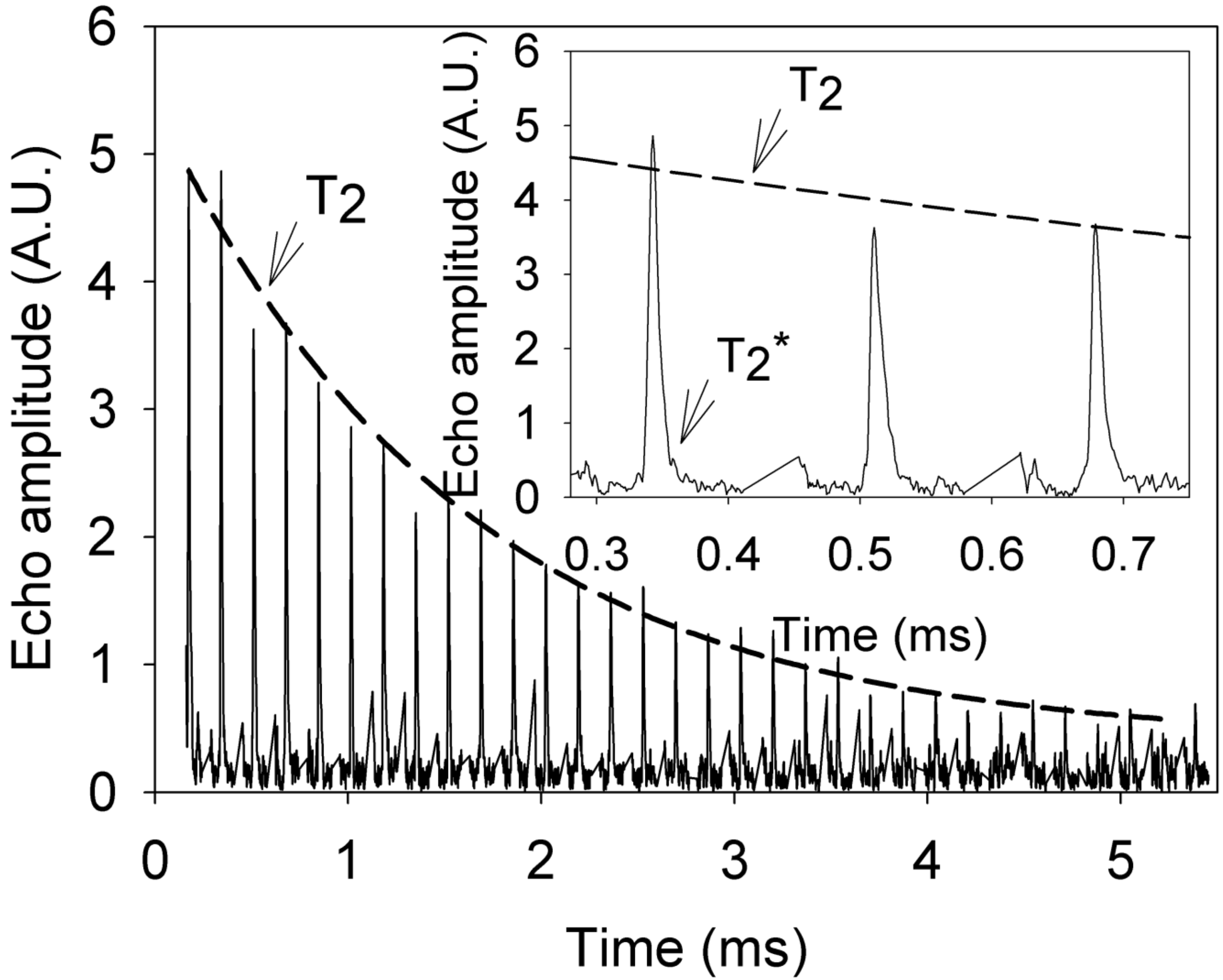
- Avoids the ‘depth of the sensitive spot’ problem by insertion into the sample.

Stack of disc magnets
3 mm above surface, 10 MHz



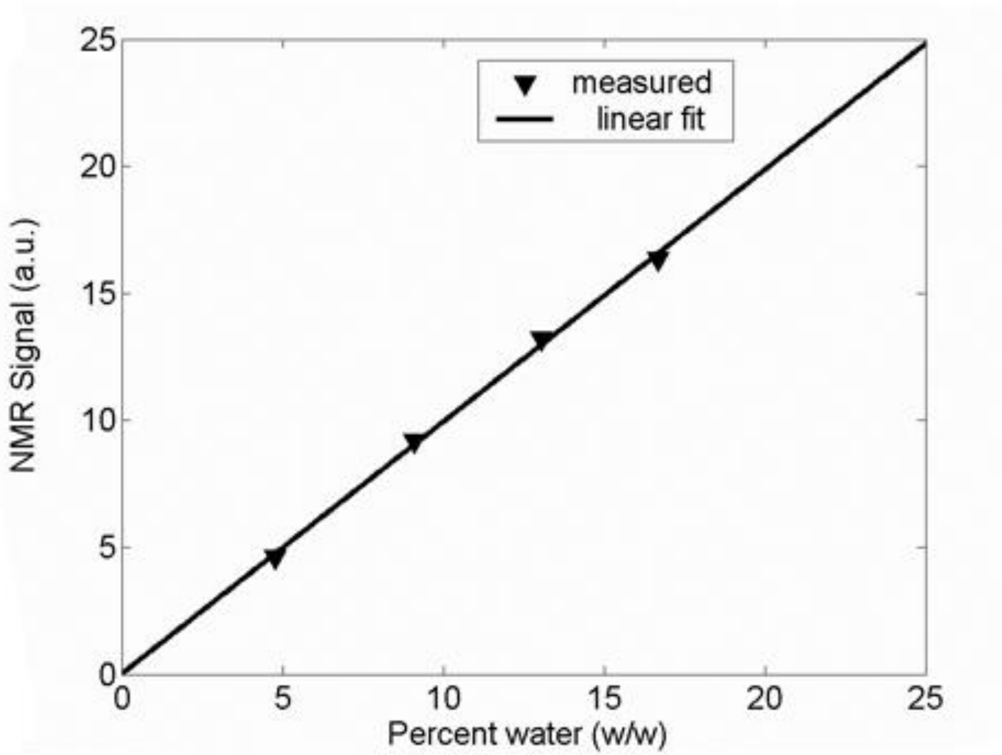
Linear gradient from 2–7 mm above magnet, 2000 Gauss/cm.

TD-NMR T_2 Measurement



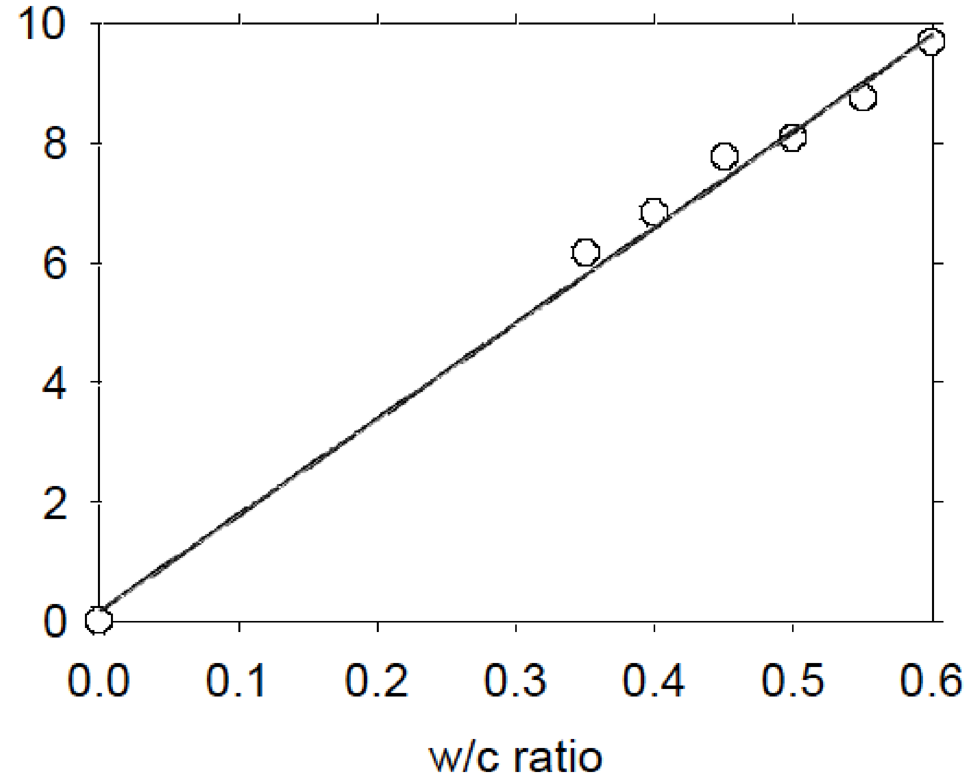
Cano-Barrita, Balcom et al Cem. Concr. Res. (2009) 39, 324-328.

Linearity ^{1}H Density MR



Calibration: Water in Sand

32 echoes, TE 200 µs, 512 avg, 9 min acq

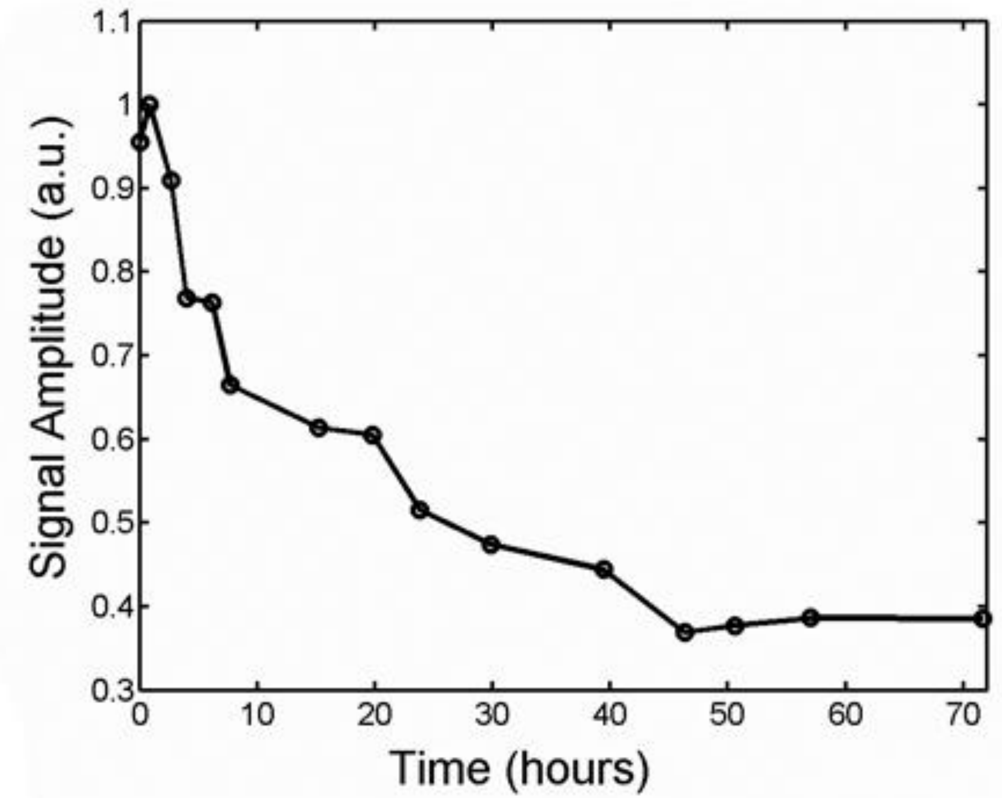


Calibration: Cement Pastes

32 echoes, TE 168 µs, 2048 avg. 7.5 min acq.

Embedded Magnet ^{1}H Evolution

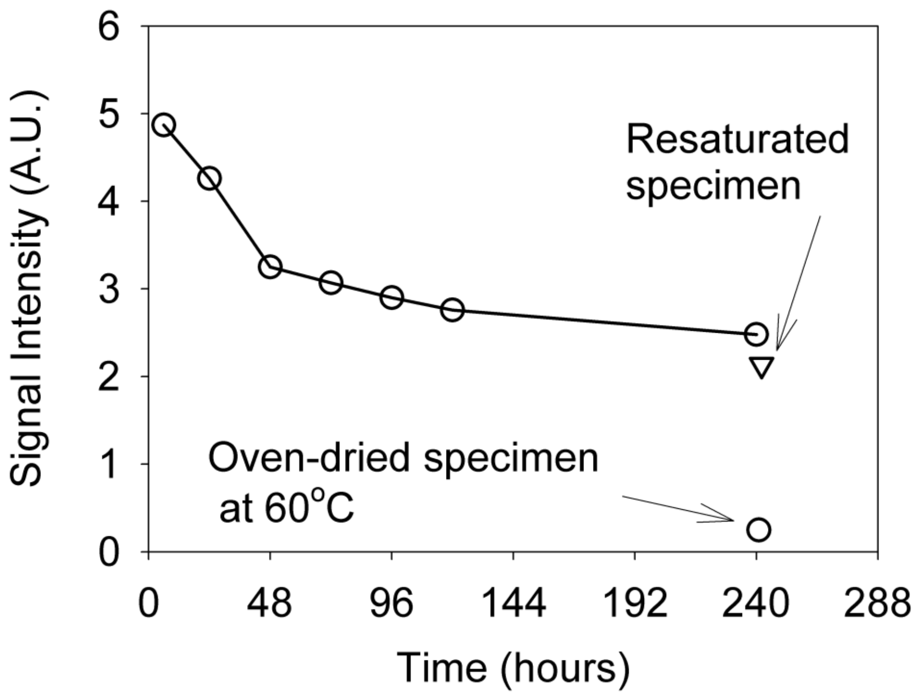
Evaporable water content (non chemically combined water) decreases as the sample hydrates.



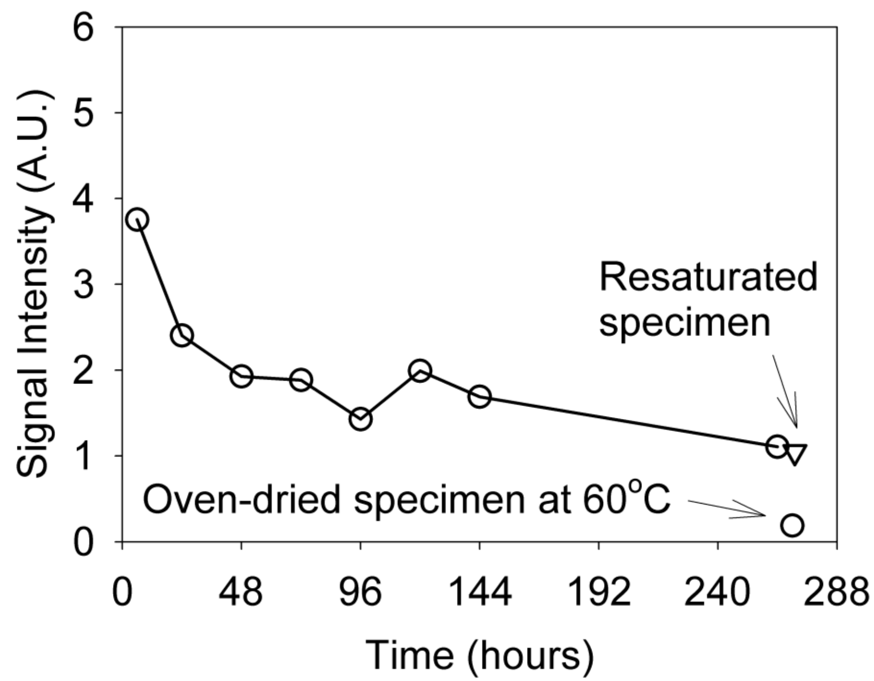
Curing mortar (w/c = 0.45). Avg. first 2 echoes, 8192 avg.

Early Age Mortar Hydration

Sealed samples



Type 1 cement mortar, w/c=0.6



Type 1 cement mortar, w/c=0.45

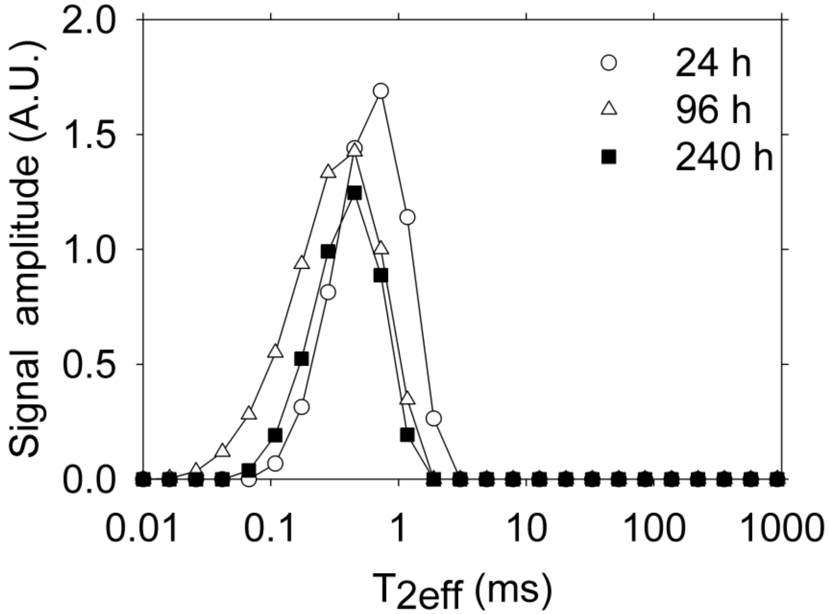
Reaction progress is measured not as heat evolved, not as product created, rather it is reagent consumed.

Evolution of Pore Structure

Time (h)	NMR Relaxation time constant		
	T_1 (ms)	T_2 (ms)	T_2^* (μs)
0	28	12	89
3	20.2 (95%)	20.4 (19%)	87
	1.4 (5%)	7.5 (81%)	
24	2.9 (65%)	4.3 (33%)	77
	0.5 (35%)	1.1 (67%)	
168	2.0 (43%)	2.6 (28%)	64
	0.4 (57%)	0.4 (72%)	

Relaxation time evolution Type 1 mortar w/c=0.6, whole sample desktop Bruker Minispec measurement. Bi-exponential fitting model.

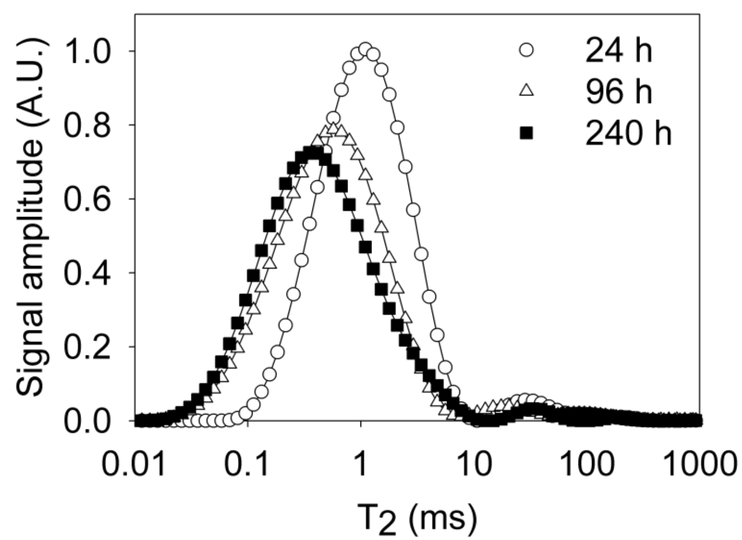
Evolution of Pore Structure



Embedded magnet T_2 distribution, w/c = 0.6.

Type 1 Portland cement mortar.

Table top magnet T_2 distribution, w/c = 0.6.



Decreased T_2 indicates smaller pores.

Cano-Barrita, Balcom et al Cem. Concr. Res. (2009) 39, 324-328.

Conclusions

- **Embedded magnets provide an in situ measure of water content variation and pore size evolution during hydration.**
- **Anticipate an order of magnitude improvement in sensitivity.**
- **Technology is still developing, applications are in their infancy. Bridge laboratory and field applications.**

UNB MRI Centre

Andrew Marble, NSERC Doctoral Prize winner, 2008.

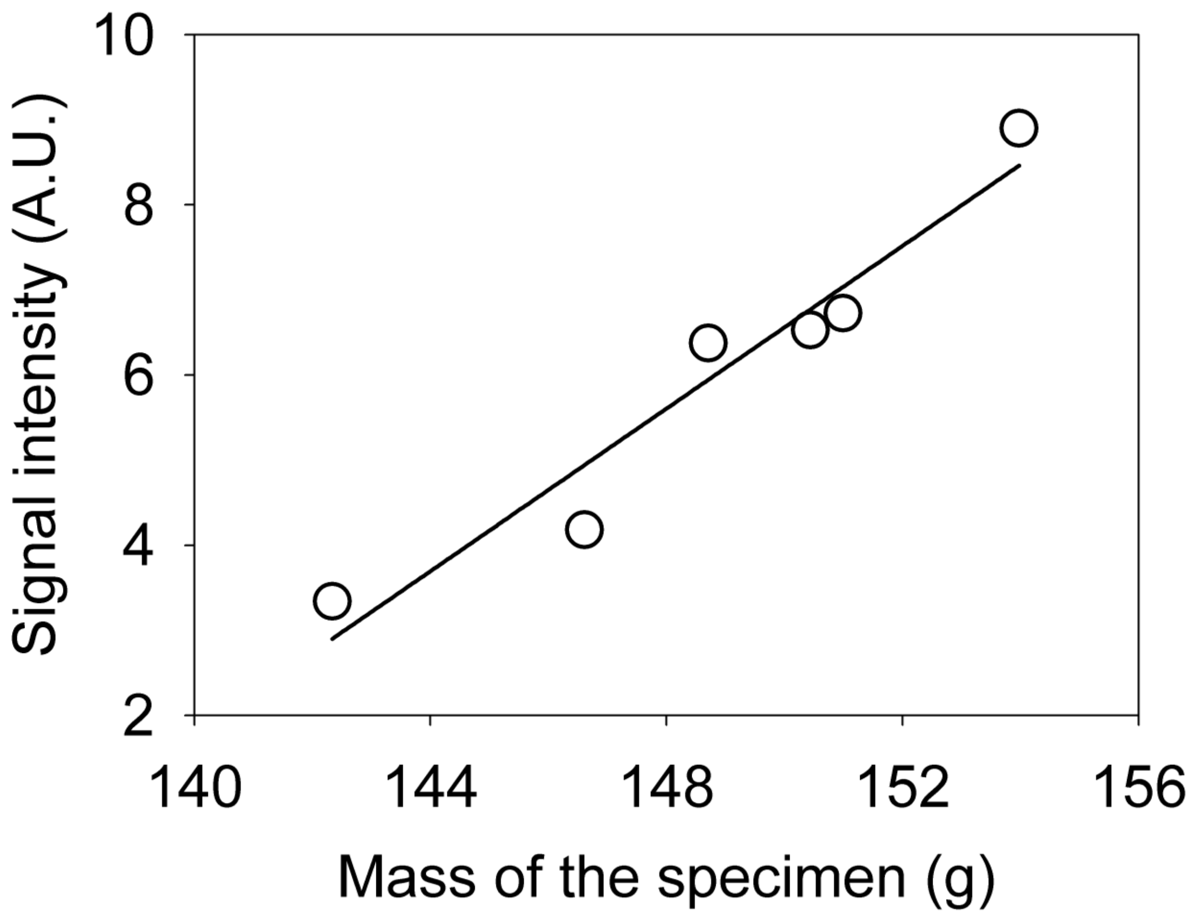
Acknowledgements

Industrial and Academic collaborators
UNB MRI Centre

T.W. Bremner, Michael Thomas, Jesus Cano, Joshua Young

NSERC of Canada

Steacie Fellowship (2000-2002)
Canada Chairs Program (2002-2016)



10
8
6
4
2
140
144
148
152
156
Signal intensity (A.U.)
Mass of the specimen (g)

MR Active Nuclei

Isotope	Spin, I	Natural abundance (%)	Resonance Frequency, 2.349 T field, MHz
^{1}H	1/2	99.98	100.00
^{7}Li	3/2	92.58	38.86
^{13}C	1/2	1.10	25.14
^{17}O	5/2	0.03	13.56
^{19}F	1/2	100.00	94.08
^{23}Na	3/2	100.00	26.45
^{35}Cl	3/2	75.53	9.81
^{27}Al	5/2	100.00	26.06
^{29}Si	1/2	4.70	19.86
^{31}P	1/2	100.00	40.48

Sensitivity -> γ^3 * I(I+1) * natural abundance * [conc.]