CRACKS AND PORES -THEIR ROLES IN THE TRANSMISSION OF WATER

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Water Transmission in cement paste

- The aim of this work is to differentiate the rate of water transmission through
  - Cracks
  - Pores
    - Capillary Pores (Diameter > 100 Å)
    - Gel pores (Diameter < 100 Å)

- Using the techniques of
  - Permeability
  - Quasi Elastic Neutron Scattering

Why this study

- Cementitious materials are used as barriers to radioactive wastes
  - Rate of transmission of radionuclides depends on rate of water transmission
- Durability of concrete related inversely to its ability to transmit fluids.
  - Hence an ability to predict future water transmission gives information on likely service life of concrete structures
- The service life of a low level repository is expected to be greater than 300 years
  - Tools to demonstrate that this is a likely outcome are desirable.

Definitions

- Concrete - cementitious materials & aggregate & sand & water
- Mortar - cementitious materials & sand & water
- Paste - cementitious materials & water

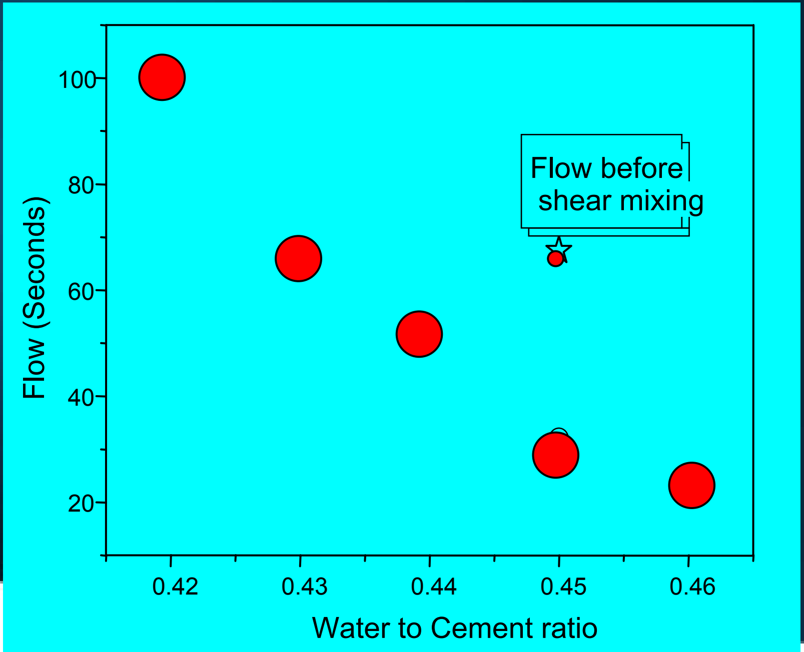
- OPC Ordinary - Portland Cement manufactured by Blue Circle Southern.
- GGBFS - Ground Granulated Blast Furnace Slag
- Marine Cement –OPC with 60% replaced with inter-ground GGBFS

Experimental I
Low & medium water pastes & mortars had similar flow.

- Paste
  - Low Water
    - W/C 0.32
  - Medium Water
    - W/C 0.42
  - High Water
    - W/C 0.6 & 0.8
- Mortar
  - Low Water
    - W/C 0.32
    - Binder/Sand 1.2
  - Medium Water
    - W/C 0.46
    - Binder/Sand 1.0

Experimental II
Shear Mixed and cured 28 days sealed

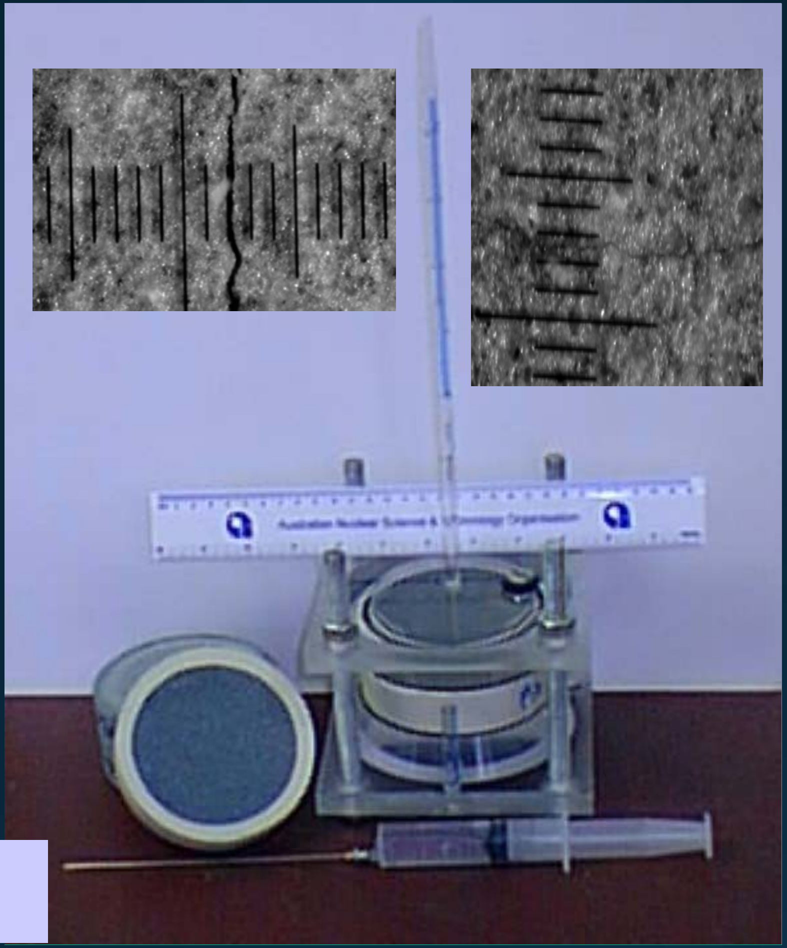
- OPC & Marine
  - Mortars Pastes
- Mixed in Wearing Blender
- Cured 28 days Sealed
- Low Medium similar flow



Ludirinia's apparatus for permeability measurement

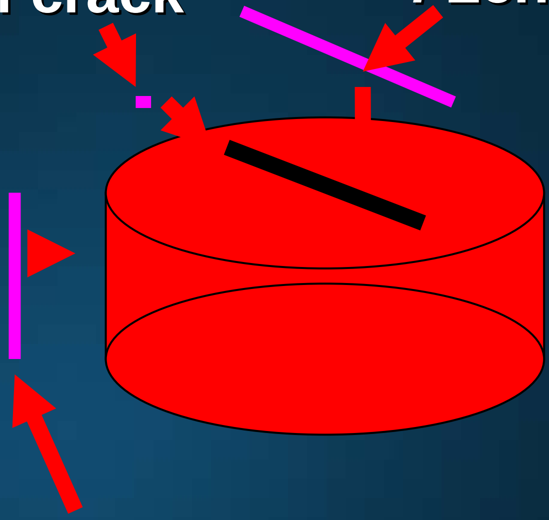
- $A'(m^2)$ - the cross section of the pipette,
- $A(m^2)$ area of specimen
- $h(m)$ the water head
  - h_o is the initial level
  - h_l the final level
- $L(m)$ the thickness
- $t(s)$ the time

- Note can only measure when $K' > 1*10^{-12}$m/s



$K' = (A' L)/(A\ t)\ \ln(h_0/h_l)$

Effect of Crack Width on Water Transmission



***w* Width of crack**

***l* Length Crack**

***d* Depth Cylinder**

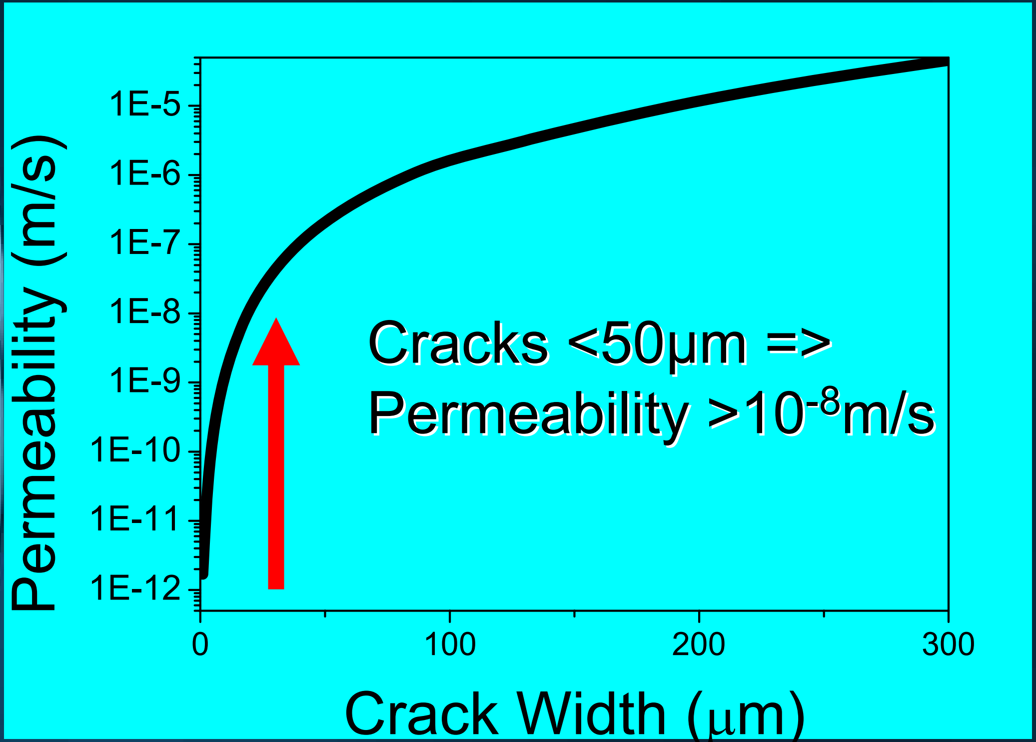
From the Navier-Stokes equation

It can be shown that

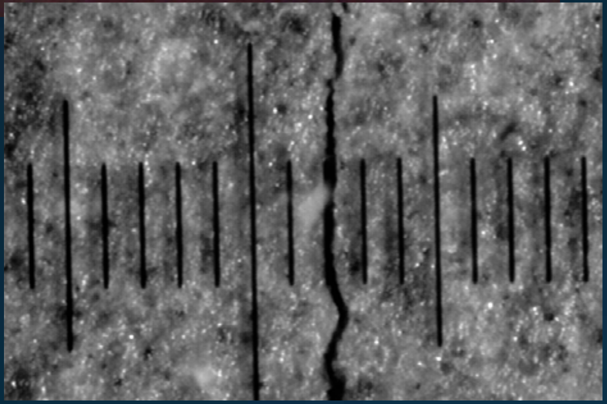
$$w^3 = 3\pi\mu d^2 K' / (\rho l)$$

Where w is the width of the crack
L is the crack length
d is the depth of the cylinder
μ is the viscosity of water at 20 degrees
ρ is the density of water
K' is the permeability of the sample

Relationship between crack width and measured Permeability



Cracks <50μm =>
Permeability >10^{-8}m/s



For pastes (uncracked) it will be the capillary pores that carry the majority of water

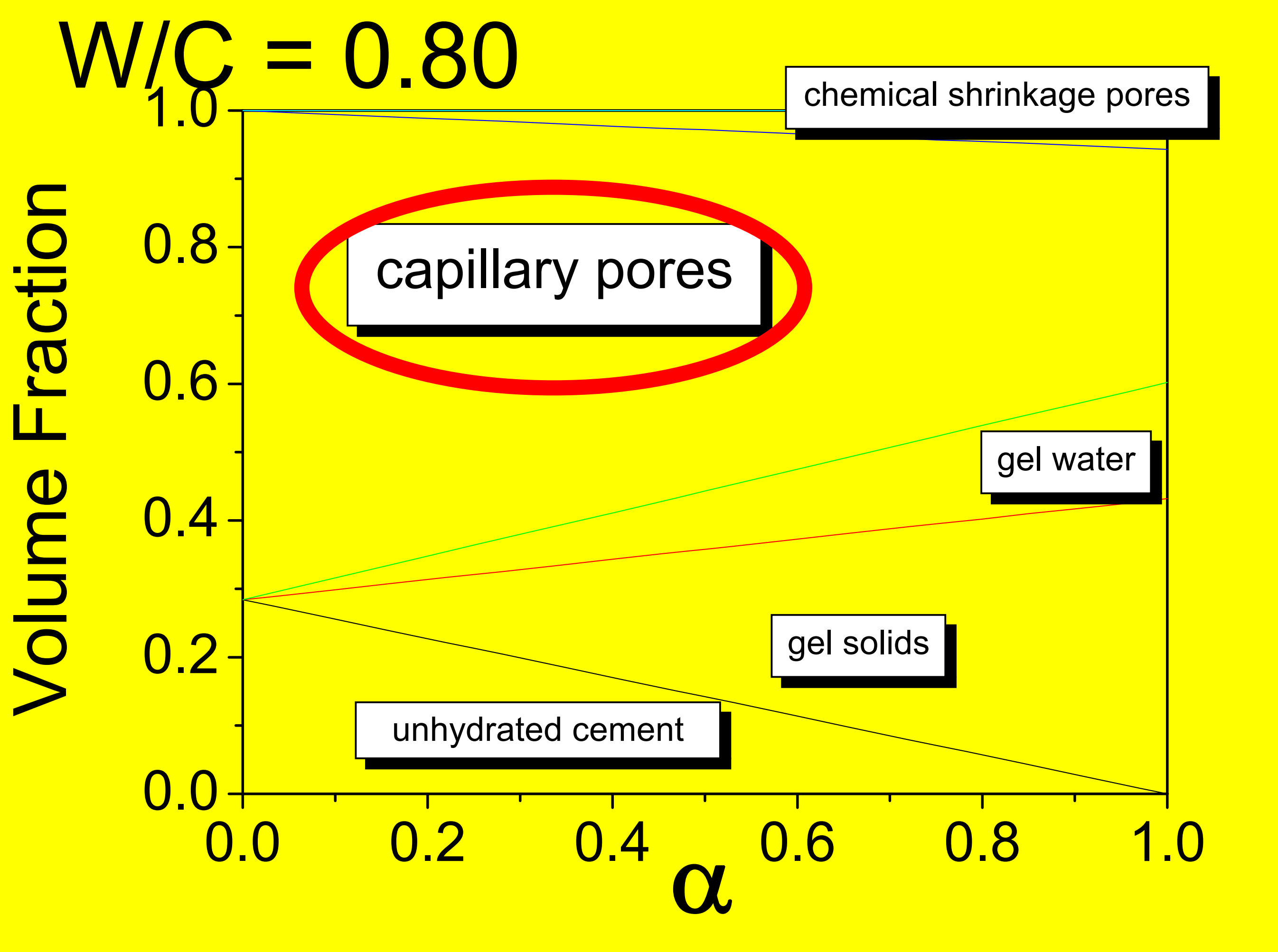
- The capillary pores are the space remaining after hydration takes place
- Thus they are highest at the start of hydration
- Paste made up
  - Un-hydrated cement
  - Hydrated cement – gel
  - Gel – pores
  - Capillary pores
  - Pores due to chemical shrinkage (capillary pores)
- Volume at a time depends on the extent of the paste hydration (α) which varies between 0 and 1

Powers Brownyard Model – Volume of components depends on α

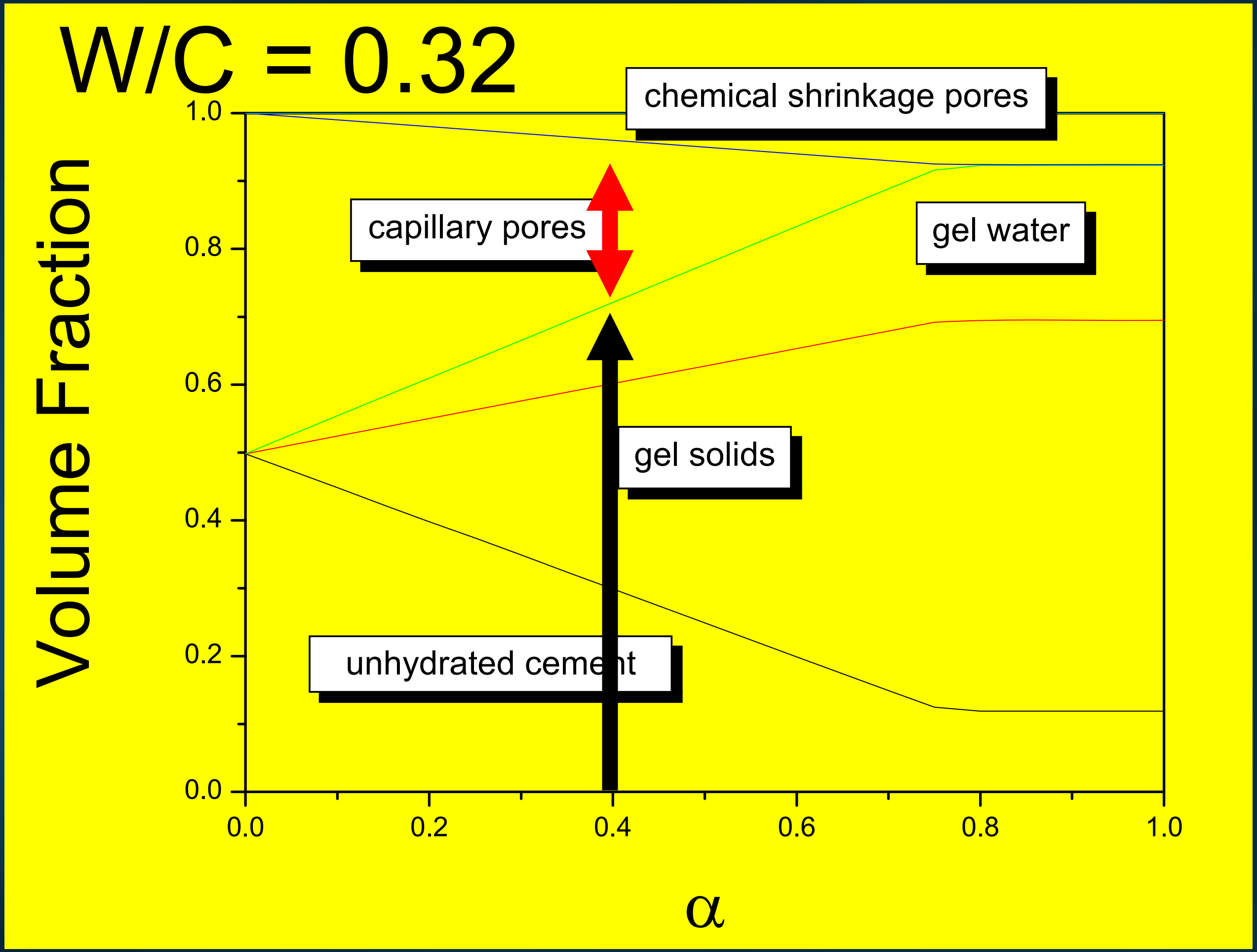
- Define p the initial porosity of the paste
  - depends on density of cement water and w/c
- Vol(chemical shrinkage) = $0.20(1-p)\alpha$
- Vol(capillary pores) = $p-1.32(1-p)\alpha$
- Vol(gel pores) = $0.62(1-p)\alpha$
- Vol(gel) = $1.52(1-p)\alpha$
- Vol(un-hydrated cement) = $(1-p)(1-\alpha)$

- Relationship depends on assumptions
  - e.g that chemically bound water (non-evaporable water) 0.23 g binds per gram of cement hydrated
  - Gel water 0.19g binds per gram of cement hydrated

So these approximations show that capillary pore volume decreases with hydration

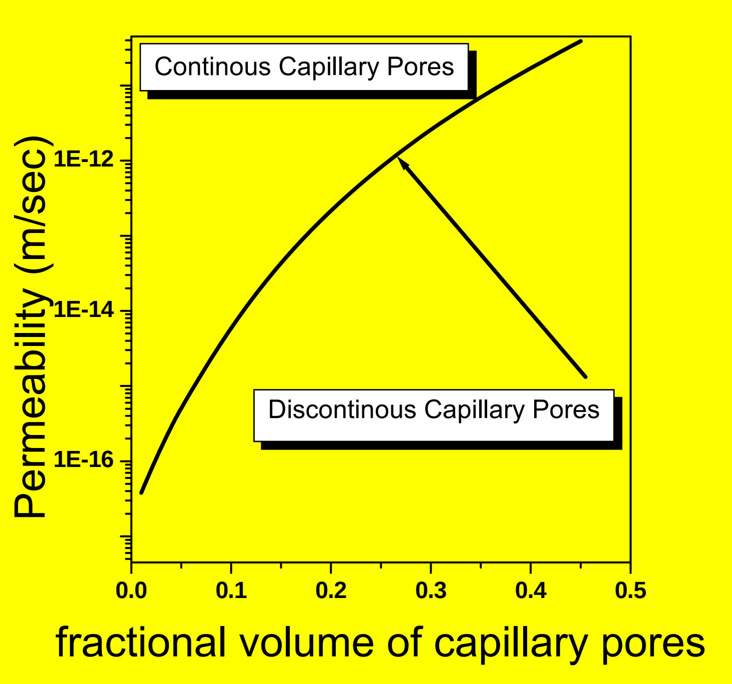


Even low w/c pastes
have large capillary pore volumes
- when uncured.



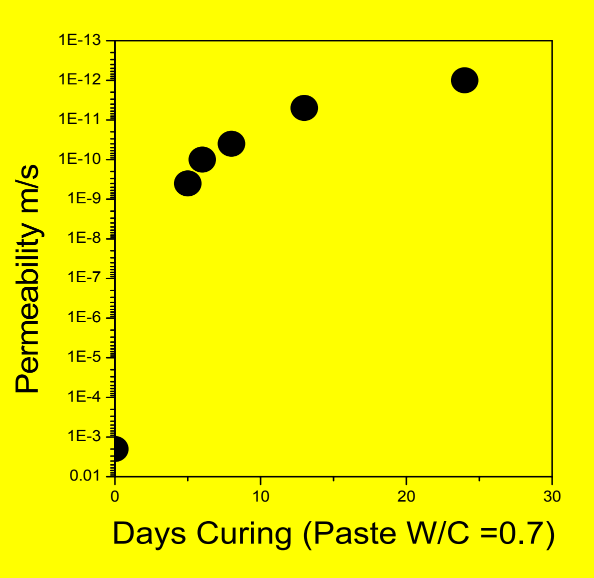
From work by Powers and his co-workers we also find that capillary pore space is related to the permeability

- Powers plotted permeability for pastes at different w/c ratios
- Pastes were almost fully saturated
- Pastes with continuous capillary pores had greater permeability than indicated by line.
- After at low pore volume the capillary pores became discontinuous and results followed the line
- The point of imitation of the discontinuous pores is indicated.

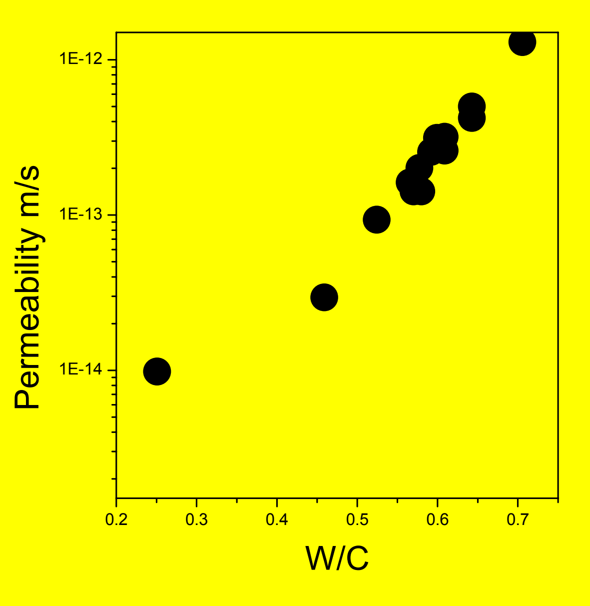


Further work by Powers and co-workers indicated the relationship between curing time and w/c ratio

- Pastes cured longer were less permeable.

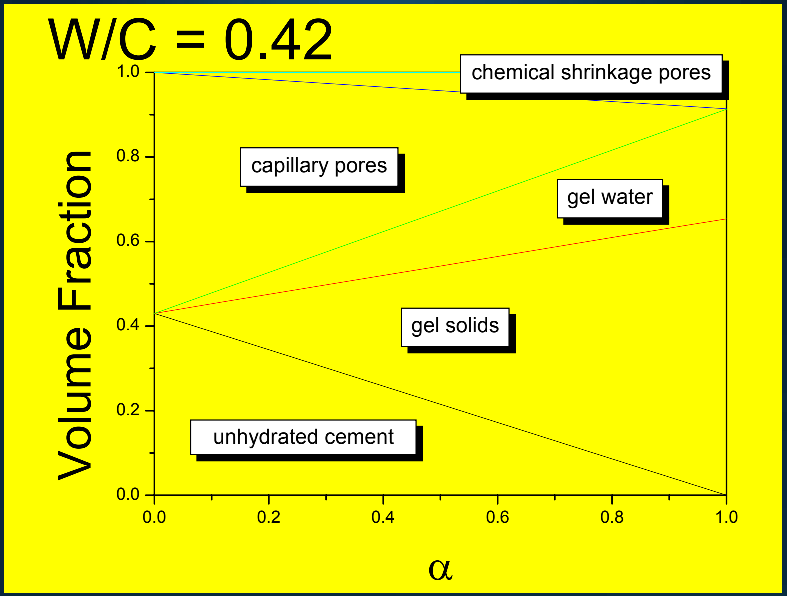


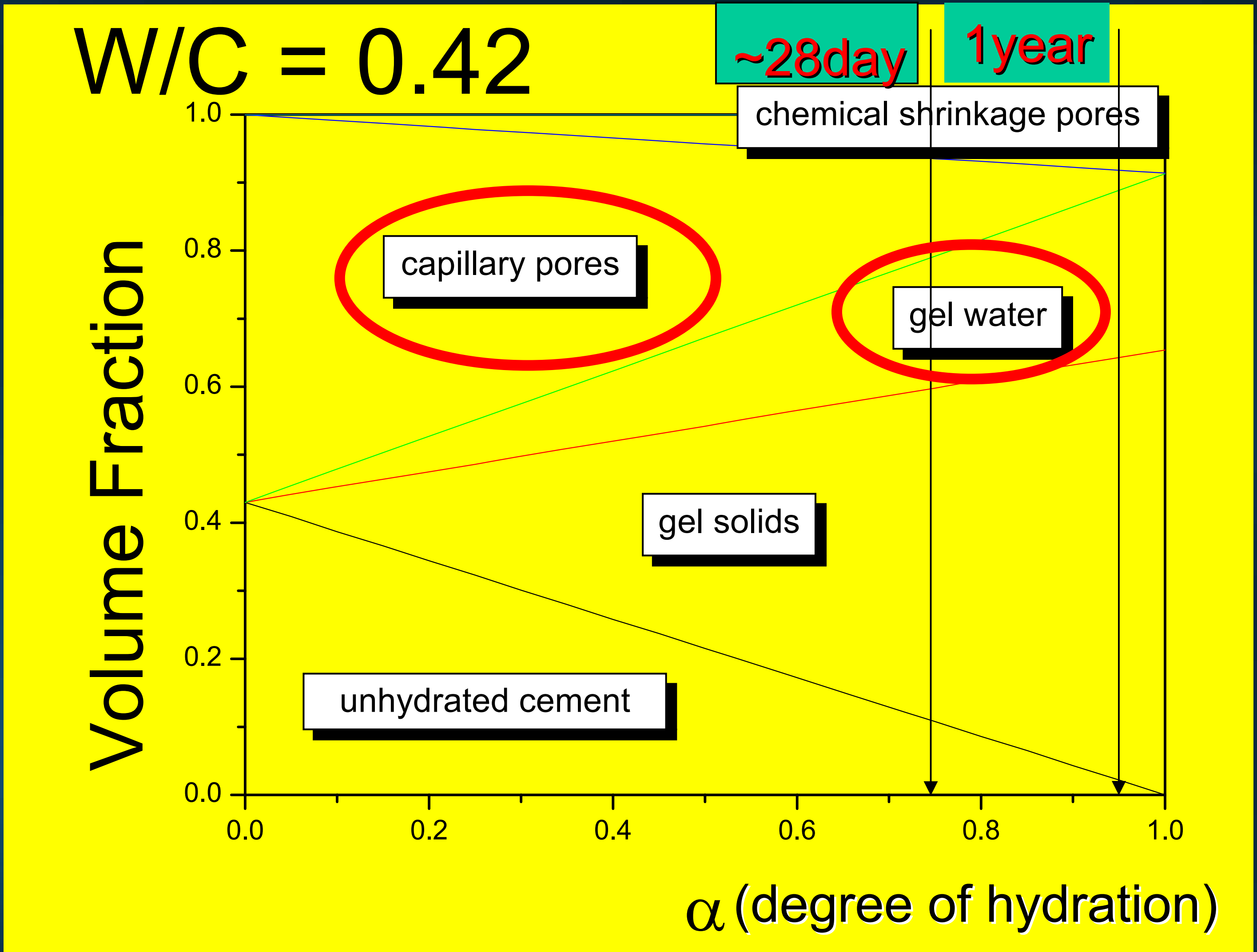
- Pastes made with greater W/C had dramatic differences in permeability



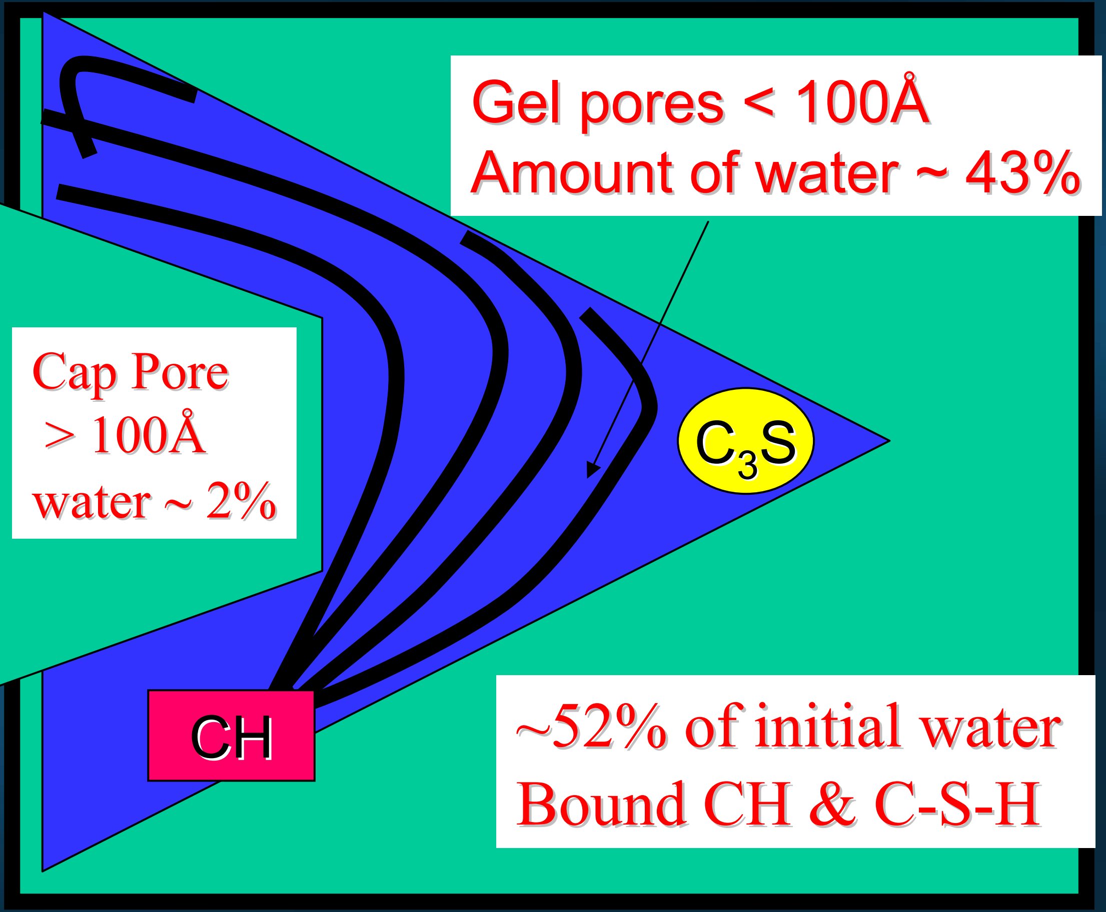
Powers work indicated that with proper curing at w/c 0.42 the pores should be discontinuous.

- At 7 days the paste with w/c of 0.45 should have an approximate degree of hydration 0.60 and have acquired a discontinuous pore structure.
- However this does assume
  - Proper Mixing
  - Proper Compaction
  - Proper Curing
- Furthermore these are theoretical estimates
  - assuming ALL cements hydrate in the same manner.




W/C = 0.42
~28day
1year
chemical shrinkage pores
capillary pores
gel water
gel solids
unhydrated cement
Volume Fraction
1.0
0.8
0.6
0.4
0.2
0.0
0.0
0.2
0.4
0.6
0.8
1.0
α (degree of hydration)

Pore Water Ratios in 1g of Fully Hydrated Pastes (1 year old α~0.95) for w/c=0.42



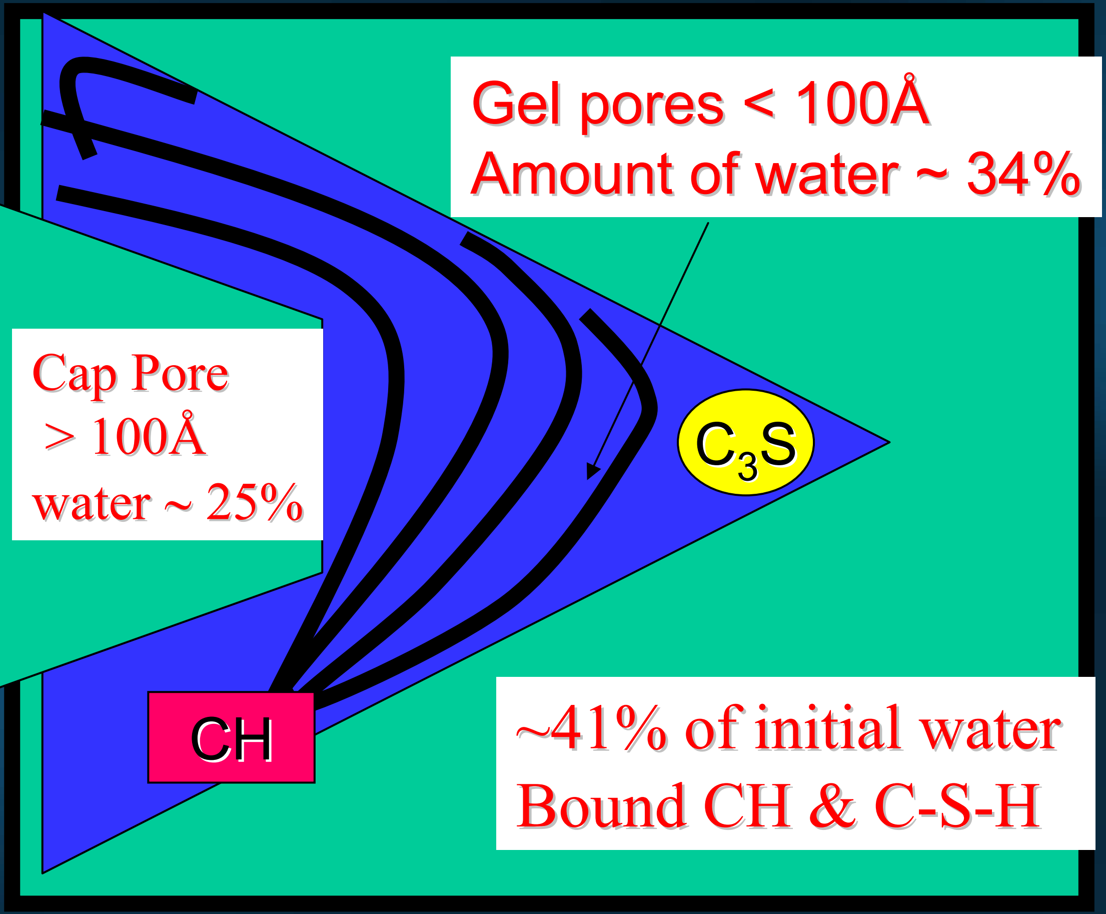
Gel pores < 100Å
Amount of water ~ 43%

Cap Pore
> 100Å
water ~ 2%

~52% of initial water
Bound CH & C-S-H

Mobile water is in both gel and capillary pores

Pore Water Ratios in 1g of Fully Hydrated Pastes (28 day cure α~0.75) for w/c=0.42



Gel pores < 100Å
Amount of water ~ 34%

Cap Pore
> 100Å
water ~ 25%

~41% of initial water
Bound CH & C-S-H

Mobile water is in the smaller pores

Water Diffusivity can be measured by QENS

- Bulk water $25*10^{-10}\ m^2/s$
- OPC Paste $12*10^{-10}\ m^2/s$ at $\Delta E = 98\ \mu eV$
- OPC Paste $6*10^{-10}\ m^2/s$ at $\Delta E = 30\ \mu eV$

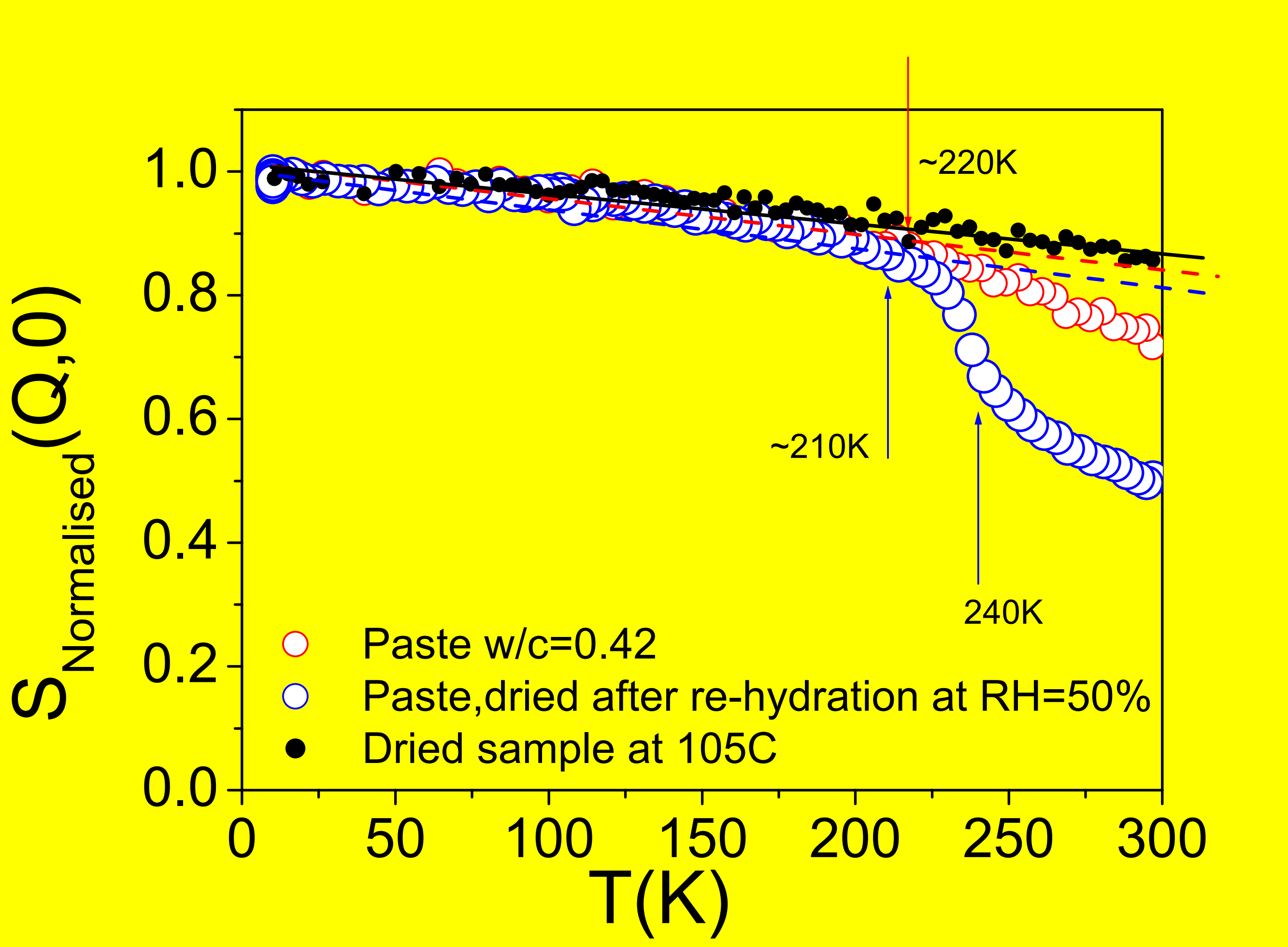
QENS Results from

1. Bordallo, H.N., Aldridge, L.P., and Desmedt, A. (2006) Water Dynamics in Hardened Ordinary Portland Cement Paste or Concrete: From Quasielastic Neutron Scattering. J. Phys. Chem. C, 110(36), 17966-6.
2. Bordallo, H.N., Aldridge, L.P., Churchman, G.J., Gates, W.P., Telling, M.T.F., Kiefer, K., Fouquet, P., Seydel, T., and Kimber, S.A.J. (2008) Quasi-Elastic Neutron Scattering Studies on Clay Interlayer-Space Highlighting the Effect of the Cation in Confined Water Dynamics. J. Phys. Chem. C, 112(36), 13982 - 13991.
3. Aldridge, L.P., Bordallo, H.N., and Desmedt, A. (2004) Water dynamics in cement pastes. Physicia B, 350, e565-e568.

QENS – Quasi-Elastic Neutron Scattering

- The signal from H dominates the spectra: We can “see water”, and the signal from the rest is very small
- By using the elastic fixed window approach that is similar to Debye-Waller evolution obtained from X-rays, we can determine the temperature where the water starts to move

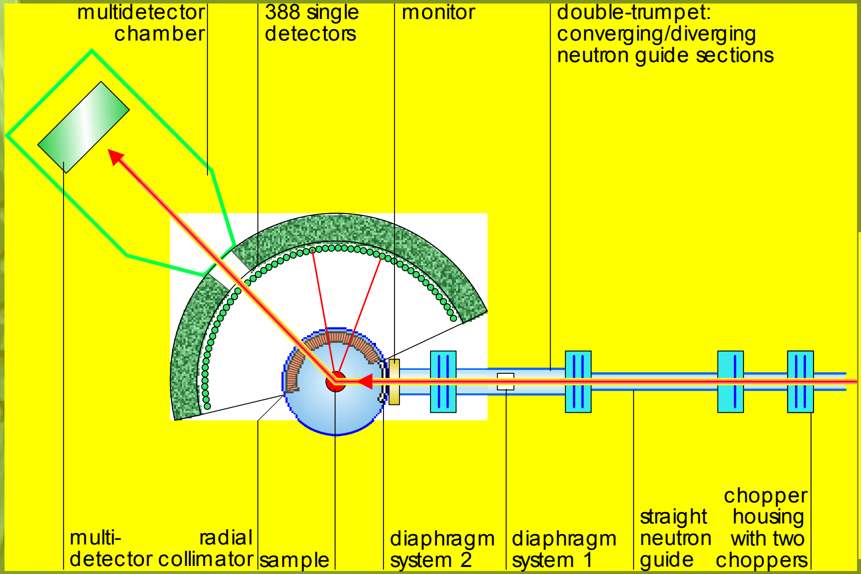
Elastic Windows on SPHERES (ns time scale) define when the water motion is unlocked!!!



QENS – Quasi-Elastic Neutron Scattering

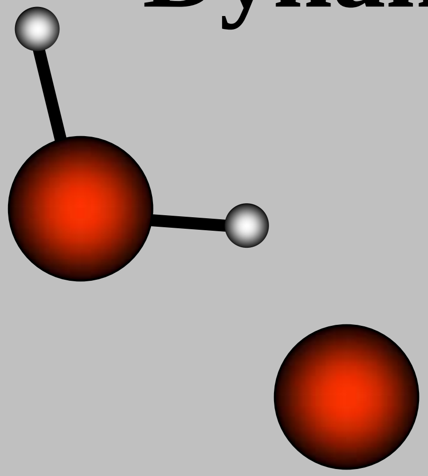
- The signal from H dominates the spectra: We can “see water”
- QENS allows measurements in different time and length scales – ΔE (Δt)
- We can differentiate between bound water and “free” water – because they move differently

NEAT - ToF Spectrometer at BENSC



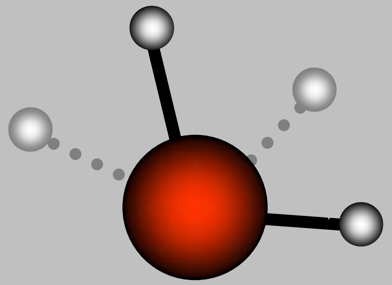
- Q: 0.4 Å^{-1} < Q < 2.1 Å^{-1}
- resolution at elastic peak: $\Delta E \sim 98$ or 30μeV
- time scale: picosecond

Dynamics Model



Oscillation
High Frequency: Stretching

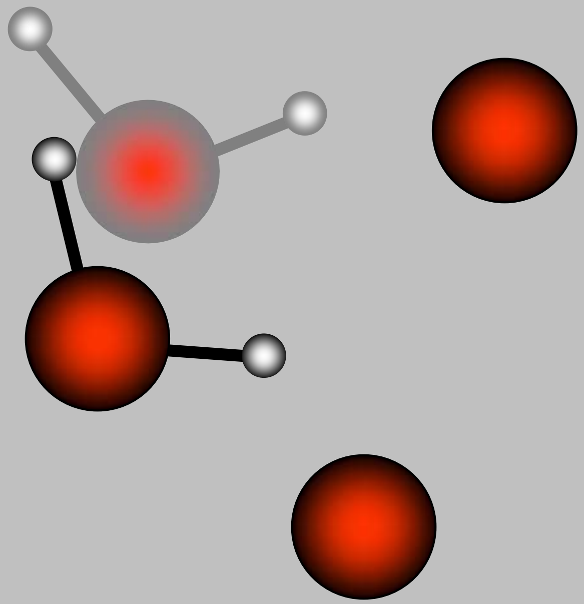
$\langle u^2\rangle^{1/2}$ Debye-Waller



Isotropic Rotation

τ_r
Rotational Correlation Time

r_g
Radius of Gyration



Jump Translational

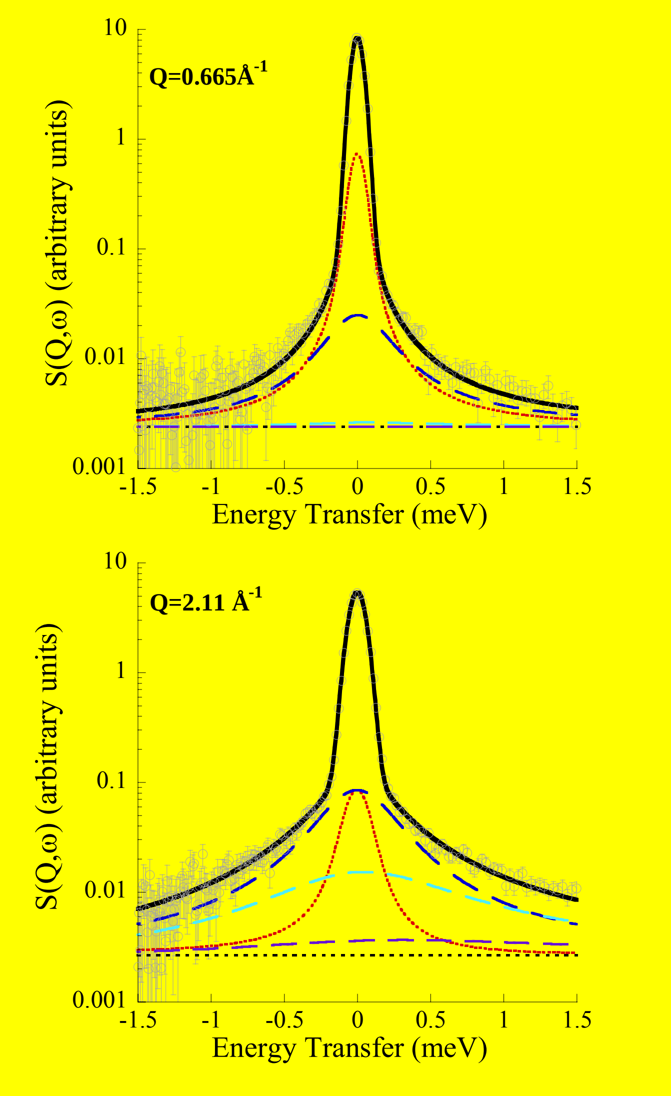
D_t
Translational Diffusion

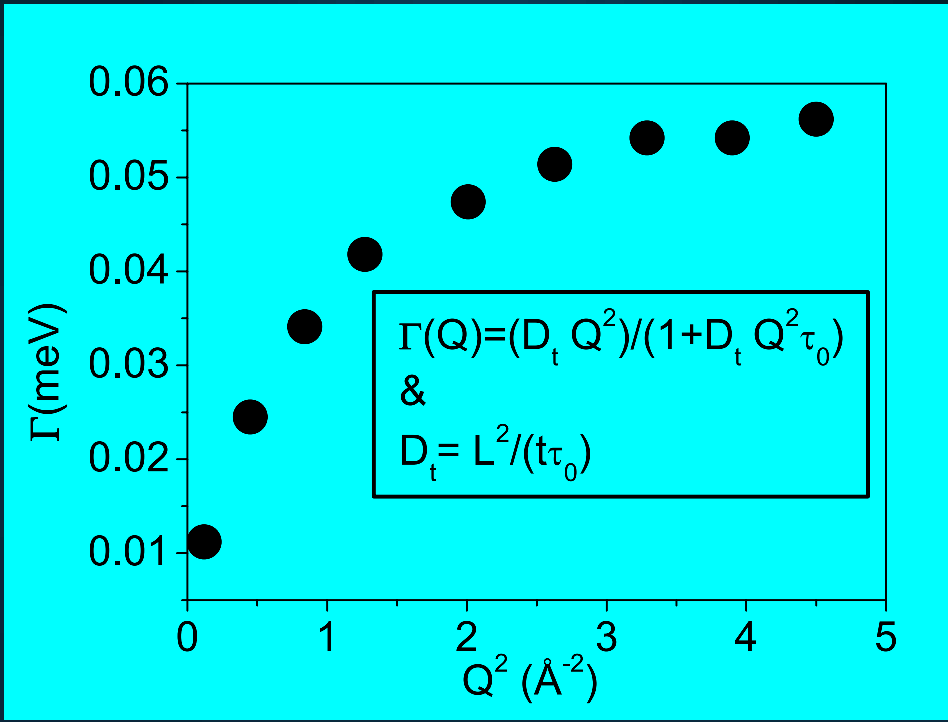
τ_t
Residence Time

L
Mean Jump Distance

$$S(Q,\omega) = \mathrm{e}^{-\langle u^2\rangle Q^2/3}\; T(Q,\omega)\otimes R(Q,\omega)$$

QENS results from NEAT



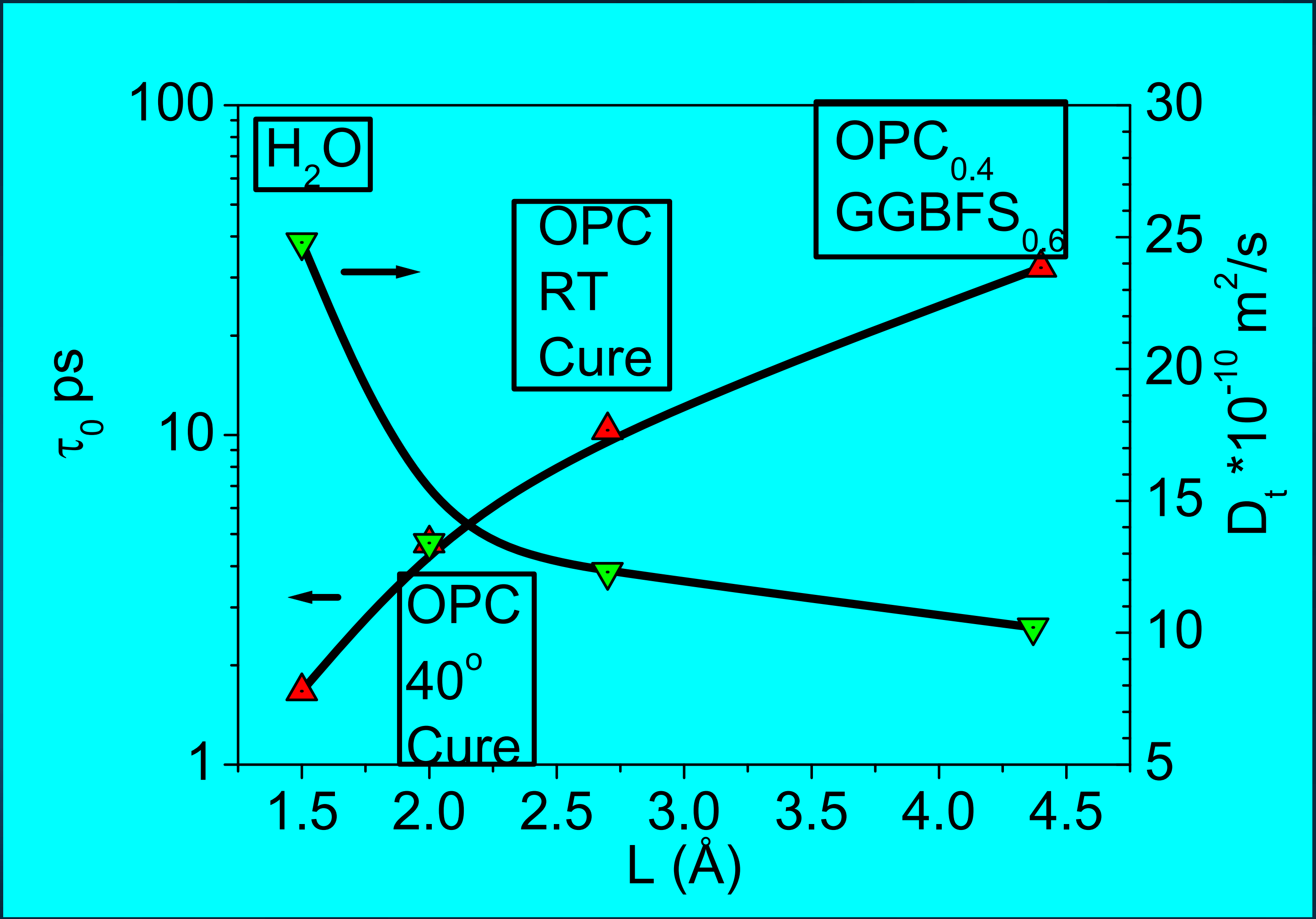


$$\Gamma(Q)=(D_t Q^2)/(1+D_t Q^2\tau_0)$$

&

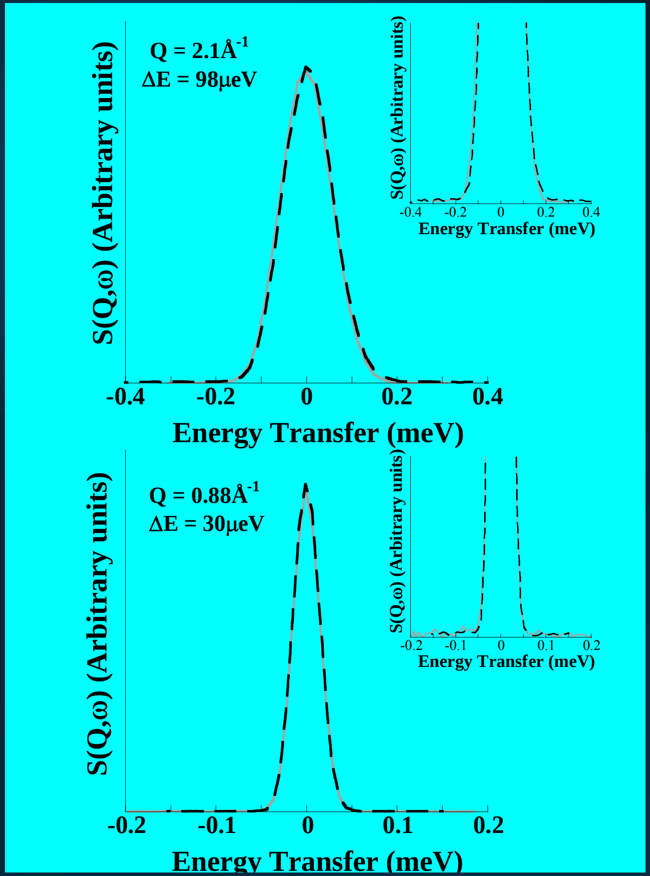
$$D_t = L^2/(t\tau_0)$$

QENS results from NEAT

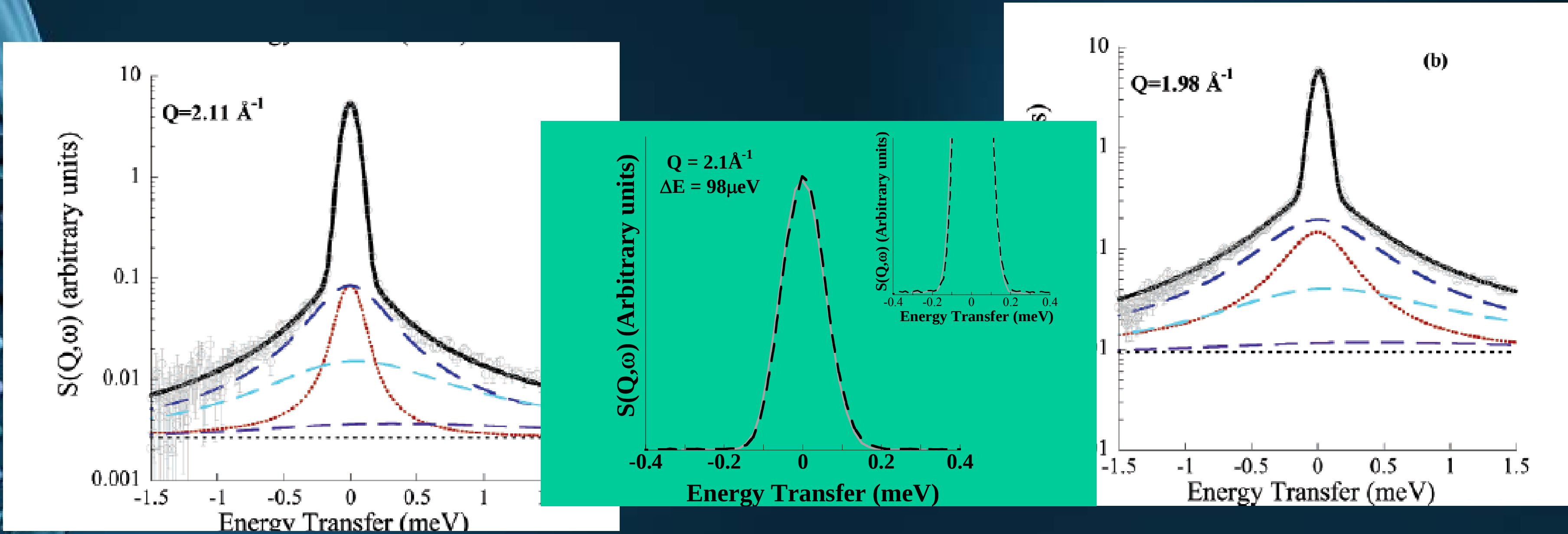


Chemically “bound” water

- Heating pastes at 105°C
  - removes both glassy and unbound water. Only chemically bound water remains.
  - No QE broadening after heating
  - Dynamics of chemically “bound” water molecules occurs on a timescale significantly slower than the pico-second.



QENS of water in paste before and after heating at 105^0C

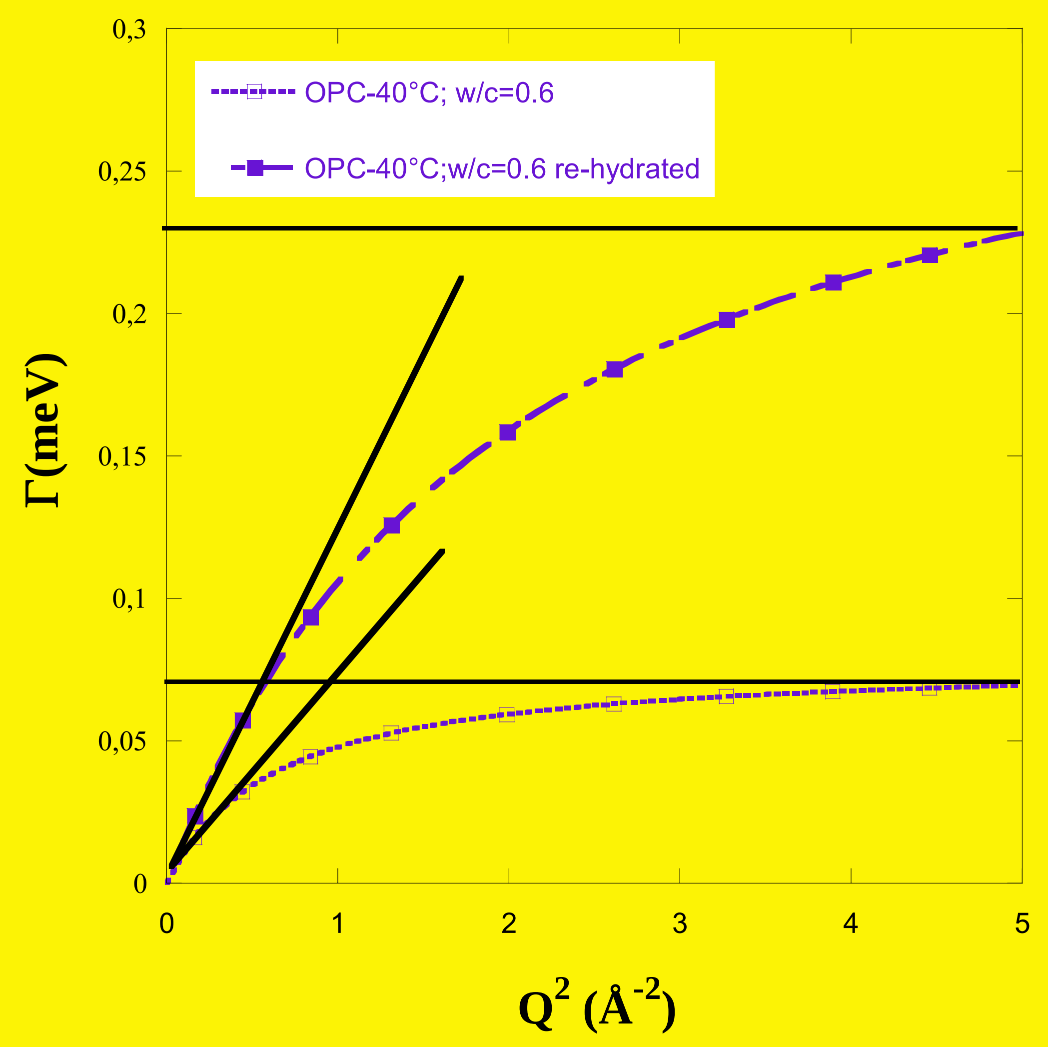


Before Heating After Heating After re-hydration

The red line (Representing translational diffusion) is about 5 times narrower on the left hand spectrum

QENS of water in paste before and after heating at 105^{0}C

- After re-hydration
  - Similar
    - To bulk
      - Water



Conclusions

- For well made cementitious based barriers
  - Cracking may dominate water transport
  - Water transport through capillary pores in cement paste can be estimated
- At low w/c ratios then water transport through gel pores should control water transport

Conclusions – Gel Pores

- Definition of water motion in gel pores is vital to understand (and measure) the durability in concrete.
- We need to understand
  - Time scale of diffusion through the gel pores
  - Time scale of diffusion into the gel pores
- We know more than we did when this work was started
- We know less than we would like
- We must characterise water motions occurring at different time scales