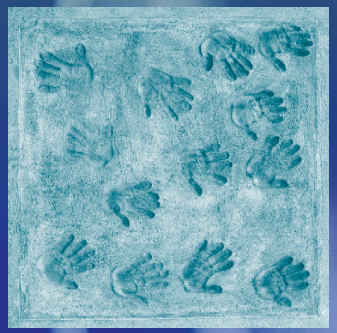
Australian Government

Australian Nuclear Science and Technology Organisation

Studying the Structure and Hydration Kinetics of Cement Systems in Real-time using Neutron Scattering



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Cement Research

- Many aspects of cement are unknown
- Cement is complex - and sensitive.
- Many factors affect the final product
- Controlling these factors is difficult.

- Understand these sensitivities ⇒ more robust material
- Optimizing chemical processes ⇒ better, cheaper product

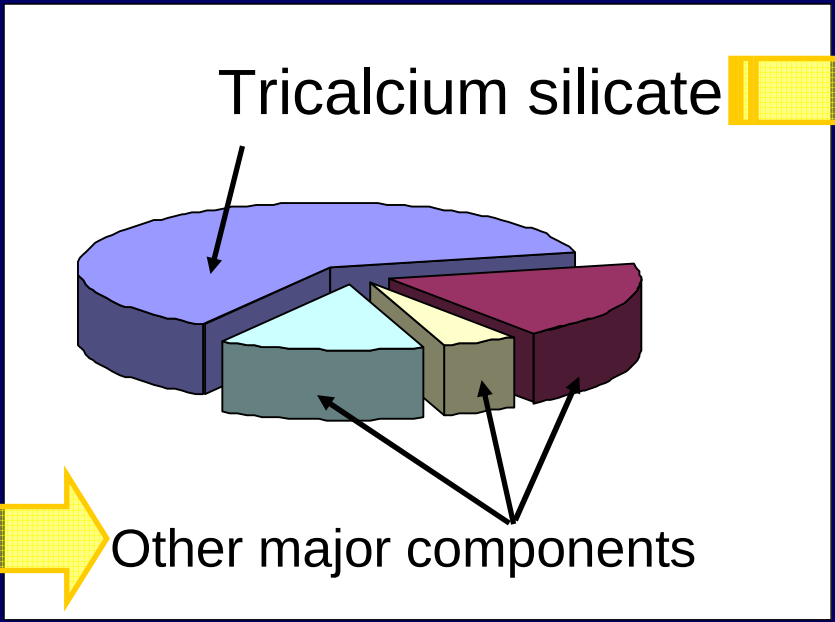
What is cement clinker?

- Tricalcium silicate is the main component of cement

Dicalcium silicate

Tricalcium aluminate

Tetracalcium aluminoferrite



> 50 %

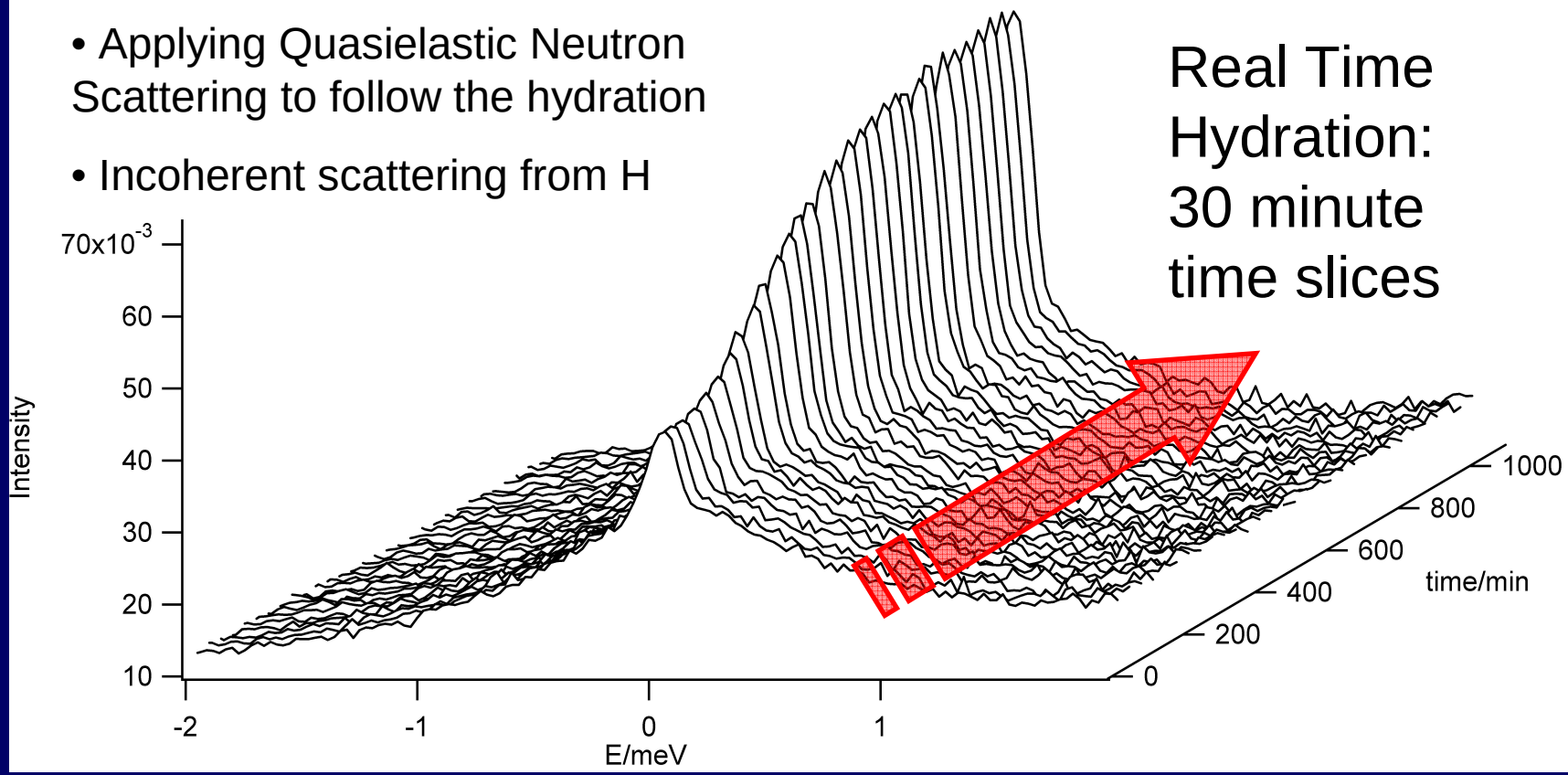
- Up to 90 %

Tricalcium silicate is the **fundamental hydraulic component** of cement

Hydration of Ca_3SiO_5: Following the hydrogen

$$Ca_3SiO_5 + (3 + y - x)H_2O \rightarrow (CaO)_x(SiO_2)(H_2O)_y + (3 - x)Ca(OH)_2$$

- Applying Quasielastic Neutron Scattering to follow the hydration
- Incoherent scattering from H

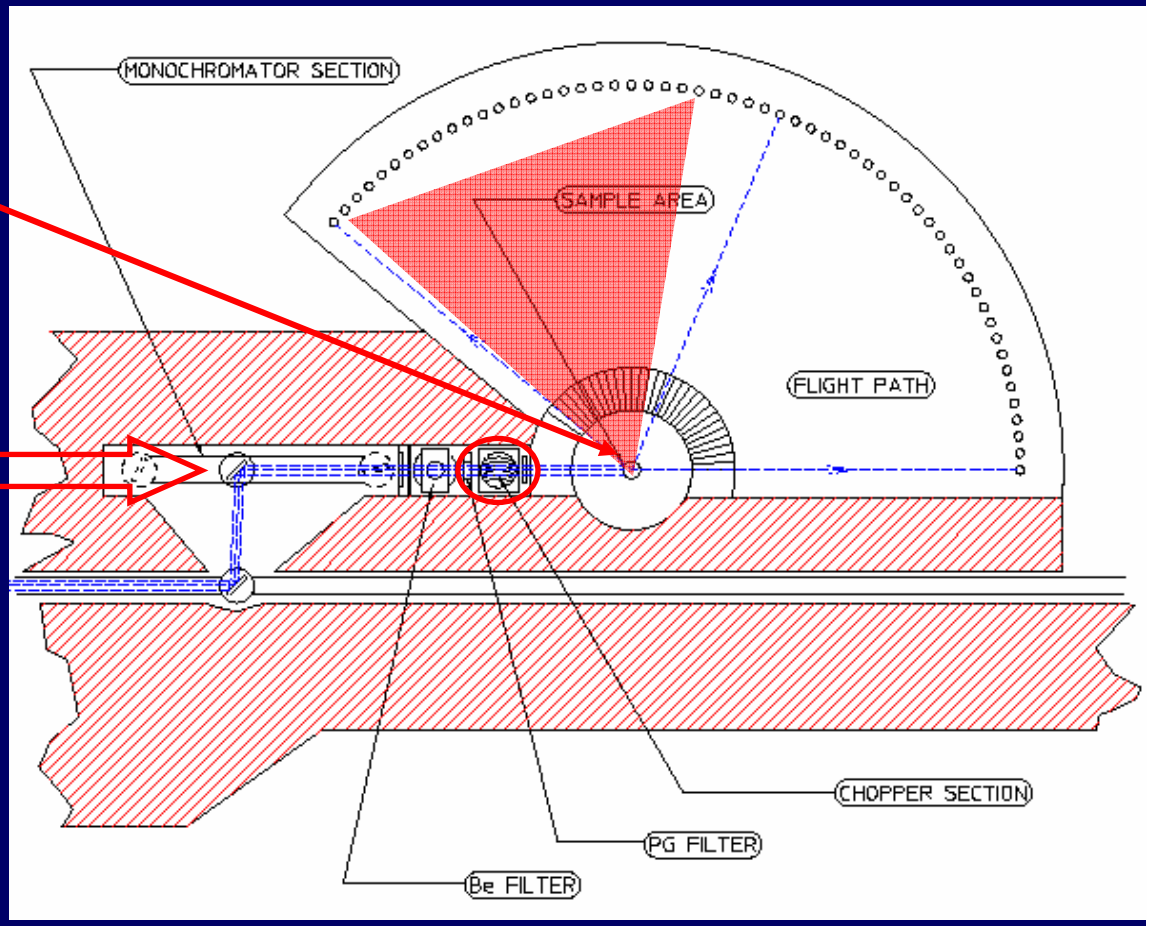


QENS: NIST Center for Neutron Research
Neutron time-of-flight Fermi Chopper Spectrometer (FCS)

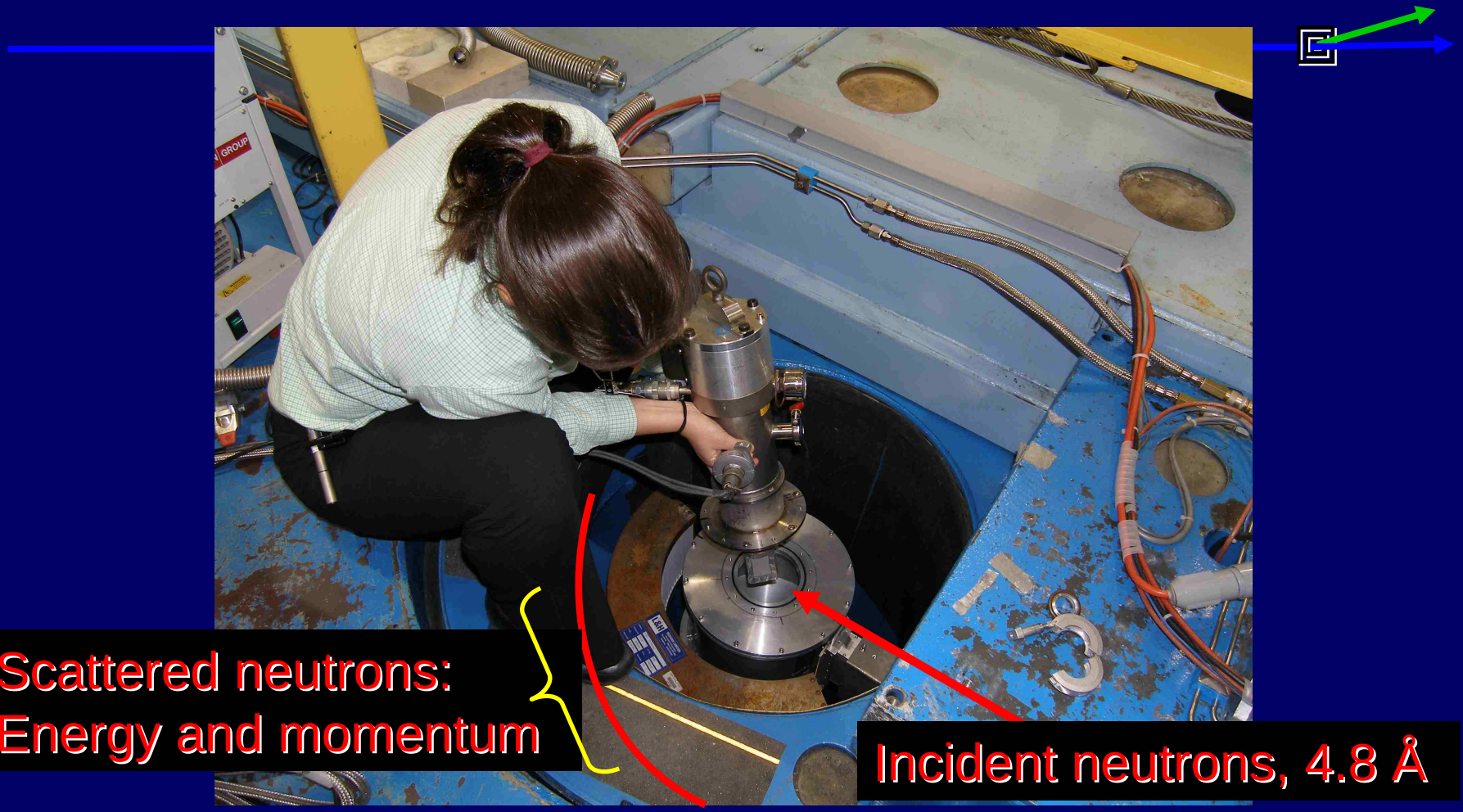
- Sample 45 º to the beam
- Reflection geometry data only used

- Incident beam λ = 4.8 Å
- Beam is pulsed by a chopper – timestamp

- Scattered neutrons arrive at a bank of detectors: 2.29 m
- The detectors record the neutron arrival time



QENS data collection & treatment

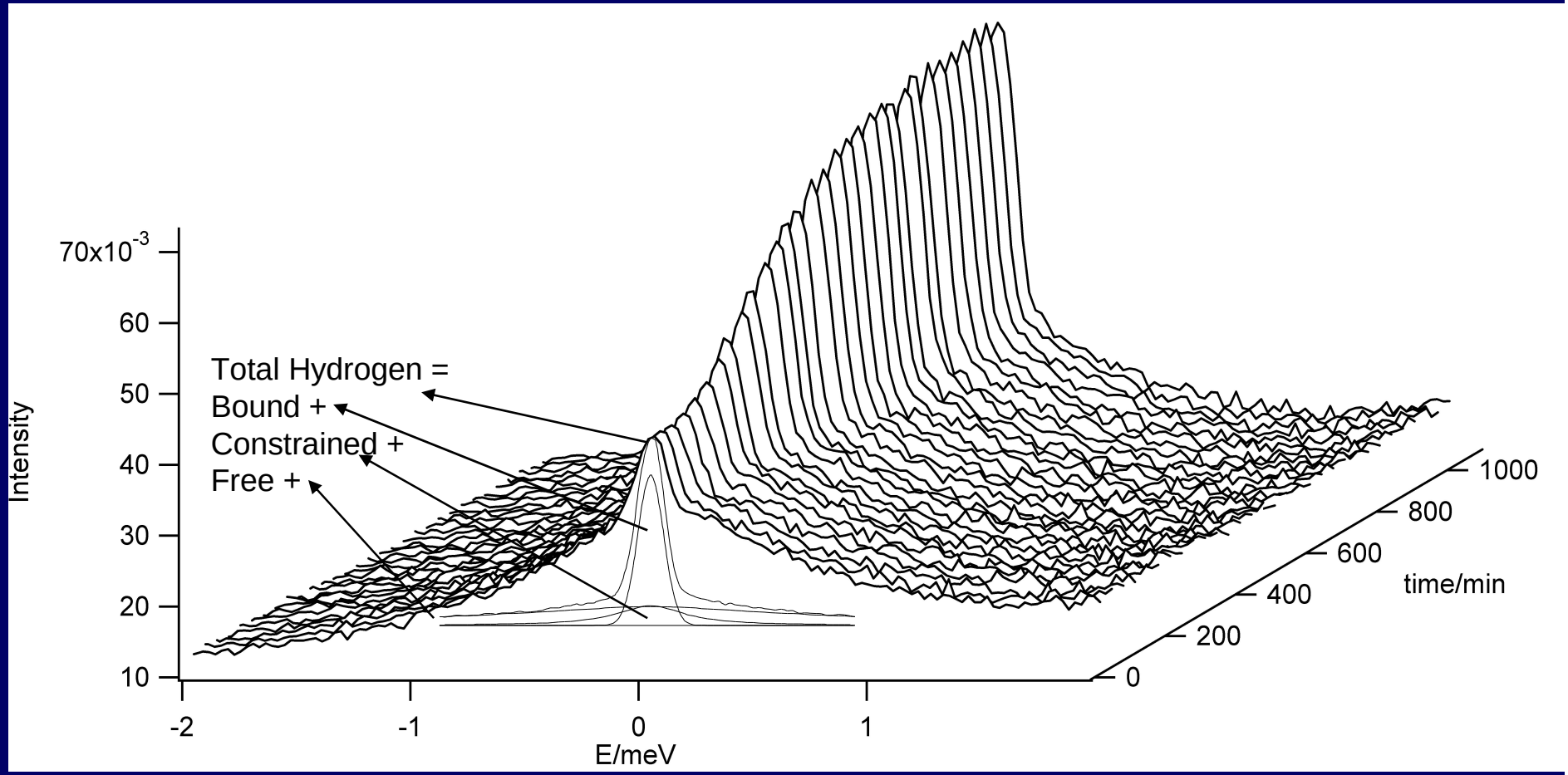


At high **Q,** QENS spectrum is **Q** independent.
Data averaged over a **Q** range (1.9–2.4 $Å^{-1}$):

- focus on rotational dynamics of water.
- increase the signal-to-noise ratio

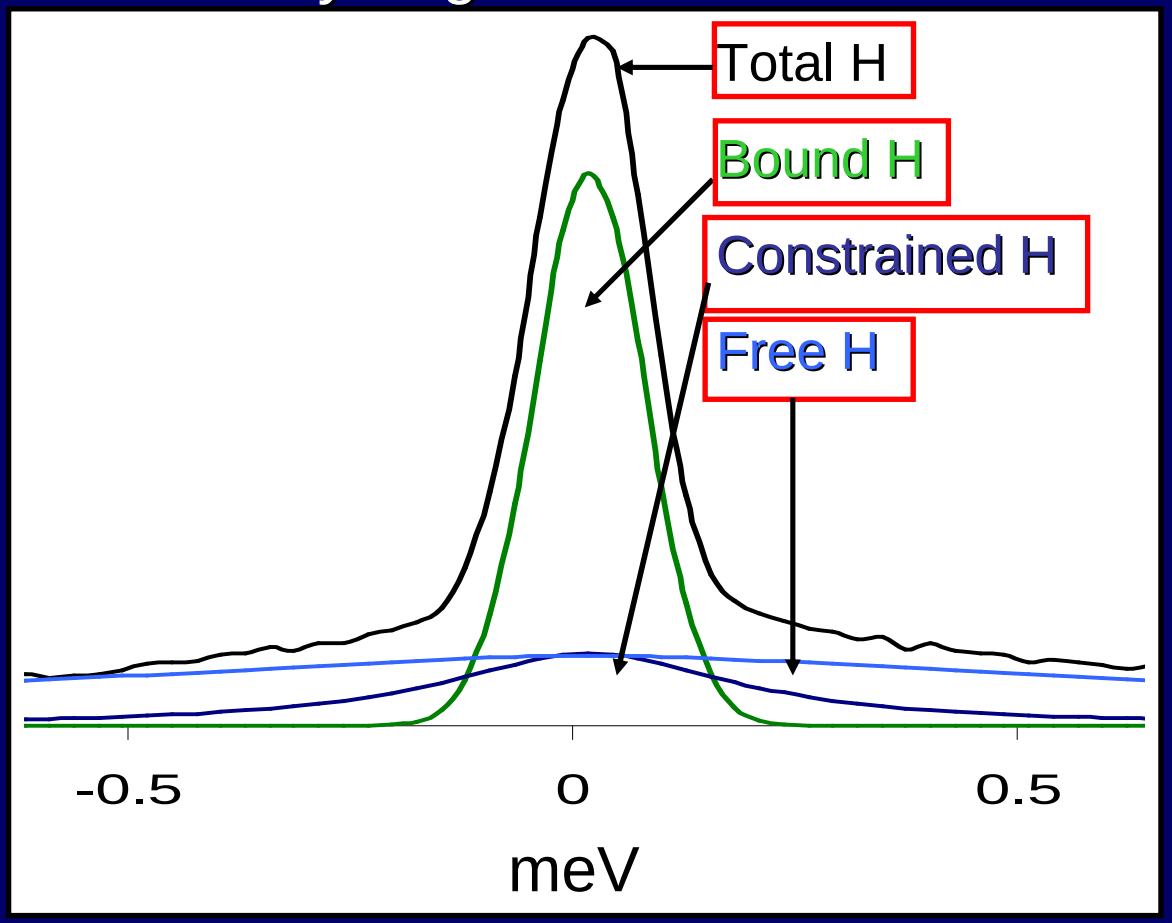
QENS: Following the hydrogen

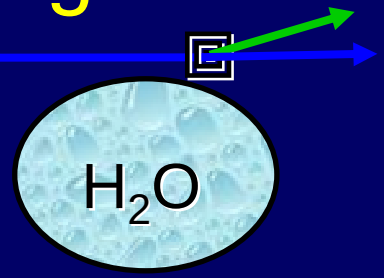
$$Ca_3SiO_5 + (3 + y - x)H_2O \rightarrow (CaO)_x(SiO_2)(H_2O)_y + (3 - x)Ca(OH)_2$$



States of hydrogen: Profile fitting

- Contribution to each QENS spectrum: States of hydrogen





H Adsorbed on surfaces

Products

- Fitted from -2 to 2 meV

Quantitative determination of H: profile fitting

Integrated areas: Quantitative information for each H state

- Very wide and wide Lorentzians: Free H
- Narrow Lorentzian: Constrained H
- Gaussian: Bound H

$$S(\mathbf{Q},\omega) = \frac{B}{\sqrt{2\pi(W_B/2.354)^2}} e^{-\frac{1}{2}\left(\frac{x-x_0}{W_B/2.354}\right)^2} + \frac{W_C}{2\pi} \frac{C}{(x-x_0)^2 + (W_C/2)^2} + \frac{W_{F1}}{2\pi} \frac{F_1}{(x-x_0)^2 + (W_{F1}/2)^2} + \frac{W_{F2}}{2\pi} \frac{F_2}{(x-x_0)^2 + (W_{F2}/2)^2}$$

x = energy transfer and x_0 is the peak center – constrained to be the same

W_B: Fixed to instrument resolution (0.147 meV)

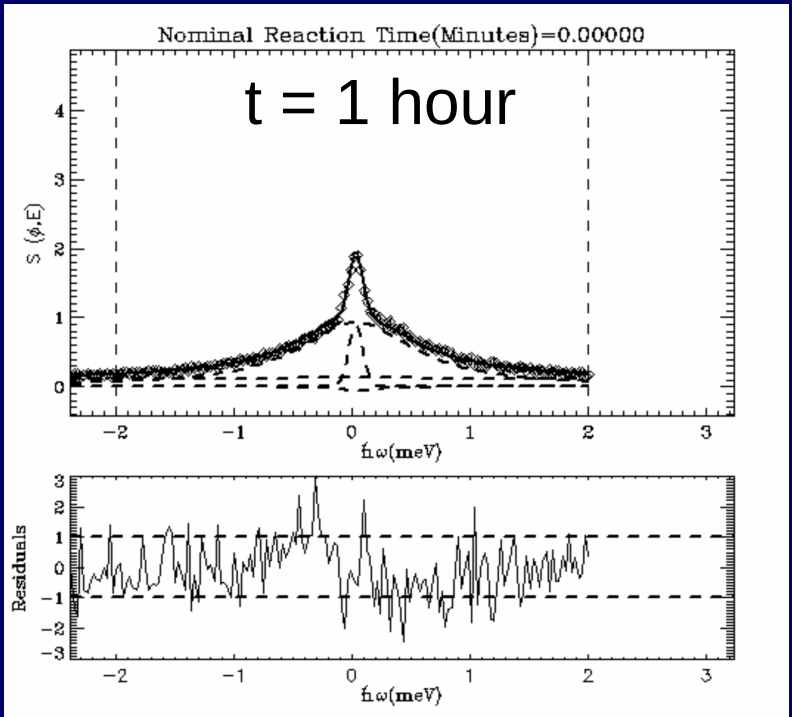
W_C: Determined for an average of the last 7 spectra

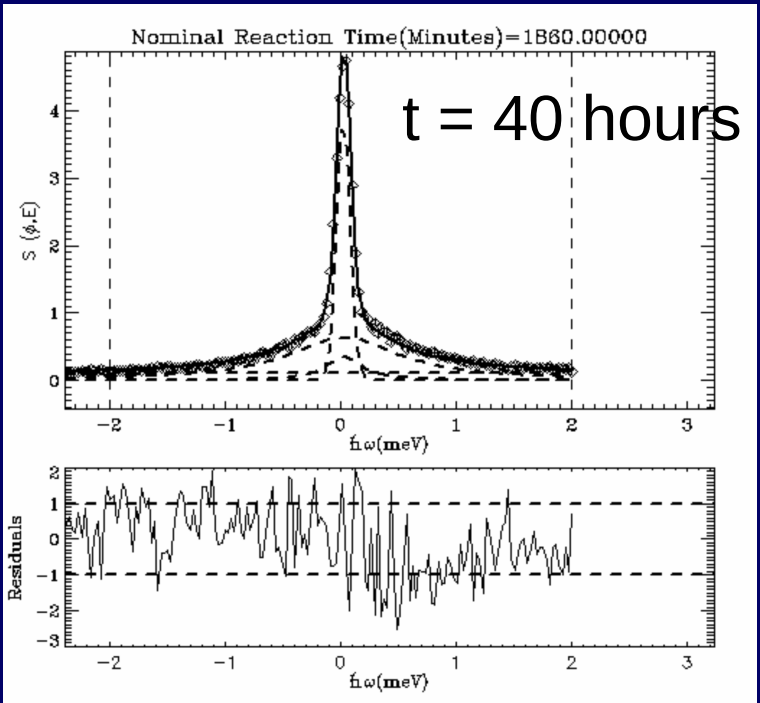
W_{F1} and W_{F2}: Determined from an average of the first 7 spectra

} Fixed

QENS profile fitting: Bound Water Index

- Can quantitatively derive the H in each state



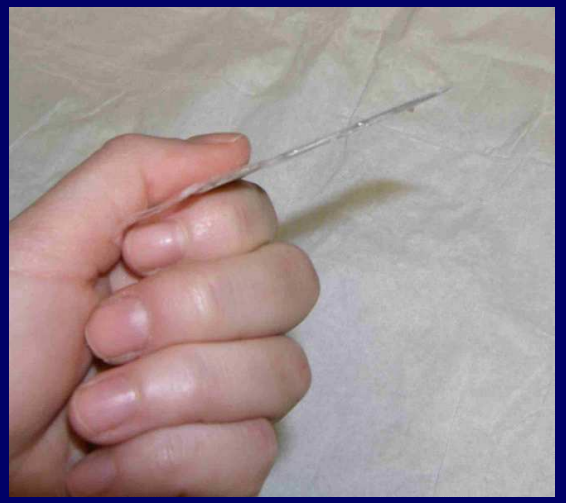


$$BWI = \frac{\text{Bound + Constrained H}}{\text{Total H}}$$

Allows the hydration to be followed

Experimental: QENS sample preparation

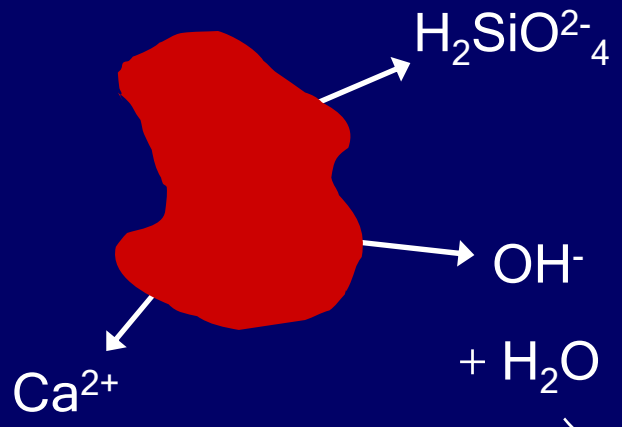
- Water to solid mass ratio of 0.4
- Mixed by hand for 3 minutes
- Sealed in teflon film



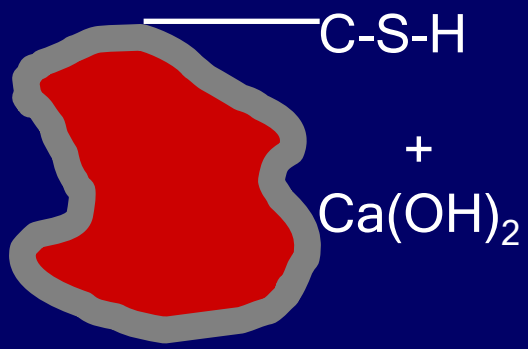
- Placed in can, sealed using In
- Can placed in a closed cycle He refrigerator, 30 °C.
- Data continuously collected for 50 hours on Fermi Chopper neutron Spectrometer (FCS).

Tricalcium silicate hydration

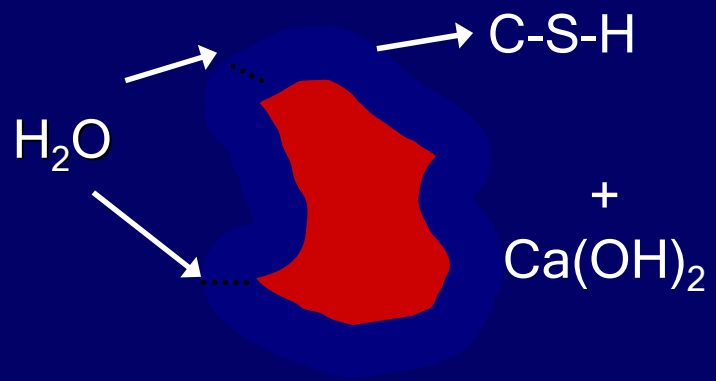
1. Induction and dissolution



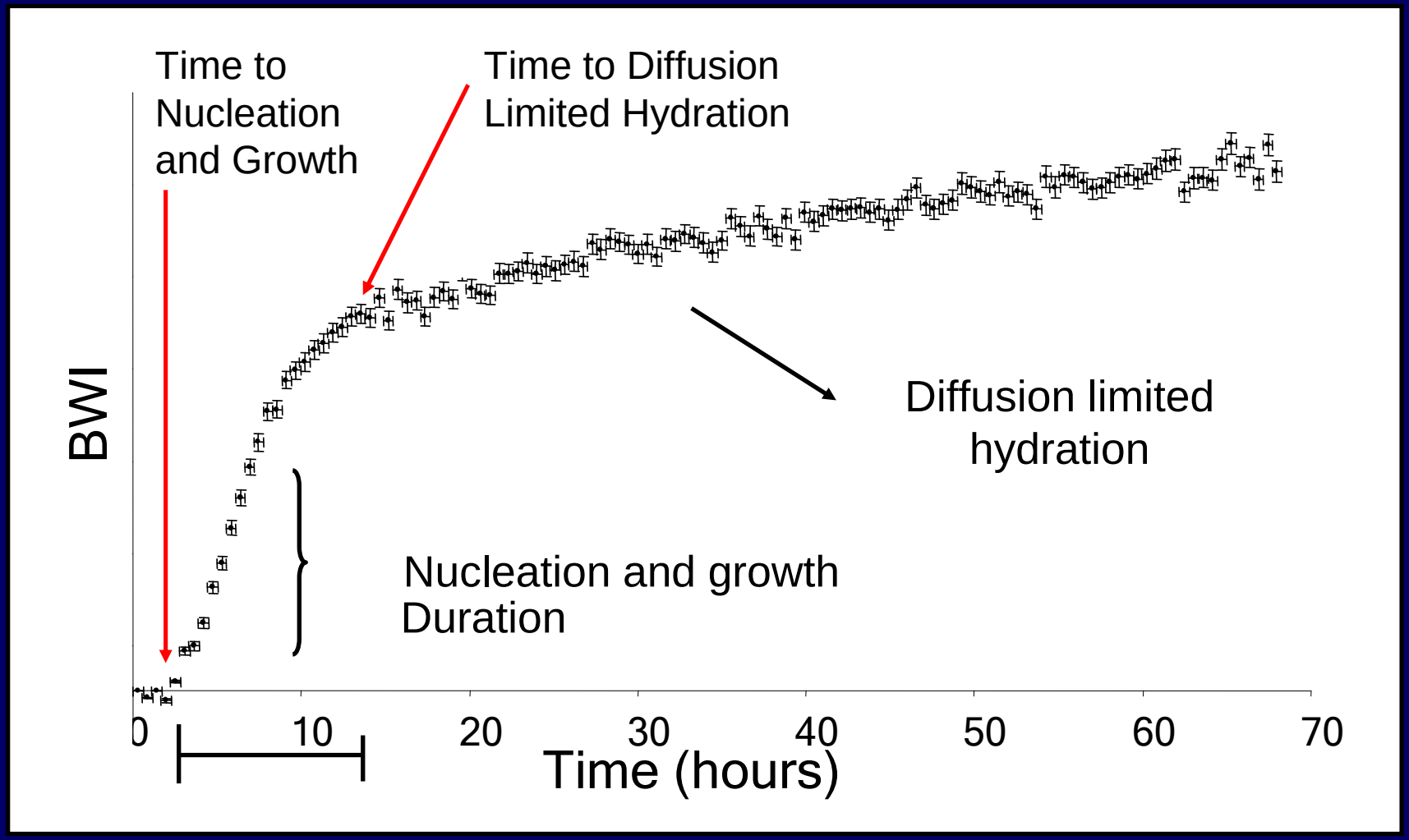
2. Nucleation and Growth



3. Diffusion limited hydration



Following hydration: BWI with time



Tricalcium silicate polymorphism

- On heating unit cell expands, then phase transitions occur

$$T_1 \xrightarrow[620\,℃]{} T_2 \xrightarrow[920\,℃]{} T_3 \xrightarrow[980\,℃]{} M_1 \xrightarrow[990\,℃]{} M_2 \xrightarrow[1060\,℃]{} M_3 \xrightarrow[1090\,℃]{} R$$

- Polymorphs stabilized in clinker at RT by impurity ions

Different forms exhibit differing strength!

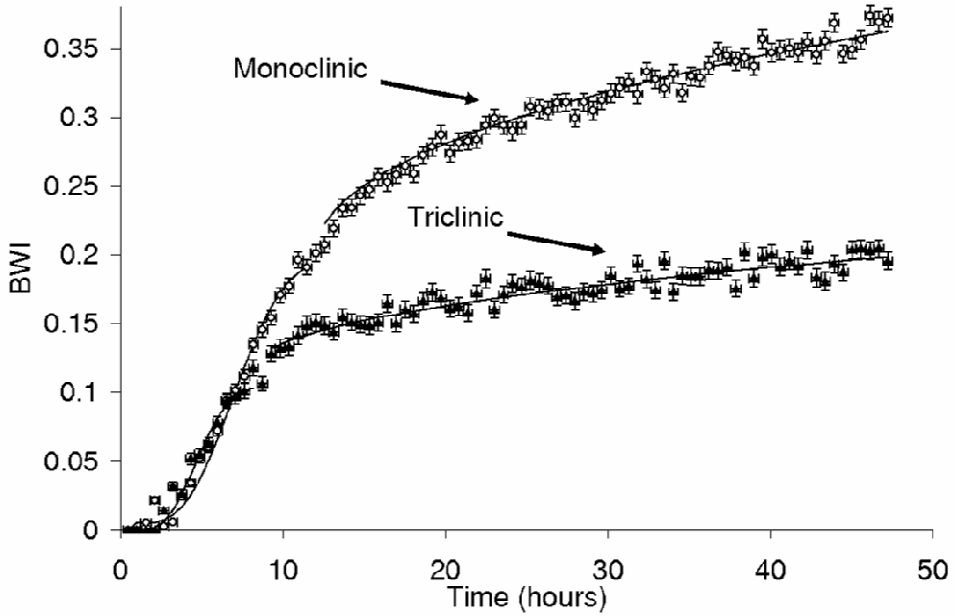
- Compressive strength has been linked to:

→ Crystal type - symmetry

→ Type of stabilizing ion

QENS: Hydration of tricalcium silicate forms

QENS data and hydration models for Mg stabilized T_1 and M_3 C_3S



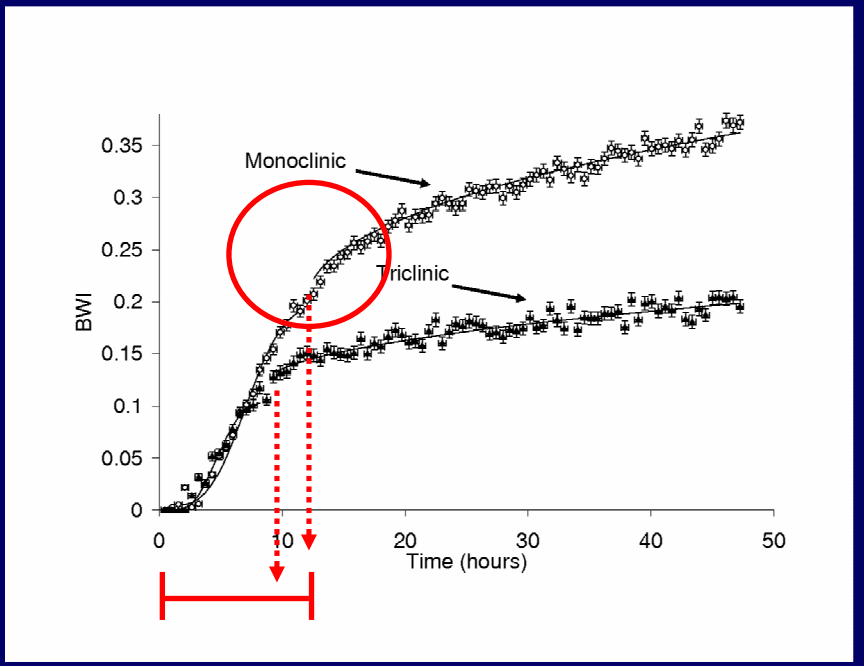
- Significant differences between hydration behaviors
- Monoclinic sample has half the surface area

Peterson, V. K. *et al. Chem. Phys. 326*, 2006.

QENS: Hydration of C_3S forms

QENS data and hydration models for Mg stabilized T_1 and M_3 C_3S

	Time to NG (hours)	Time to DL (hours)	Rate of product formation (dBWI/dt)
T_1	1.3	8.2	0.18
M_3	1.6	12	0.20



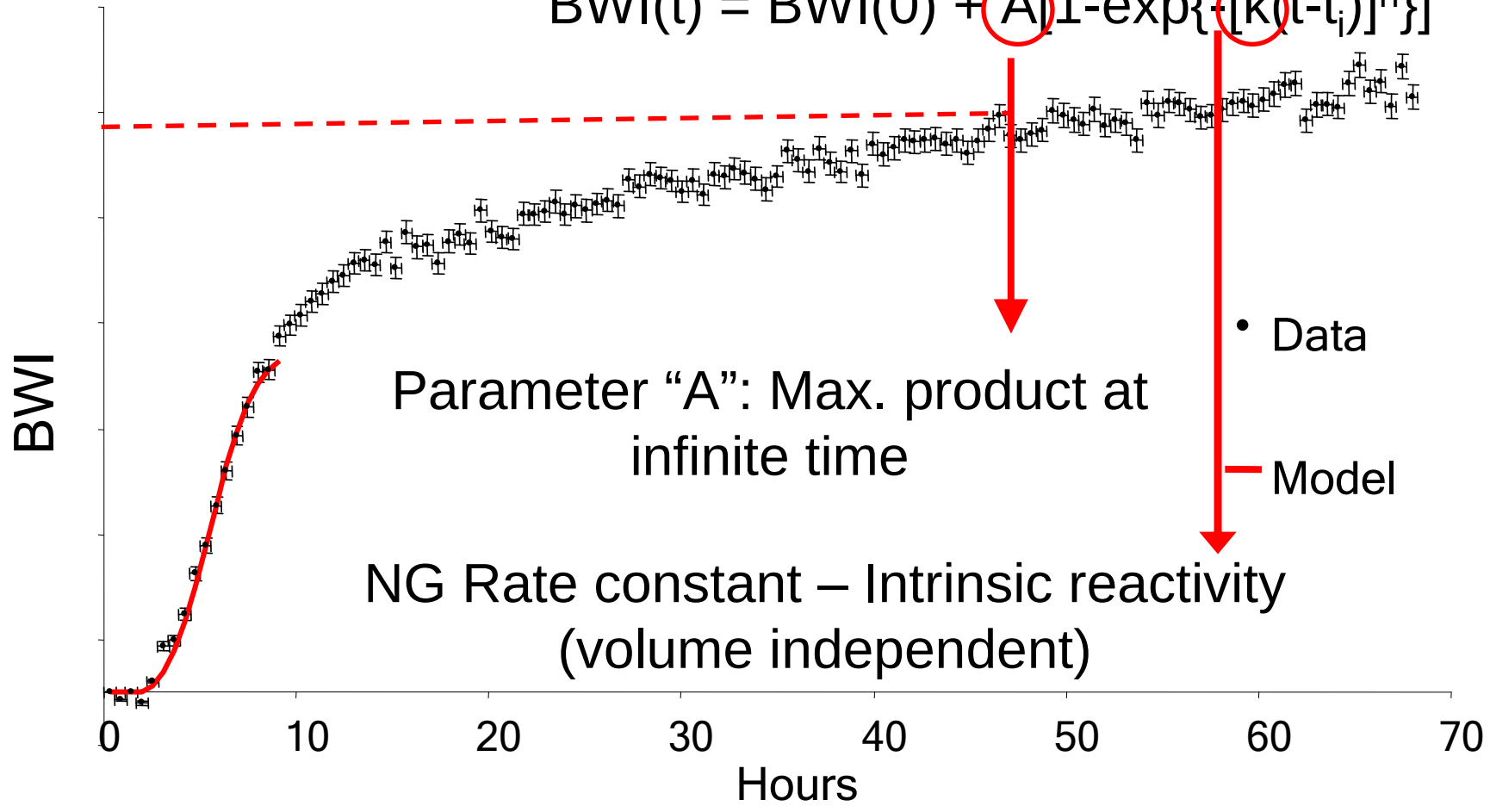
- Monoclinic has a longer Nucleation and Growth (NG) period.
- Broad tapering into the Diffusion Limited hydration from the NG period is typical for a broader particle size distribution (consistent with PSD).

Peterson, V. K. *et al. Chem. Phys. 326,* 2006.

Kinetic parameters of the hydration

Modeling of the nucleation and growth period:

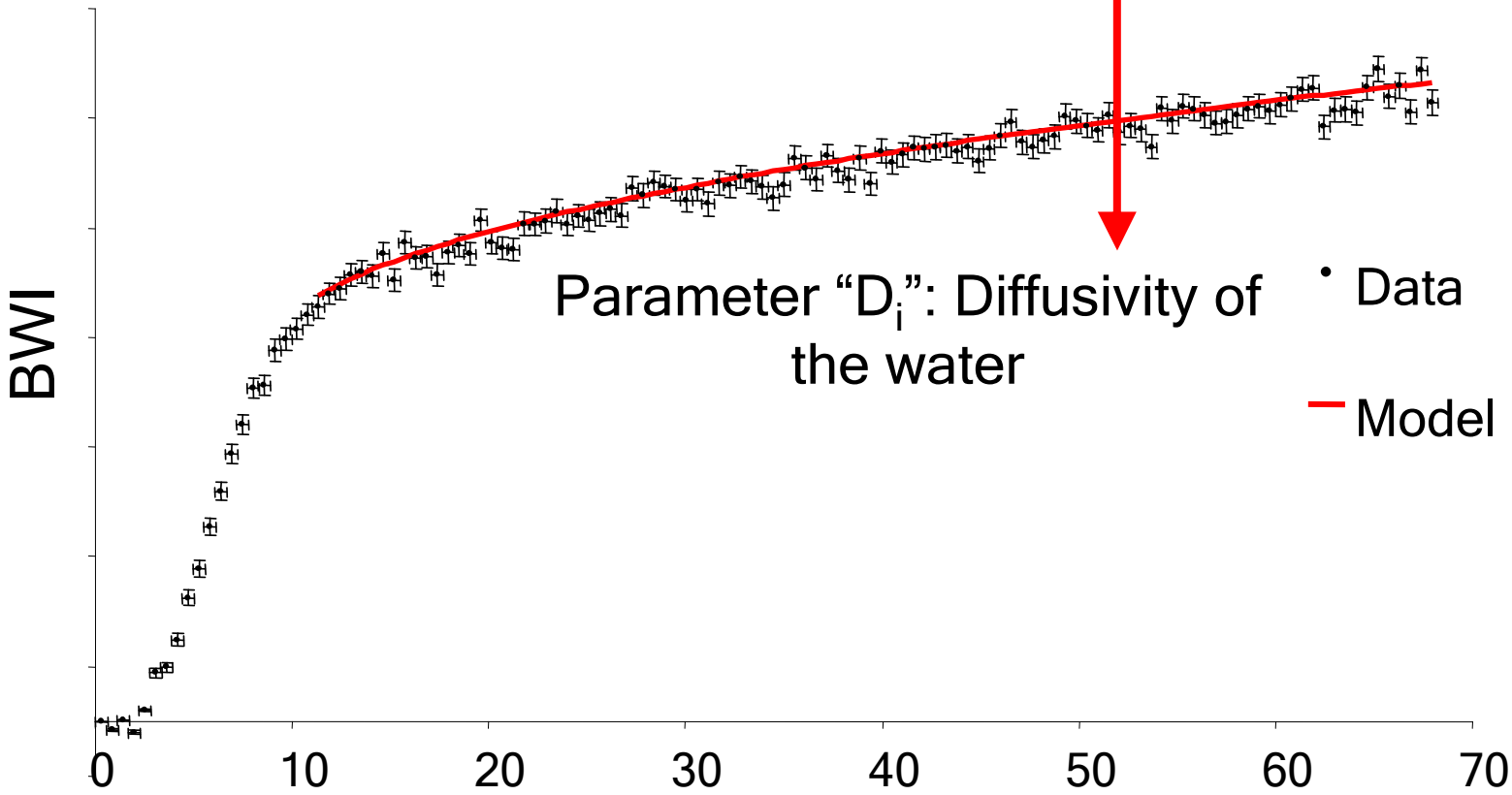
$$BWI(t) = BWI(0) + A[1-\exp\{-[k(t-t_i)]^n\}]$$



Kinetic parameters of the hydration

Modeling of the diffusion limited period:

$$BWI(t) = BWI(0) + [1-\{[1-BWI(t_d)]^{1/3} - (R^{-1})(2D_i)^{1/2}(t-t_d)^{1/2}\}^3]$$



QENS: Hydration of C_3S forms

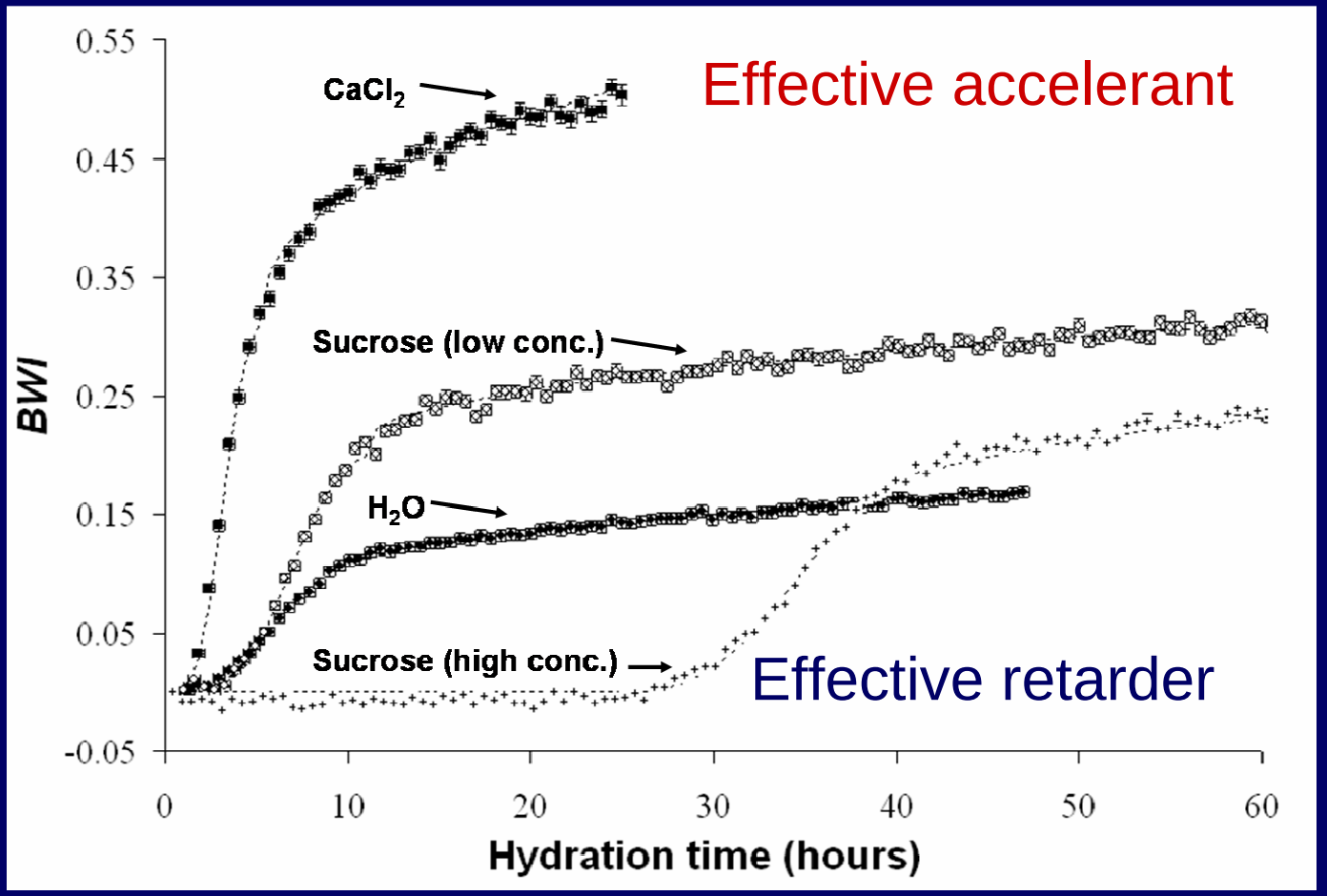
QENS data and hydration models for Mg stabilized T_1 and M_3 C_3S

	A	k ($hours^{-1}$)	D_i ($10^{-15}m^2h^{-1}$)
T_1	0.1	0.25	0.3
M_3	0.2	0.16	19

- Monoclinic:
  - Intrinsically less reactive – the way in which protons are accepted by the structure
  - Morphological effect - significant permeability of material.
  - Slower reaction and higher permeability produces more product (longer NG period)

Peterson, V. K. *et al. Chem. Phys. 326,* 2006.

QENS: Effect of additives on C_3S hydration

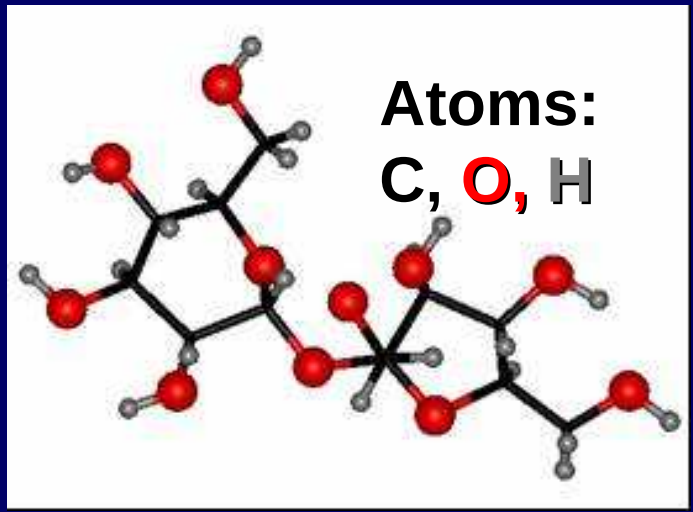


Sucrose: known hydration retarder

- Increases duration of induction period
- Some suggestion of "delayed accelerator"

Hypothesis:

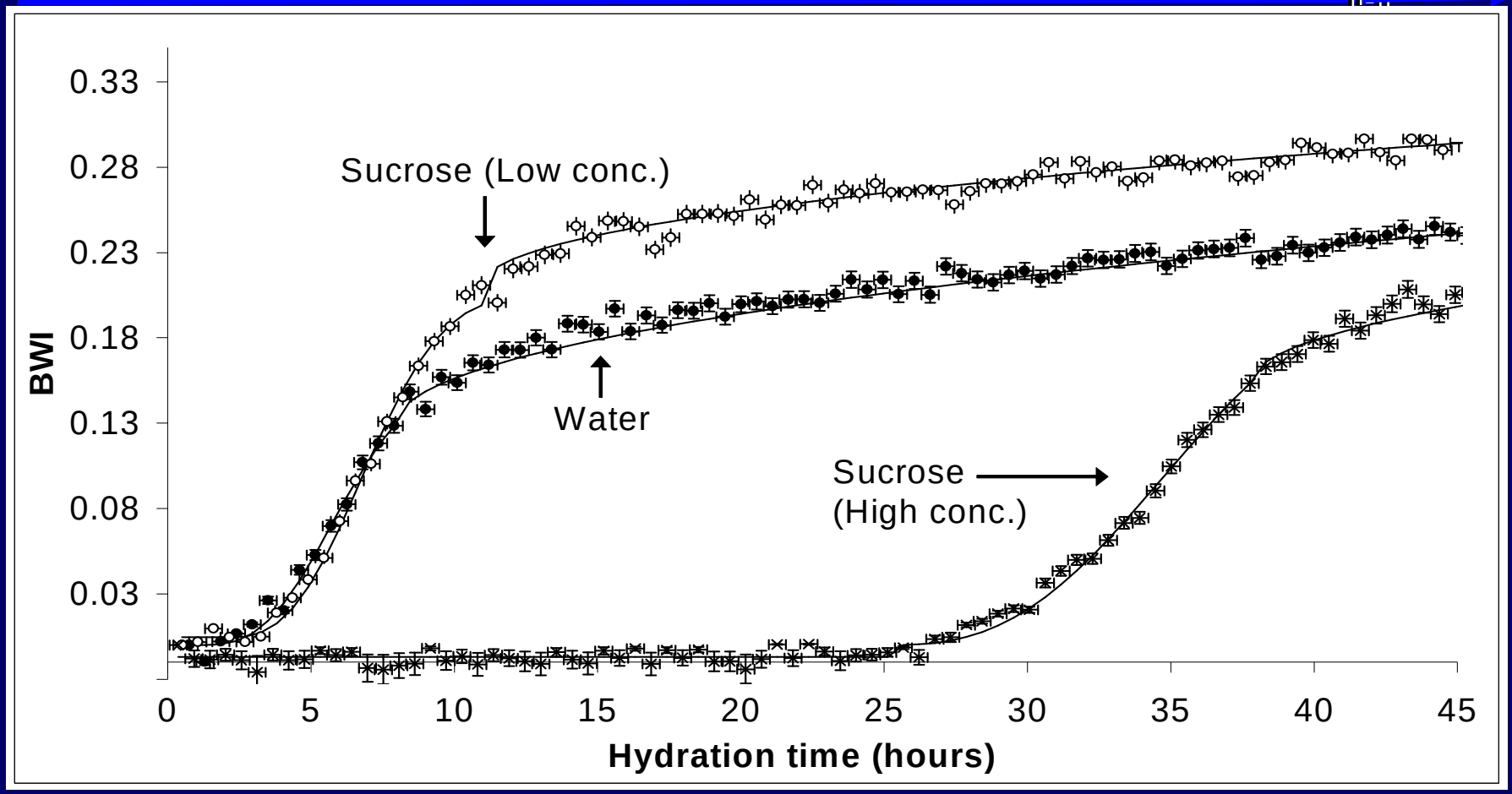
- Formation of a half-salt that poisons surfaces, disallowing nucleation.
- Intermediate ability to form this half-salt.
- Stable: does not undergo ring-opening (degradation) in the alkaline paste



- Other factors
  - Chelates with Ca^{2+} - depressing solution Ca^{2+}.
  - Solubilizes silicate in hydrating cement.

Mechanisms of effects are uncertain, particularly details on kinetics

Sucrose - QENS



Triclinic tricalcium silicate; H_2O:cement = 0.4 at 30 °C
0.01 and 0.04 wt. % sucrose

Sucrose – Kinetic Parameters

	k (h^{-1})	D_i (x $10^{-15} m^2 h^{-1}$)	t_i (h)	t_d (h)	Nucleation and Growth duration (h)
H_2O	0.19	0.60	1.3	7.9	6.6
Low % Sucrose	0.18	0.40	2.2	11.0	8.8
High % Sucrose	0.08	0.48	25.2	37.8	12.6

- Retards induction period
- Nucleation and growth rate constant reduces
- Lengthens the nucleation and growth period
- Slightly denser product, consistent with slower production

➢ Consistent with the literature, commensurate with conc. except:
  - No evidence for accelerated reaction.
  - What about the “delayed acceleration” ?

Sucrose – Kinetic Parameters

	A	d(*BWI*)/dt (h^{-1})	k (h^{-1})	D_i (x $10^{-15} m^2 h^{-1}$)	t_i (h)	t_d (h)	Nucleation and Growth duration (h)
H_2O	0.155	0.022	0.19	0.60	1.3	7.9	6.6
Low % Sucrose	0.201	0.030	0.18	0.40	2.2	11.0	8.8
High % Sucrose	0.212	0.020	0.08	0.48	25.2	37.8	12.6

- More product
- Higher rate of formation during NG

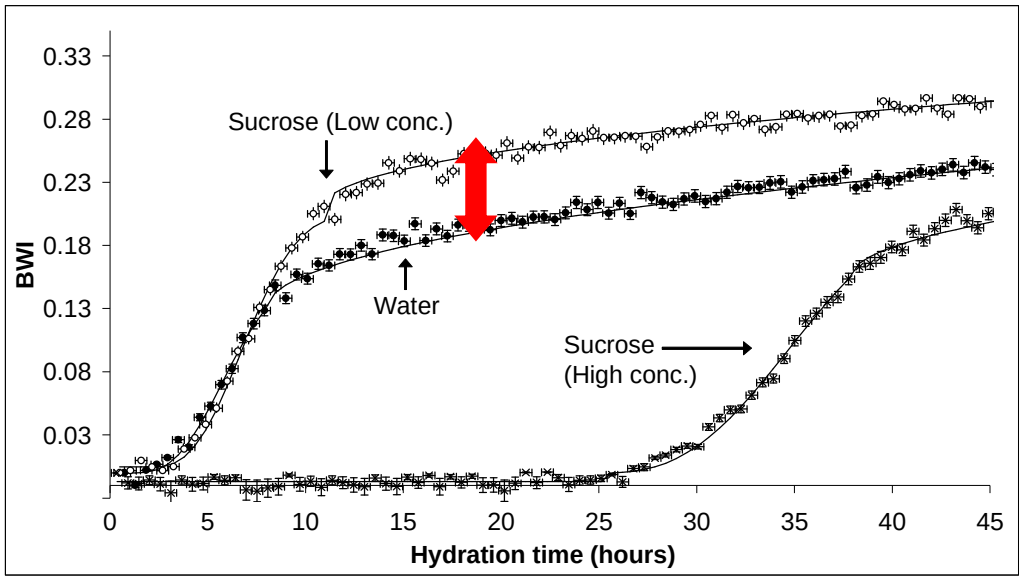
} Delayed "acceleration"

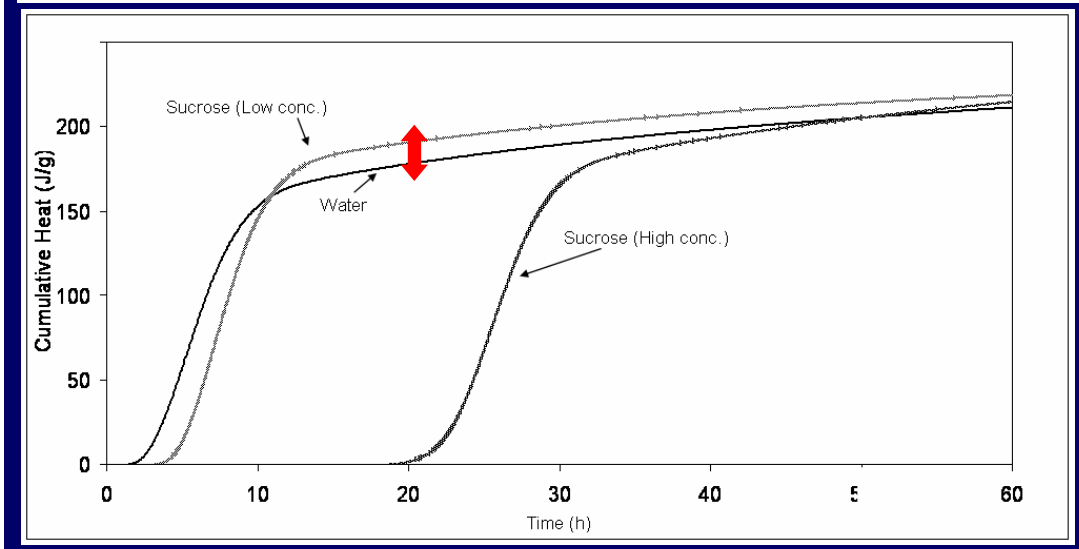
- Higher rate of formation only with low sucrose conc.
  - k is the instrinsic reactivity – volume independent
  - d(BWI)/dt is volume dependent (peaks at Akn)

Hypothesis: Solubilization of the silicate species

- Increased ions in solution (more volume, ↑ d(BWI)/dt)
- Competes with the rate constant (k) reduction
- Commensurate with sucrose concentration

Comparison of Calorimetry and QENS

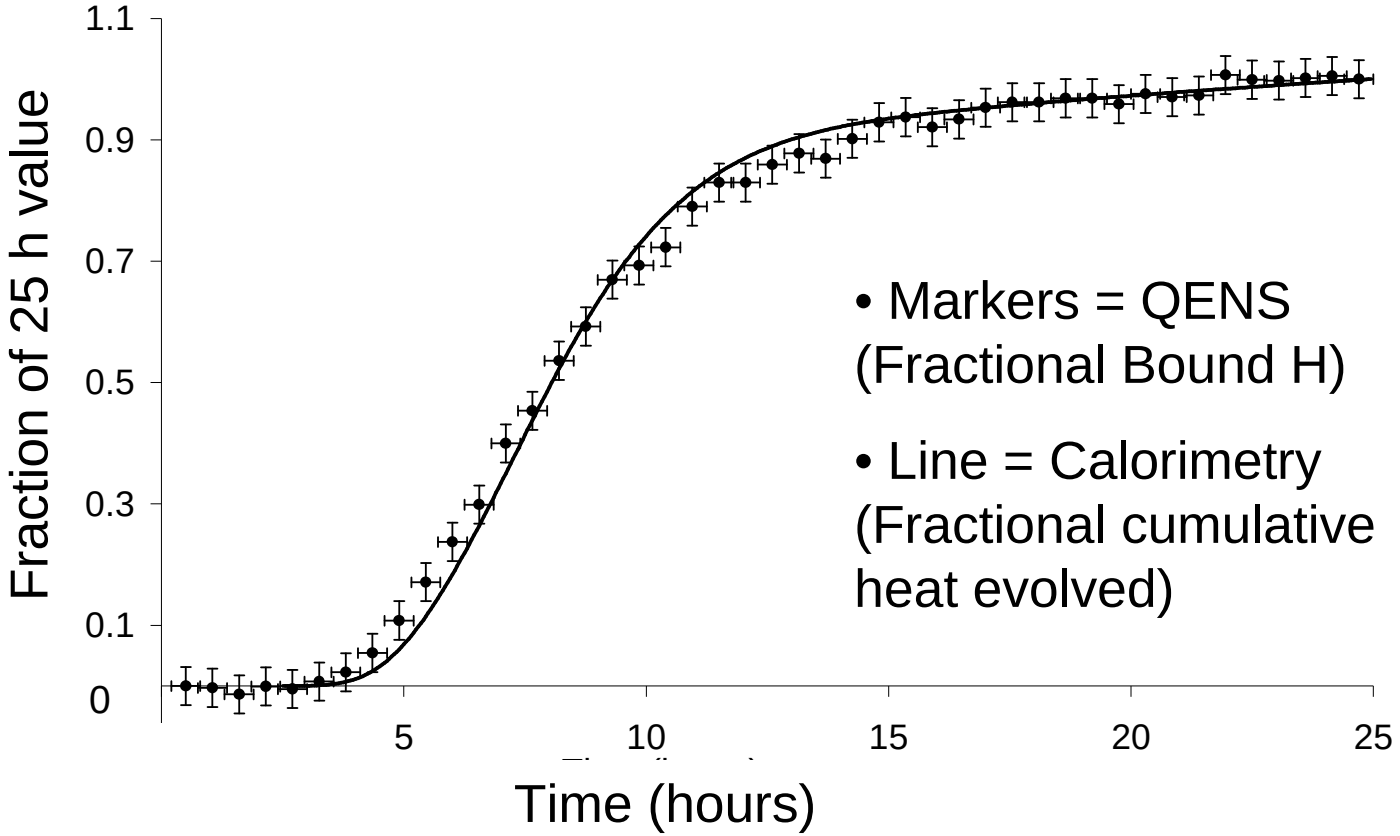




- Both QENS and calorimetry find more product at the end of NG after hydration with a low sucrose conc.
- The % increase was more with QENS than with calorimetry
- Calorimetry observes the tricalcium silicate dissolution

Calorimetry

- Measures the heat evolved during reaction
- Has been correlated to QENS results for the bound hydrogen component - reflects chemically bound H associated with $Ca(OH)_2$ and C-S-H



• QENS measures constrained and bound H

• Constrained H associated with a C-S-H phase in which water is loosely attached

Small Angle Neutron Scattering and QENS

➢ SANS for hydrating tricalcium silicate: Correlates the constrained H population (QENS) with a high surface area C-S-H phase

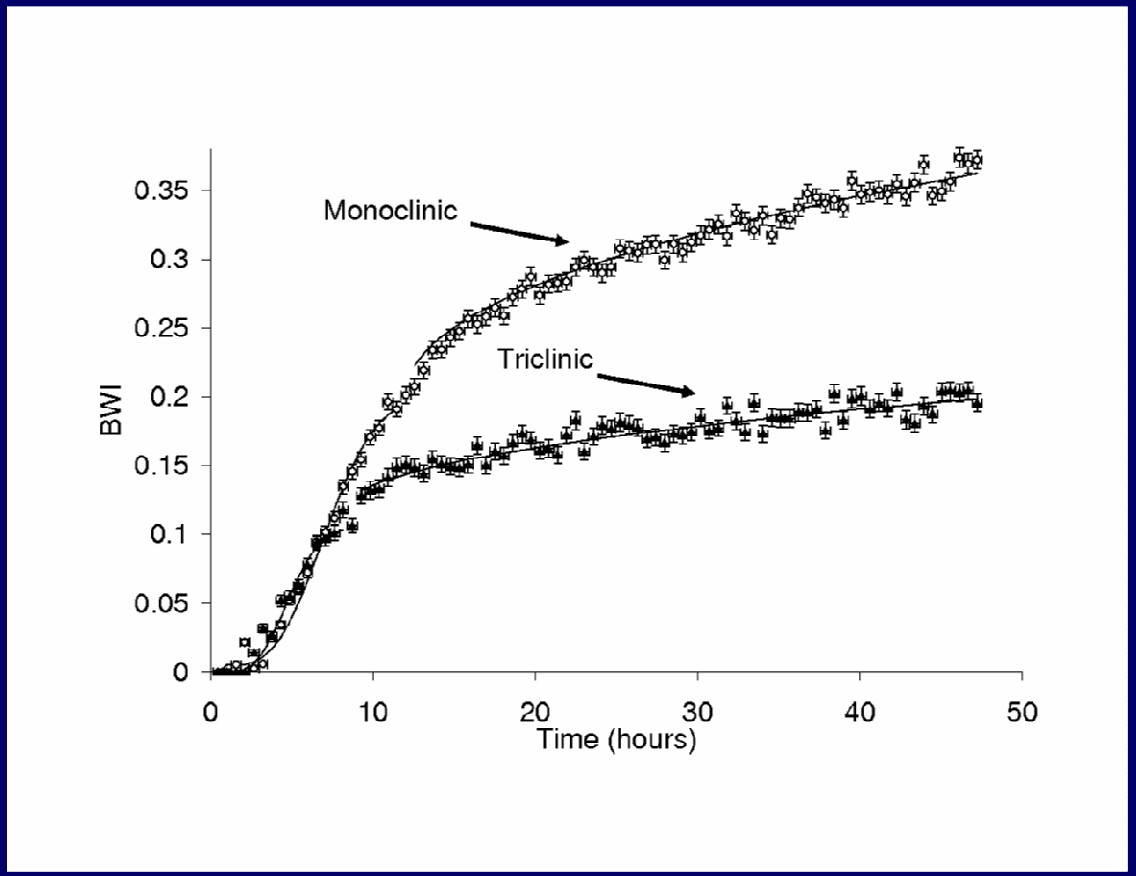
- Evidence for two different C-S-H morphologies:
  - Chemically bound H (H_S) phase = $C_{1.7}SH_{S(1.6)}$
  - Constrained and chemically bound H (H_T) phase = $C_{1.7}SH_{T2.7}$

Results suggest sucrose induces a high-surface area C-S-H phase in which water is loosely bound

Soft Synchrotron X-ray Transmission Microscopy results show a high surface area C-S-H with unique morphology
(Juenger et al, Proc. of the 11th Int. Cong. Chem. Cem., 2003)

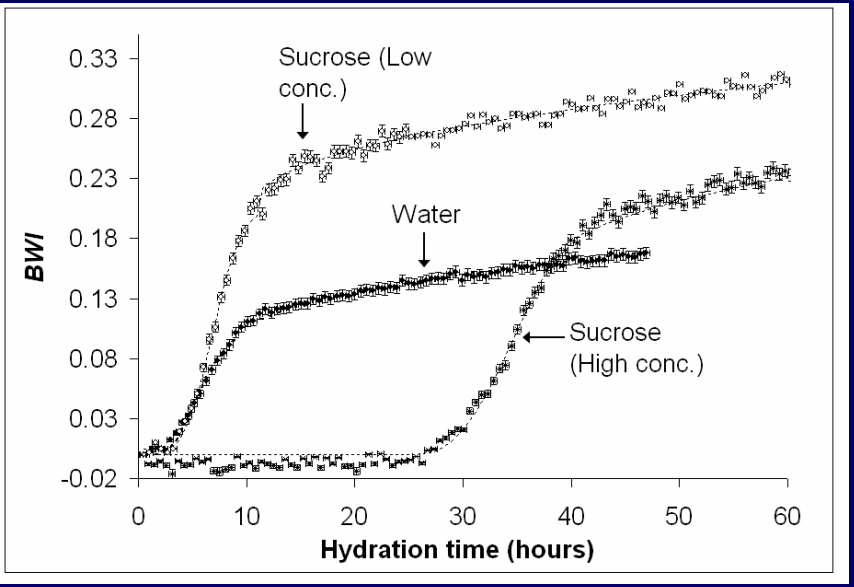
J.J. Thomas et al, J Am Ceram Soc 84 (2001).

Combined effects: Hydration of different tricalcium silicate forms + additives

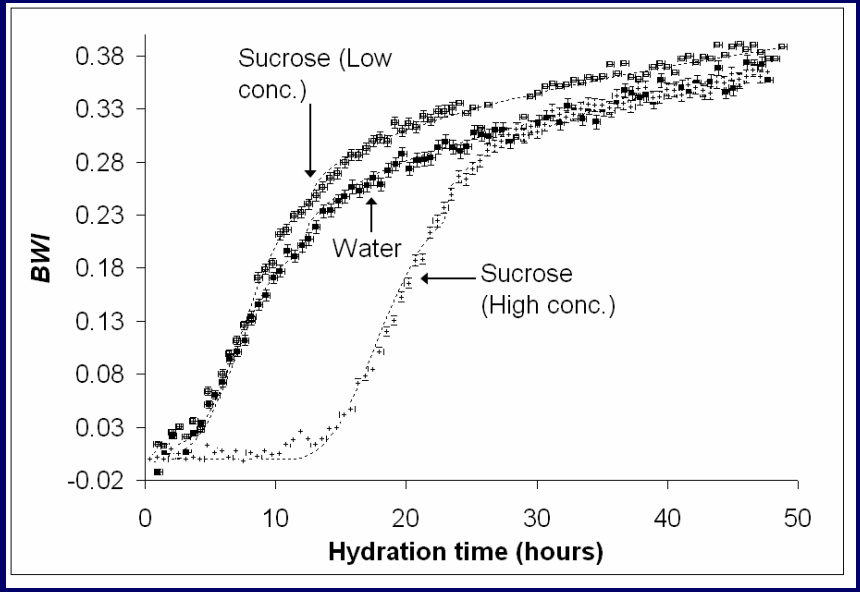


Sucrose added to different C_3S forms

Triclinic



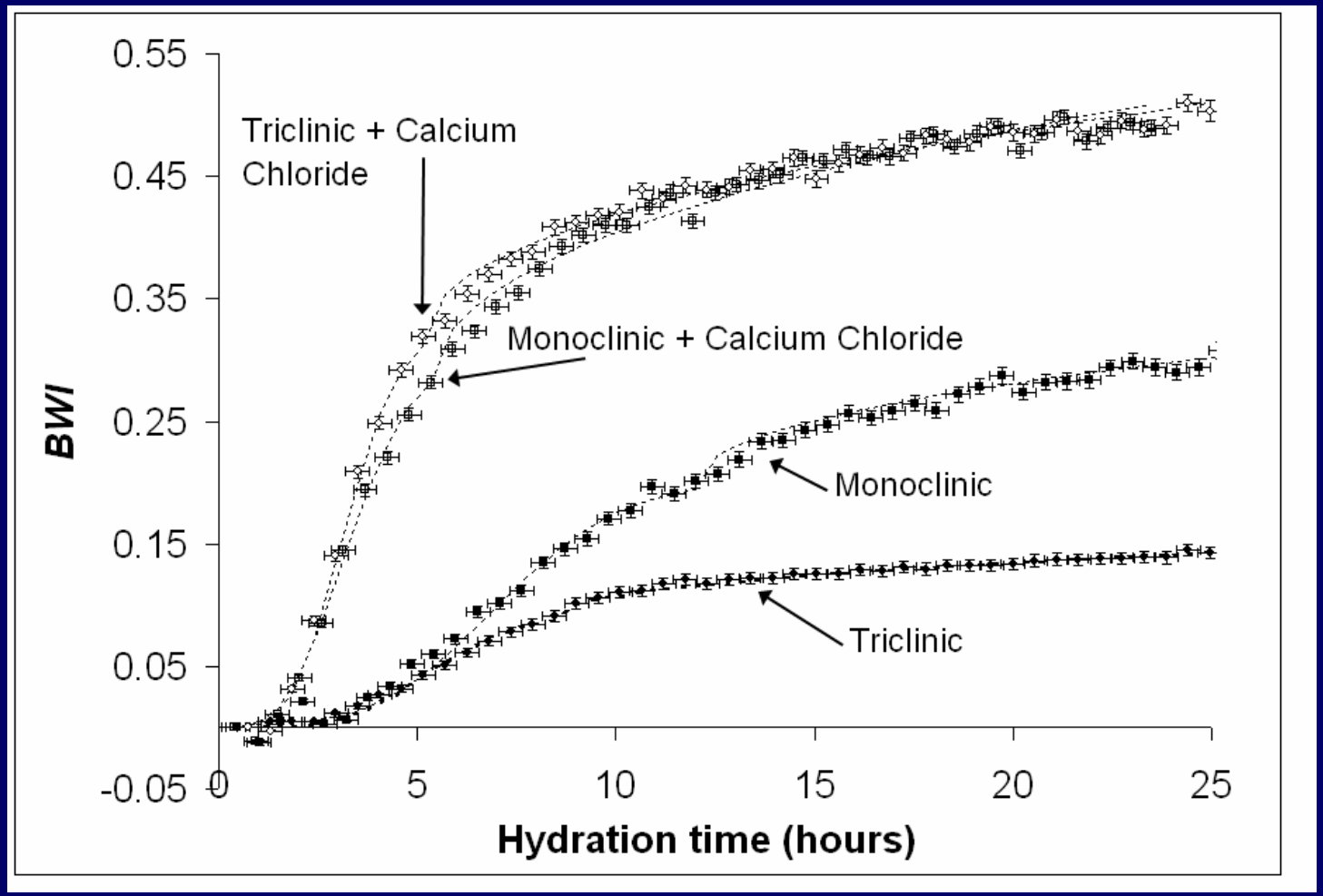
Monoclinic



- Same effects, observed to a lesser extent with monoclinic – possibly due to the lower reactivity of the monoclinic form

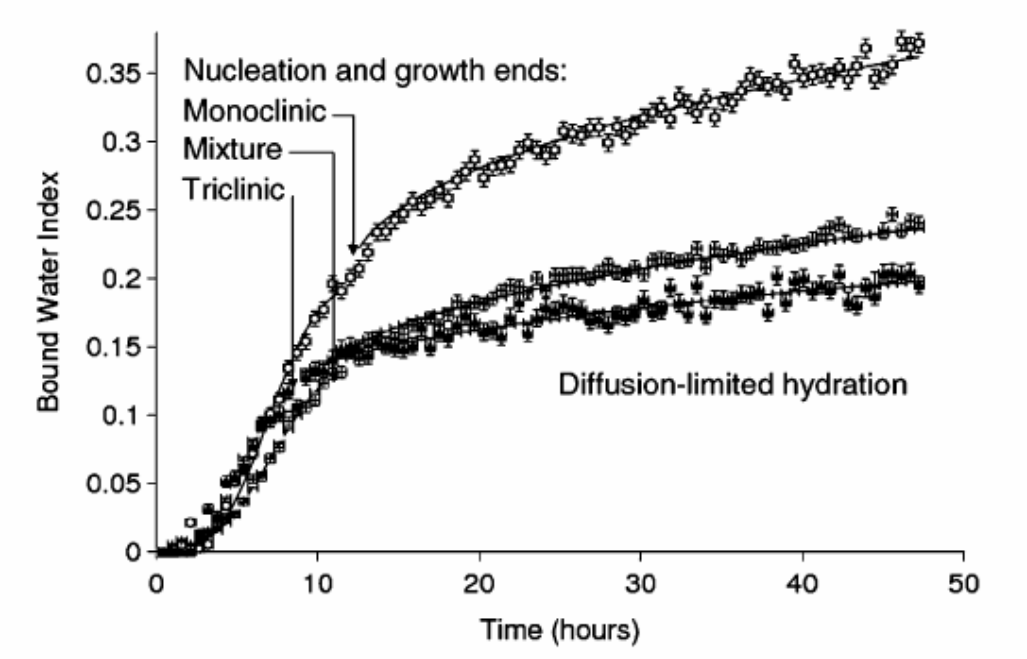
Results for the monoclinic form support hypotheses from the triclinic study

The accelerator $CaCl_2$



Hydration of mixtures

QENS data and hydration models for Mg stabilized T_1 and M_3 C_3S



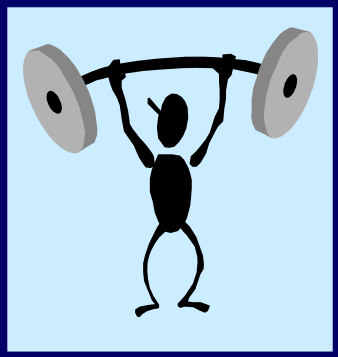
- What happens during simultaneous hydration?
- Time to NG and k both lower for the mixture!
- May arise from different product morphologies and solution chemistry

Peterson, V. K. *et al. Chem. Phys. 326,* 2006.

Interaction of Ca_3SiO_5 and Ca_2SiO_4

- Tricalcium silicate is responsible for strength up to 28 days

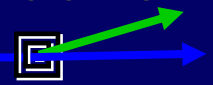
Tricalcium silicate gives cement early strength



- **Dicalcium silicate** is ~ 20 wt. % of cement
  - Adds strength later (months, years)

Ca_3SiO_5 is more reactive than Ca_2SiO_4.

Interaction of tricalcium and dicalcium silicate



- Independent hydration has been studied ✓
- Interactions are unknown !

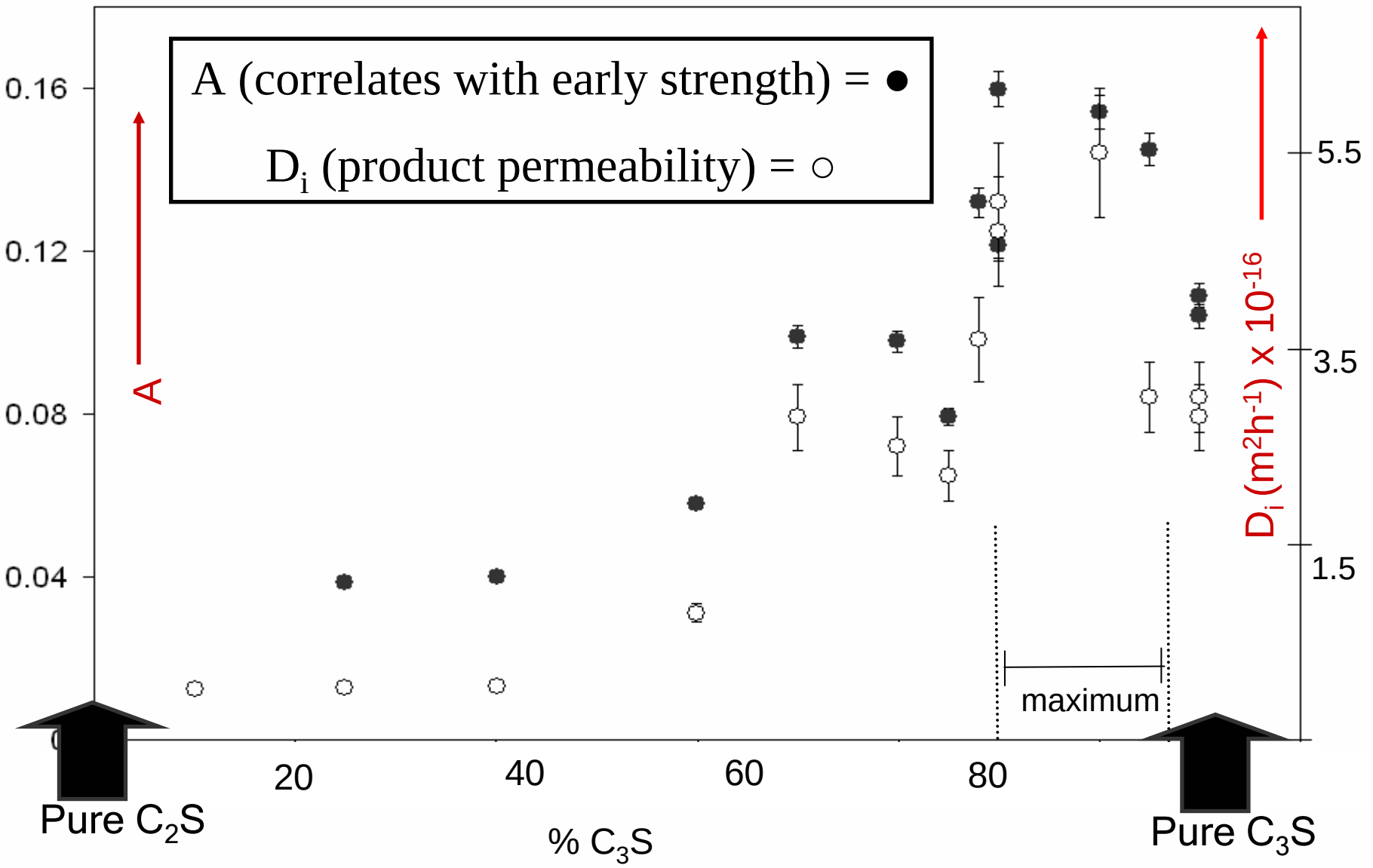
QENS: Simultaneous hydration of the calcium silicates

- Pure tricalcium silicate
- Pure dicalcium silicate
- Intermediate mixtures of the two

} Kinetic parameters as a function of composition

Owner
Date
Owner
Date

Kinetic parameters of the hydration



Application of inelastic neutron scattering

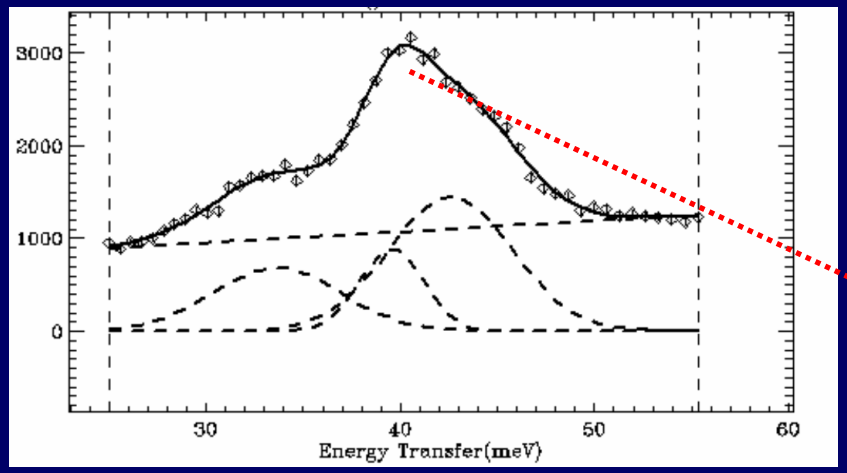
QENS: Optimization in the amount of product at 80-85 wt % tricalcium silicate.

- Confirmation by another method: formation of more product
- $Ca(OH)_2$ or $CaO\text{-}SiO_2\text{-}H_2O$: Use $Ca(OH)_2$

Inelastic Neutron Scattering: Can be done with QENS
Local interactions of atoms and molecules

- Compare sample spectrum to a reference
- Quantitative!

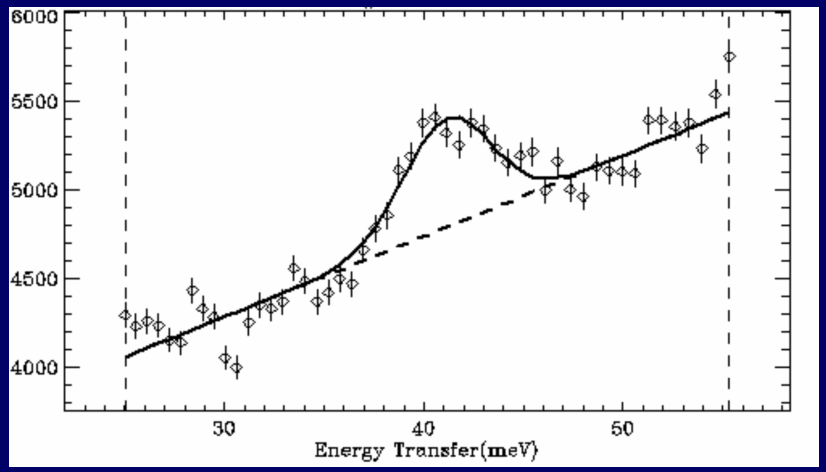
Inelastic Neutron Spectrum of $Ca(OH)_2$: Vibrational Density of States



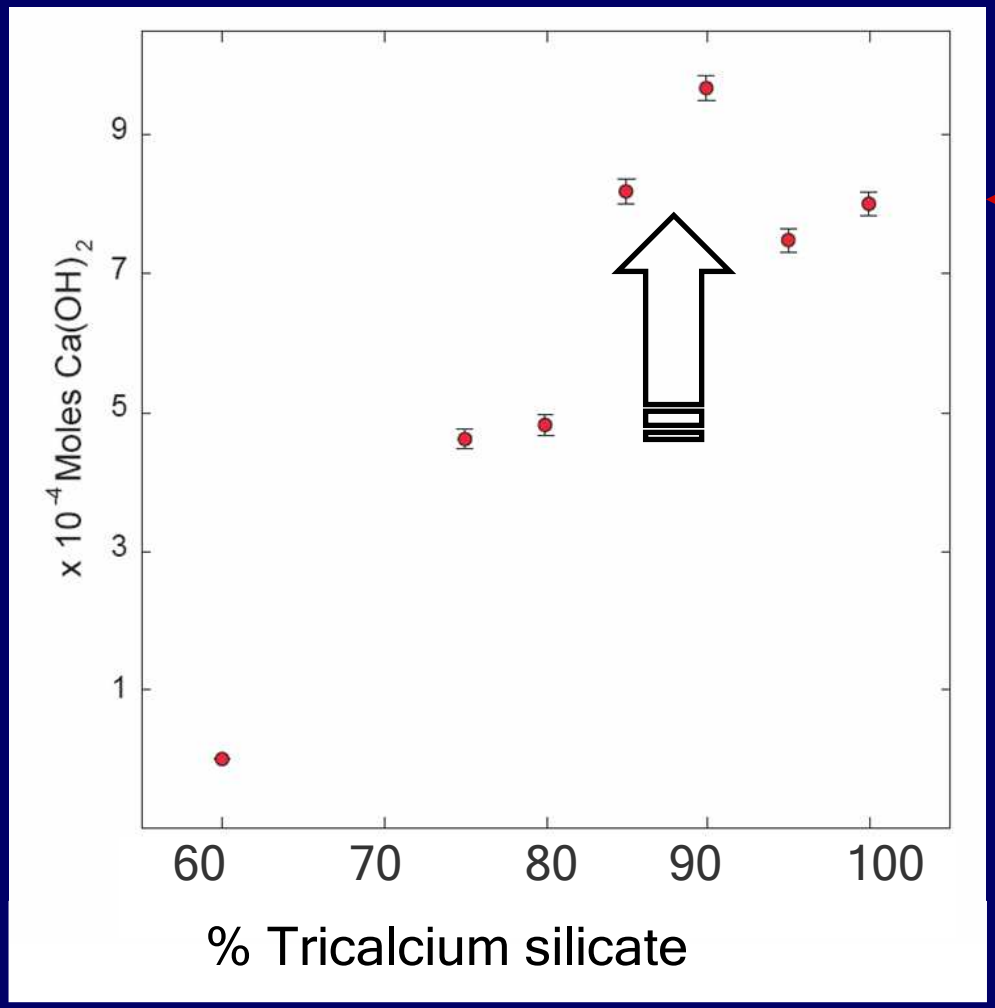
- Filter Analyzer Neutron Spectrometer (FANS)

➢ 41 meV represents the main $Ca(OH)_2$ phonon mode

- Sample data taken at 22 hours: Diffusion Limited hydration



$Ca(OH)_2$ amount with mixture composition

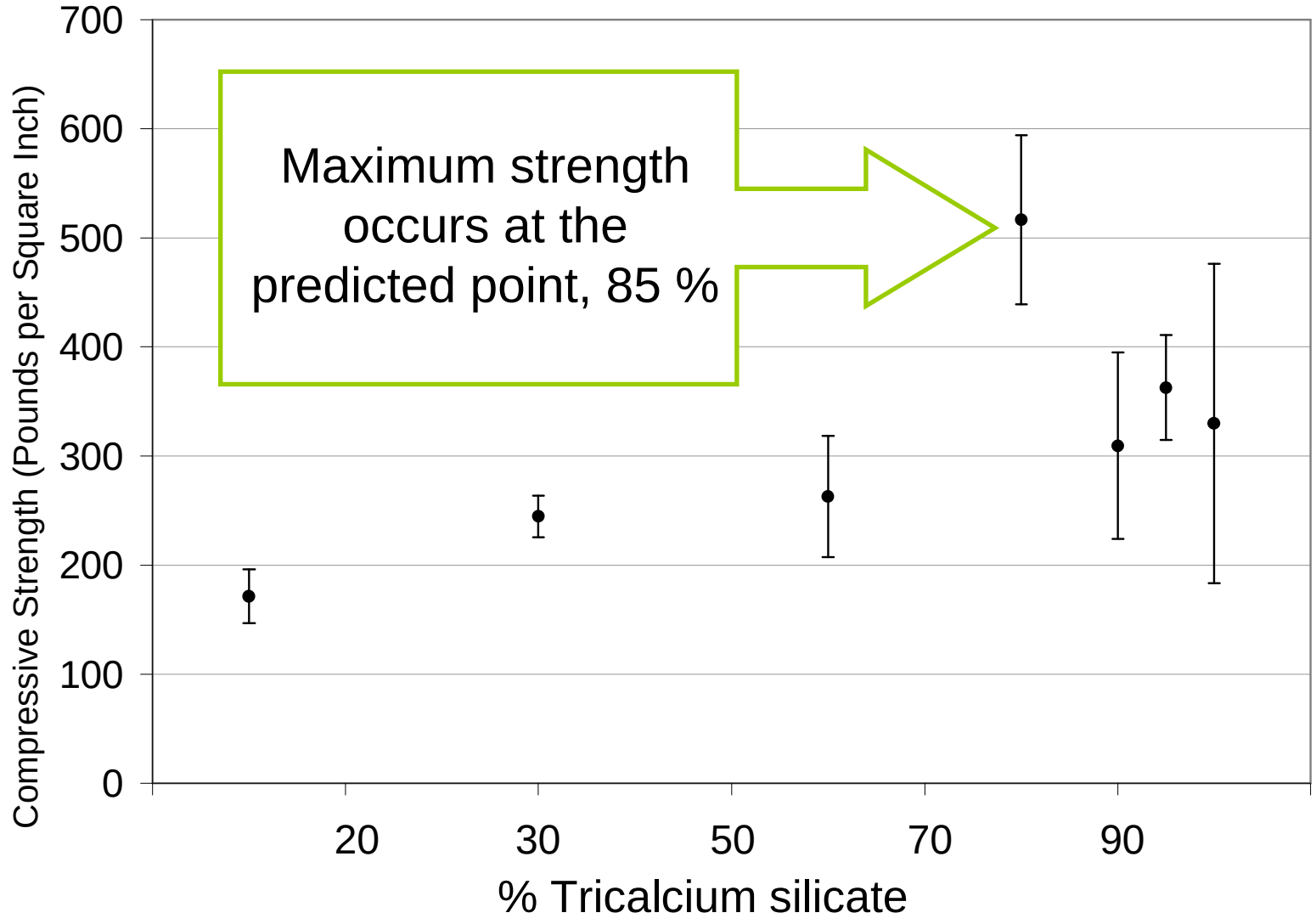


Increase in $Ca(OH)_2$ at the "critical composition" identified by QENS

Complementary analysis: 28 day compressive strength testing

- Mortars of the mixtures were prepared at 30 °C
- The QENS and INS prediction of increased strength was tested…

Strength correlates with QENS results



Cement: Significance of research

- These outcomes represent significant breakthroughs:
- New insights into the fundamental aspects of the kinetics of tricalcium silicate hydration that **relate to cement properties**
- Effects of: Structural Variation, Mixtures, and Additives

References

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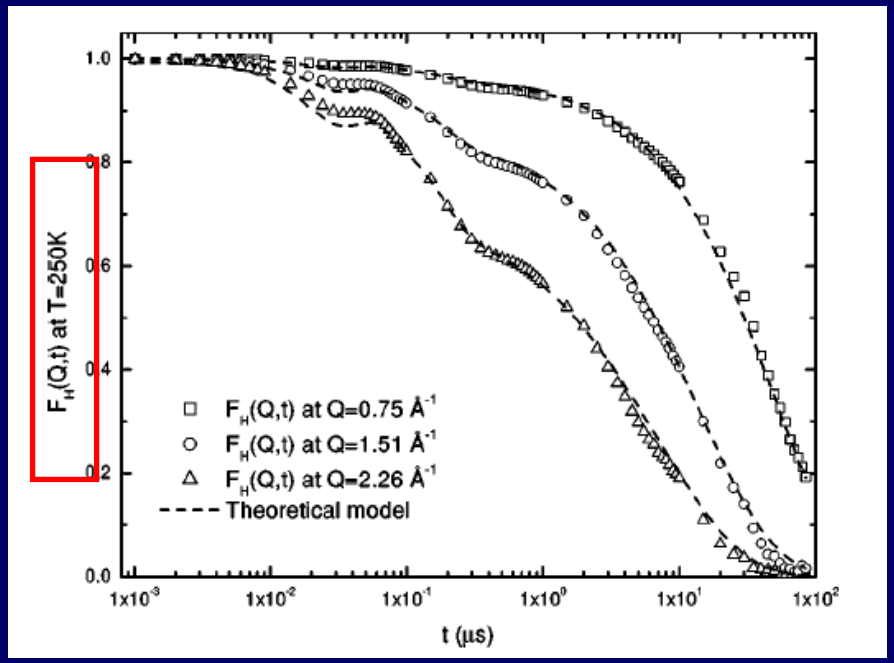
Future directions for QENS and cement:

1. Derive kinetics from models rather than fits

- Method used in this study: Profile fitting
- BWI = $(C + P)/(F_1 + F_2 + C + P)$
- Kinetic models fitted to BWI *versus* time plots

$$S(\mathbf{Q},\omega) = \frac{C}{\sqrt{2\pi\left(W_C/2.354\right)^2}} e^{-\frac{1}{2}\left(\frac{x-x_0}{W_C/2.354}\right)^2} + \frac{W_P}{2\pi}\frac{P}{\left(x-x_0\right)^2+\left(W_P/2\right)^2} + \frac{W_{F_1}}{2\pi}\frac{F_1}{\left(x-x_0\right)^2+\left(W_{F_1}/2\right)^2} + \frac{W_{F_2}}{2\pi}\frac{F_2}{\left(x-x_0\right)^2+\left(W_{F_2}/2\right)^2}$$

1. Derive new parameters from QENS models: Self-dynamics of water molecules



- Self-dynamic structure factor
- Related to S(Q,ω) via a time-Fourier transform

- Contains Intermediate Scattering Functions describing the water molecule motions as per the hydrogen atoms:

1. $F_{translational}(\mathbf{Q},t)$: Of the center of mass
2. $F_{rotational}(\mathbf{Q},t)$: Around the center of mass

Fratini *et al* Phys. Rev. E, 2001.

1. Derive new parameters from QENS models

- Data from **Q** = 0.55 to 1.24 Å^{-1}, 5 spectra for each measurement.
- Transmission geometry at low angles, reflection at high angles

$F_H(\mathbf{Q},t)$: Self-dynamic structure factor

p + → immobile fraction

$F_v(\mathbf{Q},t)\exp[-(t/\tau)^{\beta}]$ Short term **translational** vibrations of central molecule

$C_l^S \exp[-(t/\tau)^{\beta}]$ Short term lth order **rotational** correlation function

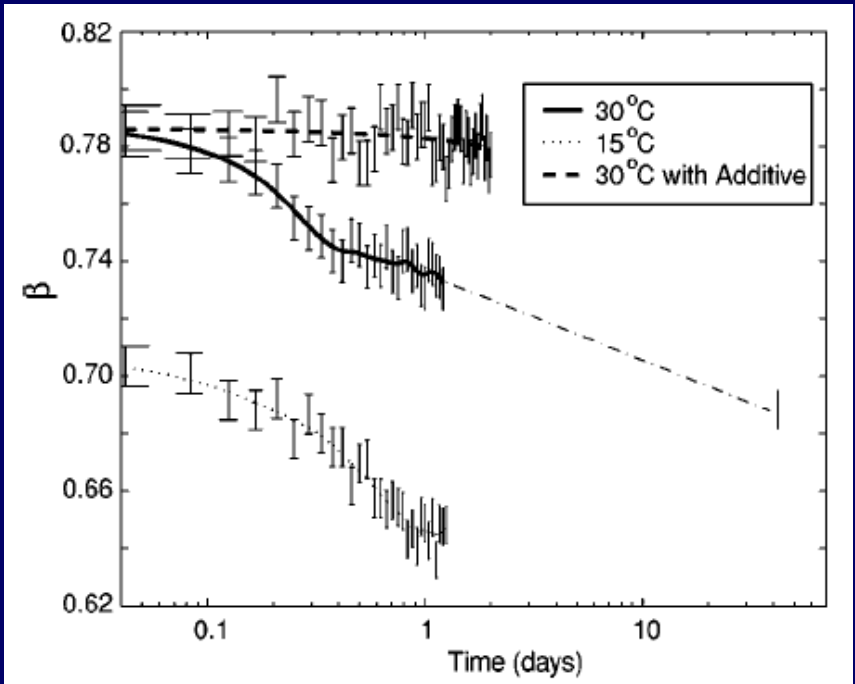
Long term component: "relaxing cage model"
α relaxation + stretching, β = 0-1.
- Lorentzian when β = 1

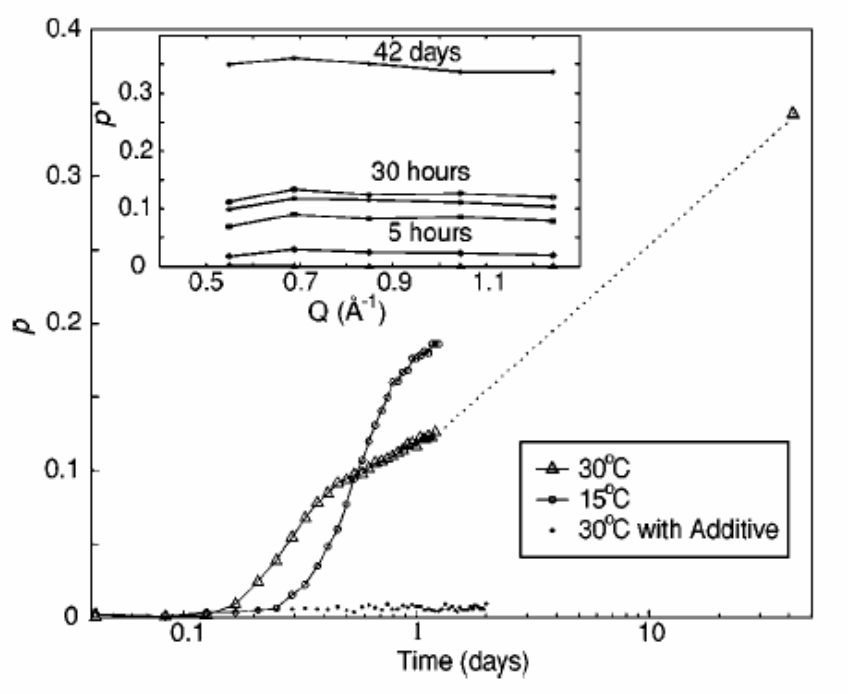
Appreciable when **Q** > 1 Å^{-1}

Fratini *et al* Phys. Rev. E, 2001. and Liu *et al* Phys. Rev. E., 2002

1. Derive new parameters from QENS models

- Time evolution of these parameters not modelled
- Bound water component for the same study shows more interesting trend with less error

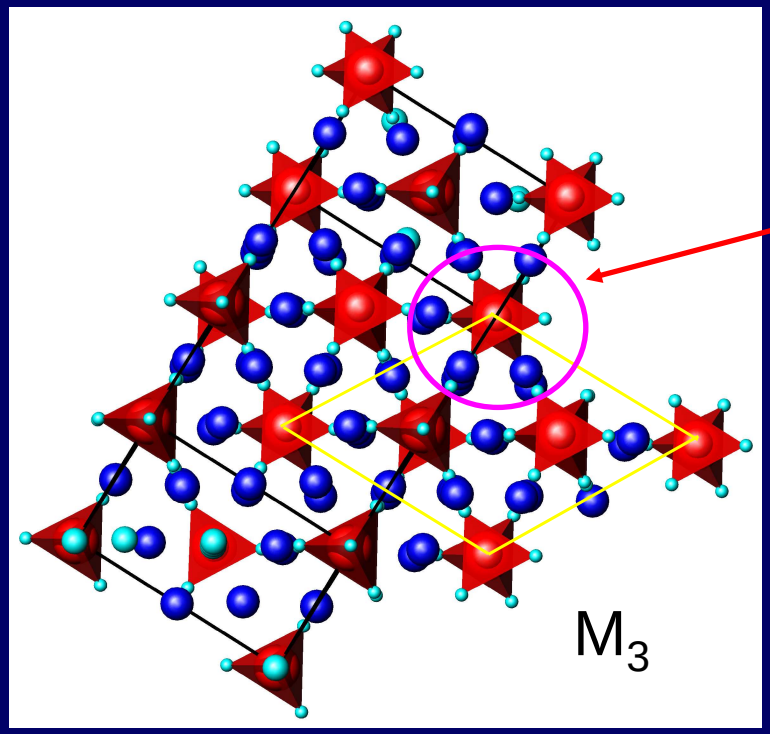


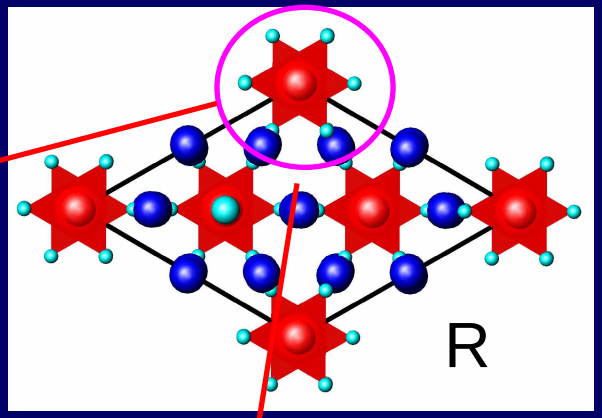


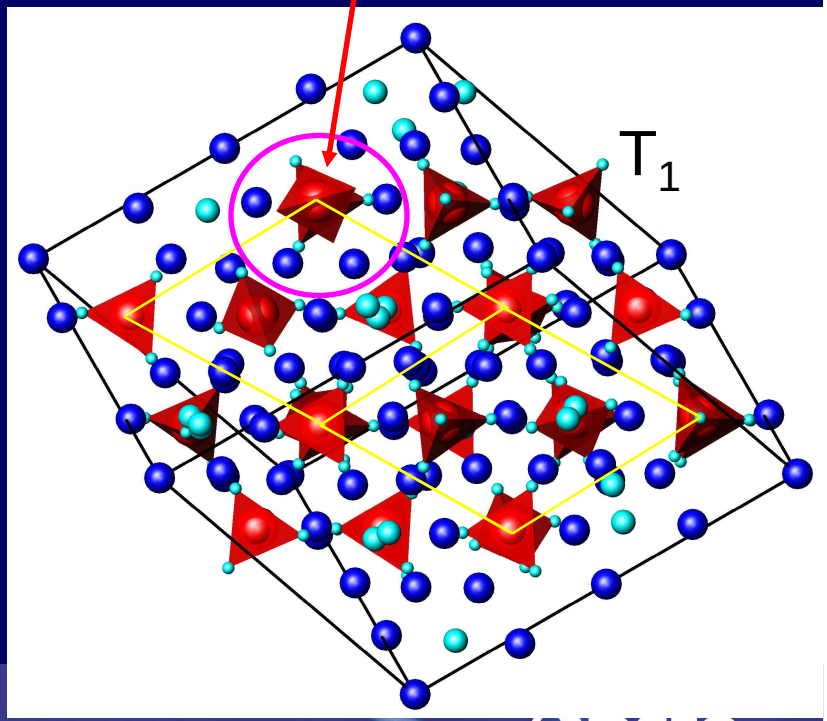
➢ Better definition of these parameters for cementitious systems may lead to application of kinetic models

Fratini *et al* Phys. Rev. E, 2001.

2. Couple kinetics with tricalcium silicate structure





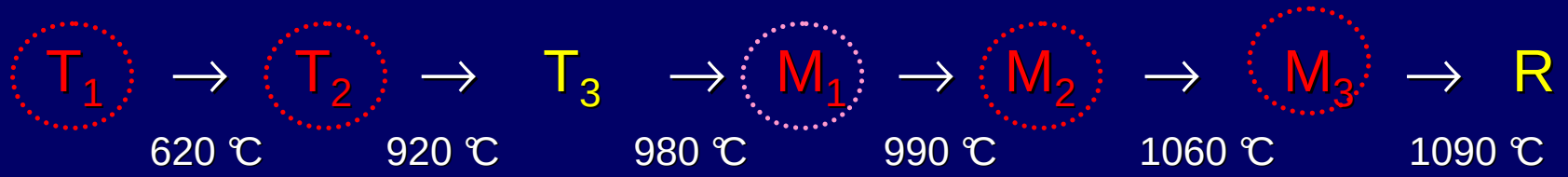


Structural differences

Orientation of SiO_4 tetrahedra: Change hydration behaviour

Tricalcium silicate: structural modulation

Electron and Synchrotron Powder Diffraction studies have revealed:



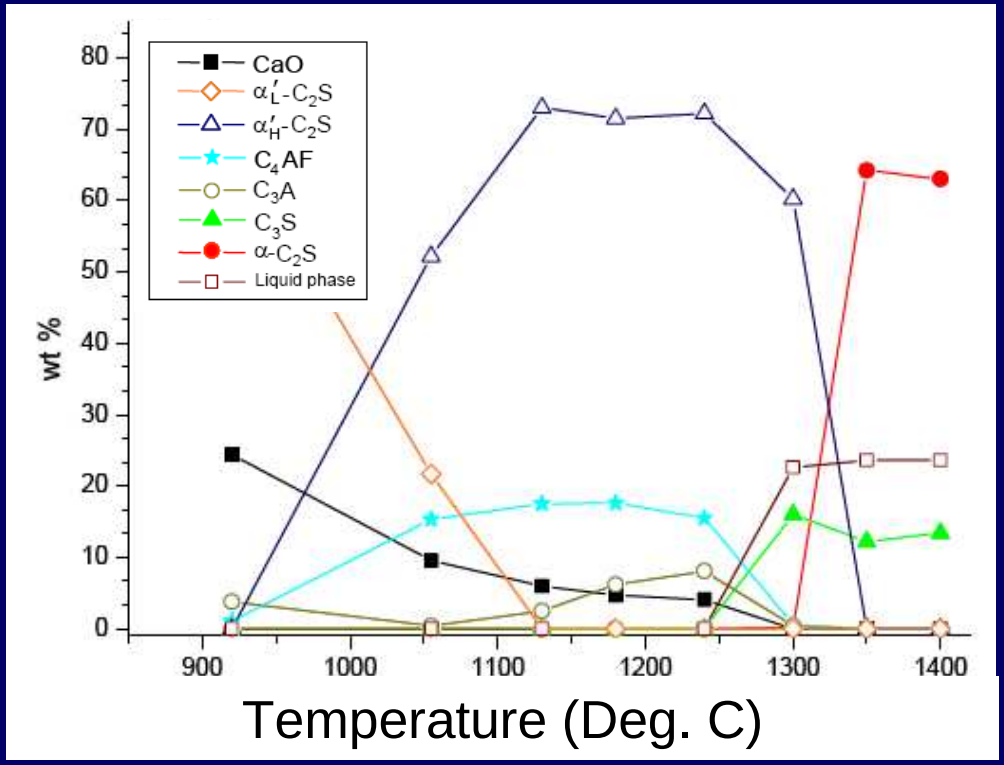
- Unmodulated
- Commensurate + incommensurate
- Positional modulation of both Ca and Si

- Existing crystal structures are averages:
- Relationship between the forms is unknown

Solve Structures and relate form to hydration behaviour: optimum structure?

3. Study kinetics of formation of tricalcium silicate: Stabilize favourable forms

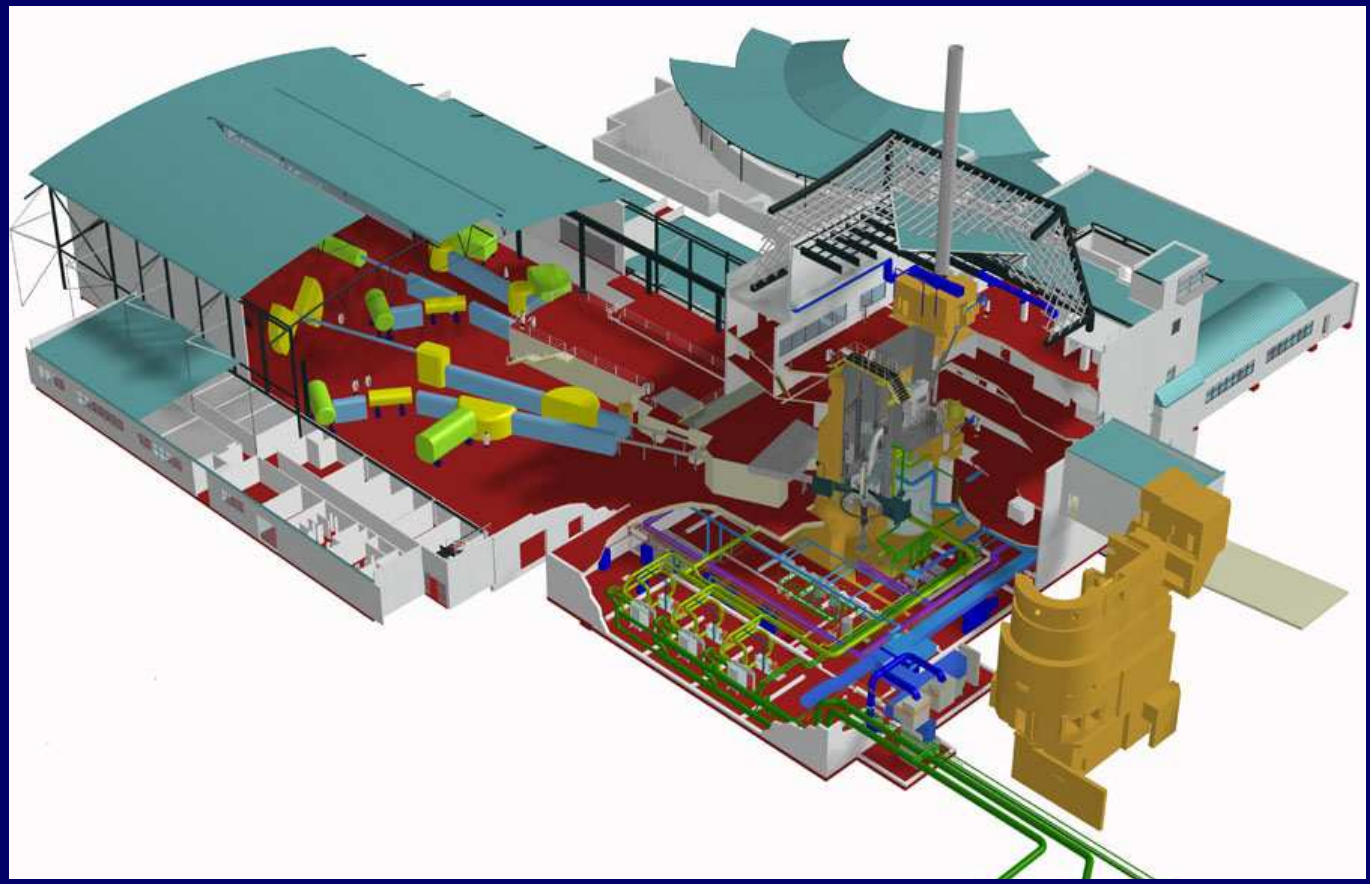
- How are these forms are stabilized: *in-situ* temperature-dependant synchrotron X-ray Powder Diffraction studies of the clinkerization (formation) processes
- Use this information to preferentially stabilize the favourable form



Better with neutrons!

Australia's OPAL 20MW reactor source

New Neutron Scattering Facility



Neutron Zoo at OPAL

Platypus
(Reflectometry)

Wombat
(Hi-Intensity Powder)

Koala
(Single Crystal)

Quokka
(Small Angle)

Kowari
(Residual Stress)

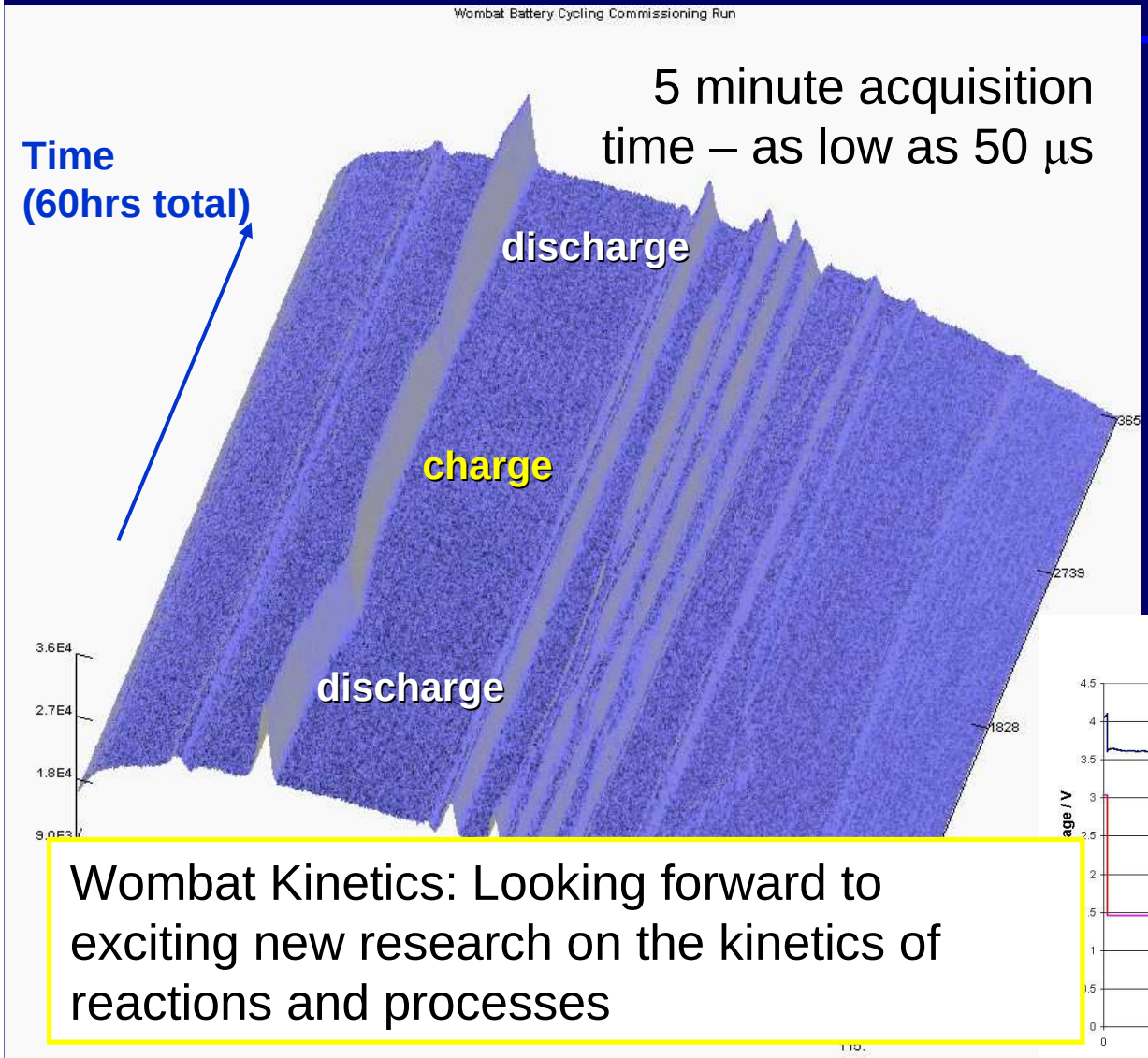
Pelican
(Polarized Quasielastic)

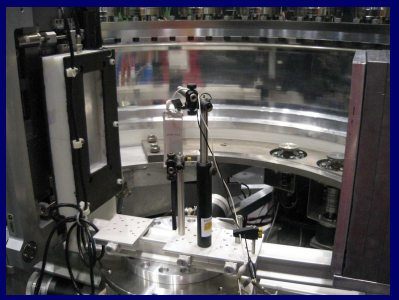
Sika
(Cold Inelastic)

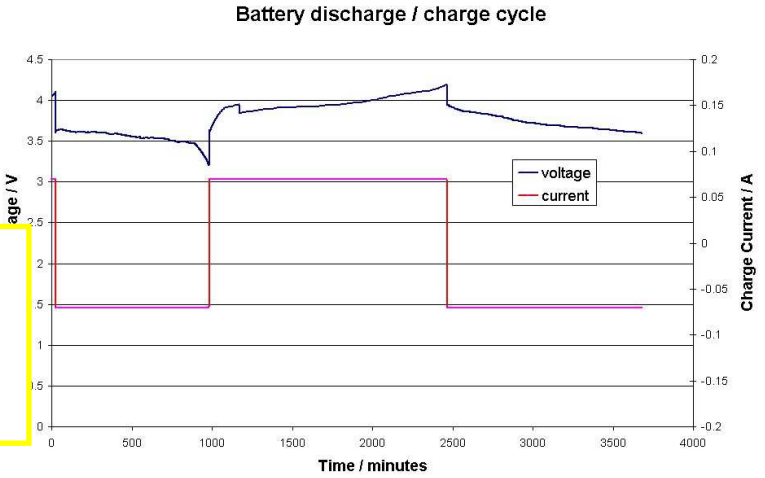
Echidna
(Hi-Res. Powder)

Taipan
(Thermal Inelastic)

In-situ battery cycling on Wombat







Wombat Kinetics: Looking forward to exciting new research on the kinetics of reactions and processes

Acknowledgements

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The University of Texas at Austin, USA
- Maria Garci-Juenger

I told you that cement was too wet…

Kinetic parameters of the hydration

Modeling of the nucleation and growth period:

$$BWI(t) = BWI(0) + A[1-\exp\{-[k(t-t_i)]^n\}]$$

n = Dimensionality of growth:

Product growth occurring in a 3-dimensional pore space

Can be determined from QENS - more precisely determined by calorimetry

- n for monoclinic pastes vary from 2.44 - 2.65.
- M_3 form has larger n (2.65) than T_1 (2.27) at 30 ºC.

➢ **Model is relatively insensitive to changes in n**

- varying n between 2.27 - 2.65 = 0.8 % change in A and 4 % in k.