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A Breakthrough: Aluminium Hydroxide Crystal Growth Pathways Revealed by Synchrotron Small Angle X-ray Scattering

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David Cookson

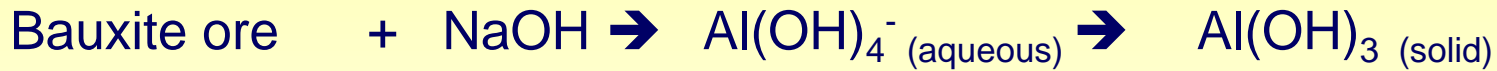
Australian Synchrotron (formerly of ASRP)

RELEVANCE



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BAYER CYCLE



Precipitation takes 2-3 days
Agglomeration very slow

CERAMICS $\text{Al(OH)}_3 \rightarrow \text{Al}_2\text{O}_3$
Size distributions for different packing densities
and packing strengths

- power insulators, abrasives, cutting tools, sparkplugs, wear resistant liners, pump parts etc...

Control of surface area

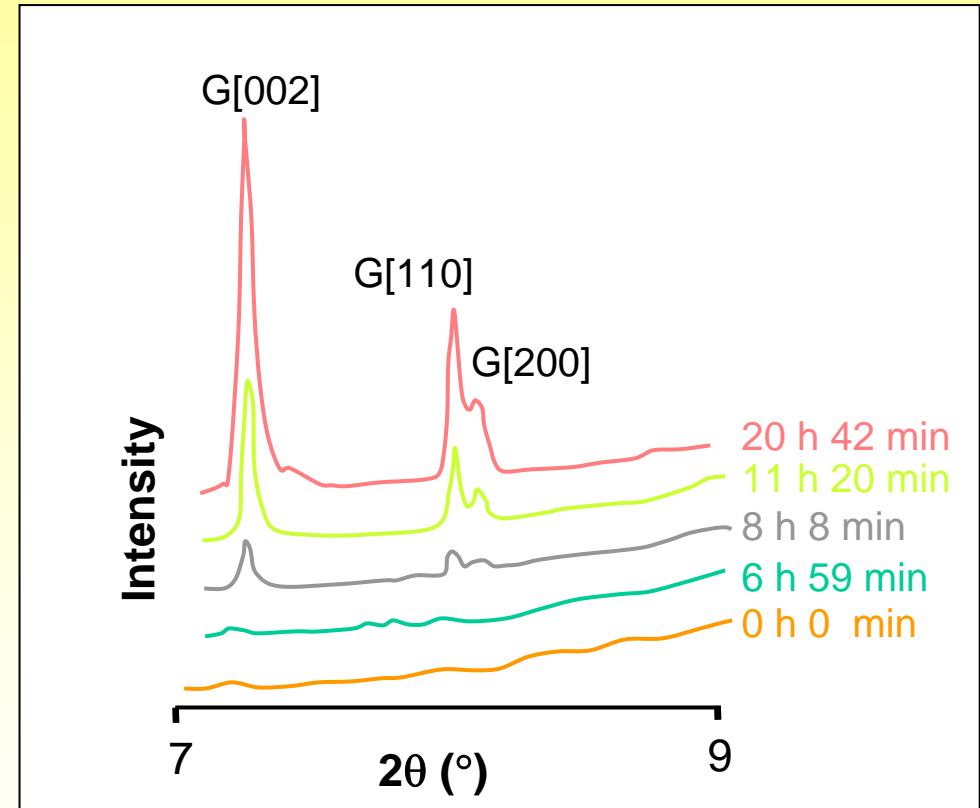
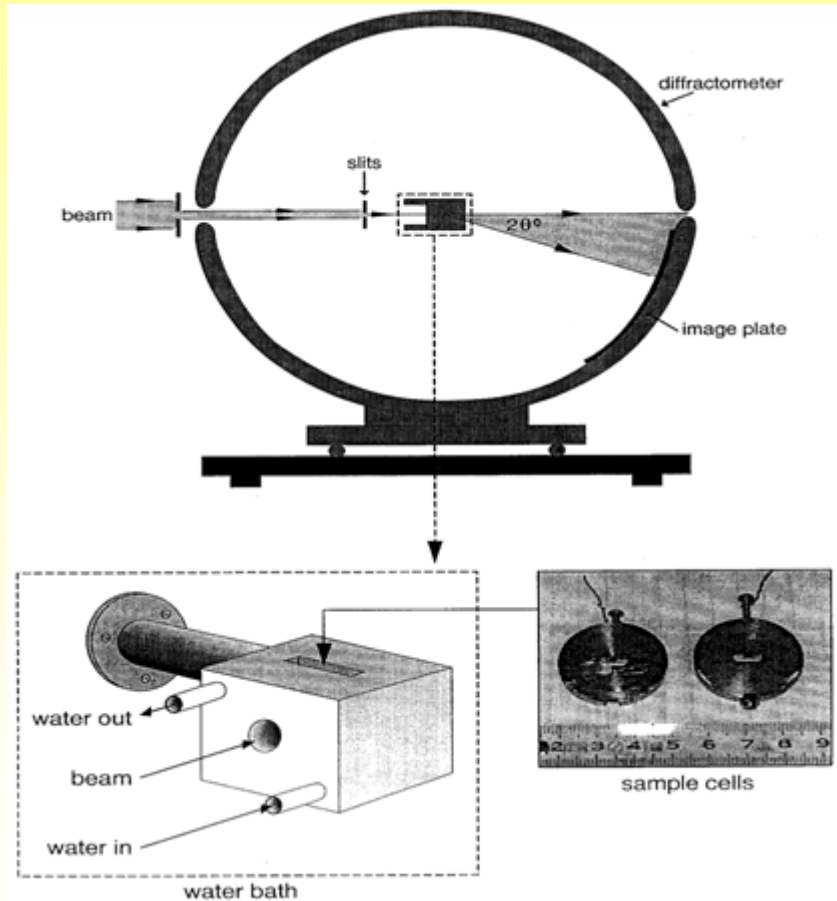
- catalysts, pigments, electro-optical and magnetic devices



HISTORY: *IN SITU* DIFFRACTION



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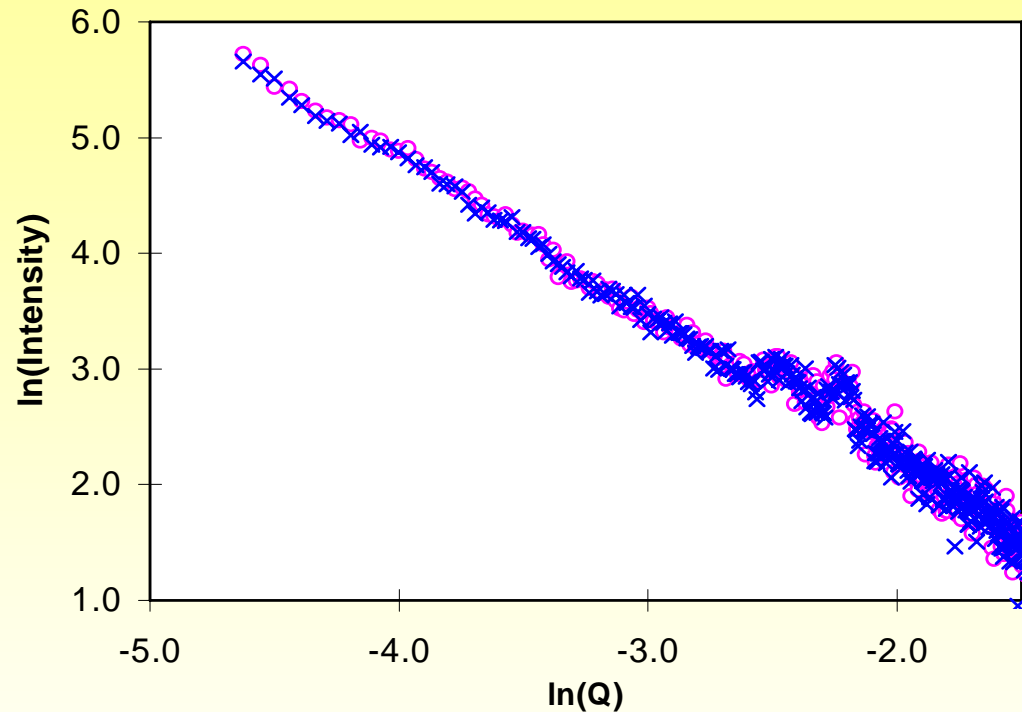


In situ X-ray diffraction patterns of gibbsite crystallising from caustic aluminate liquors. (Gerson *et al.* 1996)

HISTORY: SMALL ANGLE X-RAY SCATTERING



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Scattering length density:

$$\rho_e(\text{gibb}) = 20.9 \times 10^{10} \text{ cm}^{-2}$$

$$\rho_e(\text{sol}) = 11.9 \times 10^{10} \text{ cm}^{-2}$$

- Scattering contrast is very low at any time between a fresh solution and a fully crystallised solution.

- Indicates that the particles forming in solution have no sharp interface with the solution.
- It has been estimated that only a 5% interfacial difference in scattering length density is required for scattering.

[A.R. Gerson et al., Light Metals, 167 (1998)]

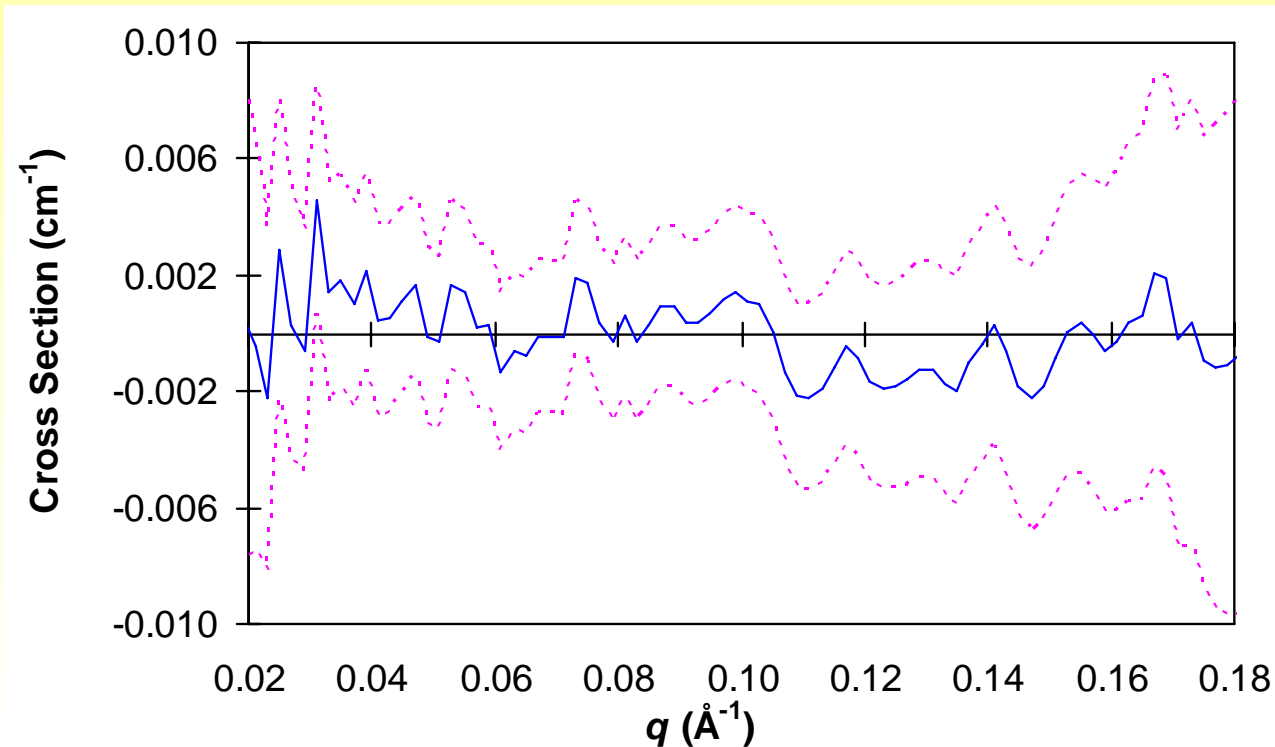
HISTORY: SMALL ANGLE NEUTRON SCATTERING



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Sufficient calculated neutron scattering length density to observe scatter.

ISIS Appleton Rutherford Laboratory (LOQ)



- ⌘ Aged solution with fresh solution subtracted.
- ⌘ All NaOD and D₂O to minimise incoherent scattering.
- ⌘ No scattering regardless of age.

A.R. Gerson et al., Light Metals, 167 (1998)

HISTORY: LIGHT SCATTERING



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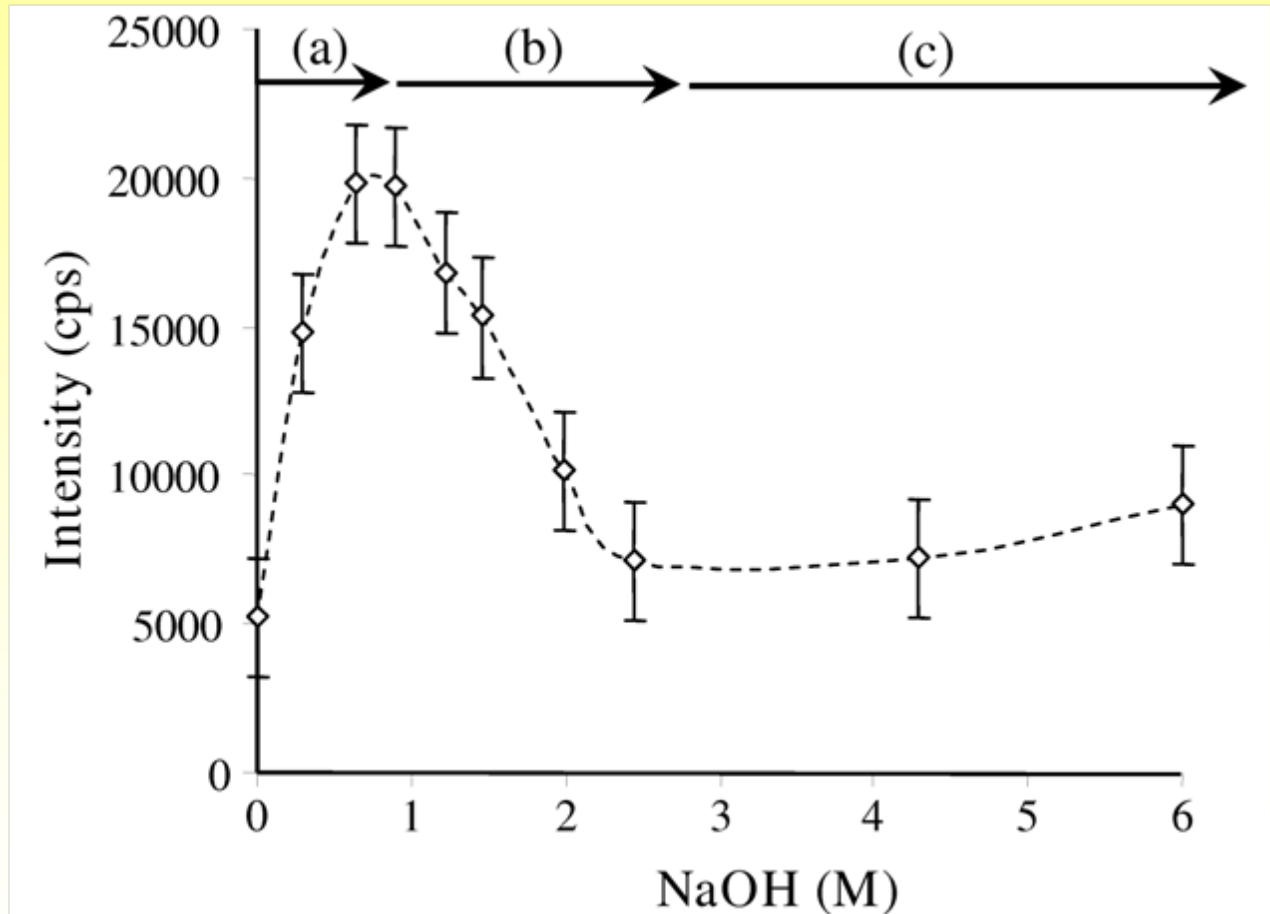
Fresh caustic aluminate
solutions.

$[\text{NaOH (M)}]/[\text{Al (M)}] = 1.22$.

(a) Increasing [Keggin ion].

(b) Decreasing [Keggin ion]
and increasing $[\text{Al(OH)}_4^-]$.

(c) $[\text{Al(OH)}_4^-]$ is the dominant
species.



Li, H.; Addai-Mensah, J.; Thomas, J. C.; Gerson, A. R. *Colloids Surf., A*.
2003, 223, 83-94.

SMALL ANGLE X-RAY SCATTERING



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ChemMatCARS at the Advanced Photon Source synchrotron (Chicago, USA).

The instrument used was 15-ID-D.

A long camera of 7 m was used to record the X-rays scattered by the sample.

The azimuthally integrated scattering data was calibrated against pure water to give absolute differential scattering cross section per volume (units of cm^{-1}). The initial scattering from the fresh solution has been subtracted as background.

Crystal Growth and Design 2008



SMALL ANGLE X-RAY SCATTERING



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1.0 M NaOH

$[\text{NaOH (M)}]/[\text{Al (M)}] = 1.22$

Keggin ion region

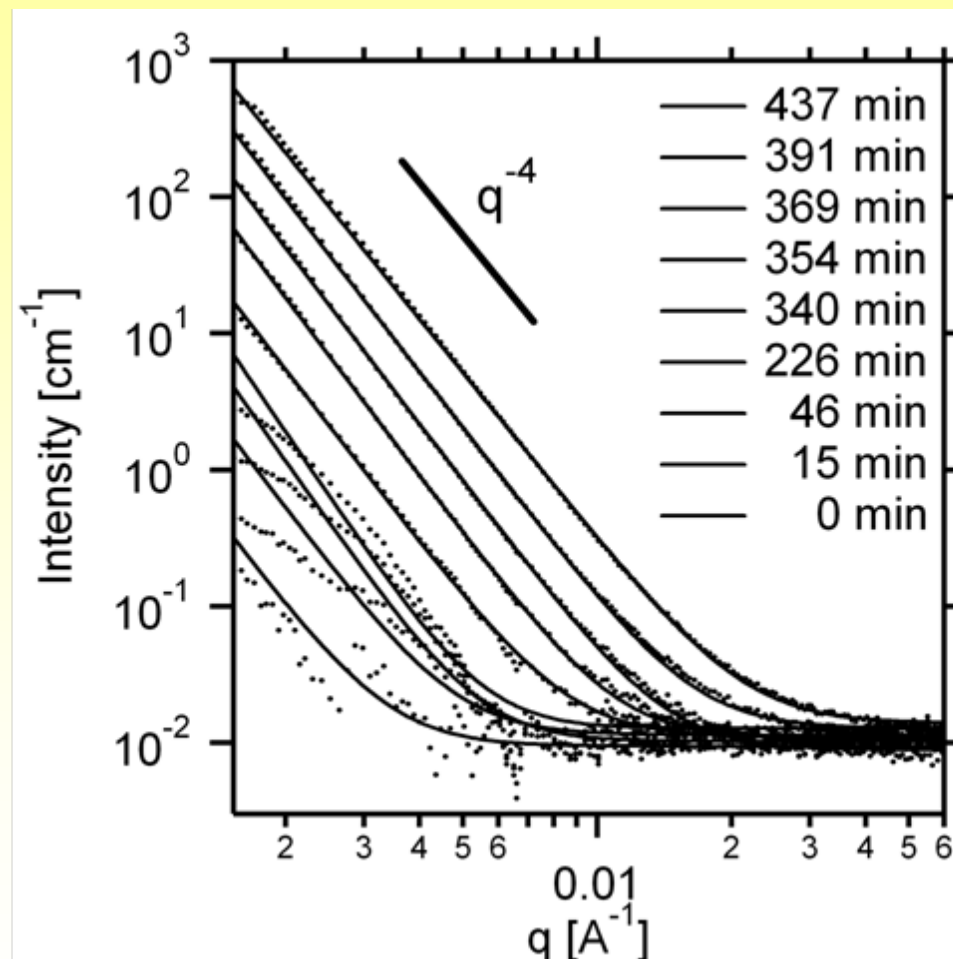
Fitted to simple power law

$$I(q) = B \cdot q^P + C,$$

$$q = 4\pi \sin(\theta)/\lambda,$$

Parasitic instrumental scatter accounts for the significant deviation of the data from the fitted function at low q , and becomes less significant with increasing aging time.

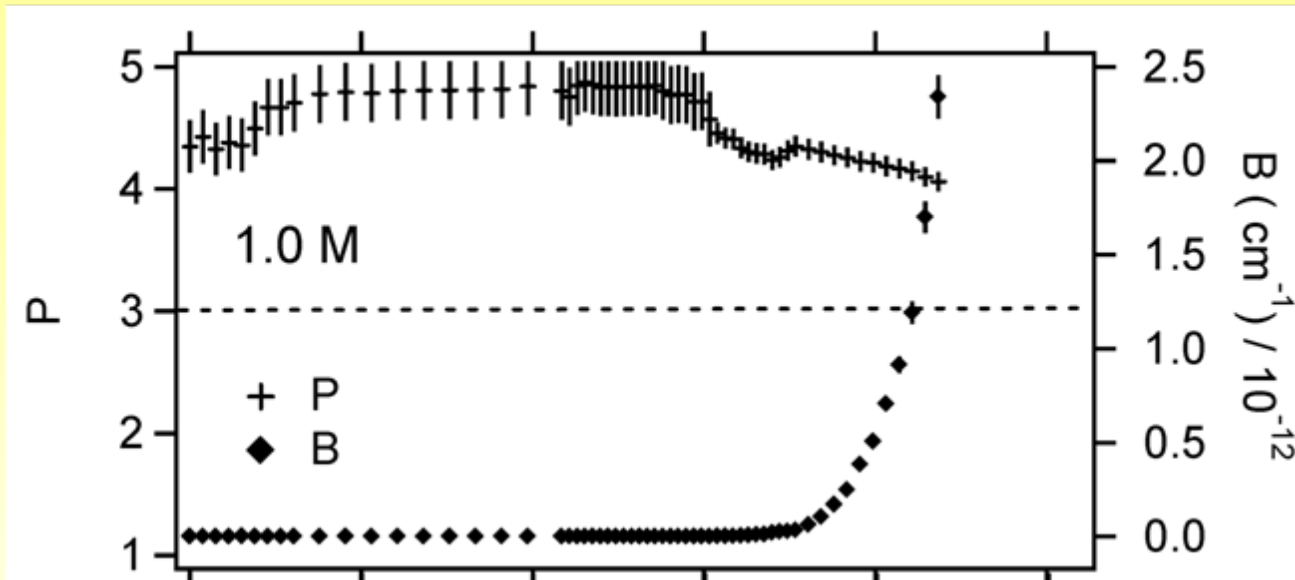
Can't see a Porod 'knee' therefore can't determine particle size ($> 1000 \text{ \AA}$)



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$$I(q) = B \cdot q^P + C,$$

$4.0 < P < 5.0$ is usually attributed to a steep gradient of electron density from solid to liquid phase consistent with a thin layer of less dense recently accreted material on the surfaces of large fully-dense particles.

B monotonically increases for the 1.0 M NaOH solution.

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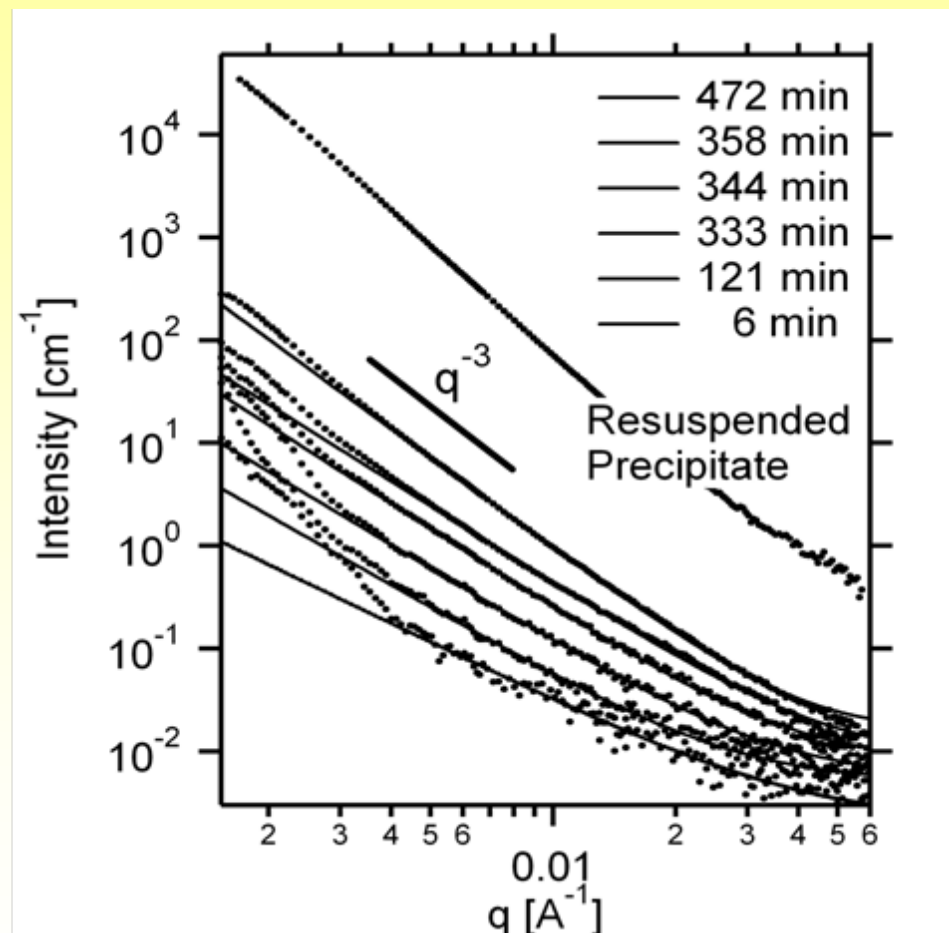
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3.0 M NaOH

$[\text{NaOH (M)}]/[\text{Al (M)}] = 1.22$

Al(OH)_4^- region

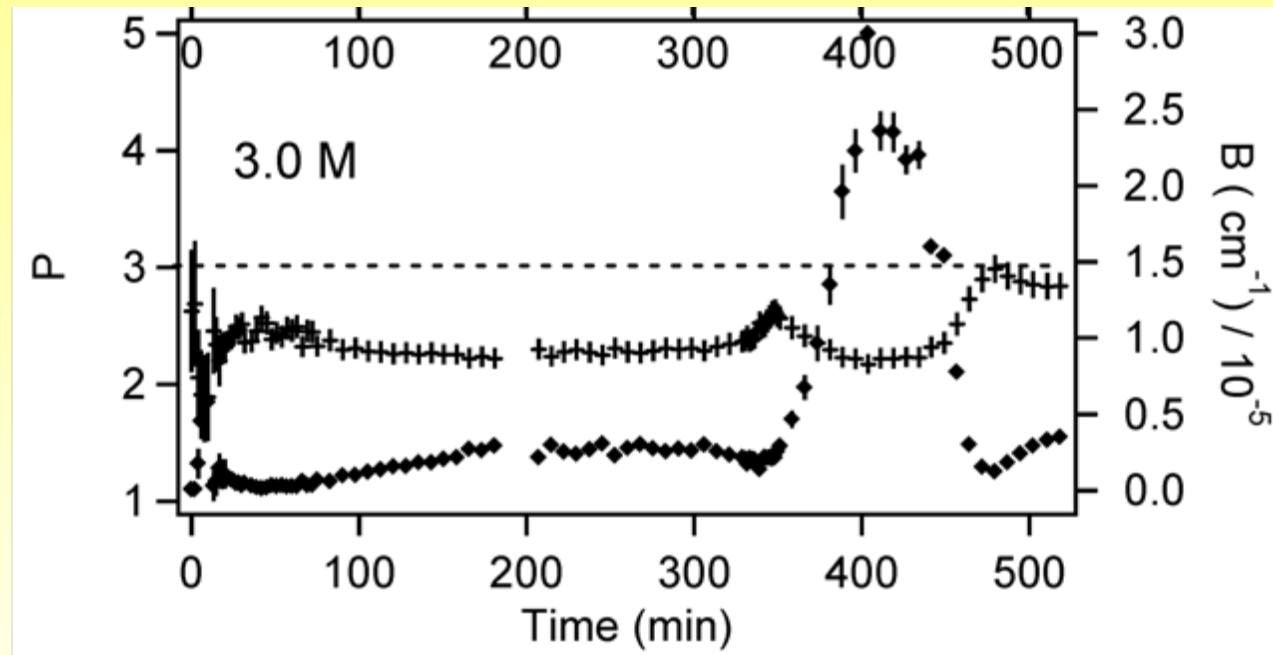
Data resulting from a re-suspension of about 10 % of the precipitate after 48 h of aging is shown.



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P oscillates between 2.5 and 3.0, consistent with large mass fractal particles. P value of 3.0, the cut-off between surface and mass-fractal behaviour. P of resuspended material 3.4, suggesting a solid particle with surface fractal structure.

B undergoes a significant maximum on 420 min and B is strongly correlated to the movement in P suggesting that the overall mass fractal nature of the large particle ensemble is labile.

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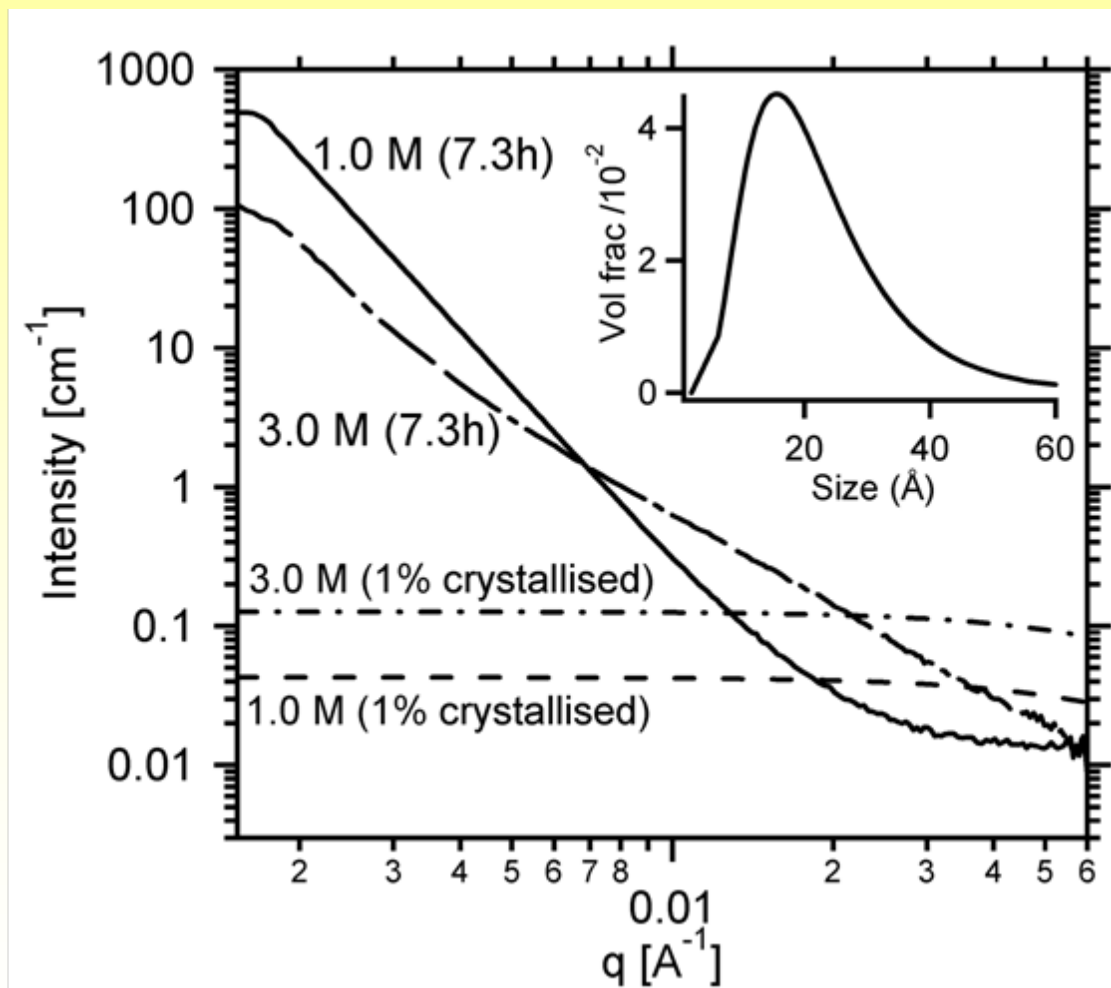


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Late-maturation profiles for 1.0 M and 3.0 M NaOH solutions.

The flat dashed profiles indicate the theoretical SAXS intensity that would be seen if only 1 % of the available solute crystallised as hard (*i.e.* fully densified) particles with the log-normal size distribution shown (inset).

Both theoretical profiles significantly exceed the measured scatter for $q > 0.02 \text{ \AA}^{-1}$. From this it is clear that if solid particles are nucleating at a size of only a few tens of angstroms, they do not grow smoothly within our SAXS-sensitive range of 40 to 1000 \AA .

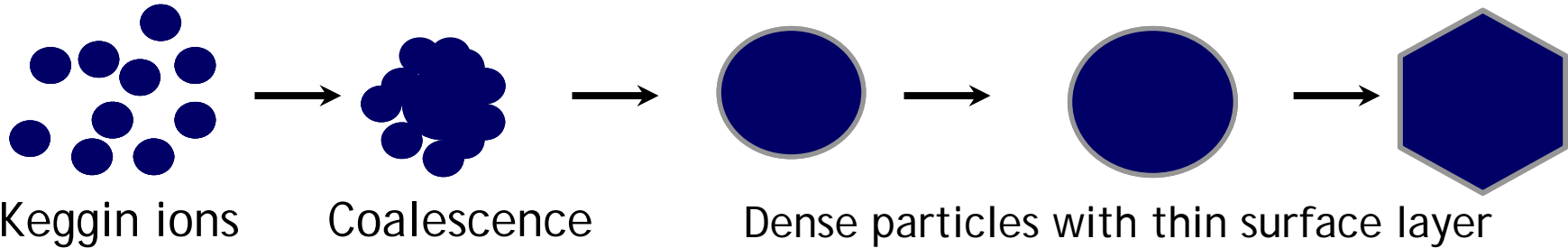


CONCLUSION: PROPOSED GROWTH MECHANISMS

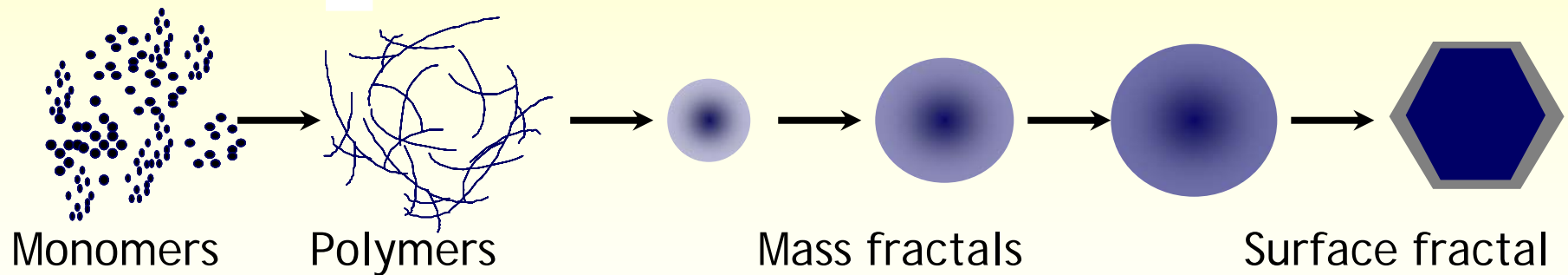


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Dilute Caustic Aluminate Solutions



Concentrated Caustic Aluminate Solutions



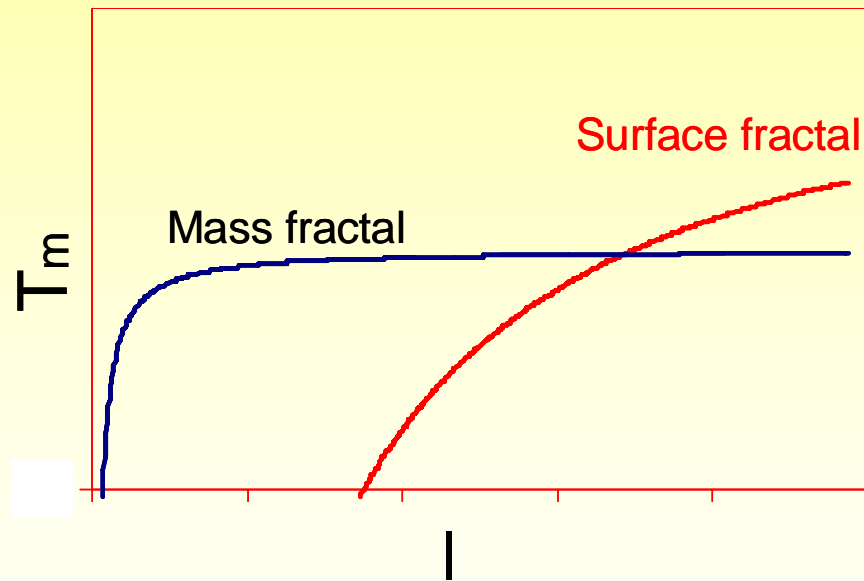
The presence of fractal interfaces inhibits the rapid agglomeration of particles as would be expected in highly concentrated Bayer liquors.

PHASE INVERSIONS AND POLYMER CRYSTALLISATION



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- The stability of a phase can be related to the size of particles of that phase.
- The stability of two polymorphs can invert with particle growth.



$$T_m = T_m^0 \left(1 - \frac{2\sigma}{l\Delta H}\right)$$

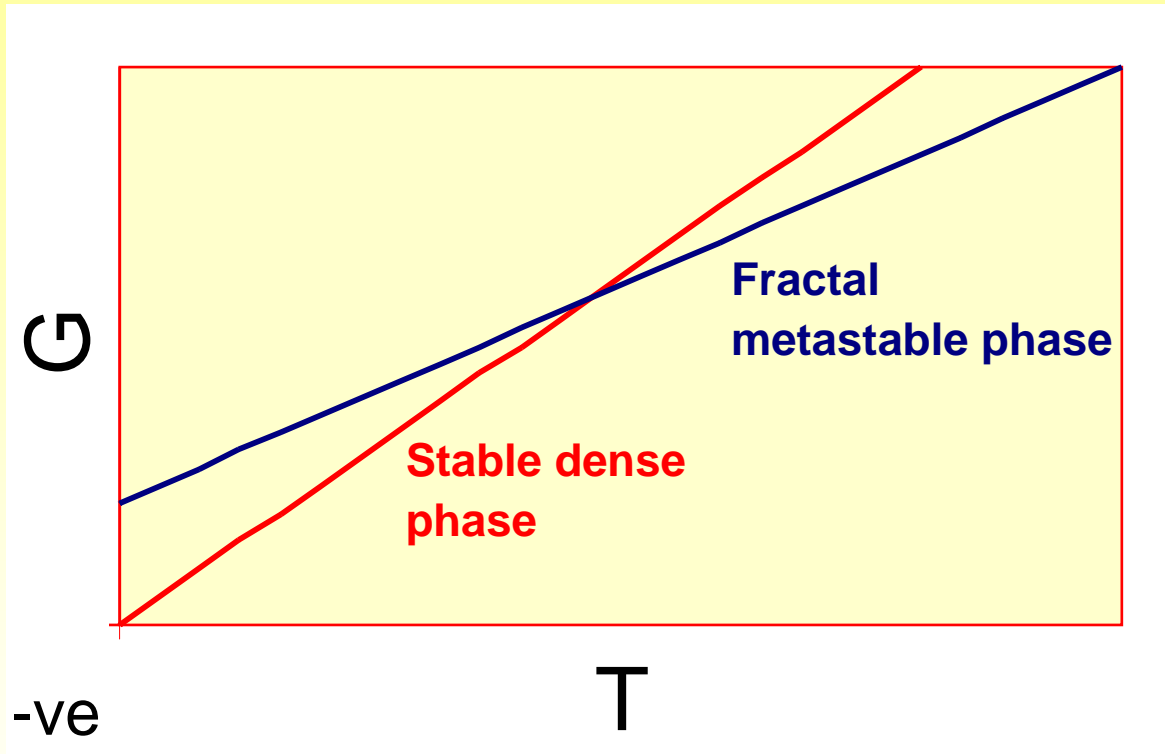
T_m is the melting point of the crystal of size l ,

T_m^0 is the melting point of a crystal of infinite size,

ΔH is the heat of fusion

σ is the mean surface free energy.

At small particle size the structure with a more stable interface will be favoured at the expense of the bulk structure, whereas at a large particle size the phase with the increase heat of fusion will be favoured (e.g. SiO_2). However, in the case of the concentrated liquors the both requirements are fulfilled with a stable crystalline interior and a fractal exterior.



Theory: Stability of fractal interface driven by entropic energetics.

$$-H_{\text{dense}} > -H_{\text{fractal}}$$

$$-S_{\text{dense}} < -S_{\text{fractal}}$$

Densification can be driven artificially by decreasing the temperature of solution or naturally on increasing particle size.

ACKNOWLEDGEMENTS



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ISIS

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AXAA 2008 Schools,
Advanced Workshops,
Conference and Exhibition