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Using Low-field NMR Relaxation to Optimise Particulate Dispersions of Silica

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Measure Interpret Apply

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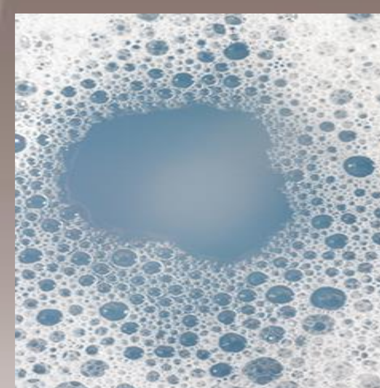
Silica Materials

Can be natural (processed) or synthetic (manufactured)
→ different sizes/shapes; porous/nonporous

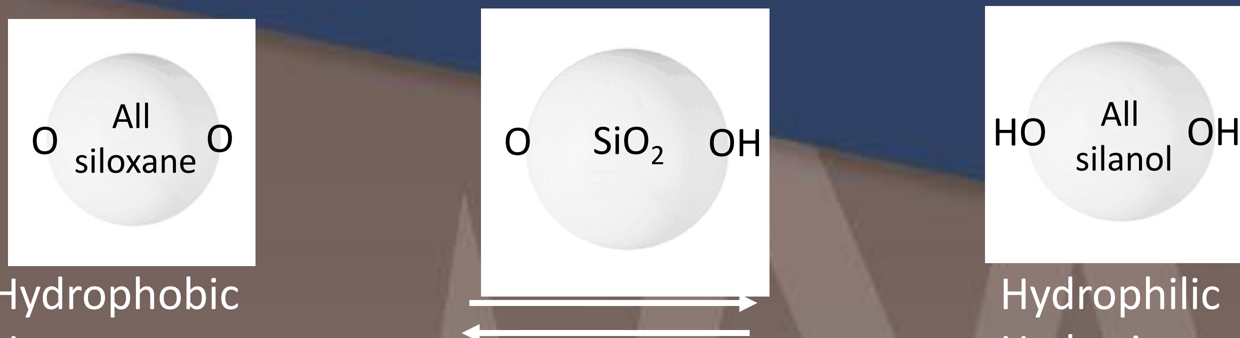



Extensive usage in wide range of applications


Silica Surface Chemistry: Complex

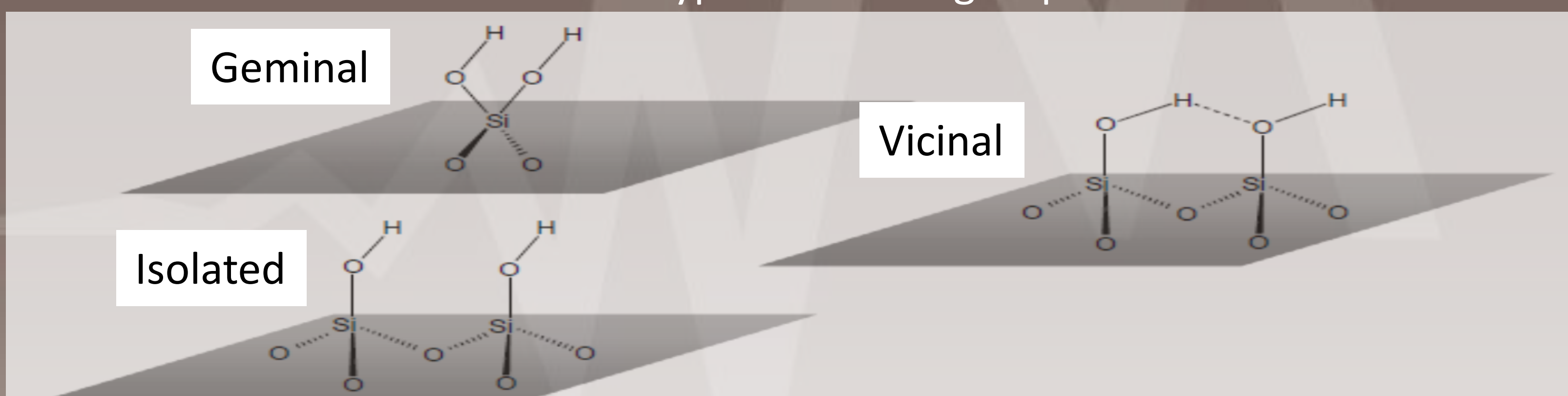
Different ratio of silanol:siloxane groups



Hydrophobic
Heat treatment

Hydrophilic
Hydration

Different types of silanol groups



RK. Iler *Chemistry of Silica*, Wiley-VCH Verlag, Weinheim (1979)

- surface physical and chemical characterization can be challenging
  - wetted surface area different for each silica type
  - important in formulation → ability to tailor silica properties to suit an application provides economic benefits

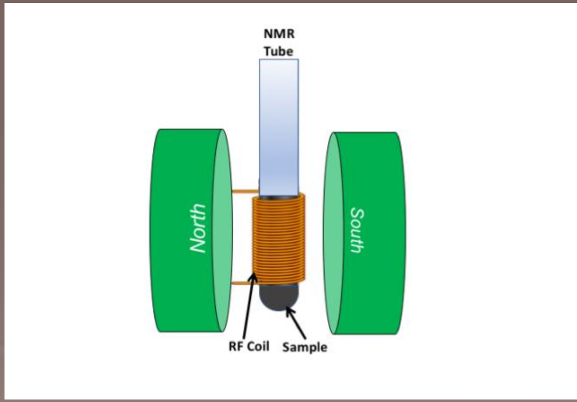
NMR Relaxation

NMR solvent relaxation times sensitive to:

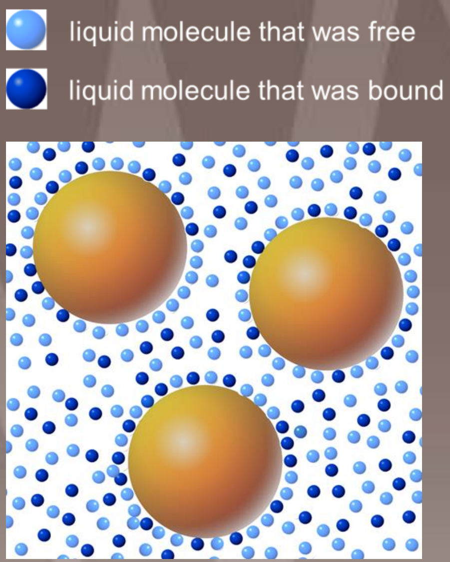
the available (wetted) surface area in a dispersion of particles in a fluid

the specific nature of the particle's interfacial characteristics

NMR Spectrometer



Magnet and RF Coil Assembly



Both have a characteristic relaxation time, T, and a relaxation rate, R (=1/T)

Free Liquid: Long Relaxation time (sec)

Bound Liquid: Short Relaxation time (msec)

Observe a single relaxation that is a weighted average

$$R_{av} = R_f (1-\varphi) + R_b \varphi$$

φ: proportion of bound liquid

R_b: relaxation rate of bound liquid

R_f: relaxation rate of free liquid

NMR relaxation measurements are fast, non-invasive, and can be made at industrially relevant concentrations in virtually any type of liquid

Wetted Surface area of Particulate Suspensions

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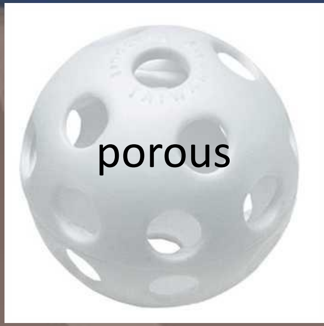
Surface area measurement by gas adsorption (N_2/BET) only suitable for dry powders

Surface Area: Size and Shape

Three spherical particles same geometric diameter



Calculated surface area based on *diameter* is the same

- Non-imaging particle sizers → Equivalent Spherical Diameter (ESD)
  - Surface areas calculated from such data can be erroneous and misleading

NMR relaxation measurements can provide **direct** determination of **wetted** surface area* of particulate suspensions without dilution, and irrespective of size or shape

* C.L. Claves *et al*, Surface Area Determination via NMR: Fluid and Frequency Effects, *Powder Technology*, 54(4) 261 (1988)

Determination of Wetted Surface Area: Basic Equation

Conversion of relaxation time to surface area simple, straightforward calculation*

$$R_{av} = \mathbf{SA}\,[\varphi_p\, L\, \rho_p\, (R_s - R_b)] + R_b$$

All parameters are known or can be independently measured or calculated

Contrast to LLS instruments → raw scattered/diffracted intensity data de-convoluted using complex algorithms (sums of exponentials or Bessel functions)

Using suitable reference sample → define a calibration constant, k_A:

$$k_{\mathbf{A}} = L\, \rho_{\mathbf{p}}\, (R_{\mathbf{s}} - R_{\mathbf{b}})$$

Then,

$$\mathbf{SA} = R_{av} / [k_{\mathbf{A}}\, \varphi_{\mathbf{p}}] + R_{\mathbf{b}}$$

Normalize out effects of solvent by defining a specific relaxation rate constant, R_{sp}:

$$R_{sp} = [R_{susp}/R_{solv}] - 1$$

* C. L. Cooper *et al*, The use of solvent relaxation nmr to study colloidal suspensions. *Soft Matter*, 9(30) 7211 (2013)

Silica samples*

Silica	N_2/BET Surface area (m^2g^{-1})
A	287
B	246
C	404
D	92
E	89
G	184
H	180
I	174
J	136

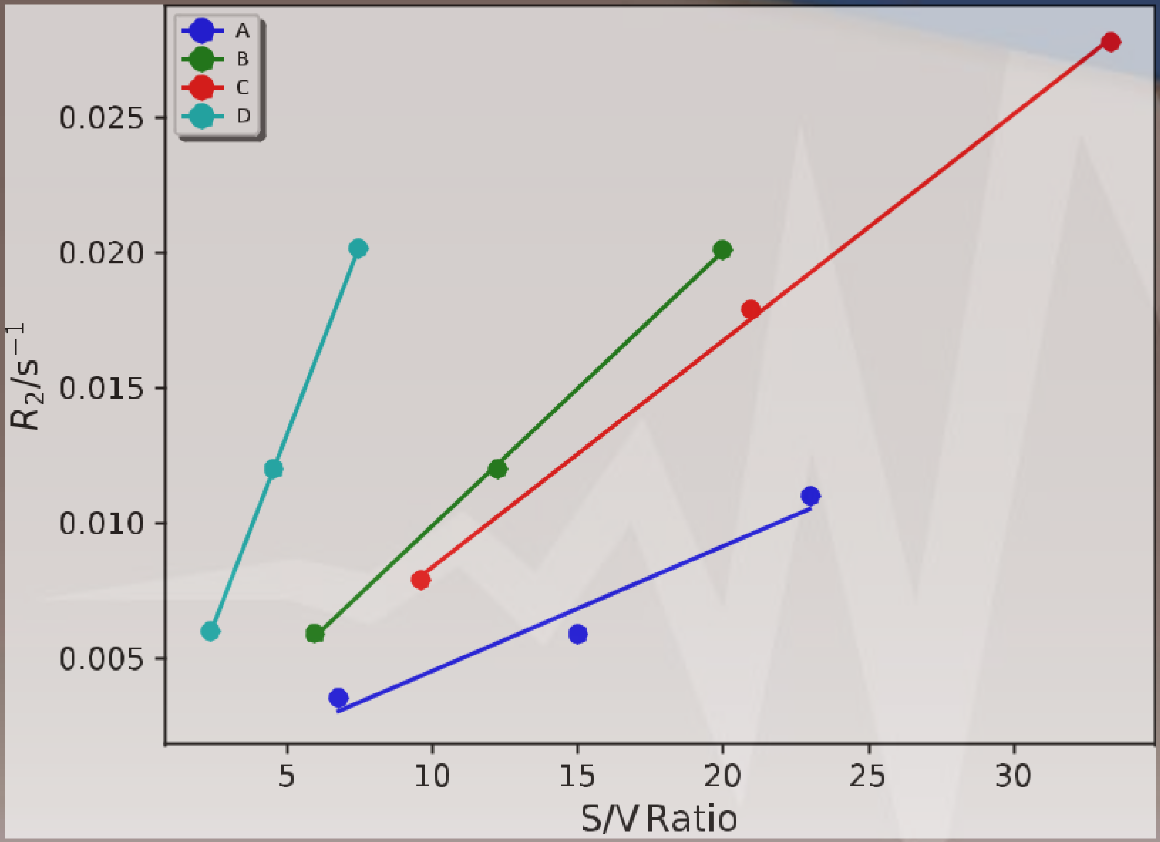
Representative SEM

Silica aggregates
→ non-spherical, irregular morphology
→ fused *bodies* 10's of nm in diameter
→ PSD from 100 of nms to 10's of microns
ca 5 silanol groups/nm^2
→ fully hydrated

* Samples supplied by PQ Silicas, Warrington, UK

NMR Surface area

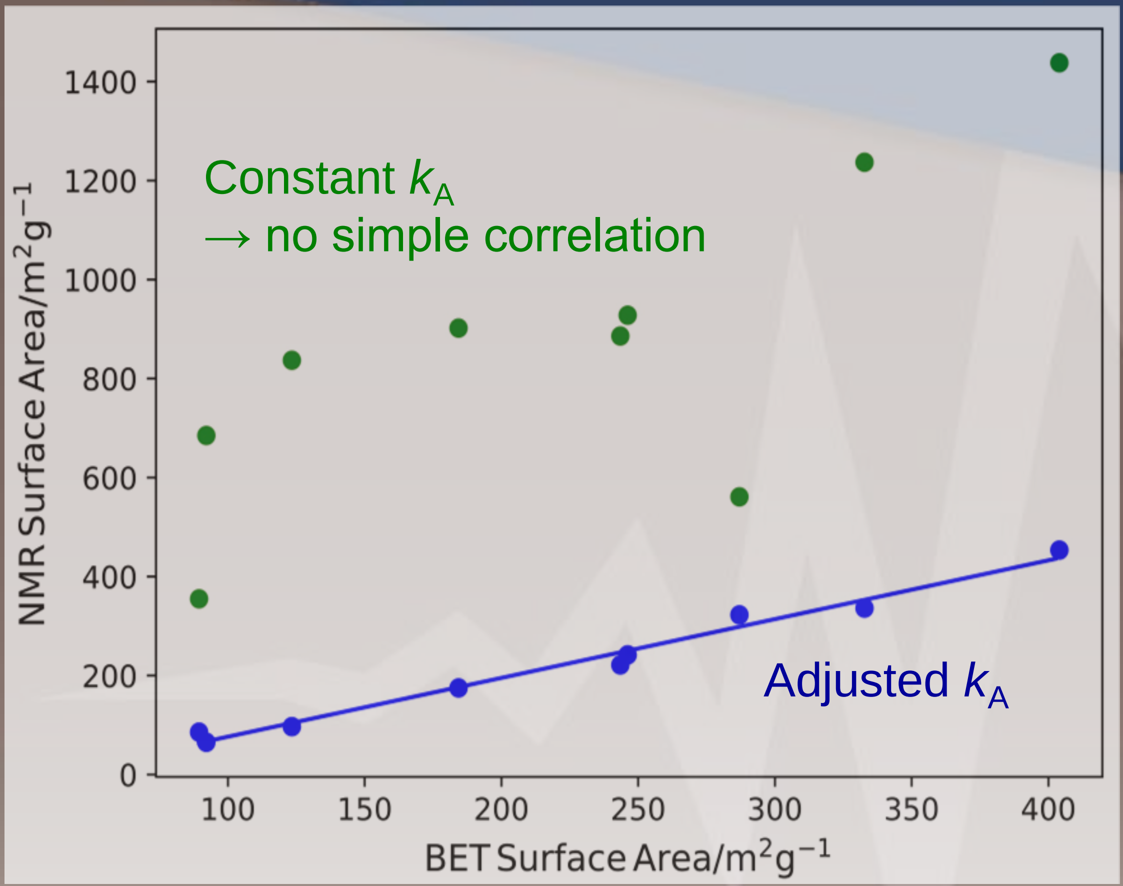
Relaxation rate, R (=1/relaxation time, T) as a function of surface:volume ratio



Different slopes:
→ R depends on *both* size and chemical/physical structure of the surface
→ calibration curve for k_A
→ values vary widely

NMR relaxation measurements characterize the strength of interaction between water (or other liquids or additives) and silica surface functional groups

Impact of k_A value on Surface Area



Silica	k_A (gm^{-2}/s)/10^{-5}
A	46
B	101
C	84
D	277
E	109
G	136
H	155
I	151
J	134

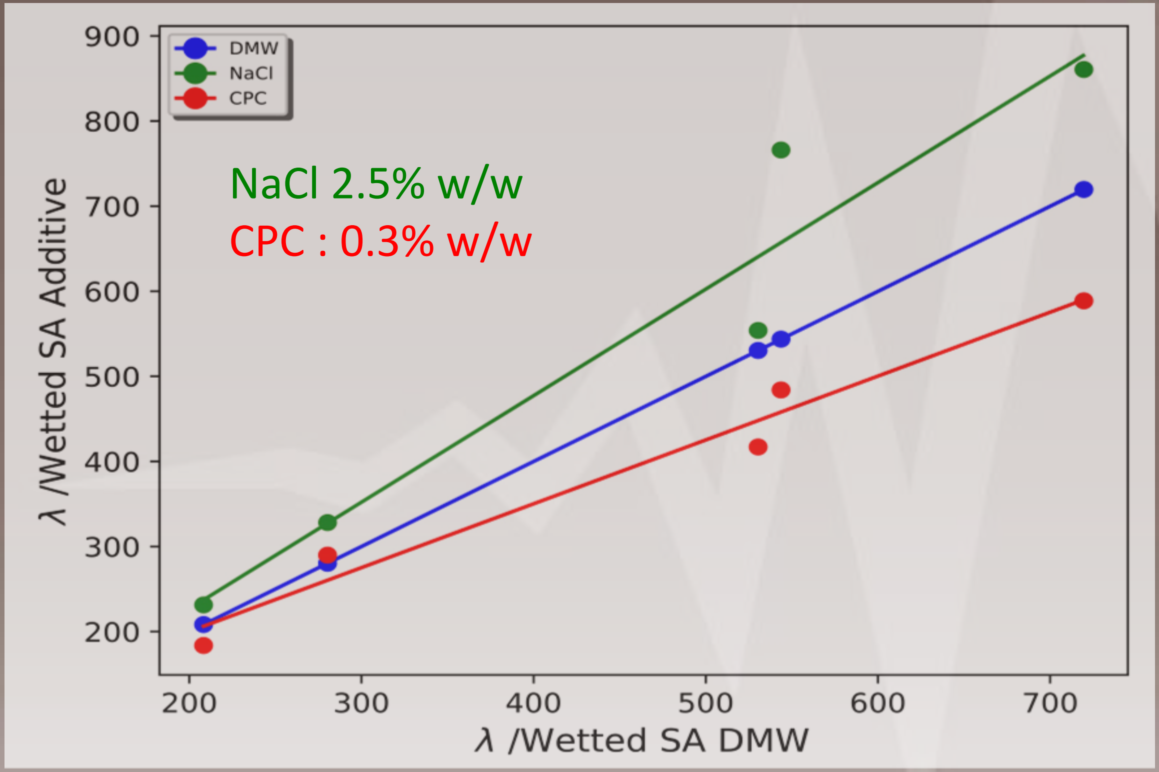
Gas adsorption not be able to distinguish between subtle differences in surface chemical/physical structure of silica
→ N_2 non-specific; H_2O high degree of specificity

Comparison of Effect of Additives

Plot R_{sp} *vs* φ (volume fraction of particles) for silica samples A to E

Slope, $\lambda = \mathbf{SA}\ k_A/R_b$

λ is dimensionless - independent of BET



Higher λ in DMW → larger wetted area available for surface interaction with an additive

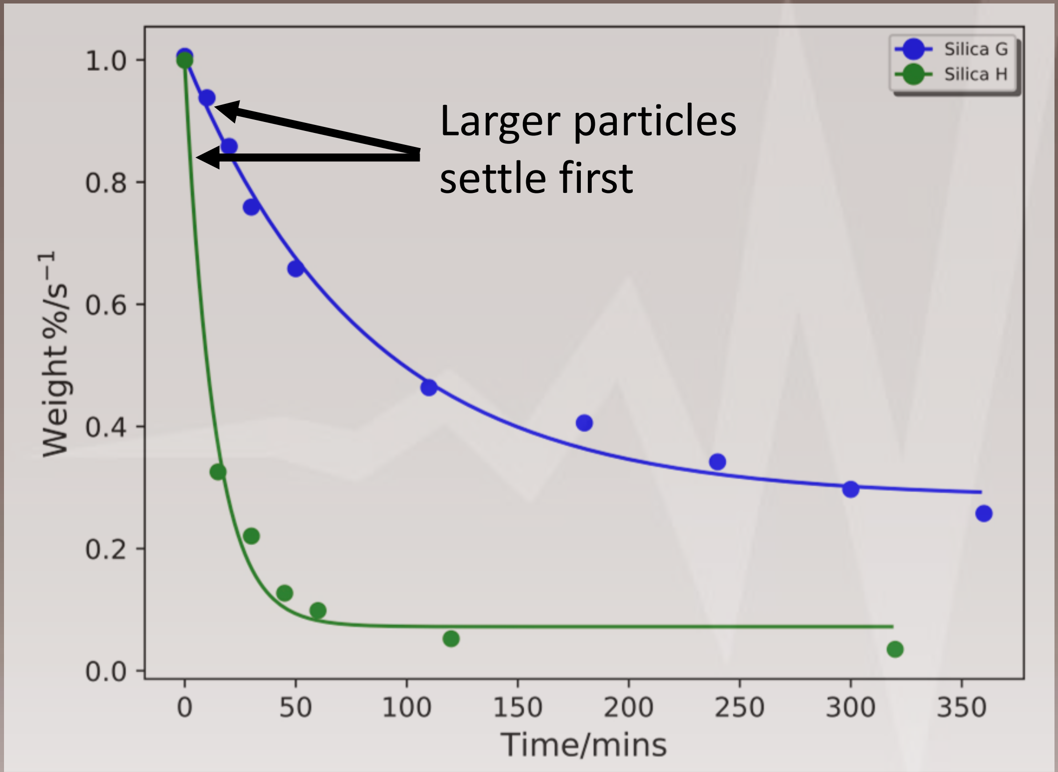
Addition of NaCl:
Changes most pronounced for those silicas having a *higher* λ in DMW

Addition of CPC: same silicas show the greatest *decrease* in λ

Measurements of λ in DMW
→ guide of how those silicas behave in the presence of additives

Sedimentation: Determination of Fines content

Silica	TBD (g/L)	BET SA (m^2g^{-1})	d_{50} size (µm)
G	111	184	13.5
H	151	180	19.7



Silicas have vastly different behavior → related to PSD

Silica G:
Slower initial rate
large fraction of smaller particles still remain in suspension after 200 minutes

Silica H:
Faster initial rate
virtually all particles settle

Relaxation data consistent with traditional methods of investigating stability
→ tapped bulk density
→ particle size by LLS

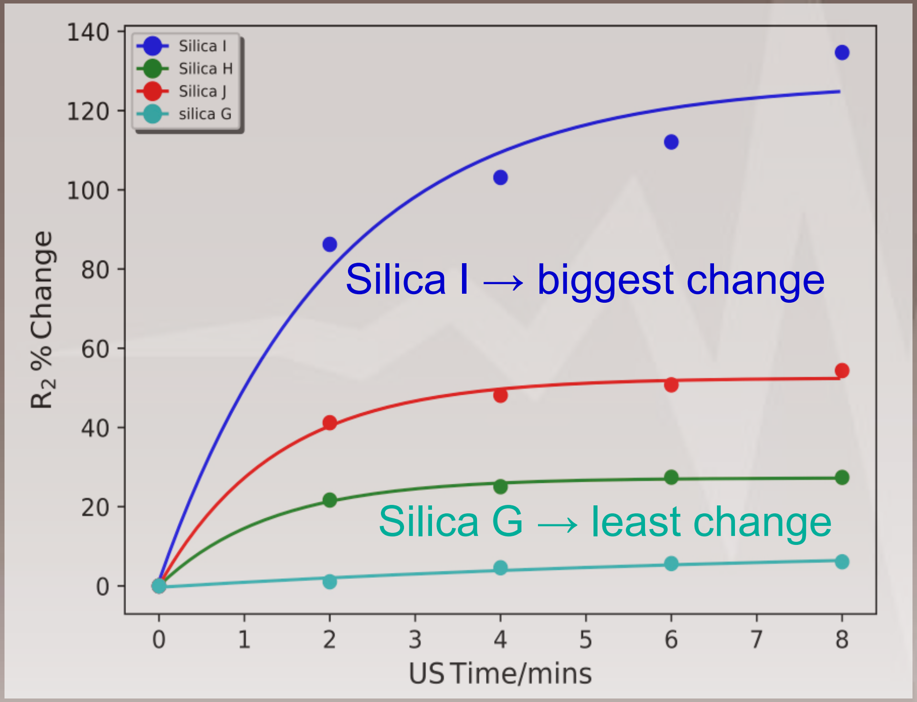
NMR method allows rapid determination of the proportion of fines and sedimentation rate

Effect of Ultrasonic Treatment

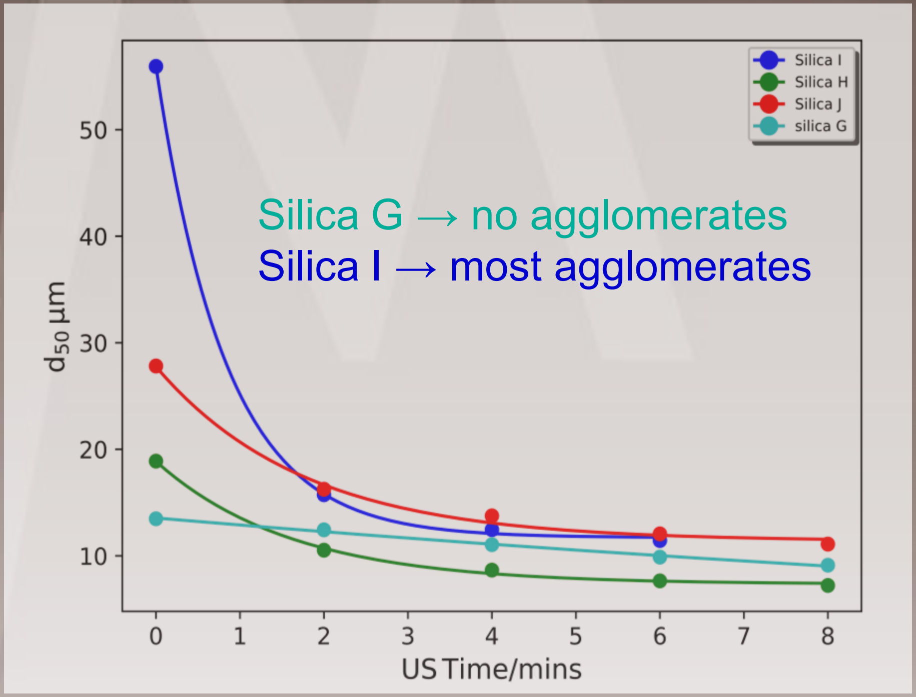
Silicas manufactured under different processing conditions
Silica G → aggregates; Silicas H, I and J → deliberately agglomerated

5%w/w slurries prepared by stirring in DMW

Relaxation rate, R as a function of dispersing time

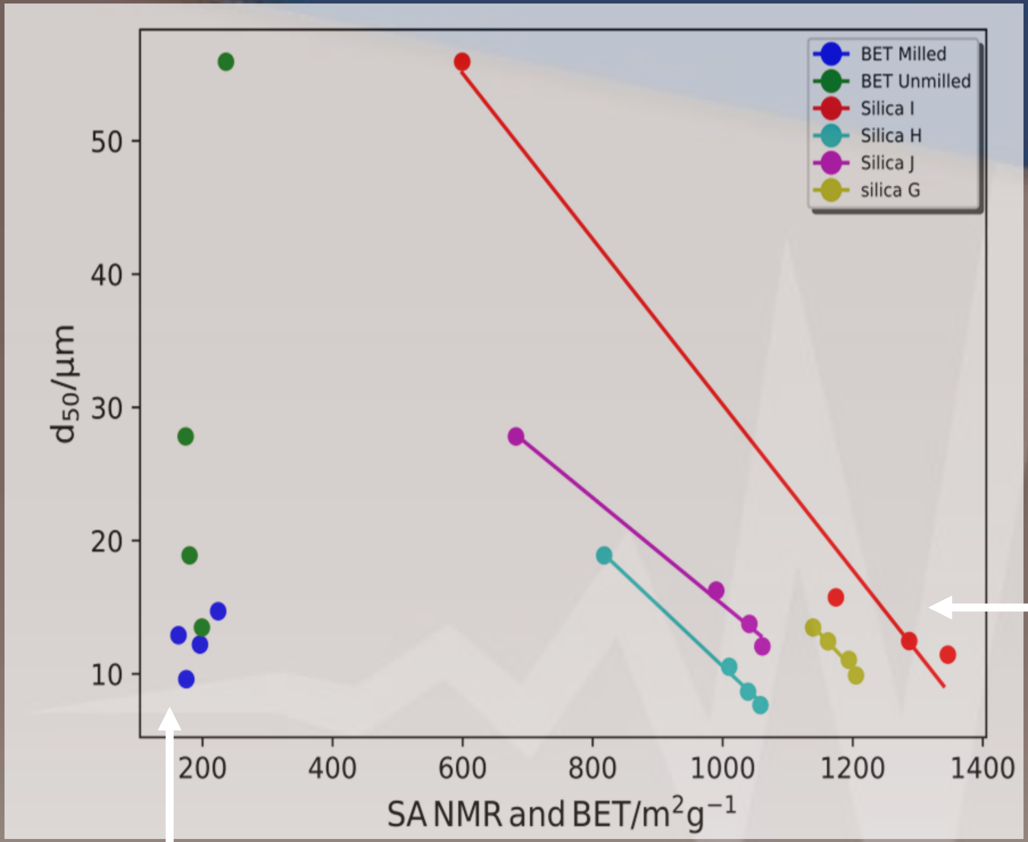


Change in median size (d_{50}) as a function of dispersing time



NMR data on processing can be obtained directly, in real-time and without dilution

Comparison of Surface area: NMR *vs* BET* with changing d_{50}



* Surface areas by N_2/BET gas adsorption measured for Silicas G, H, I and J after dry-milling to approximately same d_{50} values obtained with ultrasonic breakdown (*ca* 10 µm) after 6 minutes

NMR SA values differ widely as d_{50} decreases

All BET SA values – milled, or unmilled – are invariant as d_{50} decreases

NMR relaxation provides information about structural nature of agglomerated silicas not available by BET analysis

Hydrogel Quality Control

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HYDROGELS

→ made from sols having a wide range of silica concentrations → contain large amounts of water
→ mechanical properties change continuously with time → quality control in manufacture is critical

Silica Sample	Water Content (%)	BET Surface Area (m^2g^{-1})	Relaxation Time (ms)
B1	75.45	544	20.4
B2	75.13	554	19.0
B3	73.54	548	15.0
B4	74.12	477	58.0
B5	74.70	450	54.0
B6	73.76	425	76.2
B7	74.01	526	12.7
B8	74.17	528	15.6

Clear correlation between NMR relaxation time and BET surface area

Silicas that are in-specification all have relaxation time <**30ms**
→ corresponds to *largest* BET surface areas

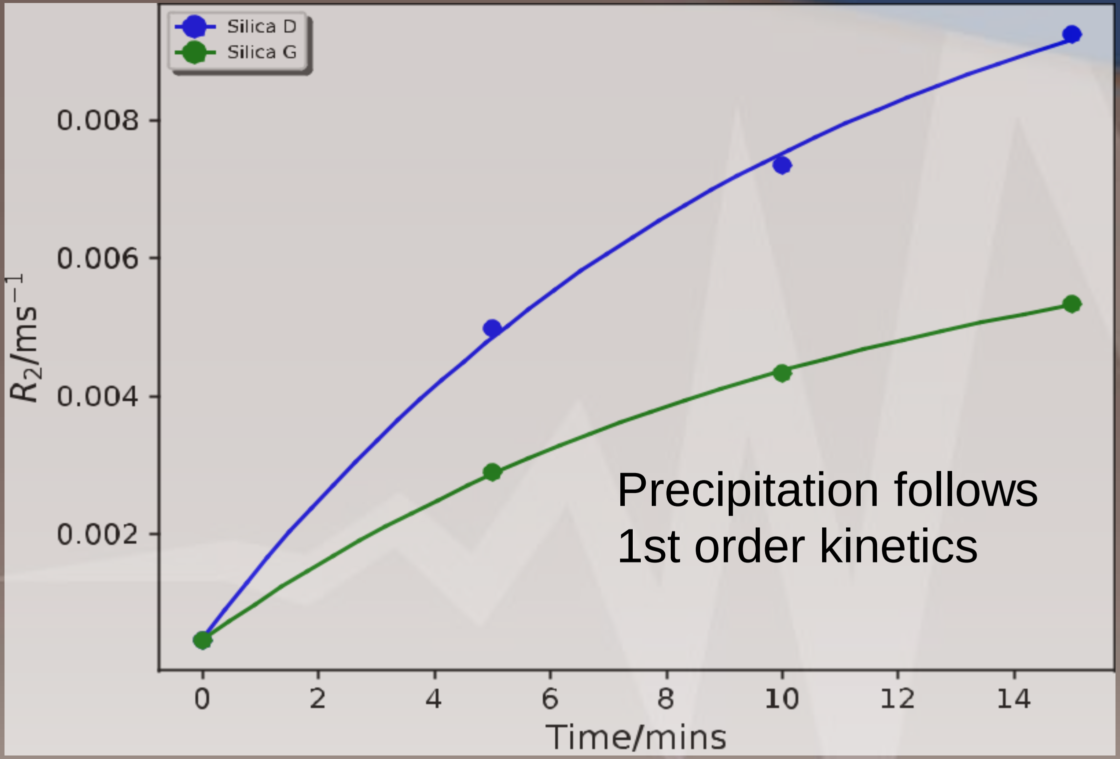
Sample preparation of hydrogels for BET analysis complicated and time consuming
→ not ideal for QC

NMR data obtained directly on hydrogels in minutes with no sample preparation
→ ideal for QC

Chemical Reaction Profiling

SILICAS

→ precipitation from silicate solutions



Relaxation time decreases → R (=1/T) increases as the available surface area increases → increase in size and number density

NMR relaxation useful monitoring precipitation/aggregation processes → measurements made in as little as 3 seconds fast → kinetic processes (coagulation and flocculation) can be monitored

Technique is non-destructive → samples can be stored for re-analysis → ideal for very long-term processes (shelf-storage)

Conclusions

- NMR relaxation is a useful complimentary techniques to traditional particle characterization techniques

- NMR relaxation measurements can:
  - characterize strength and interaction between water and particle surface functional groups
  - monitor the formation and stability of silica dispersions
  - examine the effects of additives (surfactants, polymers)
  - study dispersion techniques

- NMR relaxation measurements not limited to silicas → can be used in aqueous and non-aqueous dispersions → virtually any type of nanoparticle → virtually any type of liquid → minimal sample preparation → rapid measurements

Thank you!

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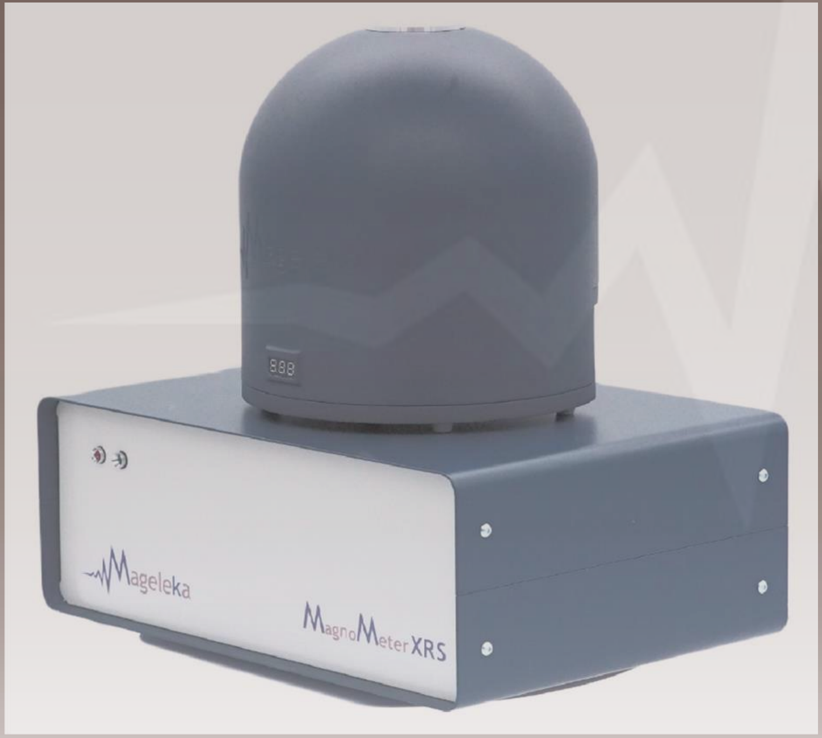

***Magno*M*eter XRS™ *Relaxo*M*eter**

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