**Script for ACS Spring Meeting 2022 Oral presentation**

**SLIDE 1: Characterization Studies of Silica Suspensions using Low-field NMR**

 **Solvent Relaxation**

Good afternoon. I first want to acknowledge various co-workers who all contributed to the work in this presentation.

Although my talk today is concerned with how NMR relaxation can be used to characterize aqueous dispersions of silicas, the methodology and analysis employed is not limited to these and can be applied to any applications involving aqueous or non-aqueous dispersions of any type/grade of nanoparticle.

**SLIDE 2: Silica Materials**

Silicas can be natural (processed) or synthetic (manufactured) and come in a wide variety of different sizes/shapes that porous/nonporous.

They are used ubiquitously in a wide range of applications. Uses include surface coatings, rubber reinforcement, toothpaste abrasives and as thickening agents.

**SLIDE 3: Silica Surface Chemistry**

In addition to the different physical properties, the surface chemistry can be quite complex. So, it is important to recognize that the *wetted* surface area will be different for each case.

Precise surface physical and chemical characterization can be challenging. This is important since, in formulation, the ability to tailor properties of a silica to suit an application is of great value.

**SLIDE 4: NMR Relaxation**

In the time allowed I will not go into details of how to measure NMR relaxation - if anyone is interested, please contact me – I will simply point out that

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

**SLIDE 5: Wetted Surface area of Particulate Suspensions**

Surface area measurement by gas adsorption (typically N2/BET) are only suitable for dry powders. As I hope to demonstrate, it cannot provide information about the *wetted* surface area of particles in suspension – which, in turn, depends critically on how the particles are dispersed.

Unfortunately, surface areas calculated from particle sizing 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.

**SLIDE 6: Determination of Wetted surface Area: Basic Equation**

In contrast to LLS instruments where the raw scattered/diffracted intensity data has to be de-convoluted using complex algorithms (sums of exponentials or Bessel functions) conversion of the NMR relaxation time to a surface area value is a simple, straightforward calculation.

We can normalize out effects of a solvent by defining a specific relaxation rate constant, Rsp, - which is a useful dimensionless parameter.

**SLIDE 7: Silica samples**

The Silica samples in the Table were all supplied by PQ Silicas (UK).

These silica materials exist as aggregated particles with sizes ranging from 100’s of nanometres to 10’s of microns in diameter. The aggregates are comprised of individual bodies of *ca* 10’s of nanometres that are fused together; this structural hierarchy is shown in the SEM. Further, the surfaces are fully hydrated - having approximately 5 silanol groups per nm2 (equal to the Zhuravlev constant)

**SLIDE 8: NMR Surface Area**

This Slide shows data for the relaxation rate (which is the reciprocal of the measured relaxation time) plotted as a function of surface-to-volume ratio, for a series of four silicas (A to D in the Table in Slide 7) dispersed in demineralized water.

All the data are linear but clearly exhibit different slopes.

The graphs are essentially calibration plots of the constant, kA (in Slide 6) for the silicas and it shows how the kA value can vary widely depending on the silica.

**SLIDE 9: Impact of kA value on Surface Area**

In this slide we compare the surface area values obtained from NMR relaxation and BET analysis.

The top plot shows the effect of assuming the *same* kA value for each silica: there is no simple correlation between the two data sets.

It is obvious that NMR relaxation - which measures the silica in a liquid (here water) - is giving a different picture of the surface compared to BET gas adsorption (measured on dry silica).

This should not be surprising as nitrogen is generally agnostic in terms of its ability to adsorb at a surface (whether porous or non-porous). In contrast, the adsorption of water onto surfaces is complex because there is a high degree of specificity in the interactions of water with solid surfaces and it depends very much on the surface chemistry (as shown for silicas in Slide 3).

In contrast, the lower plot uses adjusted (variable) values for kA values (calculated using the BET dry surface area values in Slide 7) and is now linear. However, this now assumes that the surfaces are identical – chemically – and this linear change reflects only the difference in physical characteristics between the silicas.

Thus, these different kA values are essentially measures of the degree of specific interaction of water with the various silica surfaces. That the kA values do differ for the silicas and since the silica surfaces are fully hydrated, implies that the silanol functional groups cannot be the same.

NMR relaxation is known to be a sensitive probe of liquid mobility in a local environment and so what this Slide demonstrates, here, is that such measurements can be used to characterize the strength of interaction between water (or other liquids or additives) and particle surface functional groups.

**SLIDE 10: Comparison of Effect of Additives**

In addition to changes in pH and ionic strength, many formulations often use additives such as polymers or surfactants to control or improve dispersibility, or to induce flocculation.

A useful way to represent the data is through the slopes of the data of a plot of specific relaxation rate, R2sp *vs* volume fraction of particles, φ.

The slope, λ, is dimensionless and samples with higher values of λ have higher wetted surface areas.

Importantly, λ is now a measurement which is *independent* of BET, and therefore it can provide more information about how a silica will behave in a real application - for example in a toothpaste, where a BET measurement is simply not practical but can be measured directly using NMR relaxation.

As can be seen, λ values increase with addition of NaCl and these changes are most pronounced for those silicas having a higher λ in DMW.

Interestingly, those latter silicas show the greatest decreases in λ with addition of Cetyl Pyridinium Chloride. CPC has a hydrophilic head group which is in interaction with the silica surface displacing water, and its hydrophobic tail is preventing access of bulk water to the silica surface.

Therefore, measurements of λ in DMW can be used as guide of how those silicas will behave in the presence of additives. A higher λ in DMW suggests a larger wetted area available for surface interaction with an additive.

**SLIDE 11: Sedimentation: Determination of Fines content**

Sedimentation is simply the time-dependent deposition of particles due to gravity. The higher the density of the material, the faster is rate at which particles will settle. It impacts, for example, storage of suspensions.

At short measurement times, settling is dominated by the largest particles in any particle size distribution (PSD) and there will be an initial increase in relaxation time, i.e., a decrease in relaxation rate, R2. However, and importantly, at longer measurement times the rate of increase of relaxation time will very much depend upon the fraction and size of any fines in the PSD.

So, comparing relaxation time measurements of suspensions undergoing settling can provide a quick and facile method to differentiate them.

The slide shows the change in w/w% with time for two different silica dispersions - samples G and H.

The long-time value of R2 should, in the limit of all the particles having settled, go to that of the bulk fluid. This is close to that value for sample H but not for sample G which clearly contains a much larger fraction of smaller particles that remain in suspension even after 200 minutes.

These data are consistent with more traditional methods of investigating stability. The Table above the graph shows the tapped bulk density (TBD), surface area (BET) and light scattering estimates of the median particle size (d50 values) for these two samples.

As expected, samples with a higher TBD will sediment more rapidly than ones with lower TBD. Also, samples with a lower d50 value contain a higher portion of fine material, and, hence, a larger surface area, and so will sediment more slowly.

**SLIDE 12: Effect of Ultrasonic treatment**

Silicas G, H, I and J were made from the same precipitated silica feedstock.

H, I and J were spray dried but under different conditions to produce “agglomerated” (i.e., aggregates of aggregates) silicas of varying particle size.

G was dried using a technique that avoids significant agglomeration and is better described as just containing aggregates.

This Slide shows two graphs – both are a function of ultrasonic treatment time. The one on the left-hand side plots NMR relaxation data.

The silica G shows little change because it comprises primarily an aggregated structure. In contrast the Silicas H, I and J are agglomerated particles that break down under application of ultrasound. The largest change is seen for Silica I.

The graph on the right-hand side are median (d50) values from laser light scattering, obtained by diluting the samples in a standard way.

The results presented show significant changes in relaxation time that clearly correlate with the changing particle size but it is useful to again emphasize that the NMR data can be obtained directly and without dilution.

**SLIDE 13: Comparison of Surface Area**

Subsequently, these same starting silica samples were dry milled to achieve similar d50 values to those achieved with ultrasonic breakdown (approximately 10 micron after 6 minutes).

This then made it possible to generate a BET SA *vs* NMR SA comparison with changing d50 -as shown in the Slide.

Surprisingly, the results for the BET area of the silicas – whether milled (blue points), or unmilled (green points) - did not vary.

Once again, NMR relaxation is providing information about the structural nature of agglomerated silicas in aqueous suspension not available by BET analysis (on the dry material).

**SLIDE 14: Hydrogel Quality Control**

Hydrogels can be made from sols having a wide range of silica concentrations, but they all contain large amounts of water; the mechanical properties change continuously with time. Hence quality control (QC) in manufacture is critical.

Hydrogels of silica typically contain 70-90 % water and these can be measured “as-is” (i.e., no sample preparation) in an NMR spectrometer.

Samples which were considered to be “in-specification” were all characterized by a relaxation time of < 30 ms - which correlates with the higher BET surface areas.

But, as can be seen, the measured NMR relaxation values are a more sensitive metric for these hydrogels.

Also, in the case of hydrogels, because they are so high in water content, an additional initial drying step is needed (prior to outgassing). However, since drying a hydrogel can be detrimental to its structure, this drying step must be performed much more carefully than for regular silicas. Hence, it is less than ideal for use in QC.

In contrast, NMR data can be obtained directly on the hydrogels in minutes with no sample preparation. For such materials, the advantages of using the NMR method could be substantial.

**SLIDE 15: Chemical reaction Profiling**

The previous examples have focused on the characterization of materials. Here we will suggest how NMR relaxation could be useful in monitoring precipitation processes which are often important in the manufacture of materials. As an illustration, we use the simple precipitation of silica from a silicate solution.

As can be seen, as the precipitation proceeds then the relaxation rate increases as the total available surface area increases (owing to an increase in particle number density).

The increase of relaxation rate, R2 with time for two different silica samples (D and G) follow 1st order kinetics shown by the fitted curves. The results compared well with traditional sampling methods.

Since a relaxation time measurement can be made in as little as 3 seconds, fast kinetic processes such as aggregation (coagulation and flocculation) and accelerated aging can be readily monitored.

**SLIDE 16: Conclusions**

In conclusion, I hope that I have been able to persuade you that NMR relaxation is a useful complimentary technique to traditional particle characterization techniques and that NMR relaxation measurements can be used to:

characterize the 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) and study dispersion techniques.

**SLIDE 17: Thank You!**

Finally, I want to thank MAGELEKA for the use of their instrument.