Project 1.2 Summary: Effect of Particle Hydrophobicity on Incorporation and Break-up of Four Nanoscale Silica Cluster Grades using the In-Line Rotor-Stator Ytron ZC1

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Objectives and Scope of Work

1.2 Effect of Particle Hydrophobicity on Incorporation and Break-up of Four Nanoscale Silica Cluster Grades using the In-Line Rotor-Stator Ytron ZC1

The aim of this project is to study:

➢ Study the effect of hydrophilicity/hydrophobicity on powder incorporation and particle break-up using the in-line Ytron ZC1.

► Using four different Aerosil grades (fumed silica) with different degrees of hydrophilicity
Materials: Structure of Silica Particle Clusters

- **Aggregates:**
  - Primary particles joined mainly at surfaces
  - Cannot be broken by hydrodynamic stresses (sintered)

- **Agglomerates:**
  - Collection of primary particles and aggregates joined at edges and corners
  - Held together by Van der Waals forces and hydrogen bridges between surface silanol groups (-Si-OH)
Materials: Hydrophilic Silica Grades

- **Aerosil 200V**: Commonly used in DOMINO work. Naturally hydrophilic silica produced by flame pyrolysis. The V indicates that this material has been “densified”, i.e., prior to packaging the material has been mechanically compressed, which increases its bulk density.

- **Aerosil 200**: same as 200V but not “densified”. Not used in DOMINO before.
Materials: Hydrophobic After-treatment

- Hydrophobic silica grades are produced by treating hydrophilic silica with a silane chloride, siloxane, or other materials, immediately after production (continuous process).

- Surface silanol groups are permanently replaced by hydrophobic organic groups.

- There are fewer hydrogen bridges between particles.
Materials: Hydrophobic Silica Grades

- **Aerosil R816**: partially hydrophobic fumed silica. Based on Aerosil 200, treated with a hexadecylsilane. Surface silanol concentration ~30% of initial value. Used in last year’s work and previously in DOMINO particle-liquid affinity studies.

- **Aerosil R202**: fully hydrophobic fumed silica. Treated with polydimethylsiloxane. Used in previous DOMINO particle-liquid affinity studies (dispersed in silicone oil).
# Materials – Physical Properties

<table>
<thead>
<tr>
<th>Type of silica</th>
<th>Aerosil 200V</th>
<th>Aerosil 200</th>
<th>Aerosil R816</th>
<th>Aerosil R202</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary particle size, nm</td>
<td>12</td>
<td>12</td>
<td>12</td>
<td>14</td>
</tr>
<tr>
<td>Tapped density (approx. value), g/l</td>
<td>120</td>
<td>50</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>Specific Surface Area (BET), m²/g</td>
<td>200</td>
<td>200</td>
<td>190</td>
<td>100</td>
</tr>
<tr>
<td>Carbon content, wt%</td>
<td>–</td>
<td>–</td>
<td>0.9 - 1.8</td>
<td>3.5 - 5.0</td>
</tr>
</tbody>
</table>
Equipment: Ytron ZC1

- 3 mm rotor
- 3 mm stator
- 1.5 mm stator
Equipment: Ytron ZC1

- Powder inlet
- Rotor-stator
- Pump
- Incorporation hose
- Incorporation funnel
Wettability Tests
Powder Wettability Technique

- Measurement of the rate at which a given amount of dry powder sinks in water – details in DOM09
- Theoretically, this method allows estimating the powder’s contact angle with the liquid but data are usually difficult to analyse – used in the past for qualitative comparison
Wettability Equipment and Method

- Measures height of a powder surface above water using a laser.
- Signal from the laser module monitored and saved by a computer running a bespoke DAQ program.
- Vessel below the laser contains approximately 100ml of distilled water.
- A plastic film is placed to seal in the water and allow the placement of dry powder above.
- When the film is withdrawn, the wettability experiment commences.
Summary of Wettability Tests

- Aerosil R202 did not go into the water at all.
- 200 faster to wet than 200V, possibly due to compression of 200V (200 has larger pores for the water to penetrate – capillary effect)
- Wettability results consistent with hydrophilicity/hydrophobicity
Incorporation Tests
Background: Hydrophilic vs Hydrophobic Surface Addition

**Aerosil 200V**

- Before Addition
- $t = 0$
- $t = 1$ min
- $t = 2$ min

**Aerosil R816**

- $t = 0$
- $t = 1$ min
- $t = 10$ min
- $t = 40$ min

- 1%wt addition, T/3 Ekato Dissolver, 2000 rpm, T = 0.3 m (PROFORM)
- $t_{incorp.}$ is one order of magnitude higher with hydrophobic silica
There is an optimum range of flow rates for incorporation

Air velocities are higher for 3 mm head at a given water flow rate
Previous Work: Incorporation of R816

- Longer incorporation time with hydrophobic particles (R816) compared to those with the hydrophilic particles (200V)
- Difference due to hydrophilicity? It was postulated during the last SCM that it may be due to a difference in “conveyance” in the hose and it was proposed that tests using the funnel may clarify this.
Background: Hose vs Funnel (Ytron Y)

- Incorporation of Aerosil 200V much faster when using the funnel, compared to the hose, with the Ytron Y (in-tank device)
Background: Hose vs Funnel (Ytron ZC1 - Zeolite)

- Very fast incorporation of Zeolite: 3 – 6 seconds per 1%wt addition
- Zeolite is much heavier than Aerosils (tapped density ~ 400 – 480 g/l)
Experimental Set-Up – Incorporation

- Ytron ZC1 in the re-circulation loop of a T=0.60 m tank with a PBT
- Rotor Diameter: $D_{\text{out}} = 0.095$ m
- Fine Rotor-Stator: 3.0 mm separation
- Constant speed device: $N = 6,500$ rpm
- Flow rate: $Q = 1.9$ l/s
- Total suspension volume = 0.1 m$^3$
- Additions of 1%wt (1kg) Aerosils using the funnel up to 4%wt
Incorporation Results

- Incorporation time of R816 higher than with 200V. Consistent with hose results.
- Almost no difference in incorporation time between R816 and 200.
- Low incorporation time with R202 (only one addition was possible).
- Apparent maxima at 2%wt...

Incorporation Time, s

Aerosil Concentration, %wt
## Incorporation Data Analysis

<table>
<thead>
<tr>
<th>Conc.</th>
<th>$t_{\text{incorp.}}$</th>
<th>$m_{\text{incorp.}}$</th>
<th>$Q_{\text{incorp.}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>%wt</td>
<td>s</td>
<td>kg/s</td>
<td>L/s</td>
</tr>
<tr>
<td>200V</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>14.2</td>
<td>0.070</td>
<td>0.59</td>
</tr>
<tr>
<td>2</td>
<td>23.7</td>
<td>0.053</td>
<td>0.44</td>
</tr>
<tr>
<td>3</td>
<td>23.2</td>
<td>0.049</td>
<td>0.41</td>
</tr>
<tr>
<td>4</td>
<td>17.9</td>
<td>0.051</td>
<td>0.42</td>
</tr>
<tr>
<td>200</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>33.2</td>
<td>0.030</td>
<td>0.60</td>
</tr>
<tr>
<td>2</td>
<td>41.7</td>
<td>0.027</td>
<td>0.53</td>
</tr>
<tr>
<td>3</td>
<td>43.7</td>
<td>0.025</td>
<td>0.51</td>
</tr>
<tr>
<td>4</td>
<td>22.2</td>
<td>0.028</td>
<td>0.57</td>
</tr>
<tr>
<td>R816</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>35.8</td>
<td>0.028</td>
<td>0.47</td>
</tr>
<tr>
<td>2</td>
<td>50.8</td>
<td>0.023</td>
<td>0.39</td>
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<tr>
<td>3</td>
<td>44.8</td>
<td>0.023</td>
<td>0.38</td>
</tr>
<tr>
<td>4</td>
<td>36.8</td>
<td>0.024</td>
<td>0.40</td>
</tr>
<tr>
<td>R202</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>18.0</td>
<td>0.056</td>
<td>0.93</td>
</tr>
</tbody>
</table>

**Conc.**: Cumulative Aerosil concentration in %wt (1%wt = 1kg of dry Aerosil).

**$t_{\text{incorp.}}$**: time to incorporate a 1%wt (1 kg) Aerosil addition.

**$m_{\text{incorp.}}$**: mass incorporation rate:

$$m_{\text{incorp.}} = \frac{m_{\text{Aerosil}}}{\sum t_{\text{incorp.}}}$$

**$Q_{\text{incorp.}}$**: incorporation flow rate:

$$Q_{\text{incorp.}} = \rho_{\text{Aerosil}} m_{\text{incorp.}}$$

\[ \begin{align*}
\rho_{200V} &= 120 \text{ g/l} \\
\rho_{200} &= 50 \text{ g/l} \\
\rho_{R816} &= 60 \text{ g/l} \\
\rho_{R202} &= 60 \text{ g/l}
\end{align*} \]
Incorporation Flow Rate

- Small differences in $Q_{\text{incorp.}}$ among 200V, 200 and R816 – calcs. based on approx. tapped density values. – will be confirmed with cert. of analysis.
- Significantly higher $Q_{\text{incorp.}}$ with R202 – see next slide
Incorporation Funnel

Due to its strong hydrophobicity, R202 has the lowest affinity for the funnel (stainless steel).

This results in less material sticking to the funnel and faster incorporation despite its low tapped density.
Incorporation of Aerosil R202

Incorporation of Aerosil R202
Ytron ZC1 - 1.9 l/s
1%wt
Break-up Tests
Comparing based on specific energy, which takes into account the differences in $Q$, shows that breakup in water is faster with R816 – consistent with older work and with R816 having fewer $H_2$ bridges.
Background: Previous Work with R816 & 200V

- No difference in the size of fines generated using either Aerosil - Consistent with previous DOMINO work with these materials.
Experimental Set-Up – Break-up

- Ytron ZC1 in the re-circulation loop of a T=0.60 m tank with a PBT at 150 rpm
- Rotor Diameter: $D_{out} = 0.095$ m
- Fine Rotor-Stator: 3.0 mm separation
- Constant speed device: $N = 6,500$ rpm
- Flow rate: $Q = 1.9$ l/s
- Total suspension volume = 0.1 m³
- $1^{st}$ 1%wt (1kg) addition of Aerosils recirculated for 2 hours taking samples as a function of time (200V, 200, & R816)
- Samples taken from tank
- PSD measured using laser diffraction
Particle Size Distribution Evolution – Aerosil 200V

- PSD evolution broadly consistent with erosion being the predominant breakup mechanism
Difficult to tell which break-up mechanism dominates, could be shattering or a combination of shattering and erosion.
Particle Size Distribution Evolution – Aerosil R816

- Evolution of coarse peak seems consistent with erosion.
- Bimodal fines peak – not observed before with Aerosils, except a case of bead contamination or damage in the mill – difficult to explain.
Fines Generation Rates

- Faster break-up with 200 (almost 40% fines at t = 0) – Consistent with higher porosity (lower tensile strength)
- R816 initially faster than 200V – Consistent with fewer hydrogen bridges and previous results
Fines Average Particle Size

- No difference between 200 and 200V, larger (but still mostly within usual range) fines with R816 (due to bimodal peak).
Coarse Particle Size Reduction

- Large variability with 200, possibly due to shattering being significant – shattering indicates weaker agglomerates
- 200V and R816 more consistent with erosion. R816 seems to plateau
Rheology Tests
Rheological Measurements Summary

- 4%wt 200V and 200 samples and 1%wt R816 affected by secondary flow error at all shear rates – Viscosity ~ 1 – 2 mPa·s
- R202 Samples not measurable due to separation

<table>
<thead>
<tr>
<th>Concentration, %wt</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>200V</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>Y</td>
</tr>
<tr>
<td>200</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>Y</td>
</tr>
<tr>
<td>R816</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
</tr>
<tr>
<td>R202</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>N</td>
</tr>
</tbody>
</table>
Rheological Measurements – R816

- Even at low concentrations (2 – 3%wt), R816 has a strong effect on rheology.
Conclusions
Conclusions

- Incorporation and break up tests were carried out using Aerosils (fumed silica) with different degrees of hydrophilicity and different tapped densities.

- Wettability tests indicate that the wetting behaviour (in water) of the Aerosils is consistent with their hydrophilicity:
  - The hydrophilic grades (200 and 200V) go readily into water. The difference between them can be explained by the fact that 200V is compressed and, therefore, it is more difficult to penetrate the powder via capillary effect.
  - The partially hydrophobic grade (R816) is wetted but at a slower rate.
  - The fully hydrophobic grade (R202) is not wetted by water at all.
Conclusions

- Previous work on incorporation via surface addition of 200V (hydrophilic) and R816 (partially hydrophobic) is consistent with wettability behaviour: R816 takes an order of magnitude longer to incorporate. The difference in tapped density alone does not seem to justify such large difference. Therefore, the hydrophilic nature of the powder must have an effect.

- Incorporation using the ZC1, on the other hand, does not seem to be affected by the hydrophilic/hydrophobic nature of the material, other than the fact that the more hydrophobic grade (R202) tends to adhere less to the surface of the funnel, which results in lower friction and therefore faster incorporation time.

- 200V incorporates faster than 200 and R816 but only because it is more dense.
Conclusions

- Even though R202 (fully hydrophobic) is easy to incorporate using the Ytron ZC1, it can be difficult to maintain in suspension due to its strong hydrophobicity.

- Break up tests with 200V, 200 and R816 show that:
  - 200 (hydrophilic) is the easiest to break up. Consistent with the lack of compression resulting in larger pores (fewer contact points between agglomerates and therefore fewer hydrogen bridges)
  - R816 (partially hydrophobic) is easier to break up than 200V (hydrophilic), at least initially. This is consistent with previous work with these materials and due to fewer hydrogen bridges due to the hydrophobic aftertreatment (and possibly due to lack of compression?)
Potential Future Work

- Carry out similar tests with other silica grades or other materials?
- Suggestions welcome