Particle Characterization: Petroleum Applications

Mark Bumiller
Range of Applications

Exploration Completion
Drilling fluid Proppants

Processing
Oil in water emulsion Solid particles

Refining
Catalysts

Techniques used: laser diffraction, dynamic image analysis, Acoustic spectroscopy, surface area analysis
Exploration: Drilling Rig

1. Mud tanks
2. Shale shaker
3. Mud suction line
4. Mud pump
16. Drill pipe
20. Rotary table
26. Drill bit
Drilling Fluid (Mud)

- Remove cuttings from well
- Suspend and release cuttings
- Control formation pressures
- Seal permeable formations
- Maintain wellbore stability
- Minimizing formation damage
- Cool, lubricate, and support the bit and drilling assembly
- Facilitate cementing and completion
Types of Fluids

- Water-based mud (WBM)
  - Water, then clays and other chemicals
  - Most common is bentonite
  - Other chemicals for viscosity control, shale stability, enhance drilling rate, cooling, etc.

- Oil-based mud (OBM)
  - Base fluid is a petroleum product such as diesel fuel

- Synthetic-based fluid (SBM)
  - Base fluid is a synthetic oil
Particle Size of Drilling Fluids

- Standard methods include sieves & sedimentation
- Report residue > 75 µm & < 6 µm
- Diffraction can report this, + distribution information
  - D10, d50, d90
  - Quicker, more reproducible
- Recommended practices for barite:
  - RI: 1.64, 0.1 in 1.33 (water)
  - Dispersant: 1 g sodium pyrophosphate in 1000 cm³ water
  - Mix paste of barite powder, dispersant
  - Add to system, %T not < 90-85%
  - Ultrasound for 60 sec
  - Measure
Particle Size of Drilling Fluid

Composition:
Bentonite 29 g/L
Xantham gum 2.9 g/L
P.A.C. (polymer additive) 2.9 g/L
Barite 15 g/L
NaOH 0.7 g/L

Procedure:
RI for barite = 1.64, 0.1
5 g of barite added to a beaker.
Dispersant* added to barite drop wise until smooth paste was created.
*Dispersant solution: 1 g of sodium pyrophosphate/1000 cm³ of solution.
Sampler was filled with DI water.
Barite sample added the sampler using clean spatula to desired concentration:
   Transmission = 80-90%
Sampler circulation setting = 5
Ultrasound at level 7 applied to sample for 60 sec
Wait 30 sec after turning off the ultrasound
Perform particle size measurement
Repeat these steps for a total of 3 sub-samples from the original paste
Particle Size of Drilling Fluid

LA-950
Particle Size of Drilling Fluid

LA-930
Particle Size of Drilling Fluid

Diameter on %:
1. 10.00 (%) - 0.875 (µm)
2. 50.00 (%) - 8.999 (µm)
3. 90.00 (%) - 40.147 (µm)

LA-300
Smaller, portable, better for field work
55lb/25 kg
Hydraulic Fracturing Proppant

20/40 sand
Proppants

- Keep fractures open
- Improves permeability
- Often sand, specified by sieve sizes
  - 12/20, 16/30, 20/40, 40/70 (95% passes between these sieve sizes)
- Higher tech proppants, more expensive, higher performance
Ceramic Proppant Patent

“The resulting pellets have a sphericity of about 0.8-0.9, as determined using the Krumbein and Sloss chart.”

<table>
<thead>
<tr>
<th>ASTM U.S. Standard Mesh Size</th>
<th>Equivalent Diameter</th>
<th>Particle Grade</th>
<th>Intermediate PSD-1</th>
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<tbody>
<tr>
<td>16 1.18 mm</td>
<td>&gt;1.18 mm</td>
<td>0.0</td>
<td>0.5</td>
</tr>
<tr>
<td>18 1.18 mm</td>
<td>1.18 mm</td>
<td>0.0</td>
<td>6.0</td>
</tr>
<tr>
<td>20 0.85-1.0 mm</td>
<td>0.85-1.0 mm</td>
<td>2.0</td>
<td>27.9</td>
</tr>
<tr>
<td>25 0.71-0.85 mm</td>
<td>0.71-0.85 mm</td>
<td>36.0</td>
<td>24.7</td>
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<tr>
<td>30 0.6-0.71 mm</td>
<td>0.6-0.71 mm</td>
<td>33.0</td>
<td>21.2</td>
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<tr>
<td>35 0.50-0.60 mm</td>
<td>0.50-0.60 mm</td>
<td>24.0</td>
<td>12.8</td>
</tr>
<tr>
<td>40 0.425-0.5 mm</td>
<td>0.425-0.5 mm</td>
<td>3.0</td>
<td>6.0</td>
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<tr>
<td>45 0.355-0.425 mm</td>
<td>0.355-0.425 mm</td>
<td>0.0</td>
<td>0.5</td>
</tr>
<tr>
<td>50 0.30-0.355 mm</td>
<td>0.30-0.355 mm</td>
<td>0.0</td>
<td>0.01</td>
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</table>
## Proppant Spec Sheet

<table>
<thead>
<tr>
<th>Properties</th>
<th>Units/Method (API)</th>
<th>Intermediate Density Bauxite</th>
<th>High Density Bauxite</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>VersaProp®</td>
<td>12/18 Interprop®</td>
</tr>
<tr>
<td>Typical Sieve Analysis</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Min 90% Retained Between Designated Sieves</td>
<td>% Retained</td>
<td>18</td>
<td>25</td>
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<tr>
<td>Median Particle Diameter</td>
<td>mm inches</td>
<td>0.740</td>
<td>1.367</td>
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<tr>
<td>Specific Gravity</td>
<td>grams/cc</td>
<td>3.2</td>
<td>3.2</td>
</tr>
<tr>
<td>Acid Solubility</td>
<td>%</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>Shape/ Sphericity</td>
<td>Krumbein &amp; Sloss</td>
<td>0.9</td>
<td>0.9</td>
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<tr>
<td>Absolute Volume</td>
<td>gal/lb</td>
<td>0.0374</td>
<td>0.0374</td>
</tr>
<tr>
<td>Bulk Density</td>
<td>grams/cc lbs/ft³</td>
<td>1.88 117</td>
<td>1.88 117</td>
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<tr>
<td>Crush Resistance @ Stress %</td>
<td></td>
<td>5,000 1.4</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>7,500 1.4</td>
<td>2.2</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>10,000 3.5</td>
<td>4.4</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>12,500 3.5</td>
<td>---</td>
<td>7.6</td>
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<tr>
<td></td>
<td>15,000 3.5</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

* SAINT-GOBAIN PROPPANTS

Explore the future

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Proppants: CAMSIZER

Size and shape from 30 µm – 30 mm
CAMSIZER Proppant Data*

- API crush test of proppants:
- Mechanical forces compresses proppant in cell to desired P
- PSD is measured after release
- Crush resistance = wt% of proppant passing smallest sieve of originally specified PSD
- Only one sieve tray required, entire PSD changes during test
- Measuring entire PSD reveals more information

“An optical size analyzer can extract more information than physical sieve analysis about the behavior of proppants under stress while significantly reducing analysis time.”

*Stephens et. al., Statistical Study of the Crush Resistance Measurement for Ceramic Proppants 2006 Annual SPE Meeting
CAMSIZER Proppant Data*

PSD before and after crush

*Stephens et. al., Statistical Study of the Crush Resistance Measurement for Ceramic Proppants
2006 Annual SPE Meeting
CAMSIZER Proppant Data*

50th percentile before and after crush

10th percentile before and after crush

*Stephens et. al., Statistical Study of the Crush Resistance Measurement for Ceramic Proppants 2006 Annual SPE Meeting
Production Fluid Separation

Gas
Oil
Water
Solids (particles)

Oil/water separator

1. Trash trap (inclined rods)
2. Oil retention baffles
3. Flow distributors (vertical rods)
4. Oil layer
5. Slotted pipe skimmer
6. Adjustable overflow weir
7. Sludge sump
8. Chain and flight scraper
Want to separate all phases
Need to measure phase separation
  ● Improve by adding surfactants
Need to measure ppm oil in water
  ● Required to measure if pumping water into ocean (off shore rigs)
  ● Oil is valuable, separate as much as possible
Possible to differentiate oil droplets from particles?
Emulsion Stability

- Want to promote phase separation
- Recover oil, discharge water
- May want to add water to oil to reduce viscosity, easier to transport (orimulsion)
Emulsion Stability: DT1201

Measure particle size & zeta potential w/no dilution
Zeta potential (CVI) predicts dispersion stability

Colloid vibration current (CVC) $\Rightarrow$ zeta potential
Bitumen Emulsion Stability*

- Bitumen diluted 1:1 w/toluene
- Diluted w/D$_2$O 2-30 wt %
- Homogenize 125 watt, 30,000 RPM

DT-1200 w/homogenizer

Bitumen Emulsion Stability*

[Graphs showing CVC signal magnitude, mean diameter, standard deviation, and conductivity over time.]

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Crude Oil Demulsification

Problem: Break the crude oil emulsion
   – In the shortest time
   – With less additive
   – Leave an unpolluted water phase

Solution:
   – Find the optimal additive (cost, efficiency)
   – Need to be tested on each oil batch

Identify the best surfactant for demulsification
Crude Oil Demulsification

Study from French Institute of Petroleum (IFP)*

- **Turbiscan test**
  - Qualitative & Quantitative study
  - Selection of the best additive
  - Optimization of the additive concentration
  - Criteria:
    - width of T peak = height of separated water
    - height of T peak = Limpidity of separated water

*C. Dalmazzone, C. Noïk, «Development of New «green» Demulsifiers for Oil Production », SPE65041
C. Dalmazzone, C. Noïk, «Development of New «green» Demulsifiers for Oil Production », SPE65041
Crude Oil Demulsification

« Separation rate » => %T = f(time)

300 ppm is the best concentration

C. Dalmazzone, C. Noïk, «Development of New «green» Demulsifiers for Oil Production», SPE65041
Orimulsion: Emulsification

- Bitumen: sticky, tar-like form of petroleum so thick & heavy must be heated/diluted before it will flow
- World's largest deposit in Orinoco Belt, Venezuela
- Orimulsion made by mixing bitumen with ~ 30% fresh water + small amount of surfactant
- The result behaves similarly to fuel oil
- Used as commercial boiler fuel
- D50 ~ 14 µm

Orimulsion droplets

LA-950 result
Oil in Water after Separation

Flow chambers
50um – 1mm
2mm-6 mm
Droplets vs. Particles

Distinguishing between two would be easy if they looked like this

Oil droplets                            Iron sulfide particles

Distinguishing between two would be easy if they looked like this
Droplets vs. Particles

Agglomerated droplets

Sand
Pattern Matching Algorithm

- User selects examples of droplets, iron sulfide, sand particles
- Software looks at many size/shape values
- Chooses how to discriminate
- Bins each particle by type, counts
- Can calculate ppm oil
Refining: Catalysts

- Size, shape and specific surface area (SSA) affect catalyst performance
- Measure size using laser diffraction
- Measure size/shape by CAMSIZER
- Measure SSA using BET: SA-9600
  - Flowing gas BET method
  - Low price, operating costs, maintenance
  - Easy to use, fastest measurement time
  - No vacuum system required
  - Single or multi-point
  - Up to three samples simultaneously
Catalysts Size/Shape by CAMSIZER

- Spherical catalysts
  - Easy, no special effort

- Cylindrical catalysts
  - Length, width

- Bended extrudates
  - Use other parameters

\[
x_{\text{length}} = \sqrt{(x_{Fe\max})^2 - (x_{c\min})^2}
\]

\[
x_{\text{stretch}} = \frac{A}{x_{c\min}}
\]
Catalysts Size/Shape by CAMSIZER

- Tri & quadralobe
  - Possible to distinguish between different diameters
  - Shorter green distribution = length
  - Taller maroon distribution = width
Summary

- Particle size, shape, surface area, other properties important from exploration to refining

- Key applications:
  - Drilling fluid
  - Proppants
  - Oil/water/solids separation
  - Catalysts

- Talk to HORIBA about all these requirements

Thank-you