Hydrate Analysis Methods

- 325 Mesh: Air Jet vs. Wet Sieve
- Particle Size Distribution: Lecotrac (Microtrac) vs. Sedigraph
- Specific Surface Area and Pore Volume
Hydrate Analysis Methods

ABSTRACT

Interpreting published results of the physical properties of any compound can be misleading. The publication of numbers without “units” is meaningless; the publication of numbers with the same “units” are not always equivalent. This is particularly so in the case of Hydrated Lime (Calcium Hydroxide) manufactured for the purpose of sulfur trioxide (SO₃) gas scrubbing. Specific values of interest are particle size distribution, surface area, and pore volume. It is critical that published results should not only indicate the “units” but also the test method employed. If results are obtained through the use of differing test methods, they cannot be reliably compared. Differing results due to the test method employed may actually be equivalent but are often interpreted as being different. The purpose of this technical bulletin is to clarify the differences that can be expected from the commercially available test methods and to provide a better understanding of the published results of the physical properties of these products.

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INTRODUCTION

Hydrated Lime (Calcium Hydroxide) is an industry proven reagent utilized in many environmental applications – two of which are Water/Wastewater Treatment and Flue Gas Treatment. The product specifications are as different as their applications. There are two ASTM methods for determining the particle size of hydrated lime – Air Jet and Wet Sieve.

It only makes sense that a Water/Wastewater application would use the Wet Sieve method, and a Flue Gas application would use the Air Jet method as each method is more representative of its application. Yet inconsistencies arise when reporting the percent passing 325 mesh (i.e. % -325 mesh).

ANALYSIS

Two samples from Plant 1 were tested using the Air Jet and Wet Sieve methods. Several tests were performed on each sample, and the results are summarized in Table 1. Air Jet results averaged 86% passing 325 mesh, and Wet Sieve results were about 88%. Air Jet results were more consistent with a standard deviation of ~0.5 compared with the more erratic Wet Sieve with a standard deviation > 5. The Wet Sieve method dissolves hydrated lime. This method introduces some variability in the procedure through the force of water, length of washing and brushing that may break up agglomerates. These factors would explain the erratic results.

The Technology Center results for wet sieving were quite different and much lower compared to the Plant 1 results. The dilemma is that although washing appears complete when the rinsate runs clear, hydrated lime agglomerates continue to slowly break down or disassociate with continued washing. A result of ~97% passing 325 mesh was observed when wet sieving until no further material passes. This is typical of what is reported by Plant 1.

Table 1

<table>
<thead>
<tr>
<th>% Passing 325 Mesh</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample No.</td>
</tr>
<tr>
<td>-------------------</td>
</tr>
<tr>
<td>Reported by Plant 1 (Wet Sieved)</td>
</tr>
<tr>
<td>Air Jet (Technology Center)</td>
</tr>
<tr>
<td>Wet Sieve (Clear Rinsate)</td>
</tr>
<tr>
<td>Wet Sieve (to completion)</td>
</tr>
</tbody>
</table>

Table 1
Plant 2 results were closer to the Technology Center results. The Plant 2 "Hydrate Residue Method" calls for washing until the rinse water from the bottom of the sieve is clear. This requires some judgment on the part of the technician such that over or under washing may occur. This point was much easier to determine due to the better consistency of the Plant 2 hydrated lime. The same sample, when washed to completion as in Plant 1, achieved > 99% passing 325 mesh.

Below are some photos to illustrate the different washing techniques. The photographs on the left side are from washing until the rinse water runs clear as performed by Plant 1 on Sample 2. The material provided by Plant 2 has more consistent characteristics than the Plant 1 material. This is evident based on the reported standard deviation for the Wet Sieve technique when washing until rinsate looks clear. Only when washing to completion will the standard deviations become comparable.

### % Passing 325 Mesh

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Sample 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reported by Plant 2 Wet Sieve</td>
<td>88.8 0.32</td>
</tr>
<tr>
<td>Air Jet (Technology Center)</td>
<td>87.0 0.32</td>
</tr>
<tr>
<td>Wet Sieve (Clear Rinsate)</td>
<td>84.4 0.92</td>
</tr>
<tr>
<td>Wet Sieve (to completion)</td>
<td>99.4 0.28</td>
</tr>
</tbody>
</table>

**Table 2**

<table>
<thead>
<tr>
<th>Washed Until Rinsate Looked Clear</th>
<th>Washed To Completion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Residue from Hydrate of Plant 1</td>
<td>Residue from Hydrate of Plant 2</td>
</tr>
<tr>
<td>86% Passing 325 Mesh</td>
<td>84% Passing 325 Mesh</td>
</tr>
<tr>
<td>Residue from Hydrate of Plant 1</td>
<td>Residue from Hydrate of Plant 2</td>
</tr>
<tr>
<td>97% Passing 325 Mesh</td>
<td>&gt; 99% Passing 325 Mesh</td>
</tr>
</tbody>
</table>
SUMMARY & CONCLUSIONS

The Air Jet sieve method is much more consistent than a Wet Sieve analysis and is the recommended method to be used to determine the % -325 mesh in hydrated lime to be used for flue gas treatment. When the Wet Sieve method is run to a clear rinsate, the Wet Sieve results, although not as repeatable as the Air Jet, are somewhat consistent with the Air Jet results. A correlation or correction factor could not be discerned in large part due to the Wet Sieve inconsistencies.

**Air Jet Method (Recommended):**

- is more consistent with better reproducibility
- reduces technician time/effort required
- limits technician bias
- provides quicker turnaround
- avoids interaction of sample with soluble liquid
- is from an actual ASTM method: C110 Section 19
  - ASTM recommends 20 grams sieving for 6 minutes.
  - Experimentation at the Carmeuse Technology Center with hydrate has indicated that this time is not sufficient. The recommended method is to use 10 grams of hydrate and Air Jet sieve for 15 minutes
- has a more accurate and significant sample weight (0.1 g error in weight translates to 1.0 %)
- requires additional equipment (Equipment is being or has been installed in all Carmeuse hydrate plants that supply the flue gas treatment market).

**Wet Sieve:**

- is more inconsistent in terms of repeatability
- makes it difficult to detect stopping point (unless material coaxed through screen)
- provokes more technician bias
- requires more technician time/effort
- has no ASTM equivalent; the closest is ASTM 110 Section 22 which is for agricultural material down to 200 mesh which approximates wet washing until rinsate looks clear.
Particle Size Distribution: Lecotrac (Microtrac) vs. Sedigraph

INTRODUCTION

Carmeuse found that a competitor routinely reports lower average particle size by the sedigraph method on their hydrate than Carmeuse measures using a Lecotrac (Microtrac) method, (2 µm versus 5 µm). Consequently, samples of hydrate were sent out for sedigraph analysis as well as analyzed in house by Lecotrac and the results compared.

LECOTRAC/SEDIGRAPH COMPARISON

**Lecotrac Method**

The Lecotrac is a laser light scattering instrument. It works on the theory that particles will scatter light at various angles relative to their particle size. Large particles scatter light at small angles while small particles at large angles. The particle size relates to the diameter of a sphere that scatters light at the same angle and intensity.

**Sedigraph Method**

A Sedigraph measures particle size by the velocity at which particles settle and their concentration by x-ray absorption. The determination is based on Stokes’ law of sedimentation to calculate the size of a sphere passing through the fluid. It takes into account density of the particles and viscosity of the fluid media.

RESULTS

Table 3 below compares results from the two analyses. Lecotrac numbers are on the left, the Sedigraph results on the right. All units are in microns.

<table>
<thead>
<tr>
<th></th>
<th>Lecotrac</th>
<th>Sedigraph</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mv (Mean)</td>
<td>5.48</td>
<td>4.27</td>
</tr>
<tr>
<td>Mn</td>
<td>1.34</td>
<td>- - -</td>
</tr>
<tr>
<td>Ma</td>
<td>3.31</td>
<td>- - -</td>
</tr>
<tr>
<td>Mode</td>
<td>4.63</td>
<td>1.59</td>
</tr>
<tr>
<td>d50 (Median)</td>
<td>4.14</td>
<td>1.86</td>
</tr>
</tbody>
</table>

Table 3

**MEAN/AVERAGE PARTICLE SIZE DEFINED**

There are three types of mean or average particle size reported by the Lecotrac. All are mean diameters. Historically, Carmeuse has always reported the Mv, or the average volume distribution. This represents the center of gravity of the distribution. This more or less correlates to the sedigraph analysis average particle size.

Mv is the mean diameter of the number distribution. It is weighted to the small particles and is related to the population.

Ma is the mean diameter of the area distribution. The area mean is less weighted than mv by the presence of coarse particles, and therefore shows smaller particle sizes. It represents a particle surface measurement.

Mode is the size with the highest frequency of particles in it. That is to say, it’s the size at the peak or highest point of the size distribution.

The median or d50 is the particle size in the 50th percentile of the distribution. It is possible Mv values may be erroneously compared to their median value from the sedigraph method. In this case the Mv of 5.48 may mistakenly be compared to the median value of 1.86.
Particle shape will affect particle size run by methods based on different mathematical models. The more it deviates from spherical the more difficult it is to analyze. In the Lecotrac, the orientation of irregularly shaped particles will affect the way light scatters. Typically, these orientations are averaged out over the measurement and will result in a broadened distribution. In the Sedigraph, flat or plate like particles will settle more slowly similar to a leaf floating down from a tree. This effect results in a finer distribution. In the Sedigraph, it is suspected that hydrate agglomerates or forms flocs that settle slowly resulting in a smaller particle size.

Surface area would also affect the Sedigraph analysis. A given spherical particle with a smooth surface will settle more rapidly than a similar sphere with a high surface area. This is due to increased friction on the high surface area particles. The Lecotrac results would not be impacted by surface area.

The largest problem encountered when measuring hydrate by Lecotrac is agglomeration. It is very difficult to keep hydrate particles separated while testing. Ultrasound can be used to separate particles prior to testing.

**SUMMARY & CONCLUSIONS**

LECOTRAC/SEDIGRAPH COMPARISON GRAPH

The chart below plots the Lecotrac values along with those from the Sedigraph. It is clearly visible that there is a difference between the two tests. The Sedigraph analysis shows a finer distribution. However, we would caution it is very difficult to make a direct comparison of products from two different tests. To begin with, it is important to note that Lecotrac results are based on a volume while Sedigraph results are based on mass fraction.
Measurement of Specific Surface Area and Pore Volume

FOUR STAGES OF GAS PRESSURE

<table>
<thead>
<tr>
<th>Lab No.</th>
<th>Sample ID</th>
<th>Single SSA (m²/g)</th>
<th>BET SSA (m²/g)</th>
<th>Total Pore Vol. @ P/Po = 0.984 (cm³/g)</th>
<th>MV (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>09-1570</td>
<td>Hydrate Plant 1</td>
<td>20.82</td>
<td>21.40</td>
<td>0.0832</td>
<td>5.96</td>
</tr>
<tr>
<td>09-1600</td>
<td>Hydrate Plant 2</td>
<td>18.80</td>
<td>19.34</td>
<td>0.0774</td>
<td>6.48</td>
</tr>
</tbody>
</table>

Table 4

Diagram 2

Courtesy of Micromeritics Instrument Corporation, Norcross, Georgia
SUMMARY & CONCLUSIONS

- **Single SSA - Single Point Specific Surface Area:**
  - Uses 1 point to calculate SSA
  - Comparable to Flowsorb results

- **BET SSA - Multipoint Specific Surface Area:**
  - Preferred method reported by Carmeuse
  - Uses 5 (or more) points to calculate SSA
  - Measured with a Micromeritics Tristar

- **Total Pore Volume:**
  - MV - Mean diameter of volume distribution - average

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