Gypsum: Use of Electric Power Generation By-Product in Wallboard, Cement and Plastics

Instrument: SYNC

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Introduction: Gypsum Production

Minerals are available in many forms. Some are mostly valued as gemstones while others are used for abrasives. An abrasive is a material that often is a mineral that reduces a surface by friction and rubbing. Some minerals that have good abrasive qualities include diamond, garnet, silicon dioxide, and aluminum oxide. Abrasives find use in all facets of life including chemical mechanical planarization manufacture of computer and DVR / CD discs, sandpaper, grinding wheels, cutting wheels, removing human skin blemishes and birthmarks, floor skidproofing, milling, toothpaste, kitchen and bathroom cleaners, hand cleaners, etc.

Coal burning produces many substances such as sulfur dioxide, nitrogen oxides, particulate and carbon dioxide. Electric power companies have reduced the emission of these substances considerably during the last 20 to 30 years. The adoption of Clean Coal Technology has been beneficial to controlling emissions. Devices known as “scrubbers” have been used successfully since 1980 to remove sulfur by a process known as flue-gas de-sulfurization. Since 1980 USA emission of SO_2 has been reduced by about 40%. In this use of wet or dry scrubbers, sulfur dioxide is flowed past dry or slurried limestone or lime to react to form calcium sulfate where up to 90% of the emission is eliminated. At the same time, a useful product (gypsum) is produced by converting SO_2 gas to $CaSO_4$. Typically, a wet flue system is used due to its low operating costs, high reliability, and efficient removal of SO_2. The converted SO_2 is collected at the bottom of the scrubber as a solid or slurry. It is also collected by bag-houses or electrostatic precipitators. Figure 1 shows the diffraction
particle size distribution as measured using the Microtrac SYNC.



Fig. 1: *Sync Analyzer (left) and Diffraction Particle Size Measurement of Gypsum Produced from Scrubber Reaction*

The chemical reaction occurring to remove the gas is shown below.

$$CaCO_3 + SO_2 + \tfrac{1}{2}\ H_2O \rightarrow (CaSO_3 \bullet \tfrac{1}{2}\ H_2O)s + CO_2$$

$$Ca(OH)_2 + SO_2 \rightarrow (CaSO_3 \bullet \tfrac{1}{2}\ H_2O)s + \tfrac{1}{2}\ H_2O$$

Scrubber sludge contains a compound known as gypsite, but it also contains a number of impurities such as $CaSO_4 \bullet \tfrac{1}{2}\ H_2O$ and $CaCO_3$. The process can be of two types where natural conditions cause oxidation of the gypsite to gypsum ($CaSO_4$) or forced oxidation can be used as shown in Figure 2. Forced oxidation results in nearly 100% conversion of gypsite to gypsum (named synthetic gypsum). Gypsum is the primary component of wallboard, so the scrubbing activity provides a means for producing gypsum in addition to the time-tested mining method. Impurities in the synthetic gypsum affect hardening rate of wallboard so it must be purified prior to use, but the purified product has found wide acceptance due to its cost effectiveness.

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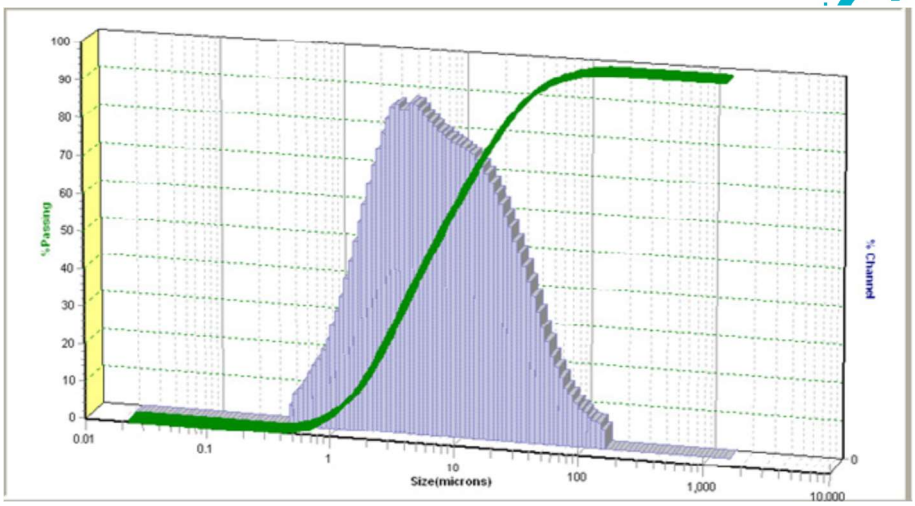


Fig. 2: *Pre-reacted limestone. Microtrac SYNC diffraction particle size distribution*

By-products Used in Portland Cement

Synthetic gypsum along with bottom ash and fly ash from bag houses or electric precipitators has also found use in cement where the material is added to clinker or final cement product. Over 420,000 tons of power plant scrubber products are used annually in cement production. Fly ash decreases permeability and increase long term strength, while gypsum is used in the finish mills of Portland cement. Thus two by-products normally sent to land-fills are used. Cement kiln dust (by-product of cement manufacture) is mixed with synthetic gypsum to produce a powder to be added to finish mills. Combining the materials thus reduces environmental stress by reducing emissions as well as reducing land-fill use.

Plastic Filler Substitution with Coal-Burning By-Products

A final example of using by-products of electric power generation is the addition of fly-ash as filler to plastics. Plastic fillers enhance properties of plastics to improve performance and reduce costs. Due to its chemical and physical properties, fly-ash is considered a mineral such as alumina, kaolin, talc and mica, which are used as fillers. However, flyash has a particle size distribution that contains too much particulate above approximately 5 microns. Thus, flyash must be treated to reduce the presence of coarse particles before it can be used. A typical Microtrac particle size distribution is shown for fly-ash. Figure 3 shows comparison data obtained using n SYNC diffraction particle size measurements.

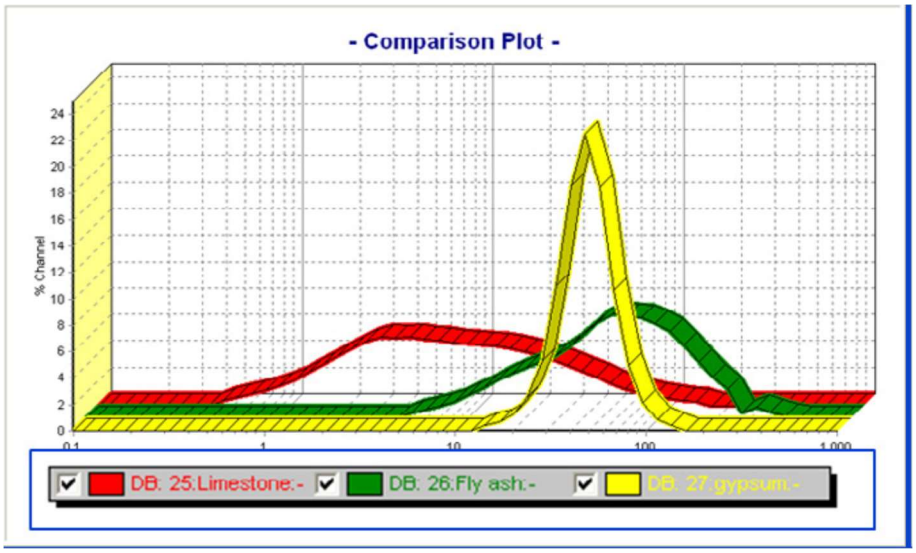


Fig 3: *Comparison plot of Limestone, Gypsum and Fly Ash. Distributions obtained by Microtrac SYNC. Three-dimensional effects using Microtrac FLEX software.*

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SYNC Image Analysis

Image analysis was performed on a commercially acquired gypsum from a local building supply store. This was to compare data between laser diffraction and image analysis. It is important to recognize that different technologies are being applied to the sample to obtain characterization data. Laser diffraction particle size measurement distributions are volume distributions based upon light scattering theories. Dynamic image analysis data are based upon photographs of individual particles upon which various geometric calculations are applied. Each method provides particle size information based upon the implementation of the respective theories and concepts. Since the methods are different and have separate approaches to defining volume distributions of particle distributions, the data often will not agree. The data for the present sample of gypsum is an example of the slight discrepancy. The "beauty" of the use of the 2 methods is that each provides opportunity to fully characterize size and shape using one instrument (Microtrac SYNC) that simultaneously measures size and shape. Table 1 shows the SYNC diffraction measurement for a commercially obtained gypsum.

Percentile	Diffraction	Image Analysis, size definition Da	Image Analysis, size definition FWidth	Image Analysis, size definition FLength
10	6 µm	25 µm	18 µm	33 µm
50	32 µm	56 µm	43 µm	78 µm
90	100 µm	116 µm	96 µm	165 µm

Diffraction provides a very valid volume distribution (popularly known as a particle size distribution). The addition of shape information by image analysis provides another dimension to characterization since information on shape is available simultaneously. In the present case with the commercial gypsum, the above table shows that the FWidth (often considered a good approximation to sieve sizes) is the parameter that provides the best agreement to diffraction. The issue with using the imaging FWidth for qualification s that it may not agree historical values for specifications based on diffraction measurements. However, the advantage of the SYNC is the ability to obtain diffraction size and images on the identical sample. As shown below (Figure 4, left) in columns 3 (Da, Sphericity), 4 (FLength, L/W ratio) and 5 (FWidth, Sphericity) for this material, the values for the parameters show constancy. This suggests that the particles are very similar in shape (will not segregate according to size), not very spherical (will not segregate according to shape and may represent a sieve "cut" (since the FWidth is constant). Graphical representation of the data is show in Figure 4 (right). This type information is not available by diffraction measurements. Thus, it adds to the full characterization of the sample.

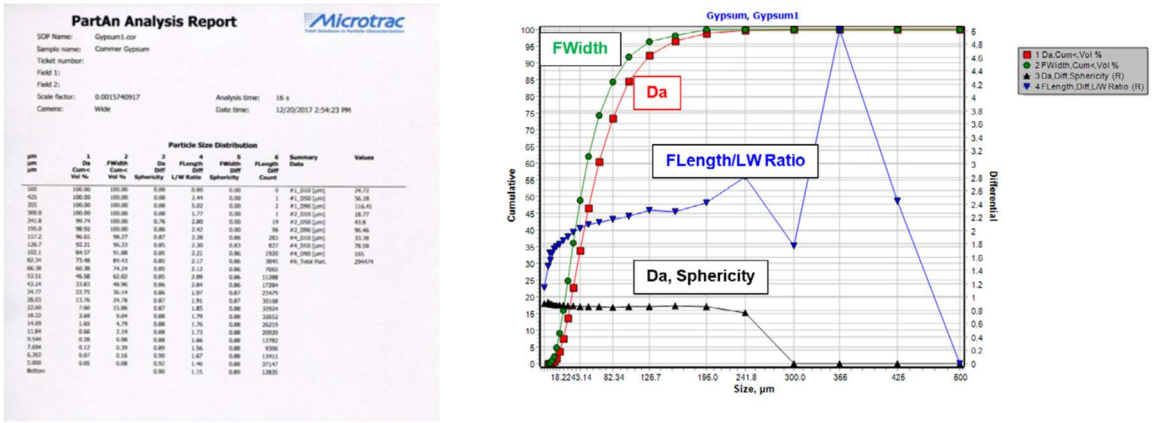


Fig. 4: *SYNC image analysis: Size and shape data can be displayed in tabular (left) or graphical form (right).*

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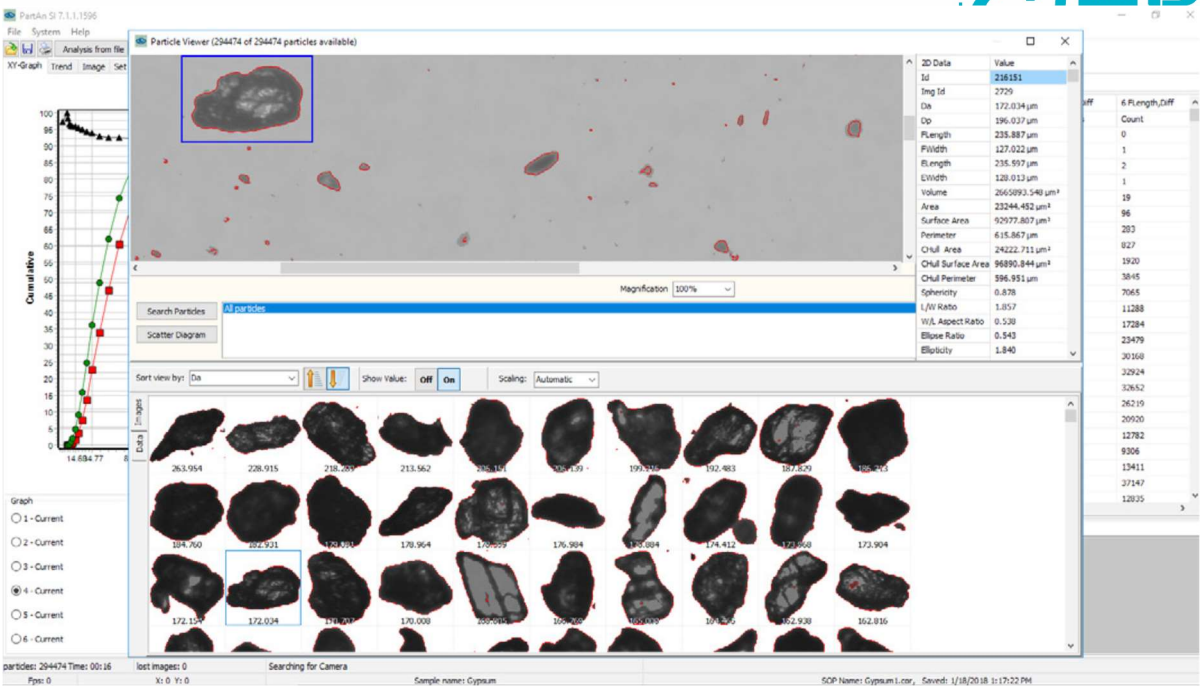


Fig. 5: *Images obtained by SYNC: a small portion of the more than 200 000 particles measured. Tabular data are for the particle outlined in blue color rectangle.*

Sample Preparation and Measurement

Note that the sample particles are slightly soluble in water. Usually our lab receives sample as a dried “cake” which results from processing. It can further be dried to produce a powder form which results in agglomerates that require some extra time for final dispersion using ultrasonic energy.

Recirculator carrier fluid: 99% Isopropyl Alcohol, Refractive Index: 1.38
Particle Refractive Index: 1.53
Particle Shape: Irregular

Transfer well mixed powder sample to 60ml of IPA contained in a 100 ml beaker. Evaluate the sample by microscope to determine the presence of agglomerates. If agglomerates are present, treat the slurry of IPA and powder with 10 seconds ultrasonic energy if powder is from a cake or 60 seconds of ultrasonic energy if the cake has been dried. Its best to check the preparation by microscopy to be sure that particle agglomerates are completely dispersed. Once the sample is dispersed, stir the beaker preparation with an overhead stirrer. While the prep is stirring, remove portions of the dispersion using a pipette and transfer the portion to the recirculator containing IPA. Repeat transfer of portions until loading is acceptable.
Microtrac Particle Size Analyzers are used in over 20 of the largest and most modern electric power plants where coal is used as a fuel source and Clean Coal Technology is being practiced. New processes are being developed to reduce environmental stress of all power plant emissions. Laser particle size measurement by Microtrac instruments will be ready to assist these developments.

Summary

The data and experiments conducted show that the combination of imaging technology with diffraction particle size measurements can provide timely information over a large particle size range. Diffraction measurements simultaneously with image analysis provides the best approach to characterizing a given sample thus avoiding representative sampling issues when performing measurement on separate or new samples.

References:

- Huang,X., Hwang, J.Y., and Gillis, J.M., Processed Low NOx Fly Ash as a Filler in Plastics. Journal of Minerals and Materials Characterization & Engineering, Vol2, No 1, p11-31, 2003
- Kawatra, S.K., Eisele, T.C., and Shoop, K., Separation of Flue Gas Scrubber Sludge into Marketable Products, Michigan Technological University, Dept of Metallurgical and Materials Eng., For the US DOE, Pittsburgh Energy tech Center, Pittsburgh, PA August 1997.
- Portland Cement Association, Sustainable Manufacturing Fact Sheet. Power Plant Byproducts. July 2005, PCA Website.

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