

A Lens to the Nanoscale - Precision Measurement of Ultrafine Particles

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Introduction

The characterisation of high purity alumina (HPA) particles is principally achieved through wet laser diffraction particle size analysis, a technique capable of providing excellent insight into the particle size distribution (PSD), typical known as D10, D50 and D90 fractions, of alumina in either powder or slurry form.

The choice of measurement technique often depends on the end user's requirements. It is very important for the recipient to determine their application and needs in terms of particle size distribution; either wet or dry. This will help us to identify the most suitable method that best represents the target application.

The typical challenge in the determination of particle size is linked to the fact that fine particles tend to agglomerate, like in Fig. 1, and stick to each other via Van der Waals bonding; which means they are relatively easy to break into smaller particles via non-intrusive agitation methods such as sonication. This means that sometimes the operator measures the size of the agglomerates and not the primary size of the particles. The measurement of the true particle size dimensions by laser diffraction can present a number of challenges, in particular interpreting the different results obtained by different characterisation techniques or methods (SEM imaging) or particle size distribution (PSD) measurements in a coherent manner. This article will address the main difficulties associated with measuring alumina agglomerates by laser diffraction (wet route) during the process of wet grinding, drying of the alumina suspension and dry re-grinding of the clogged alumina to the size desired by our customers. '

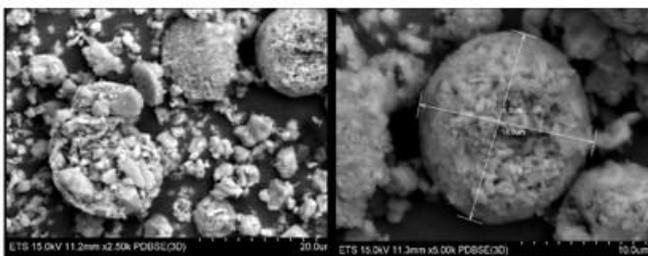


Figure 1. Agglomerates

Challenges in Measuring the PSD of Sub-micron Alumina Agglomerates:

As said before, the distribution and size of finely ground alumina particles is often affected by the presence of agglomerates, linked to ripening, aggregation or agglomeration phenomena. Agglomeration of alumina nanoparticles can have a significant impact on PSD results.

Understanding these phenomena and controlling the complete and uniform dispersion of solid particles will enable us to determine whether additional dispersive energy (agitation, heating, sonication, etc.) is required to obtain representative results for the product. Otherwise there is a risk of obtaining erroneous distribution results, i.e. an overestimate of particle size and/or an underestimate of the number of fine particles in the sample.

In order to choose the right measurement method, it is very important to take SEM or optical microscope images to qualitatively characterise the shape of the particles and to assess the rate and type of agglomeration of the alumina particles (Figure 2). It should be noted that SEM is a qualitative technique that in no way provides reliable statistics or results on particle size. It is therefore essential to use a suitable technique to measure the size distribution of fine particles or nanoparticles (submicron alumina). The process of agglomeration is very complex and it is summarized in Figure 3.

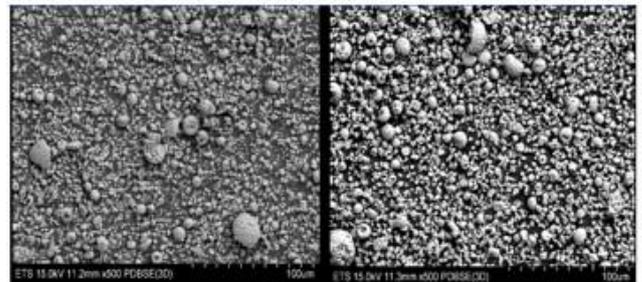


Figure 2. SEM images of fine powder w/o statistical analysis

Ripening - A phenomenon which depends on the solubility of alumina in water. Smaller particles have a tendency to present more surface deformation, resulting in higher surface energy and increased solubility. The preferential solubility of small particles will be greater than that of larger particles. Over time, the population of small particles will dissolve in solution. The dissolved part of the small particles will then be deposited on the larger particles, and the alumina particles will become larger. This process is known as Ostwald ripening.

Aggregation - Primary particles can come into contact, sticking together to form strong chemical bonds over a small area or point of contact. The mechanism is called aggregation or coagulation. Aggregates of very small or few primary particles can still be found in the colloidal size range. Because of the bonds between the primary particles, they are usually quite difficult to separate using simple techniques such as stirring, heating or sonication.

Agglomeration - Agglomeration is a phenomenon whereby fine alumina particles adhere to each other to form larger particles by means of intermolecular bonding and are often measured as a single larger particle. Unlike individual smaller particles that form agglomerate, this type of agglomeration is generally easy to break up by simple means such as agitation, heating or sonication. Agglomeration of fine particles can also affect the shape and size distribution of particles.

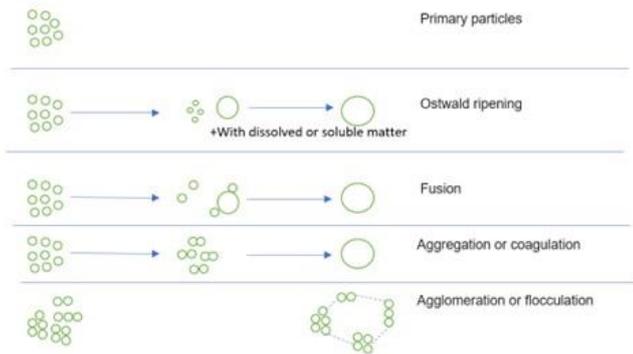


Figure 3: Types of colloidal particles and their agglomeration phenomena

A primary particle is the smallest identifiable subdivision in a particulate system. Primary particles can stick together to form "soft/fragile" (easily dispersed) or "hard" (fused) agglomerates.

The stability of a colloidal system or suspension depends on a number of factors including pH, ionic strength, temperature and the 'history' of the dispersion, because in many suspensions the colloid 'remembers' its history from the primary particle.

Finely ground metal oxides, and more specifically alumina, are materials that tend to form agglomerates, which means that individual fine particles can come together to form larger structures.

The agglomeration of metal oxides particles can be caused by several factors, such as the physio-chemical characteristics of the surface of fine alumina particles (pH, conductivity, etc.), electrostatic forces, Van der Waals forces (attraction and repulsion), micronisation (grinding) and certain storage conditions can also make these particles (generally <math><10\ \mu\text{m}</math> in size) more likely to absorb small quantities of water. This can lead to partial dissolution at the surface of the metal oxide particles – in the case of alumina particles, water-soluble aluminium hydroxide species are formed. Fine particles in contact with each other can fuse completely or partially to form what are known as hard or brittle agglomerates. Hard agglomerates cannot be easily separated without fracturing the newly formed assembly of individual particles, unlike brittle agglomerates, which are easier to break up with sonication or agitation (simple or vigorous).

However, it is important to point out that most of the aggregates that are observed at industrial level are easy to break. In this regard, figure 4 shows a powder with aggregates that are quickly broken into the constituent particles after a quick sonication.

Conclusion

The key to obtaining reproducible and representative results of particle size distribution by wet laser diffraction is to prepare a good, stable dispersion of the particle suspension (colloidal system).

A well-dispersed suspension is a colloid in which the minimum particle size has been reached and operationally defined by a constant (minimum) particle size distribution. This results in complete de-agglomeration of the metal oxide suspension particles (wet process), which will enable us to obtain identical or similar results with or without sonication.

If the addition of a surfactant, mechanical agitation or heating is not sufficient to separate the fragile agglomerates, ultrasonic energy can be applied.

A time study using ultrasound can be useful to determine the sample preparation parameters when fragile agglomerates are present and when they do not reflect the main objective of the particle size analysis, we can cross-check internal methods with other orthogonal techniques such as:

- Particle size analysis using DLS (Dynamic Light Scattering)
- Centrifugal liquid sedimentation analysis (CLSA)
- Particle Imaging Analysis (PIA) to accurately measure the particle size distribution of agglomerated particles.
- Nanotrak Nanoparticle analyser.

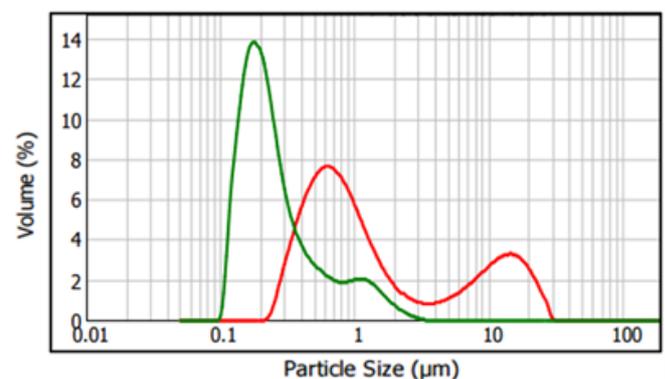


Figure 4: Graph showing the change in particle size profiles between a sample without sonication (Red) and after sonication (Green).