Aluminum Oxide Surface Area using the Acorn Area™

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Aluminum oxide, or alumina, is widely distributed in nature usually in combination with silica and other minerals. It is an important constituent of the clays used for making porcelain, bricks pottery and refractories. The chief uses for alumina are for the production of aluminum metal and for abrasives; corundum, natural Al_2O_3, is extremely hard (Mohs hardness 9) and second only to diamond. Alumina ceramics are the hardest, strongest and stiffest of the oxides; they are used for electrical insulators. It is used in glass and vitreous enamels to increase strength and luster.

Activated alumina is a porous form used for drying liquids and gases and is used as a catalyst in chemical processes; hydrated alumina is used as filler in plastics and in cosmetics. Fumed alumina is nano-sized and used as a reinforcing pigment in rubber and plastic and in the production of ferrite ceramic magnets. The high surface area provides fast adsorptive capacity making them ideal for high quality inkjet coatings. They tend to be supplied as high solids wet slurries that are cationic (positively charged) and this feature is used to effect in the fixing of dyes. The surface chemistry of aluminum oxides has been extensively reviewed (1).

It is obvious that the surface area of porous alumina is important but the small particle size of colloidal alumina also brings with it an important characteristic. While it is evident that as the particle size of a material is reduced the surface area increases (as $1/d^2$), what may be less obvious is the exceptionally large surface area-to-volume ratio per given mass for the particles involved. This is an essential characteristic common to all nanoparticulate dispersions. It matters little what the particle shape is - the surface area per mass of any colloid is orders of magnitude larger than it is for particles of even only a few micrometers in size. This huge increase in surface area dramatically effects not just adsorption of chemicals and other moieties onto the particle surface but also the interaction between particles and, importantly from a commercial perspective, system properties such as suspension rheology, coating and adhesion. Thus, the surface area of any nanoparticulate alumina is a vital metric in quantifying the performance of the material. Further, many aluminas are intrinsically wet suspensions of particles so it is essential that the surface area be measured directly on these materials as supplied.

The Acorn Area

The **Acorn Area** is a new instrument using a patented technique based on NMR relaxation to determine the wetted surface area of suspensions of particulate materials such as alumina (2). The **Acorn Area** takes advantage of the fact that liquid that is bound to a particle surface has a much lower relaxation time than the free or bulk liquid. Thus, a sample with a high surface area will have a lower total relaxation time than a low surface area sample because there should be more of the fluid bound to the surface. Unlike the measurement of particle size by, for example dynamic light scattering, where the raw intensity data has to be de-convoluted by means of complex algorithms, here the relaxation time is converted into the absolute surface area by means of a simple calculation. As in BET gas adsorption method, there is a basic assumption of monolayer coverage of fluid onto the particle surface.

The most common method of surface area determination is nitrogen (N_2) gas adsorption (3, 4). In this method N_2 is adsorbed on a sample kept at liquid N_2 temperature at a series of different pressures. This method is useful only for dry powders and requires that the sample be degassed to drive off any adsorbed material (sample conditioning); this requires a source of liquid N_2 to maintain the proper sample temperature; and this is also a critical experimental requirement (5). In contrast, the Acorn Area measures suspensions directly and requires no sample pretreatment or temperature control. It is inherently a much simpler measurement technique; and as little as 0.1mL of sample is needed.

To calculate the surface area from the measured relaxation time, the following formula is used:

$$R_{av} = \psi_p S L \rho_p (R_s - R_b) + R_b \qquad (1)$$

where:

R_{av} is the average spin relaxation rate constant

ψ_p is the particle volume to liquid volume ratio

S is the total surface area per unit weight

L is the surface layer thickness of liquid,

ρ_b is the bulk particle density,

R_s is the relaxation rate constant for the bound solvent

R_b is the relaxation rate constant for the free or bulk solvent

Using a standard reference material we can define a constant, $K_a = L \rho_b (R_s - R_b)$ so that the equation 1 reduces to:

$$R_{av} = K_a S \psi_p + R_b \qquad (2)$$

The surface area can then be calculated from:

$$\text{Surface Area} = R_{sp} R_b / K_a \psi_p \qquad (3)$$

where, $R_{sp} = R_{av}/R_b - 1$

A more precise method is to use the slope of a plot R_{sp} as a function of different volume ratios, ψ_p , (i.e. concentrations).

Results of Surface Area Measurement

To demonstrate the applicability of the Acorn Area to the measurement of the surface area of alumina suspensions, we chose an industrial material, AERODISP W630, that is supplied by Evonik (formerly Degussa) as a high solids (30wt%), slightly acidic, slurry used to fix dyes and for high quality inkjet coatings. The slurry is considered to be cationic (positively charged). The zeta potential, which is a measure of the surface charge (6) was determined by electrophoretic light scattering (ELS) to be +58 mV.

Prior to the surface area analysis, the particle size distribution (PSD) of a sample of the AERODISP W630 was measured using X-ray disc centrifugation, a technique ideally suited to oxide materials (7). The mean particle size was determined to be 47nm (diameter) with a narrow PSD (Figure 1); the polydispersity index (the ratio of D_v:D_n) was 1.08. Assuming that the alumina particles are spherical, the mean surface area was estimated to be 32m^2 g^{-1}.

The sample was measured as a function of concentration: full (as received at 30 wt%), diluted 10:20 from full concentration using deionized water : diluted 5:20 from full, and diluted1:20 from full. The results of the relaxation measurements using the Acorn Area are shown in Figure 2 below. The relaxation times (in milliseconds) varied as expected; the more dilute sample has less available surface area, a larger relaxation time and hence R_{sp} is smaller. The mean surface area, as calculated from the slope of the plot of R_{sp} vs. Volume Ratio, ψ_p, is 31m^2 g^{-1}.

All measurement data are summarized in Table 1.

TABLE 1

Material	Particle Size	Zeta Potential	Surface Area	
	(nm)	(mV)	(m^2g^{-1})	
			Estimated	Measured
AERODISP W630	47	+38	**32** (16-46)*	**31** (SD:7.1, CV:0.23)

* SA values calculated using 90th and 10th percentiles of the PSD

The agreement between estimated and measured SA for the AERODISP W630 material is excellent.

REFERENCES

1. S. Goldberg, J.A. Davis and J.D. Hem in “The Environmental Chemistry of Alumina”, G. Esposito (ed), 2nd Edition, CRC Press, New York, 1996.
2. US Patent, 7,417,426, August 26, 2008.
3. S. J. Gregg and K.S.W. Sing, “Adsorption, Surface Area and Porosity“, 2nd Edition, Academic Press, London, 1982.
4. S. Lowell and J. E. Shields, “Powder Surface Area and Porosity“, Chapman Hall, London, 1984.
5. K.S.W. Sing, “The Use of Gas Adsorption for the Characterization of Porous Solids“, *Colloids and Surfaces*, 38 113 (1989).
6. P. McFadyen and D. Fairhurst, “Zeta Potentials of Nanoceramic Materials - Measurement and Interpretation”, *Proc. British Ceramic Society*, 51, 175, (1993).
7. P. McFadyen and D. Fairhurst, “High Resolution Particle Size Analysis from Nanometers to Microns”, *Clay Minerals*, 28, 531, (1993).