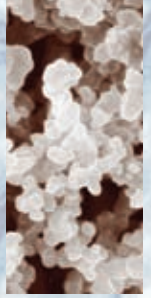


# PARTICLE WORLD



Technical papers on QUANTACHROME particle analysis techniques

1<sup>st</sup> English issue

Dear Reader,

with our first English „Particle World“ we want to inform you about newest developments in the field of **Characterization of Fine and Porous Systems**, but also about relevant analysis methods, results, potential problems and their solutions.



We, as QUANTACHROME in Germany offer sales, service and support for four product lines of innovative analysis instruments around the “world of particles”. We have experience with **CILAS** laser granulometers for particle sizing and with **QUANTACHROME** analytical instruments for characterization of fine and porous particles for more than 15 years. In 1999 we started as the EUROPEAN DISTRIBUTOR for **DISPERSION TECHNOLOGY** scientific instruments to determine particle size and zeta potential of concentrated liquid dispersions. Since 2005 we are distributor for **FORMULACTION**, the innovative company for characterization of stability of dispersions in original concentration and without the need to change the sample. **FORMULACTION** started in 2006 with a worldwide new principle – **HORUS**, the analytical tool for characterization of drying processes of thin film layers.

A complete **PARTICLE CHARACTERIZATION LAB** is available for your test and contract analyses! Please mark this on the fax answer sheet to get more information.

As business manager in Germany as well as member of the German DIN norm group for surface and pore characterization I look forward to maintain contacts with you.

Please, feel invited to visit us at [www.quantachrome.de](http://www.quantachrome.de) or the manufacturers of the excellent particle characterization equipments at their homepages. Especially the fax answer of this “Particle World” could be the starting point for further information, discussions and cooperation. Don't hesitate to contact us!

*D. Klank*

Yours sincerely Dr. Dietmar Klank

## QUANTACHROME Application Lab for characterization of fine and porous systems:



Excellent results, reliable and fast reports and professional information

QUANTACHROME particle analysis technique does not only offer analysis methods and the instruments themselves but also an excellent application lab. The **QUANTACHROME Particle Characterization Lab** provides not only test analysis of samples to search out the adequate analysis method but also the service for contract analysis in case that your number of necessary measurements should not be substantial enough to make the use of own instruments economic. Our support is also very valuable in case that you have only single samples or if you want to see if special analysis methods and the resulting parameters respectively could be the methods to solve your applications in your lab. The **QUANTACHROME Particle Characterization Lab** has all instruments of four product lines around the characterization of fine and porous systems available and sends excellent reports with comments and explanations to understand the determined parameters and the methods themselves.

The **QUANTACHROME Particle Characterization Lab** is acknowledged for particle size measurements, surface and pore characterization methods and other analyses “around the particle”, respectively for results according to international and/or national norms and new developed innovative methods:



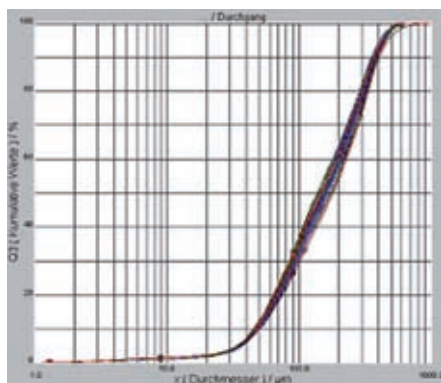
**Particle size in liquid and dry mode** with laser diffraction (ISO 13320)  
**Particle shape**  
**Particle size in concentrated dispersions** from 5 nanometers  
**Zeta potential in concentrated dispersions**  
**BET surface area** (ISO 9277 / DIN 66131)  
**Surface and pore characterization:**  
- Micropores (DIN 66135)  
- Mesopores (ISO 15901-1 / DIN 66133 and ISO 15901-2 / DIN 66134)  
- Macropores (ISO 15901-1 / DIN 66133)  
**Chemisorption** (DIN 66136) and **TPD/TPR/TPO**  
**Density of solids** (DIN 66137)  
**Tap-Density of Powders** (DIN 53194, ISO 3953)  
**Open/Closed cell content of rigid foams** (ISO 4590)  
**Sorption of water vapour** and other vapours (draft DIN 66138)  
**Stability of liquid dispersions**  
**Characterization of drying processes of thin film layers**

The **QUANTACHROME Particle Characterization Lab** has the equipment and the experienced staff to take representative samples respectively to divide the samples into representative small samples and to find out and propose specific preparation and measurement conditions according to your application. We are capable to measure your single sample as exact as periodic samples or large numbers of samples in really short period. You can load the necessary sample forms directly from our Homepage [www.quantachrome.de](http://www.quantachrome.de) and can fill the deadline according the need when you should have the results via email, fax or letter. If necessary you can clarify to get results overnight or as express service respectively. For more information about all the possible measurements please use the fax answer sheet.

**Articles in this issue** Page 2 40 years CILAS Experts in Laser Particle Size and Shape Analysis for 40 years  
Page 4 Surface and pore characterization by means of gas adsorption and mercury porosimetry (Part 1)  
Page 5 Determination of particle size and zeta potential of concentrated ceramic slurries  
**Please read furthermore** Page 1 QUANTACHROME Particle Characterization Lab, News on page 10 and 11, Fax answer sheet to copy on page 12

In the last decades, the laser diffraction has persisted against more traditional measurement methods in particle sizing. Influential reasons are considerable time saving, wider measurement ranges, higher flexibility and no need to know about parameters of the material or material mixtures in the framework of the Fraunhofer approach. For the evaluation of the measurement method, the ISO 13320 can give support. Nevertheless there are again and again new challenges and questions, which have to be evaluated and solved: a wide measurement range of a laser granulometer says nothing about the sensitivity of the special measurement equipment or the quality of the dispersion unit. Very often only a practical test gives an explanation about the automation and operation of hard- and software.

The micrometer range is a typical domain of many powders and dispersed systems which were developed in several branches of industry. The particle size analysis is an elemental tool to characterize powders, suspensions and emulsions. This concept is often reduced by the main measurement process which builds the primary base of measurement results. In the following the perception of particle size analysis is expanded to a wider meaning. In practice we have to estimate single measurements which were performed by ourselves or from which we only get a report. It is important to get an overview of the hole process: starting from sampling to the dispersing conditions and to the main measurement.

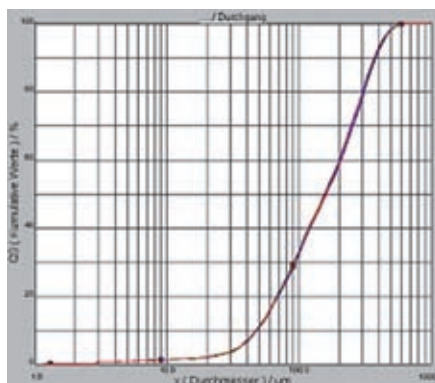


### Sampling and sample separation

Not always sampling and sample separation takes place in particle size analysis. It is strongly recommended in ISO 13320 that samples has to be representative and has to be prepared with sample separation, for example with a rotary MICRORIFFLER. By means of this instrument, several samples get separated to receive representative charges of samples for particle analysis. *Figure 1* shows the importance of representative sampling to the particle size results and the need of sample divider.

### Dispersing Conditions

Any dispersing method has advantages and disadvantages. The treatment authoritatively depends on the nature of samples, the particle size range and also on analysis tasks. If samples are soluble in common liquids and no dispersing problems are expected, a dry dispersing treatment could be favourable. Different dispersing units give caution of the limited field of applications. The liquid dispersing treatment has the advantage, that several parameters can be adjusted. These are ultrasonic time and intensity, type and nature of dispersing agents and of course the nature of solvent itself. *Figure 2* shows this principle for dispersing agents. Particles are agglomerated (left/right) with/without using additives, with additives and by use of ultrasonic agglomerates they are separated and stabilized to primary particles (middle). The amount of dispersing agent should be not to low and not to high in order to have a good dispersion of the product in the carrier liquid.



**Figure 1** CILAS 1180L Particle size analysis of feldspar without sample separation (28 measurements, left) and after use of QUANTACHROME MICRORIFFLER (28 measurements, right).



**Figure 2** Dispersing situation depending on concentration of dispersing agents.

Dispersing agents are often used in water based liquid media. For several hydrophobic samples, like carbons, carbon black or pharmaceutical products a tenside is a suitable agent to disperse such samples in water. Other (hydrophilic) samples also show excellent results of measurements without using any agent. In many cases, for example in cement industry, the use of additives could be saved by using isopropyl alcohol as liquid. Also the risk of manually dispersing errors could be prevented. The following measurements were done in isopropyl alcohol by using a CILAS 1064L adapted with an alcohol recycling unit ARU (*figure 3*).



**Figure 3** Consumption of liquid is minimized to 3 % by use of A.R.U. (Alcohol Recycling Unit).

The ARU is not only suitable with alcohols, but solvents of silicon oil or aqueous solutions are additive applications. Independent from the nature of solvent: thousands of single measurements by using only 40 litres of liquid are impressive for many users of CILAS laser granulometer for particle sizing.

### Measurement principle

The particle size analysis of laser diffraction is based on the theories of FRAUNHOFER

or the MIE approach. By sending monochromatic light through the sample, particles diffract light as illustrated in *figure 4*. The interaction of light with a single particle results in a specific angle depending on the light spectrum.

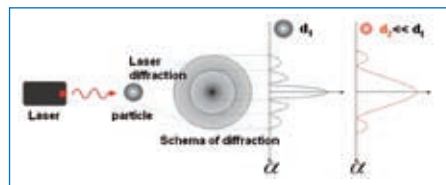


Figure 4 Principle of laser diffraction.

The diffraction pattern depends on laser wavelength, particle sizes and the optical properties of the sample. The location of minima and maxima is caused by interference. Different particle diameters result in specific diffraction patterns (*figure 5*).

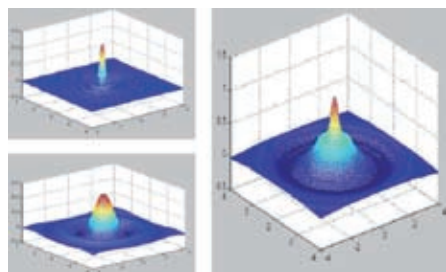


Figure 5 Diffraction patterns of large (left above), smaller (left below) and the overlay of both spectra.

The diffraction pattern of mono dispersed particles is known. The pattern of different particle sizes is an overlay of all single spectra. So the particle size distribution of an experimental diffraction pattern can be calculated by parts of theoretical curves.

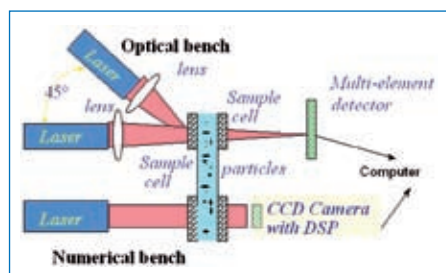


Figure 6 Optical bench of CILAS 1180 Granulometer. The patented three laser technology provides a particle size range from 0.04 to 2500  $\mu\text{m}$  in one measurement. The change from liquid to dry mode takes exactly one mouse-click only!

Figure 6 shows the technical conversion of CILAS Particle Size Analysers. For different measurement ranges CILAS provides several instruments with exactly that range for your needs and applications. The basic instrument **CILAS 930e** has one Laser (Laser 1) which gives results from 0.2  $\mu\text{m}$  to 500  $\mu\text{m}$ . To explore better at the sub-micrometer range the **CILAS 1064** Granulometer provides a

second Laser (Laser 2) in a 45° disposition. The particle size range is increased to 0.04 to 500  $\mu\text{m}$ . The hole range of particle size from 0.04 to 2500  $\mu\text{m}$  is realized with the patented “Three Laser Technology” of the **CILAS 1180**. The size distribution of large particles is determined by Laser 3 and a CCD camera within a digital signal processor. This arrangement enables a very short optical bench for a large measurement range without changing or moving any optical parts or further adjustments.

### Analyses by use of superior CILAS laser technique

If the sampling is done and optimal dispersing conditions are known or tested, the main measurement takes place. We demand reproducible measurements of well dispersed primary particles. The results strongly depend on the optical system and the arrangement of dispersing unit integrated in the instrument. The design of pumps, ultrasonic and stirring unit enables air bubble free measurements, especially in the large micrometer range.

### CILAS offers an instrument configuration with the way of ultrasound dispersion during the measurement!

In this way the particles cannot agglomerate during the measurement, this is a very useful feature for testing unknown and special suspensions, for instance in case of magnetic products! Ultrasound dispersion during the measurement works by use of up-to-date CILAS instrument version – CILAS 920, CILAS 930e, CILAS 1064 and CILAS 1180 – without air bubbles in case of measurements of water based suspensions.

### Another excellent feature of CILAS granulometers is the dispersion of particles with high density in liquid mode!

In this way, users of CILAS laser diffraction instruments are able to measure not only particles with densities of 4, 7 or 10  $\text{g}/\text{cm}^3$ , but also tungsten or gold powders with densities of 19  $\text{g}/\text{cm}^3$  because of the sophisticated liquid dispersion unit with both integrated, special designed ultrasonic bath and also special designed pump with stirrer system.

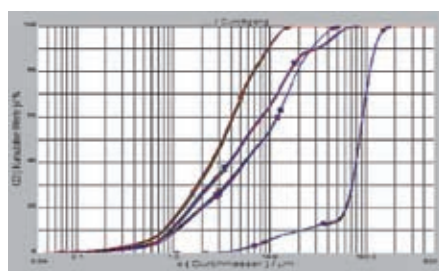


Figure 7 Experiments with CILAS 1064L from left to right: titanium dioxide (20 repeats), limestone (20), cement (100) and silica (20).

In *figure 7 and 8* the particle size distributions of several different materials are displayed. *Figure 7* shows also the investigation of reproducibility of several materials, each time 20 measurements of titanium dioxide, limestone and silica and 100 measurements of a cement sample.

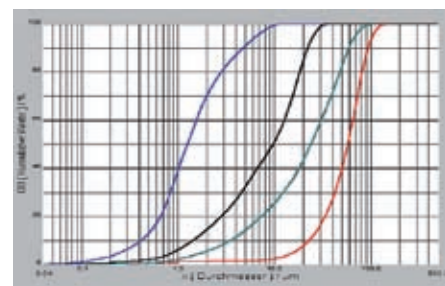


Figure 8 Experiments with CILAS 1064L from left to right: zinc oxide, graphite, lactose, milk powder.

Figure 8 shows how non-mineral powders can excellently be analysed in isopropyl alcohol without any dispersing agent. From particle size distributions, specific surfaces can also be calculated. The comparison of the particle size distributions of very different powders with the geometrical surface area and with the BET surface area, measured by use of the QUANTACHROME NOVA 2200e surface area analyser, will be discussed in our next Particle World.

### Conclusion

The laser diffraction method is the standard method for the micrometer range. The first commercial laser granulometer worldwide was produced by CILAS in 1968, a special development for building materials at that time. The laser diffraction method has been developed to the most popular and superior method for the micrometer particle size range since then. The state-of-the-art CILAS analysis instruments can characterize particle size distributions in the fine range downwards up to 0.04  $\mu\text{m}$  and in the large range up to 2.5 mm with implemented additional information about particle shape. If your interest is to be prepared for dispersion of simple but also of special samples: CILAS laser diffraction analysers offer solutions as to use ultrasound during the measurement or to analyse powders with high density in liquid dispersion!

While the sieving method is often used in the higher millimetre range, there are other analysis methods especially for the nanometer range. How even particle size distributions in concentrated dispersions can be analysed, you can read in article on characterization of concentrated ceramic slurries on page 7 of this issue.

# Surface- and Pore characterization by means of gas adsorption and mercury porosimetry

Mercury porosimetry for pore characterization up to 950  $\mu\text{m}$  (Part 1)

In this series we will discuss different aspects related to surface and pore characterization. We will describe the different measurement methods as well as the instrumental possibilities. We also explain the potential problems related to this, including the technical solutions for them.

## Pore analysis by means of mercury porosimetry

Surfaces and pores play an important role for certain applications and materials, independent of the fact whether the pores are wanted or not wanted. Therefore, the characterization of (porous) materials is often necessary, to understand the behavior of materials or to quantify its behavior. Also for production control and in the research, for developing new materials, people need to characterize the materials. This also implies the development of new instruments.

## Advantage of mercury porosimetry

If surface area is the important issue, and/or related with pore characteristics of pores smaller than 0.2  $\mu\text{m}$ , then gas adsorption is the method to use. For an extended pore structure analysis however, mercury porosimetry is often needed, especially when the pore diameters are in the micrometer range.

The main advantage of mercury porosimetry for pore characterization is the large range of pore diameters that can be covered with the measurements. The measuring range of this method, by use of the QUANTACHROME POREMASTER, is between 3 nanometers up to 950 micrometers, so it will cover more than 5 decades.

The measuring technique can be realized with the use of the POREMASTER series, manufactured by QUANTACHROME Instruments. The method is based on the fact that mercury is a non-wetting liquid, and therefore can enter the pores of materials, without changing the solid's physical characteristics nor losing its own properties. These measurements give a correlation between pressure, applied for filling the pores, and the pore diameter of the pore which is being filled. This correlation is expressed in the

Washburn-Equation which gives a direct relation between pore diameter  $D$  ( $\mu\text{m}$ ) and pressure ( $p$ ). Typically one measures the amount of mercury intruded in the pores as a function of pressure, the intrusion curve. With the aid of the Washburn-Equation these data result in a function of intruded mercury volume vs. pore diameter (see figure 1).

From that curve, one can calculate the pore volumes as well as the pore size distribution. An estimation of the specific surface area can be given, assuming that all pores are cylindrical or have a predefined structure.

## Experimental

The following results are obtained using the mercury porosimeter POREMASTER 60 (QUANTACHROME) with pressures up to 4000 bar. The samples are automatically evacuated, before starting the analysis, and automatically measured. Two porous materials, alumina (granulates) and silica gel (powder), are analyzed as well as predefined mixtures of those materials.

Mixtures of silica gel/alumina are analyzed, containing 33, 50 and 75 weight percent silica respectively. Additional gas adsorption measurements are performed using the AUTOSORB-1 (QUANTACHROME) as well as a particle size distribution analysis, using the laser granulometer CILAS 1064L.

## Interparticle voids in powders

What happens when loose powders are analyzed? The interparticle voids as well as the real pore structure is being measured. Be referred to figure 1, where the intrusion curves obtained with the POREMASTER 60 are displayed. The lower intrusion curve is related to the alumina, and the upper intrusion curve is related to the pure silica gel. In between are the mixtures as mentioned above.

Three intrusion steps are clearly seen (left to right): 100-10  $\mu\text{m}$ , 0.04-0.01  $\mu\text{m}$  and 0.01-0.008  $\mu\text{m}$ . Those steps are explainable. In this case it is an advantage to have more information about the samples. Gas adsorption for measuring BET surface area as well as characterization of smaller pores is highly recommendable. For powders, the particle size distribution can be used for interpreting the results.

## Compartmentation between pore volume and interparticle voids

Clearly seen is an intrusion step with an increasing amount of silica gel at 100  $\mu\text{m}$ , and especially at pore diameters between 40 and 20  $\mu\text{m}$ . The particle size distribution of the silica powder, measured with the CILAS 1064 L, gives an average particle diameter of 90  $\mu\text{m}$ , whereas still 10 % of the volume distribution is represented by particles bet-

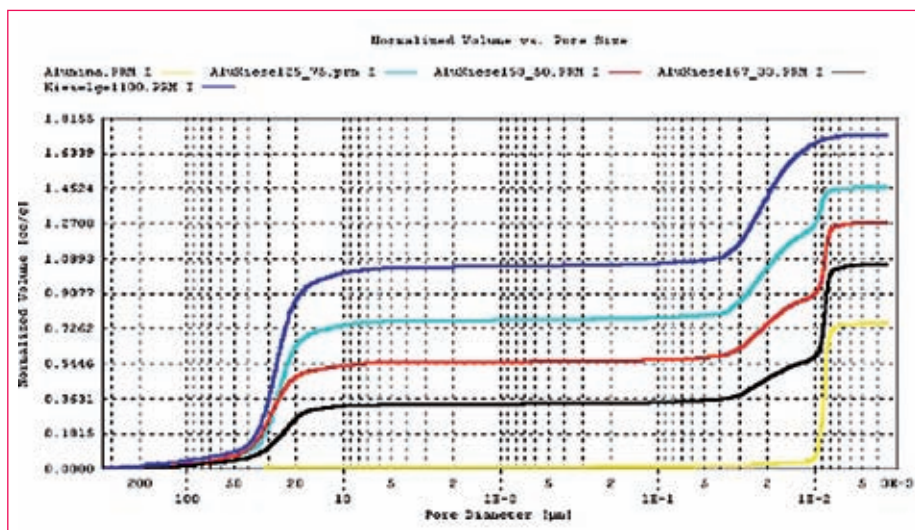


Figure 1 Intrusion curves of silica gel (upper curve), alumina (lower curve) and their mixtures.

Amount silica (%)	Intrusion Volume (cc/g)	Surface area (m <sup>2</sup> /g)	calculated amount silica (%) (from intrusion volume)	calculated amount silica (%) (from surface area)
100	0,045	22,43	100,0	100,0
75	0,202	91,58	75,8	76,7
50	0,364	170,58	50,8	50,1
33	0,478	225,79	33,2	31,5
0	0,693	319,30	0,0	0,0

Table 1 Evaluation of silica gel/alumina mixtures for pores smaller than 0.1  $\mu\text{m}$ .

ween 3  $\mu\text{m}$  and 50  $\mu\text{m}$ . This significant amount of small particles in the silica gel powders do give interparticle voids between 20-40  $\mu\text{m}$ , in the pure silica gel powder as well as in the mixtures. This is clearly seen in the curves shown in figure 1, where there is an intrusion between 20-40  $\mu\text{m}$  for all samples. The real pore filling of the silica gel starts at pores of 0.04  $\mu\text{m}$ , and of the alumina at about 0.1  $\mu\text{m}$ . The curves in figure 1 show those phenomena of the mixtures.

For the pore analysis of powder samples, not the complete curve may be used. For calculation of the average pore size, the interparticle voids should be eliminated. The POREMASTER software opens the way to exclude a certain range. This will result in compartmentation of pore volume and/or interparticle voids. Shown in table 1 is the separate examination of the pores from the used alumina (pores below 0.01  $\mu\text{m}$ ). Taking the calculation models into account, it is shown that the pore volumes of the mixtures are directly an indication of the concentration of the mixtures. The calculated and measured concentrations do match very well. This is also shown in figure 2, where the plots of the pore size distributions are overlaid. With an increasing amount of alumina, the peak at the pore size distribution shifts.

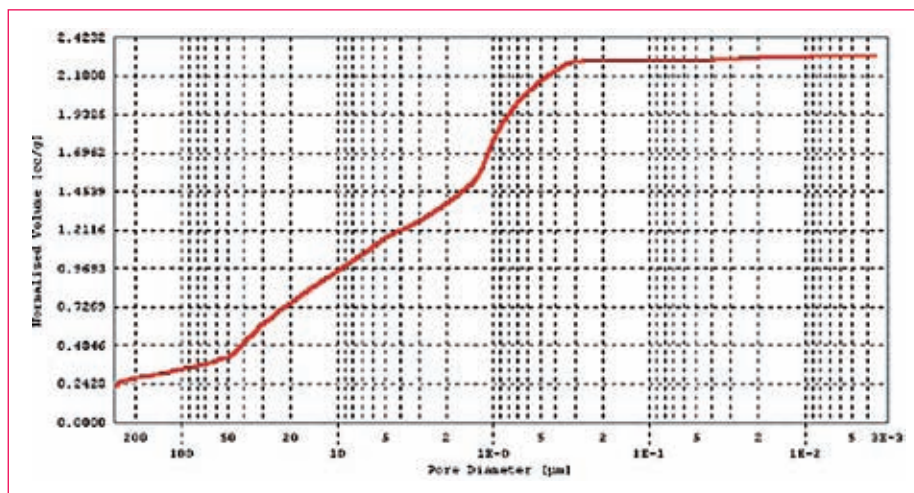


Figure 3 Mercury intrusion curve of silica gel.

There are more difficult samples, where the interparticle voids and pore filling is not as clear as in the described example. This is especially the case where the interparticle voids and pores have an overlap, how it is seen in figure 3.

The intrusion curve of silica gel shows a fraction at 1.5  $\mu\text{m}$  and an amount of pores smaller than 0.3  $\mu\text{m}$ . The latter one can be confirmed using an AUTOSORB gas adsorption measurement. On the other hand this is a sample with a high BET surface area, which indicates a large porous system

inside the material. For the silica a particle size distribution between 2 and 20  $\mu\text{m}$  was measured with the laser granulometer CILAS 1064L. For such samples, interparticle voids in the micrometer range are likely, but in the nanometer range such interparticle voids are normally not possible. After examination of the data for silica gel one can say: no significant pores below 0.3  $\mu\text{m}$ , interparticle voids are above 1.5  $\mu\text{m}$ , and the pore range of the silica is between 0.3-1.5  $\mu\text{m}$ .

### Summary

Mercury porosimetry is extremely useful for the characterization of pores over a wide range. Powder samples are showing at low pressures the interparticle voids, and at higher pressures the pore filling is shown. Those two processes are sometimes well shown, but sometimes it is more difficult to interpret the data. In the difficult cases additional techniques are needed in order to properly explain the data. The use of the gas adsorption technique (for BET surface area and small pores characterization) as well as particle size measurements can be very useful. There are not such problems with granulate or porous pieces, e.g. from building materials. For such samples you can especially use the full pore size range of the POREMASTER up to more than 950  $\mu\text{m}$ .

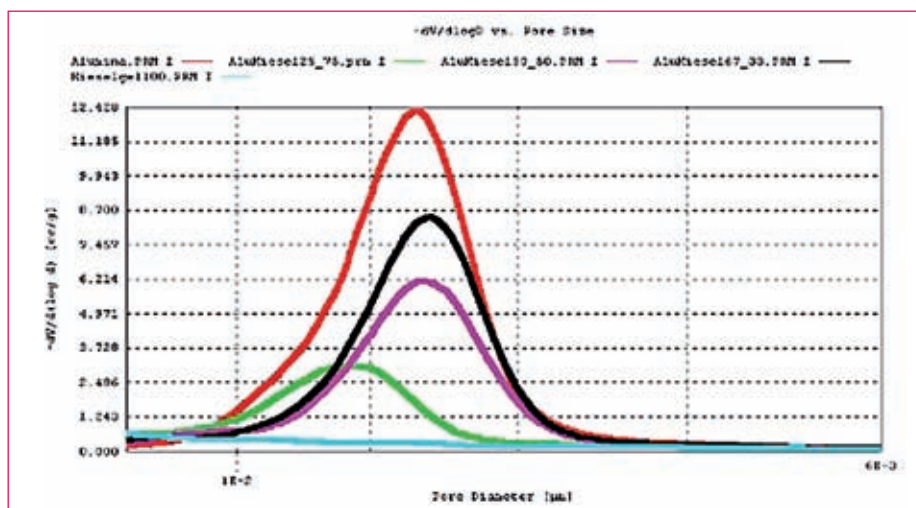


Figure 2 Pore size distributions of pores smaller than 0.01  $\mu\text{m}$ .

# Determination of particle size and zeta potential of concentrated ceramic slurries

The extensive characterization of ceramic slurries is one of the most important tasks and challenges in the ceramic industry. It is important for fields like research and development as well as quality control. The particle size distribution and the zeta potential of a ceramic slurry are of key importance in slurry characterization and in optimizing performance. The size of the particles is closely related to inhomogeneities, which in turn relate to fracture origins as well as shape distortion/cracking during drying, pyrolysis and sintering. Moreover, the zeta potential of the slurry particulates can be used as a tool for optimizing chemical dosage to achieve the desired colloid stability and size distribution.

Traditional measurements of particle size and zeta potential usually involve light scattering or sedimentation techniques and therefore require extreme dilution of the ceramic slip along with other “sample preparation” steps. Depending on the measurement technique employed, this sample preparation might include adding surfactants, sonication, and stirring.

Although the samples prepared this way may yield reproducible data, the results may be meaningless in terms of understanding the complex nature of the original ceramic slip. The sample preparation unavoidably changes both the size distribution and zeta potential of the sample, thereby distorting the very information being sought. Characterizing the concentrated sample, as is, would allow us to realistically judge the true agglomeration status of the slip and to optimize the dosage of various chemical additives *in situ*. In contrast, measurements of the diluted samples with traditional methods often reveal only the primary size of the raw materials since the sample preparation steps may have destroyed most of the useful information about the original slurry.

Ultrasound can propagate through samples that are not transparent for light, which open up many new applications. Two complementary ultrasonic techniques have been developed that allow such neat measurement of ceramic slurries, without sample preparation or dilution: Acoustic

spectroscopy for particle size measurements and Electroacoustic spectroscopy to measure the zeta potential of the slurry [1]. In both methods the interaction of sound with the dispersed particles provides useful information. However, the driving force and measured parameters are different in each case.

## Acoustic Spectroscopy for Particle Size Characterization

For acoustic spectroscopy pulses of sound are applied to the test ceramic slurries. The pulses are transmitted through the sample. The acoustic part of the instrument measures the attenuation and propagation velocity of the sound over a wide range of ultrasonic frequencies. The typical frequency range is 1 to 100 MHz. A transmitter generates acoustic pulses of certain frequency and length. These ultrasound pulses pass through the concentrated slurry. The acoustic sensor measures energy losses. Simply put: sound in – sound out (see figure 1). The most important part of the energy loss occurs while the ultrasound pulse propagates through the slurry and interacts with the particles and the liquid, but one part of the loss comes from the components of an instrument. However, an acoustic instrument can measure independently the losses in electro-

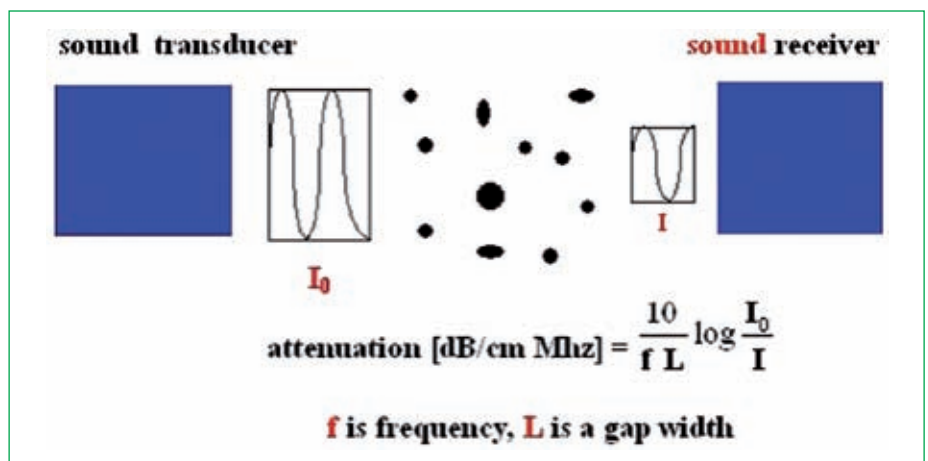
acoustic losses in transducer. In this way the colloid loss can be calculated from the total loss and can be used to calculate the particle size distribution.

The rate of change in the signal level with gap (distance from transducer to the sensor), expressed in dB/cm, corresponds to the attenuation due to losses in the colloid. It is convenient to normalize the attenuation by frequency. The experimental output of the acoustic sensor is the attenuation frequency spectra in dB/cm/MHz.

The colloid losses arise from several sources or mechanisms including the main mechanisms for the acoustic method to characterize ceramic slurries: 1. scattering, 2. viscous, 3. thermal, and 4. intrinsic loss.

For dispersions with large differences between density of the particles and density of the liquid, as in the case of ceramic slurries, the viscous dissipation mainly cause the attenuation to calculate particle sizes.

On the basis of the most well known acoustic theory for heterogeneous systems by Epstein and Carhart, Allegra and Hawley (ECAH theory) one can calculate the particle size distribution from an attenuation spectra. A key part of the acoustic method is a predictive theory which allows to calculate the expected attenuation for a given size distribution, taking into account all of the



**Figure 1 Block Diagram of Acoustic Spectrometer:** The transmitting transducer (left) converts electrical pulsed RF signal to ultrasound and launches acoustic wave pulse into slurry. The receiving sensor (right) converts the acoustic wave that passes through the slurry back into an electrical pulse. The attenuation is measured from the decrease in the received signal with increasing gap (length L).

various loss mechanisms. The particle size distribution is computed by finding that particular distribution that minimizes the difference between the experimental spectrum and that predicted by theory. The fitting error between theory and experiment provides a confidence factor for the final result.

One very attractive feature of this acoustic technique is that the colloid attenuation depends only on the rate of change of signal with changes in the gap and is independent of the actual magnitude of the signal. As a result, acoustic spectroscopy, unlike optical methods, is inherently very robust and not sensitive to fouling or contamination of the transducers and therefore very suitable for online production monitoring and control.

### Electroacoustic Spectroscopy for Zeta Potential Measurements

Electroacoustic spectroscopy measures the interaction of electric and acoustic fields from which the zeta potential can be determined. It probes the interaction between acoustic and electric fields. There are two ways to do this. In the first case, the slurry is excited with pulses of ultrasound. Ultrasound induces a motion of particles relative to the liquid. The small fluid displacements produced by this sound wave causes small periodic displacements of the electrical double-layer surrounding each charged particle. This displacement of the ionic cloud with respect to the particle surface creates a dipole moment. The sum of these dipole moments over many particles creates an electric field, which can be sensed by an antenna immersed in the slurry to record the short circuit colloid vibration current (CVI). Such an electroacoustic sensor has also two parts: a piezoelectric transducer and an electroacoustic antenna. Another design is an electroacoustic probe where the antenna is placed on the transducer.

Simply put: sound in – electrical signal out. In principle, one can do the reverse experiment, i.e. excite the slurry with an electric field, which then interacts with the particles to create an acoustic response. This reverse technique is often referred to as Electrokinetic Sonic Amplitude (ESA). Simply put: electrical signal in – sound out.

Although the normal and reverse methods appear similar, the theory for the more conventional forward CVI technique has been more extensively developed and is valid for concentrations up to 50 volume % without empirical corrections (1).

### Combination of both methods for ceramic slurry characterization

The measured electroacoustic spectrum for a given slurry contains information about both the particle size and zeta potential. At first blush, it would appear that the electroacoustic spectra would be very attractive for providing simultaneous measurement of both size and zeta potential. In practice, however, there are several disadvantages to using only electroacoustic data for such complex particle characterization. First, the electroacoustic spectra can only be measured for charged particles. Second, the desired particle size distribution and zeta potential information can only be deduced from this spectra for a limited range of conductivity and only if one makes some rather restrictive assumptions about the nature of the double layer surrounding the particle. Third, the uncertainties in the model and the underlying theory makes it most difficult to obtain any more detailed information than a simple log-normal approximation to the actual distribution.

In contrast, the acoustic spectra for a given slurry is unaffected by either the slurry conductivity or the charge on the particles. On the down side, it is not possible to obtain zeta potential from the acoustic spectra. On the bright side, however, we can obtain size data for any conductivity, and even for uncharged particles. The acoustic spectra depend only on the size distribution and the slurry concentration. Therefore, one might reasonably expect that the particle size derived from acoustic spectroscopy to be more accurate than that obtained from the electroacoustic spectra.

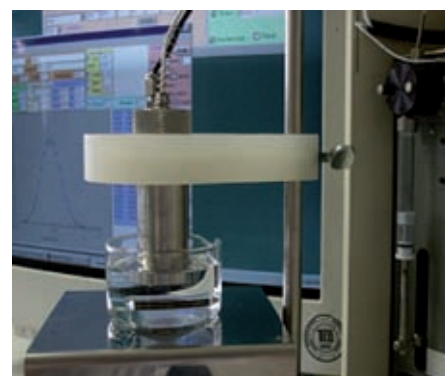
In practice, one finds that the most reliable and versatile measurements are obtained by incorporating results from both acoustic and electroacoustic spectra. The particle size is best derived from the acoustic spectra.

This size data is valid for any conductivity, whether the particles are charged or not. The electroacoustic spectra is then used primarily for calculating the zeta potential, however, a particle size determined from this data can be used as a consistency test to see how well the actual colloid fits the assumptions of the model. This high degree of crosschecking between the two independent techniques provides a high confidence in the quality of the data. Such confidence checks are often missing in some “black box” instruments, which do not have the advantage of redundant sources of data.

### Experimental

A combined acoustic and electroacoustic spectrometer DT-1200 developed by Dispersion Technology Inc. was used. The DT-1200 is a combination of the acoustic spectrometer DT-100 and the electroacoustic spectrometer DT-300 (2) and has separate sensors for measuring acoustic and electroacoustic signals. Both sensors use a pulse technique. The gap between the transmitting and receiving transducer of the DT-1200 is variable in steps from 0.15 to 20 mm and computer controlled by means of a stepping motor. The signal level at the output transducer is measured for a set of discrete frequencies and gaps. The resulting attenuation spectra are used by the DT-software to calculate the particle size distribution over a range from 0.005 to 1000 micrometers. The acoustic sensor also measures the sound speed at one chosen frequency.

For measurement of zeta potential we used the DT-1200 design of the electroacoustic sensor where the antenna is placed on the transducer. This zetaprobe is very flexible to measure the zeta potential in an external experiment, online or from small samples (see figure 2).



**Figure 2A and B, Acoustic and electroacoustic parts of the DT-1200:** Acoustic transducer (left), acoustic sensor (right), zeta potential probe (in front), smaller sensors are for temperature and conductivity measurement and for titration. The zeta potential probe can be used for external experiments, like special titrations or online-monitoring.

In just minutes, both methods provide an accuracy and precision of a few percent. The total volume of samples required is about 100 ml, measurements of zeta potential are already possible with sample volume of 5 ml. We used the automated titration equipment of the DT-1200 to invoke changes in agglomeration as a function of pH or dispersant dosage, which allows also the ceramics manufacturer to optimize performance at minimum chemical cost and operate the process under the best conditions.

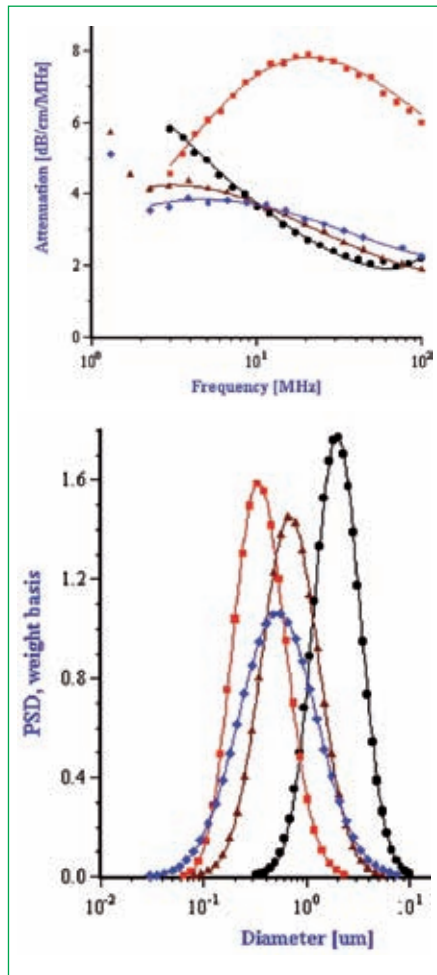
A quite unique feature of the technique is the ability to determine separate particle size distributions for individual components in mixed systems such as alumina/zirconia slurries. Although much of the experimental method is new, the overall approach is based on a well-established scientific background (1,2).

### Ceramic Applications

Acoustic and Electroacoustic spectroscopy can be used in ceramic industry and research from the very beginning to the very end of the ceramic manufacturing process. Typical applications are

- quality control of raw materials,
- control and manipulation of grinding processes (3.4),
- optimizing stability and performance of ceramic slurries at minimum chemical cost,
- operating the process under the best conditions,
- characterizing of non aqueous slurries e.g. for electrophoretic deposition processes,
- finding the optimum of flocculant dosage in ceramic waste water treatment.

Acoustics and Electroacoustics provide accurate particle size and zeta potential data for ceramic slips, neat, without any dilution or sample preparation. In some cases these acoustic techniques may agree with more traditional measurements on the diluted samples, particularly when care is taken in formulating the concentrated dispersion with an optimum level of surfactant to insure good dispersion of the primary particles. However, in many real-world cases, the final dispersant dose may have been simply extrapolated from dilute measurements and one may obtain a larger particle size in the actual slurry than predicted from these dilute measurements. It is always better to characterize the particle size and zeta potential of the actual slurry. Acoustics and electroacoustics offer this

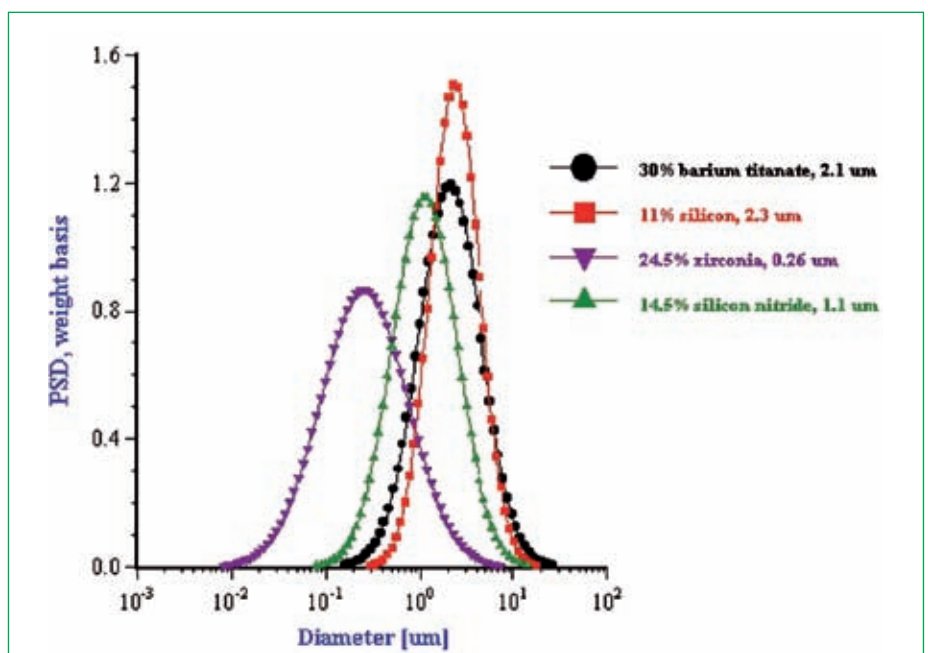


**Figure 3A and B** Acoustic Spectra for four aluminas fit precisely with theoretical curve based on output particle size distribution (weight fraction 17 % (black and red sample) and 33 % (brown and blue sample). The measured particle size distributions for same four Sumitomo aluminas demonstrate the wide particle size range capability of acoustic spectroscopy.

possibility. Examples are given in figures 3 and 4. When these measurements do not correspond with dilute measurements one needs to examine whether the chemical formulation is adequate.

For some applications it is important to recognize particle size sub-populations in the final slurry. Such bimodal distributions might result from agglomeration of primary particles caused by non-optimum dispersant addition, or perhaps from intentional addition of a second size fraction. For other ceramic applications the ceramic slip is actually a mixture of more than one solid component. Traditional optical or sedimentation techniques cannot provide correct interpretation of such mixtures and typically assume that all particles have a common set of physical properties. Today acoustic method is able to solve such applications. The commercially available software for acoustic spectroscopy has evolved to the point that allows the specification of at least two classes of disperse particles. Furthermore latest developments in ceramic manufacturing like electrophoretic deposition require characterization of high concentrated non-aqueous slurries. One example is given in figure 5.

It is not always appreciated that the particle size distribution of a slurry is not simply a function of the primary size of the constituent ingredients, but instead is a result of many complex chemical and mechanical operations on the system. The zeta potential of the system is one parameter that can be used to investigate this complex relationship.



**Figure 4** Versatility of acoustic method and the ability to provide quality control of a wide range of raw materials is illustrated by particle size distributions for a variety of ceramic materials.



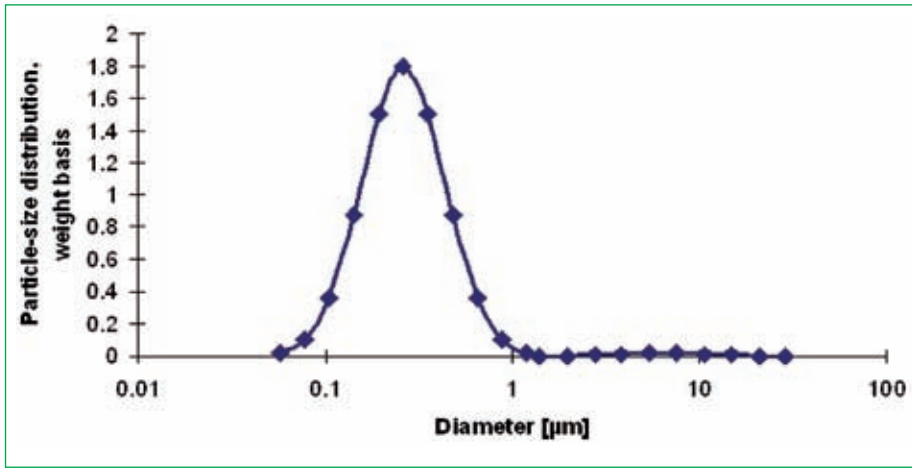


Figure 5 Particle Size distribution of a 10% alumina in Methylethylketone (MEK) used for electrophoretic depositions.

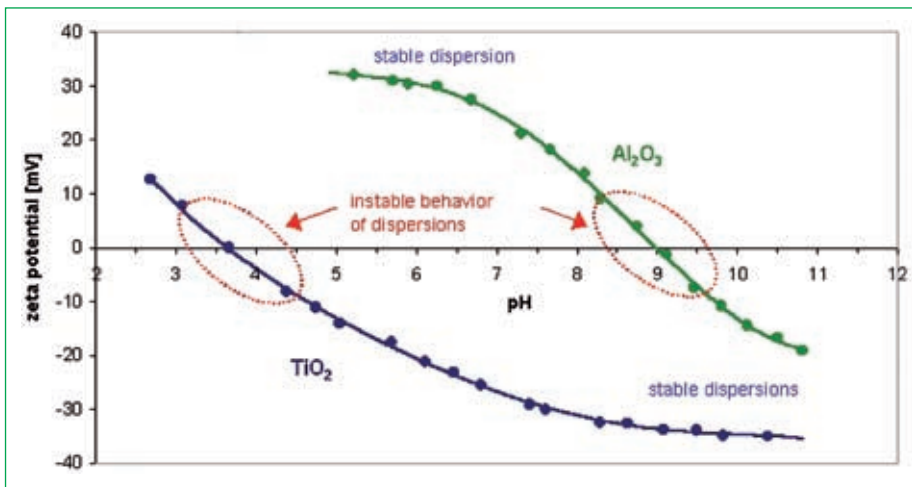


Figure 6 Slurry isoelectric point suggests optimum pH for achieving stability. Poor stability normally occurs if absolute value of zeta potential is less than 10-30 mV. Titration curve for alumina slurry suggests avoiding the range pH 9-10, whereas titania curve suggests avoiding the range pH 3-4.

The pH at which the zeta potential goes to zero is referred to as the isoelectric pH. Different materials may have quite different isoelectric points (see figure 6). If we desire good stability, then we need to operate far enough from the isoelectric point to achieve a zeta potential in excess of perhaps 20-30 mV, either plus or minus. This complex

relationship between zeta potential and particle size distribution can be easily understood using acoustic spectroscopy (see figure 7).

Zeta potentials far enough from the isoelectric point can be also reached by adding chemicals like ligninsulfonate (plastifisizer). Optimum dosage of these chemicals can be determined by zeta potential!

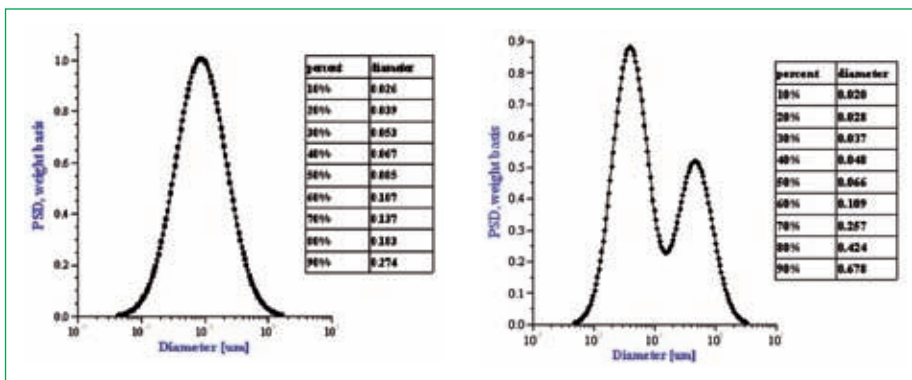


Figure 7A and B Particle size distribution of slurry depends on chemical environment. Alumina slurry at pH 4 with zeta potential of +40 mV gives unimodal distribution corresponding to the primary size of raw material. Bimodal distribution results from aggregation of unstable alumina slurry at pH 9 having a zeta potential of only +5 mV.

In the real world, the situation is sometimes even more complex. The particle size and zeta potential is not just a function of the final chemical state of the system, but may depend also on the history of how the system reached this state. In other words, the complete history of the sample may be important (figure 8).

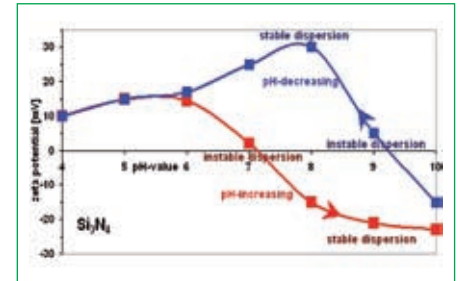


Figure 8 Case History. Slurry stability depends not only on chemical state but how one reaches this state. Laboratory titration of production silicon nitride slurry to low pH indicates high zeta potential and good stability at pH 7-8. However, process engineers found that this pH did not provide good operating performance. Actual process included an acid wash of slurry.

Subsequent back-titration to alkaline conditions shows dramatic shift in isoelectric point that required shift in plant operating conditions. The explanation for this shift in isoelectric point is quite interesting. The initial slurry had a very small level of contamination, which was insignificant in terms of the overall zeta potential and stability of the system. However, under acid conditions this minor component dissolved. Upon subsequent change to more alkaline conditions, this dissolved material then re-precipitated on the surface of the bulk of the silicon nitride surface.

This minor component, although present in seemingly insignificant quantity, nevertheless finally dominated the surface chemistry of the silicon nitride material. By realizing that the final state is dependent on the history of the sample the process could be modified to accommodate this change.

However, it can be also appreciated to work with unstable slurries near the isoelectric point. This becomes important in the case of filtration or flocculation. In many ceramic plants it becomes more and more important to recycle the process water. Waste water treatment is usually performed by flocculation. If recycling the process water the optimum dosage of flocculants is crucial. If amount of flocculant is too low particles will remain in the water.

On the other hand side overdosing leads to remaining flocculant in the process water having a devastating effect during the production process. Optimum dosage of flocculant is given by the isoelectric point and can therefore be measured by zeta potential (figure 9, next page).







## Fax answer

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### I would like to have information

- only in English       only in German       in English and German

concerning the following subjects:

- Particle Size:**  
(and Particle Shape)
- Micrometer Range (0.04 – 2500  $\mu\text{m}$ )  
 Nanometer Range (> 5 nm)
- Pore Size:**
- Gas Adsorption (0.3 – 300 nm)  
 Mercury Porosimetry (0.003 – 950  $\mu\text{m}$ )
- BET Surface Area       Density
- Zeta Potential       Chemisorption, TPD, TPR, TPO
- Sample Dividing       Water vapor sorption
- Characterization of drying processes or formation of films
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**Pictures**  
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