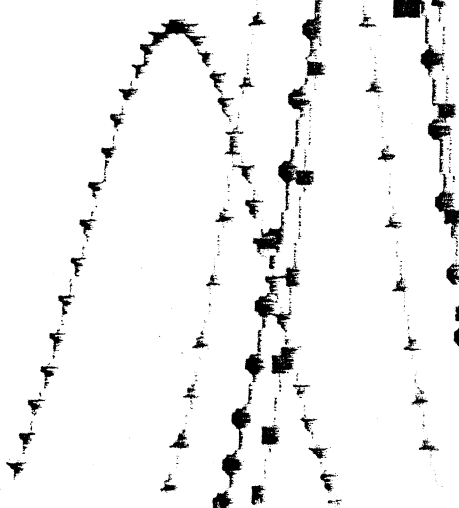


# Acoustic and Electroacoustic Spectroscopy

*Acoustic and electroacoustic spectroscopy can be used to characterize and, more significantly, provide tools to understand, optimize and control the final aggregative state of a ceramic slip.*



The zeta-potential and particle-size distribution of a ceramic slip are important in optimizing its performance. The size of the particles is closely related to inhomogeneities, which in turn relate to fracture origins and shape distortion/cracking during drying, pyrolysis and sintering. Moreover, the zeta-potential of the slurry particulates can be used to optimize 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 and other sample preparation steps. Depending on the measurement technique used, 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.

Sample preparation unavoidably changes the size distribution and zeta-potential of the sample, thereby distorting the information being sought. Characterizing the concentrated sample, as is, allows 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, because the sample preparation steps may have destroyed most of the useful information about the original slurry.

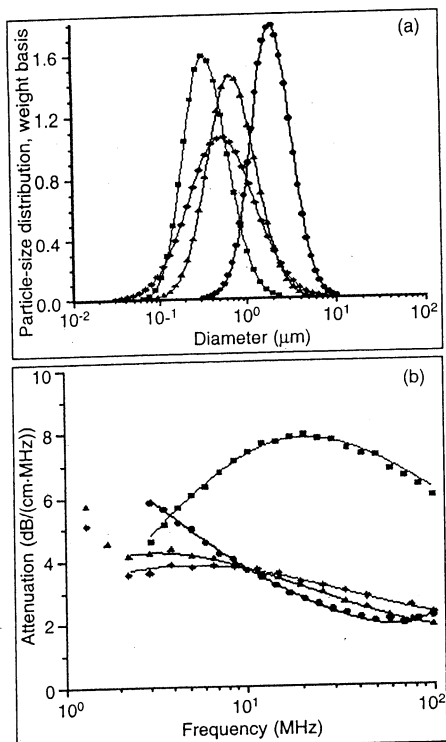
Two complementary ultrasonic techniques have been developed that allow neat measurement of ceramic slurries, without sample preparation or dilution.<sup>1,9</sup> Acoustic spectroscopy measures the attenuation and sound speed of ultrasound pulses as they pass through concentrated slurries. The measurements are made over a wide range of frequencies, and the resulting spectra are used to calculate the particle-size distribution over a range from 0.005 to 100  $\mu\text{m}$ .

Electroacoustic spectroscopy measures the interaction of electric and acoustic fields, from which the zeta-potential can be determined. Both spectroscopies are now commercially available, either separately or combined in a single instrument, such as the Dispersion Technology Model DT1200. These methods rapidly provide an accuracy and precision of a few percent on samples as small as 5–100 mL.

Automated titration equipment also is available to study changes in agglomeration as a function of pH or dispersant dosage, which allows the ceramics manufacturer to optimize

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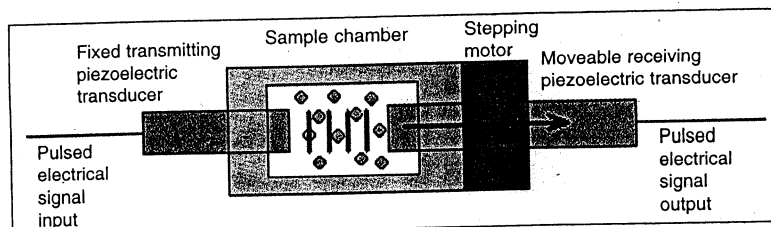


(a) Measured particle-size distributions for four Sumitomo aluminas demonstrate the wide particle-size range capability of acoustic spectroscopy and the ability to provide quality control of a wide range of raw materials ((●) AA-2, 1.9651; (■) AKP-30, 0.3193; (▲) AKP-15, 0.6838; and (◆) AKP-3000, 0.5201). (b) Acoustic spectra for same four aluminas fit precisely with theoretical curve based on output particle-size distribution ((●) AA-2, 30.67; (■) AKP-30, 30.67; (▲) AKP-15, 17.33; (◆) AKP-3000, 17.33; and (—) theory). (c) Median particle-size data from manufacturer agrees well with measured size from acoustic spectroscopy.

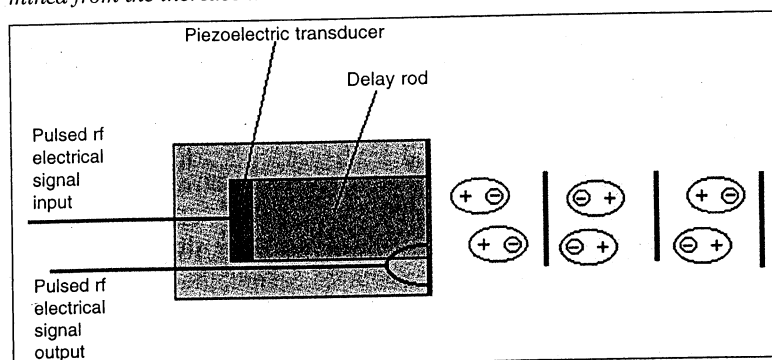
performance at minimum chemical cost and operate the process under the best conditions. A unique feature of the technique is the ability to determine separate particle-size distributions for individual components in mixed systems, such as  $\text{Al}_2\text{O}_3/\text{ZrO}_2$  slurries. Although much of the experimental method is new, the overall approach is based on a well-established scientific background.<sup>2-6</sup>

## Acoustic Spectroscopy Basics

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. For acoustic spectroscopy,



Block diagram of acoustic spectrometer. Transmitting transducer converts electrical pulsed rf signal to ultrasound and launches acoustic wave pulse into slurry. Receiving transducer converts the acoustic wave that passes through the slurry back to an electrical pulse. Gap between the transmitter and receiver is controlled by a stepping motor. Attenuation is measured from the decrease in the received signal with increasing gap. Sound speed is determined from the increase in the arrival time with gap.



Block diagram of an electroacoustic spectrometer. Transmitting transducer converts the electrical pulsed rf signal to ultrasound and launches acoustic wave into slurry. Sound wave causes the charge in the double layer surrounding the particle to be displaced with respect to the surface charge on the particle, creating small dipole moments that reverse polarity synchronously with the applied acoustic field. Center electrode inside the acoustic field detects the colloid vibration current that flows between it and a reference electrode outside the acoustic field.

pulses of sound are applied to the test slurry, and the instrument measures the attenuation and propagation velocity of the sound over a wide range of ultrasonic frequencies, typically 1–100 MHz—in other words, sound in and sound out.

The gap between the transmitting and receiving transducer is computer controlled using a stepping motor. The signal level at the output transducer is measured for a set of discrete frequencies and gaps. The rate of change in the signal level with gap, expressed in dB/cm, corresponds to the attenuation due to losses in the colloid. It is convenient to normalize the attenuation by frequency and express the final result in dB/(cm-MHz).

These losses result from several mechanisms, including scattering, viscous, thermal, and intrinsic loss.<sup>4</sup> An important part of the method is a predictive theory that allows the instrument to calculate the expected attenuation for a given size distribution, taking into account all of these 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 attractive feature of this acoustic technique is that the colloid attenuation depends only on the rate of change of the 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 robust and not sensitive to

fouling or contamination of the transducers and, therefore, suitable for on-line production monitoring and control

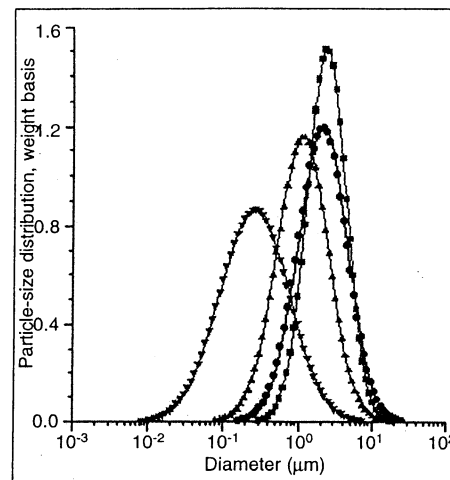
## Electroacoustic Spectroscopy Basics

In contrast to the acoustic method, which is purely acoustic, electroacoustic spectroscopy, as the name suggests, is half acoustic and half electric. Electroacoustic spectroscopy probes the interaction between acoustic and electric fields. There are two ways to do this.

- The slurry is excited with pulses of ultrasound. The small fluid displacements produced by this sound wave cause small periodic displacements of the electrical double-layer surrounding each charged particle. This distortion produces an electric field, which can be sensed by an antenna immersed in the slurry to record the short circuit colloid vibration current (CVI)—in other words, sound in and electrical signal out.

- In principle, we 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)—in other words, electrical signal in and 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 vol%.<sup>8</sup> In contrast, to date, the theory for the reverse



Versatility of acoustic method is illustrated by particle-size distributions for variety of ceramic materials ((●) 30% BaTiO<sub>3</sub>, 2.1 μm; (■) 11% silicon, 2.3 μm; (▼) 24.55% ZrO<sub>2</sub>, 0.26 μm; and (▲) 14.5% Si<sub>3</sub>N<sub>4</sub>, 1.1 μm).

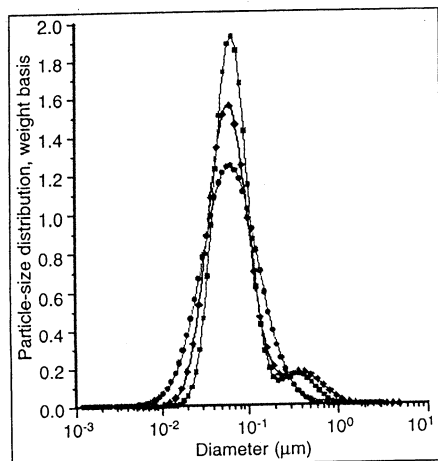
ESA technique is valid only for volume fractions <5% and relies on empirical corrections for measurement of real-world slurries.<sup>7</sup>

## Best of Both Worlds

The measured electroacoustic spectrum for a given slurry contains information about the particle size and zeta-potential. It initially appears that the electroacoustic spectra would be attractive for providing simultaneous measurement of particle size and zeta-potential. In practice, however, there are several disadvantages to using only electroacoustic data for such complex particle characterization.

- The electroacoustic spectra can be measured only for charged particles.
- The desired particle-size distribution and zeta-potential information can be deduced only from this spectra for a limited range of conductivity and only if we make some rather restrictive assumptions about the nature of the double layer surrounding the particle.
- The uncertainties in the model and the underlying theory makes it most difficult to obtain any more detailed information than a simple lognormal approximation to the actual distribution.

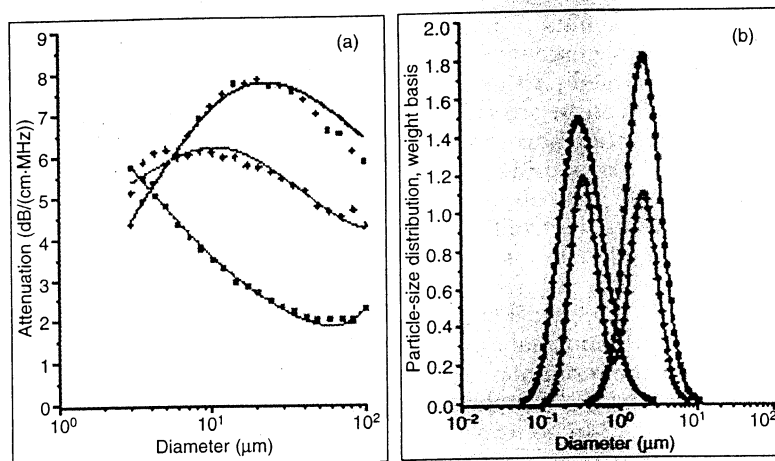
In contrast, the acoustic spectra for a given slurry is unaffected by either the slurry conductivity or the charge on the particles. On the down side, it is not possible to obtain zeta-potential from the acoustic spectra. On the bright side,



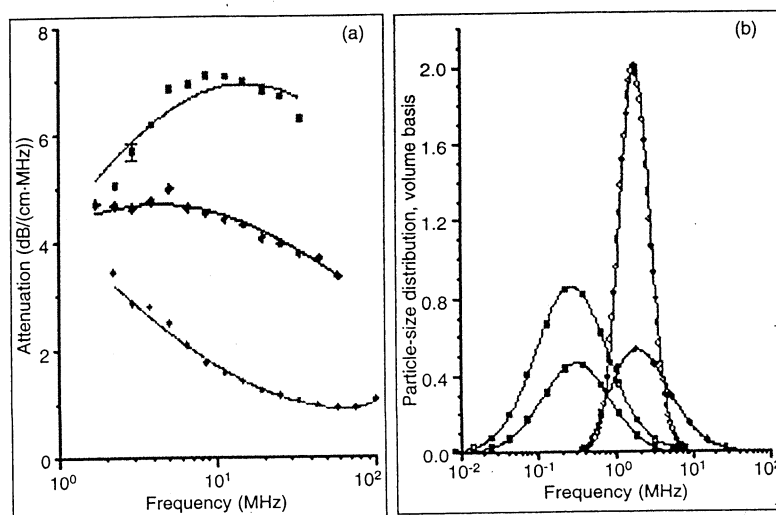
Ability to detect small subpopulation of a single 1  $\mu\text{m}$  particle per million 100 nm particles is illustrated by particle distribution of  $\text{Al}_2\text{O}_3$  slurry and same slurry with 1-wt%-added component ((●) SS25 diluted + 3.8% Geltech 0.5; (■) SS25 diluted + 2% Geltech 0.5; and (○) SS25, NVI diluted).

however, we can obtain size data for any conductivity, even for uncharged particles. The acoustic spectra depend only on the size distribution and the slurry concentration. Therefore, we might reasonably expect that the particle size derived from acoustic spectroscopy is more accurate than that obtained from the electroacoustic spectroscopy.

In practice, we find that the most reliable and versatile measurements are obtained by incorporating results from acoustic and electro-acoustic spectra. The particle size is best derived from the acoustic spectra. This size data is valid for any



(a) High sensitivity of acoustic attenuation spectra to subtle differences in samples is illustrated by the large difference in the attenuation spectra for three 10 vol%  $\text{Al}_2\text{O}_3$  slurries (0.36  $\mu\text{m}$ , 2.0  $\mu\text{m}$  and a 1:1 mixture of each). Validity of the theory is established by the good fit between the theoretical prediction and the experimental data in each case. ((●) AKP-30; (◆) 50:50 AKP-30 and AA-2 mixture; (■) AA-2; and (—) theory). (b) Each peak in the bimodal distribution for the mixed slurry agrees precisely with a corresponding peak in the size distribution for the single-component slurry. Theoretical spectra fit well the experimental data, giving high confidence in the results. ((●) AKP-30; (◆) 50:50 AKP-30 and AA-2 mixture; and (■) AA-2.)



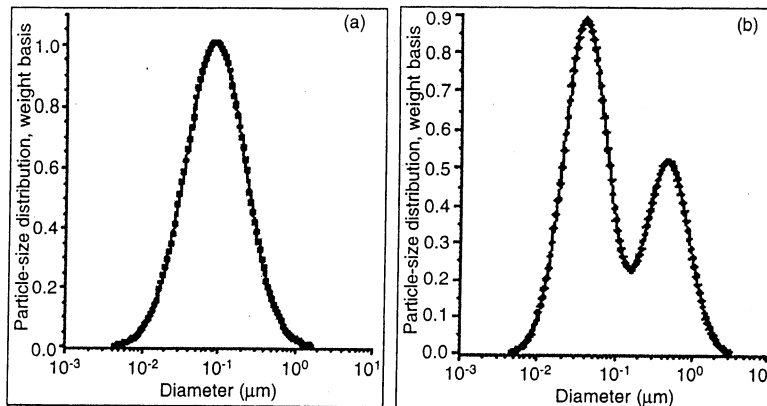
(a) Attenuation spectra for 5 vol%  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$  and 1:1 mixture of each shows that three cases have different spectra and that best-fit theoretical distribution finds a good solution for each case ((◆) 50:50  $\text{Al}_2\text{O}_3$  +  $\text{ZrO}_2$ ; (●)  $\text{Al}_2\text{O}_3$ ; (■)  $\text{ZrO}_2$ ; and (—) theory). (b) Particle-size distribution for each component in mixed slurry can be measured; size distribution for each component in the mixed slurry agrees well with the particle size for each component measured separately ((■)  $\text{ZrO}_2$  in mixture; (●)  $\text{Al}_2\text{O}_3$  in mixture; (○)  $\text{Al}_2\text{O}_3$ ; and (□)  $\text{ZrO}_2$ ).

conductivity, whether the particles are charged or not charged.

The electroacoustic spectra then are 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 cross-checking 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.

## Ceramic Applications

Acoustic and electroacoustic spectroscopy can provide accurate particle-size and zeta-potential data for ceramic slips, with no dilution or sample preparation. In some cases, these acoustic techniques may agree with more traditional measurements



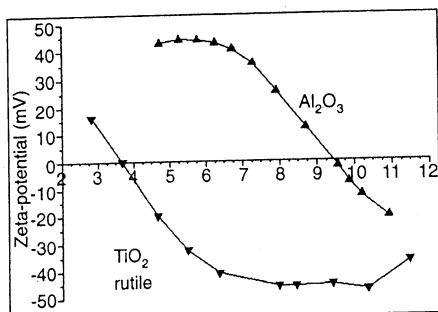
(a) Particle-size distribution of slurry depends on chemical environment.  $\text{Al}_2\text{O}_3$  slurry at pH 4 with zeta-potential of +40 mV gives monomodal distribution, corresponding to the primary size of the raw material. (10% 0.026 μm, 20% 0.039 μm, 30% 0.053 μm, 40% 0.067 μm, 50% 0.085 μm, 60% 0.107 μm, 70% 0.137 μm, 80% 0.183 μm, and 90% 0.274 μm.) (b) Bimodal distribution results from aggregation of unstable  $\text{Al}_2\text{O}_3$  slurry at pH 9 having a zeta-potential of only +5 mV. (10% 0.020 μm, 20% 0.028 μm, 30% 0.037 μm, 40% 0.048 μm, 50% 0.066 μm, 60% 0.109 μm, 70% 0.257 μm, 80% 0.424 μm, and 90% 0.678 μm.)

on the diluted samples, particularly when care is taken in formulating the concentrated dispersion with an optimum level of surfactant to ensure good dispersion of the primary particles.

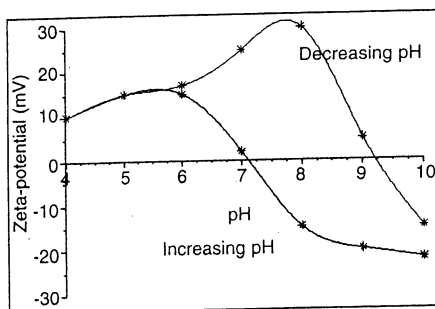
However, in many real-world cases, the final dispersant dose may have been simply extrapolated from dilute measurements,

and we may obtain a larger particle size in the actual slurry than predicted from these dilute measurements. It is almost always better to characterize the particle size and zeta-potential of the actual slurry. When these measurements do not compare with dilute measurements, we need to examine whether the chemical formulation is adequate.

For some applications, it is important to recognize particle-size



Slurry IEP suggests optimum pH for achieving stability. Poor stability normally occurs if absolute value of zeta-potential is <10–30 mV. Titration curve for Al<sub>2</sub>O<sub>3</sub> slurry suggests avoiding the range pH 9–10, whereas TiO<sub>2</sub> curve suggests avoiding the range pH 3–4.



Slurry stability depends on chemical state and how it is reached. Titration of Si<sub>3</sub>N<sub>4</sub> slurry to low pH indicates high zeta-potential and good stability at pH 7–8. However, this pH did not provide good operating performance. Actual process included an acid wash of the slurry. Subsequent back-titration to alkaline conditions showed shift in IEP that required shift in plant operating conditions. Initial slurry had little 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 reprecipitated on the bulk surface of the Si<sub>3</sub>N<sub>4</sub>. This minor component, present in insignificant quantity, finally dominated the surface chemistry of the Si<sub>3</sub>N<sub>4</sub>. By realizing that the final state is dependent on the history of the sample, the process could be modified to accommodate this change.

subpopulations in the final slurry. Such bimodal distributions might result from agglomeration of primary particles caused by nonoptimum dispersant addition, or perhaps from intentional addition of a second-sized fraction.

In other applications, it is important to be able to detect a small subpopulation of a few large aggregate particles mixed with a large number of much smaller particles. For example, chemical mechanical polishing (CMP) slurries are used in the semiconductor industry to planarize silicon wafers at various steps in the production of computer chips. One large aggregate particle can cause a major scratch and destroy circuit performance.

In many 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. In contrast, commercially available software for acoustic spectroscopy has evolved to the point that allows the specification of at least two classes of disperse particles.

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.

The pH at which the zeta-potential goes to zero is referred to as the isoelectric point (IEP). Different materials may have different IEPs. If we desire good stability, then we need to operate far enough from the IEP to achieve a zeta-potential in excess of ±20–30 mV. This complex relationship between zeta-potential and particle-size distribution can be easily understood using acoustic spectroscopy.

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 also depend on the history of how the system reached this state. In other words, the complete history of the sample may be important. ■

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