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CHARACTERISTICS OF THE CONCENTRATED SUSPENSIONS USING ULTRASONIC AND ELECTROACOUSTIC METHODS

Simultaneous determination of several characteristics such as agglomerate size, zeta-potential, pH value and conductivity are important for a better understanding and modelling of processes with submicron particles. Titania ultrasonic spectrometry was tested for its ability to determine the particle size distribution and the respective state of agglomeration in non-diluted particulate systems.

Comparative measurements of the zeta-potential were made to determine the tendency towards agglomeration of a silica suspension. In high-solid concentrations it can be measured with the colloid vibration potential. The dependence of the viscosity on the zeta-potential caused by the pH value is shown because of its importance to chemical engineering. The apparent viscosity of a titania slurry at different stirrer speed of a rotation viscosimeter was measured.

1. INTRODUCTION

Agglomerates cover the wide range between aggregates of partially molten primary particles and flocs, which can be destroyed by low-shear forces. In addition to particle interaction, chemical reactions often change dramatically the surface of the particles and the type of particle interaction. So a floc may be converted into an aggregate. For particles with nonspherical shape, mechanical interactions or mechanical fixing are possible. Often even very small amounts of additives or impurities change the properties of suspension by adsorption of particles on a surface. Thus the history of a particulate system in the production process and sample preparation may strongly influence the state of agglomeration.

Ultrasonic spectrometry should be tested for its ability to determine the particle size distribution and the respective state of agglomeration in non-diluted particulate systems. The tendency towards agglomeration should be determined by the measurement of the colloid vibration potential.

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At the Particle Characteristics and Particle Technology Laboratory of the University of Technology in Dresden various methods of particle analysis are applied (table).

Table

Methods of particle analysis

Method	Size range	Sample
Laser diffraction	0.18–1750 μm	S, P
Single particle counting	0.1–10 μm	A
(optical and coulter principle)	1.2–250 μm	S
Electrical mobility	20 nm–3 μm	A
Nuclei counting	$0–10^7$ p/cm^3	
Photometric measurements	1–100 μm	S
Sieving	5–25 000 μm	S, P
Sedimentation	0.15–50 μm	S
Cascade impactor	0.3–20 μm	A
Scanning electron microscope	> 10 nm	P
Light microscope	> 5 μm	P
Ultrasonic spectroscopy	0.1–10 μm	S

S – suspension, A – aerosol, P – powder.

Ultrasonic spectroscopy is the latest and the only method allowing measurements of high-solid concentrations without dilution.

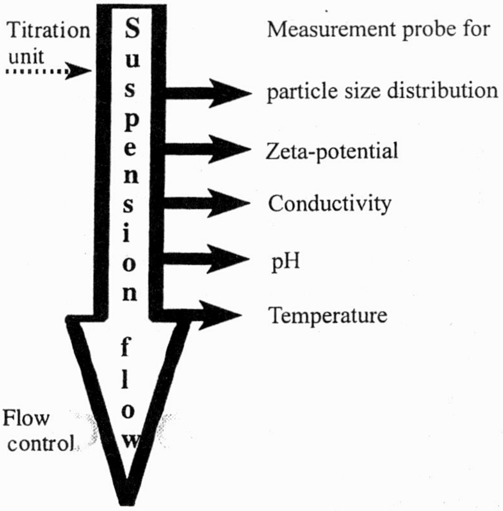

Fig. 1. Scheme of a flow through cell with several sensors to characterise the state of concentrated suspensions

Such processes as flocculation, crystallisation, dispersion and filtration and many materials, e.g. ceramic slurries, pigments, coatings and others, need the characteristics of the state of agglomeration, i.e. the degree of dispersion.

Because of the dominating surface effects and small interparticle distances the particles in the submicron range tend to agglomerate. The complex relations between particle size, surface behaviour and rheological properties of the liquid cause that agglomeration and deagglomeration are in a certain state of dynamic equilibrium. This state will change if the concentration of solids, the types of ions, or the polyelectrolytes are altered.

Therefore, simultaneous determination of several characteristics such as agglomerate size, zeta-potential, pH value and conductivity are important for a better understanding and modelling the processes with submicron particles (figure 1).

2. INSTRUMENTATION

The AcoustoPhor 8000 from Pen Kem is designed for a long wavelength regime with a frequency range from 1 to 100 MHz in the particle size range from 10 nm to 10 µm. The measured attenuation spectra are transformed into a log-normal particle size distribution as well as into monodisperse particle size and a bimodal log-normal distribution. A statistical measure for the coincidence with the experimental values allows the selection of the best hypothesis. The sample volume of 100 cm^3 suspension with up to 50 vol.% solids is pumped continuously through the measurement cell.

For zeta-potential measurement a second probe is located at the inlet of the flow through cell for ultrasonic spectrometry.

3. PARTICLE SIZE DISTRIBUTION MEASURED BY ULTRASONIC SPECTROMETRY

The attenuation of sound and dispersion of phase velocity over a wide frequency range is measured and analysed.

For the calculation of a particle size from the attenuation spectra, a number of physical constants of the phases must be known: density, sound speed, specific attenuation, viscosity, head capacity, heat conductivity and thermal expansion coefficient. In the case of suspensions of hard solid particles, the thermal losses can be neglected.

The physical background to the particle size-dependent effects is understood to be scattering of the sound waves on the particles and certain dissipation processes that are inherent in sound propagation in disperse systems [1]. The dissipation processes belong inevitably to the sound propagation, as sound waves by their nature are propagating equilibrium disturbances.

Five different loss mechanisms can be distinguished in disperse systems [2]:

1. The particle size-independent sound absorption in the fluid and disperse phase(s), the so-called *intrinsic losses*.
2. The exergy loss of particle deformation and a non-stationary heat transfer across the phase interface due to different thermo-physical properties – *thermal losses*.
3. The exergy loss of a viscous deformation of the flow field around the particle due to different inertial properties and the viscosity of real fluids – *visco-inertial* or *viscous losses*.
4. The exergy loss of alternating electric currents due to the dipole behaviour of charged particles in acoustic fields – *electrokinetic losses*.
5. The exergy loss in inelastic inter-particle links – *structural losses*.

Titania is often used in industrial applications, for example, in the paint industry. As a result of the AcoustoPhor measurement of a suspension with 5 vol.-% solids concentration we obtained in figure 2 a median particle size of 233 nm with a standard deviation of 0.325 [3]. For comparison with a similar non-diluting measurement technique [4], the material was measured with the AcoustoSizer (Matec) in the Fraunhofer Institute IKTS-Dresden at 5 vol.-% giving 245 nm as mean size and 0.35 as standard deviation [5].

This relatively narrowly distributed material was measured by laser difraction after strong dilution and dispersion with broader and slightly larger distributions. The analysis with the scanning electron microscope (SEM) shows for titania selectipur (Merck) in figure 2 a non-spherical convex shape and a broad size distribution with a median size of 142 nm (number-based) and a standard deviation of 0.4. The value transferred into a median size by weight was 229 nm [6], [7].

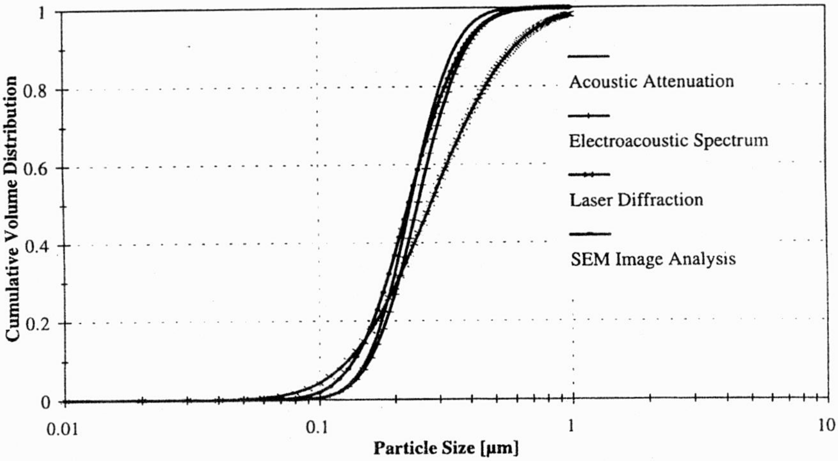

Fig. 2. Particle size distribution of a 5 vol.% titania suspension measured by different methods

4. CHARACTERISTICS OF THE STATE OF DEAGGLOMERATION

Different mechanisms of the agglomeration, e.g. solid bridges, adhesion or shape effects, cause agglomerates with a different strength of their bonds and different porosity.

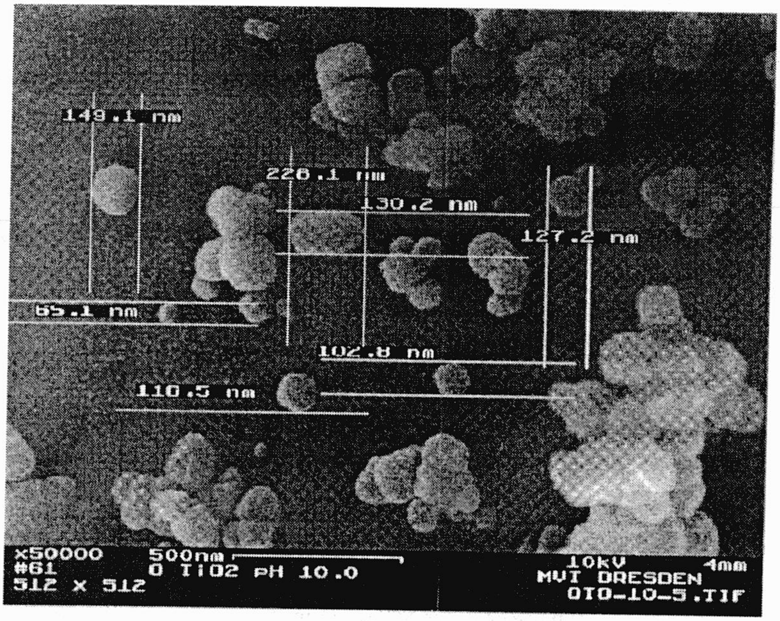

Fig. 3. Primary particles, aggregates and agglomerates of titania

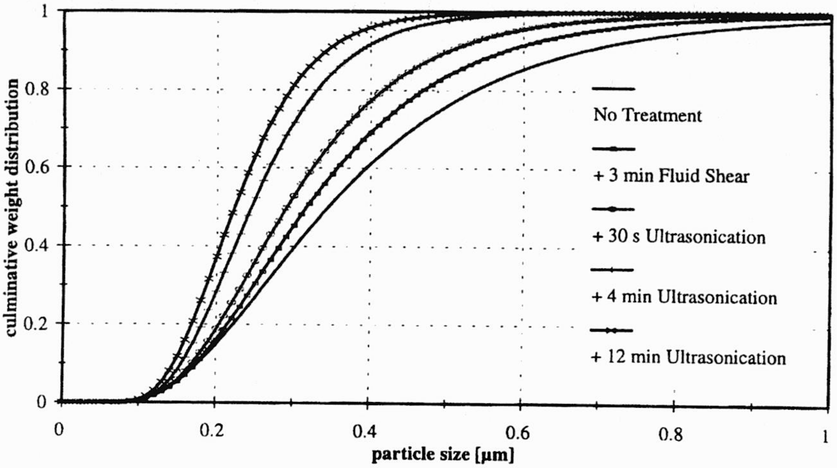

Fig. 4. Particle size distributions measured by ultrasonic spectroscopy of a 5 vol.-% titania slurry between different steps of treatment

In figure 4, a real agglomerated titania powder was suspended in a 5 vol.-% suspension without any dispersing treatment. Then a toothed-disk mill with a high-fluid shear, and after that an ultrasonic disintegrator were applied in order to disperse titania. With the passing of time the mean particle size became smaller and the standard deviation was reduced.

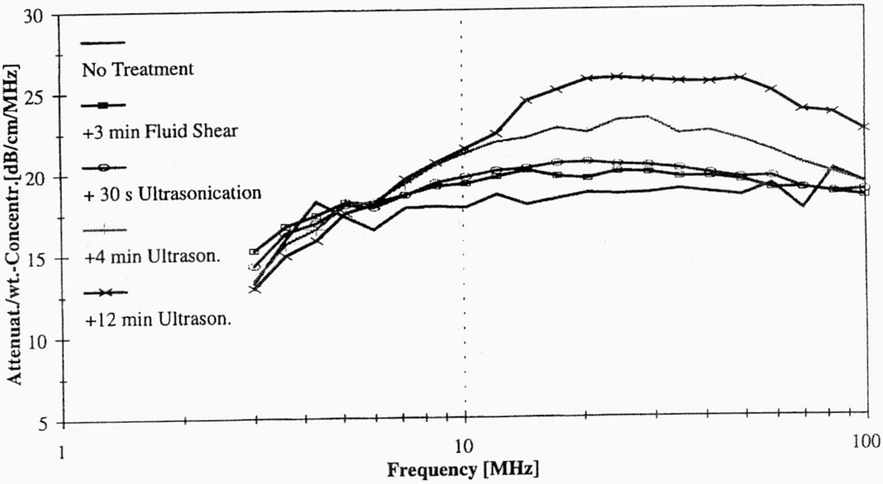

Fig. 5. Ultrasonic attenuation spectra of a 5 vol.-% titania slurry between different steps of treatment

The ultrasonic spectra showed a significant increase in the attenuation in the higher-frequency range due to an increasing amount of small primary particles over the time of dispersion in figure 5.

After dilution at constant pH and conductivity the dispersion effect could not be measured with a laser diffractometer. In the first 20 seconds of dilution, reagglomeration dominated the dispersion effect in the submicron range produced by the ultrasonic disintegrator. The drastic dilution to less than 0.1 vol.-%, necessary for optical methods, seems to cause a loss of dispersion stability because of desorption of stabilizing ions from the particle surface, even if pH changes are avoided.

5. COLLOID VIBRATION POTENTIAL

The tendency towards agglomeration should be determined by the measurement of the colloid vibration potential. As a sound wave crosses a suspension, the particles start to oscillate following the visco-inertial effect produced between particle and fluid. The resulting relative motion between fluid and particles leads to a disturbance of the diffuse ion layer around the particle. The particles become a dipole as it is known from the sedimentation potential. This acousto-phoretic effect induces a macroscopic colloid vibration potential.

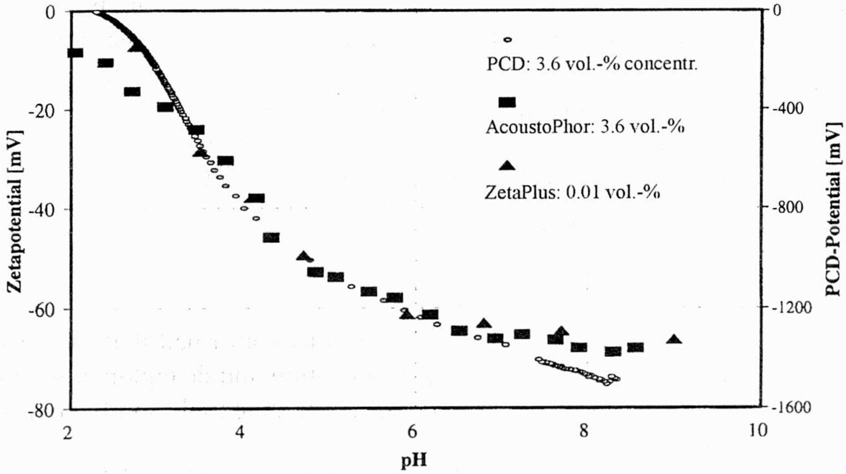

Fig. 6. Zeta-potential measured by very different methods during pH titration

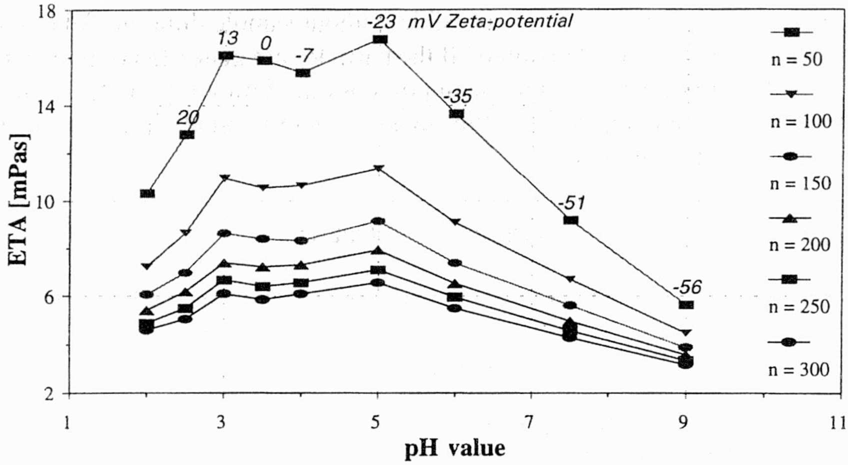

Fig. 7. Apparent viscosity ETA of a 5 vol.-% titania slurry during pH titration and respective variation of zeta-potential at different stirrer speed (rpm) of a rotation viscosimeter

Systematic investigations of the sample dilution procedure enabled us to obtain a good agreement of the zeta-potential measured by very different methods (figure 6).

Dilution of a silica suspension with supernatant liquid after filtration or centrifugation resulted in the same zeta-potential as dilution with water and controlling pH and conductivity. But this is not valid for all minerals.

The Zetaplus is the measurement of the electrophoretic mobility of individual particles. Based on the particle size, measured by photon correlation spectroscopy, the zeta-potential can be calculated. The PCD instrument allows measurement of the streaming potential of the suspension in a slit between an oscillating piston and a cylinder. It can be related only qualitatively to the zeta-potential.

The dependence of the viscosity on the zeta-potential caused by the pH value is shown because of its importance to chemical engineering (figure 7).

6. CONCLUSIONS

The experiments in dense submicron suspensions confirmed that the characteristics of the dynamic equilibrium between agglomeration and deagglomeration requires the simultaneous measurement of particle size, zeta-potential, solids concentration, pH and conductivity.

Ultrasonic spectrometry can be used to measure the size of particles below 10 μm down to about 10 nm. In particular the upper limit must be regarded because of an increasing influence of scattering effects not detectable with the AcoustoPhor 8000.

In contrast to optic methods, an online measurement for the study and optimization of the processing of dense slurries is possible without sample dilution. Additionally the solids concentration must be determined if the particles are generated or reduced.

The zeta-potential measurement basing on colloid vibration potential in high-solid concentrations can be compared to other measurement methods in dilute suspensions controlling the ion background.

ACKNOWLEDGEMENT

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REFERENCES

[1] DUKHIN A., GOETZ P., *Acoustic Spectrometry for Concentrated Polydisperse Colloids with High Density Contrast*, Langmuir, 1996, 12, 4987–4997.

[2] BABICK F., HINZE F., STINTZ M., RIPPERGER S., *Ultrasonic Spectrometry for Particle Size Analysis in Dense Submicron Suspensions*, Part. Part. Syst. Charact., 1998, 15, 230–236.

[3] HINZE F., STINZ M., RIPPERGER S., *Ultraschallspektrometrie zur Partikelgrößenanalyse*, CLB., 1997, 5, 193–196.

[4] KNÖSCHE C., FRIEDRICH H., STINZ M., *Determination of Particle Size Distribution and Electrokinetic Properties with the Acoustosizer in Comparison with Other Methods*, Part. Part. Syst. Charact., 1997, 14, 175–180.

[5] KNÖSCHE C., Diploma thesis, TU Dresden, 1995.
[6] BABICK F., Diploma thesis, TU Dresden, 1997.
[7] HINZE F., STINTZ M., RIPPERGER S., *Particle Characterisation in Highly Concentrated Submicron Suspensions by Ultrasonic Spectrometry*, First European Congress on Chemical Engineering ECCE 1, Florence, 1997.

CHARAKTERYSTYKA ZATĘŻONYCH ZAWIESIN Z WYKORZYSTANIEM ULTRADŹWIĘKÓW I METOD ELEKTROAKUSTYCZNYCH

Jednoczesne określenie wielu parametrów takich jak: wielkość aglomeratów, potencjał zeta, wartość pH i przewodnictwo jest istotne w dokładnym zrozumieniu i modelowaniu procesów, w których występują cząstki o charakterze submikronowym. Sprawdzono przydatność spektrometrii ultradźwiękowej z wykorzystaniem tlenku tytanu do określania rozkładu wielkości cząstek i stopnia aglomeracji w układach nierozcieńczonych. Dokonano porównawczych pomiarów potencjału zeta, aby zbadać, czy aglomeraty mają tendencję do występowania w zawiesinie krzemionki. W przypadku dużego stężenia ciał stałych tendencja do tworzenia aglomeratów może być określona przez pomiar potencjału wibracji koloidów. Ze względu na istotne znaczenie w inżynierii chemicznej przedstawiono zależność potencjału zeta od lepkości (w wyniku zmian pH). Zmierzono również lepkość pozorną osadu tlenku tytanu dla różnych prędkości obrotowych wiskozymetru.