Aggregation of concentrated colloidal silica dispersions in flow

Mallorie Tourbin, Sylvie Schetrite, Béatrice Biscans, Christine Frances

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M. Tourbin, S. Schetrite, B. Biscans, C. Frances
Laboratoire de Génie Chimique CNRS UMR 5503, 5 rue Paulin Talabot, BP 130
31106 Toulouse Cedex 01, France
E-mail address: Mallorie.Tourbin@ensiacet.fr

ABSTRACT

Concentrated suspensions of nanoparticles subjected to transport or shear forces are commonly encountered in many processes such as precipitation, wet comminution or filtration. In these processes, particles are likely to undergo processes of aggregation and fragmentation under physicochemical interactions and hydrodynamic forces. This study is focused on the analysis of the behaviour of colloidal silica in dense suspensions subjected to hydrodynamic forces.
The destabilization of a colloidal silica suspension is done adding sodium chloride salt to a stable dispersion, so modifying the ionic force of the system. Batch experiments, performed in an agitated vessel, were made in order to observe the behaviour of the suspended particles under fixed operational parameters. Various techniques of characterization of the particle size (photon correlation spectroscopy, acoustic spectroscopy) and of the physicochemical properties of the suspensions were used allowing defining the silica dispersions properties (particle size distribution, particle arrangement during the aggregation process, pH, zeta potential). This work presents a study of on-line particle sizing during the aggregation process of colloidal silica by ultrasonic attenuation spectroscopy.
The evolution of the particle size distribution versus time showed the different stages of the silica aggregation whose kinetic rates depend either on physicochemical or hydrodynamics parameters.

Keywords: *nanoparticles, dense suspensions, stability, aggregation, correlation photon spectroscopy, acoustic spectroscopy.*

1. INTRODUCTION

The success of nanoparticles is due to the industrial interest for many applications of this type of particles. But the usual properties of the nanoparticles (optical properties, texture, rheology, bioavailability …), in the form of powders or suspensions, are closely associated to the particle size and to their dispersion state. Processing nanoparticles induces a series of problems during the generation, handling, conveying or storage steps. An inherent problem of the different methods of generation or treatment of nanoparticles in dense suspensions is the difficulty of controlling the process of aggregation and then of preserving the quality and the stability of the products.
The physicochemical properties of the medium and the hydrodynamic conditions (shear, transport flow,…) are decisive for the aggregation phenomenon. So, it is essential to know the influence of these parameters in order to control and model this process during the generation or treatment steps.
The aim of this study is to follow the aggregation process of concentrated colloidal silica suspensions placed under conditions of flow (shearing, transport) identical to those met in real processes. One major problem deals with the characterization of the properties of dense

suspensions. Indeed, optical methods usually used to characterize size often require doing measurements in diluted conditions. However dilution can involve a change of the dispersion state of the system, modifying the physico-chemical properties of the suspension, thus inducing an aggregation or de-agglomeration process of the dispersed phase. So, the main objective of the present paper is to define an appropriate method for the characterization of dense suspensions.

2. MATERIALS AND METHODS

2.1 Materials

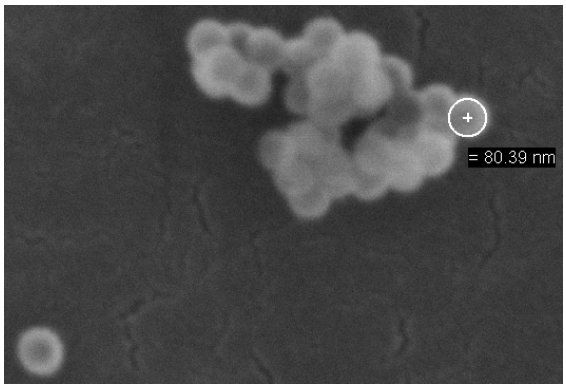

Figure 1: SEM photography of Klebosol 30R50 (x 50000)

A colloidal silica suspension, Klebosol 30R50 (Clariant, France), having an initial solid content of 30% w/w was used. The suspension is stabilised by Na^+ ions and has a pH of about 8-9. Its density is about 1.9 g/ml (silica density is 2.2g/ml) and its specific surface around 50m^2/g. *Figure 1* shows a photography of dried powder obtained using a scanning electronic microscope (LEO 435VP). Silica particles are spherical and have a diameter of about 80 nm. The particles are organised themselves into agglomerates looking like grapes when the colloidal suspension is dried on a desiccation balance.

Deionised water (pH~6 and Λ~5-7 µS) was used to prepare the diluted suspensions. The solid content of these suspensions was determined with a precision of 10^{-2} %, by the measure of the humidity rate by thermogravimetry using a Halogen Moisture Analyser HB43 desiccation balance (Mettler Toledo).

2.2 Characterization measurements

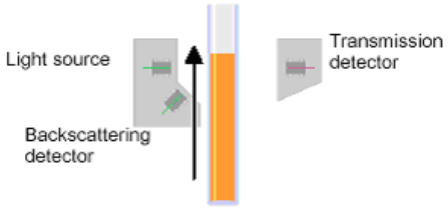

Figure 2: Principle of Turbiscan measurements

The stability of the different silica suspensions was measured with a Turbiscan MA 2000 apparatus (Formulaction, France). The studied dispersion was poured into a flat-bottomed glass cylindrical cell. A LED that emits in the near infrared (λ=850 nm) gives light to the glass tube and two photo-detectors collect the transmitted and retrodiffused light by the dispersion. The detection head scans the entire height of the sample (about 65 mm), acquiring transmission and backscattering data. The apparatus allows detecting the phenomenon of particles migration (creaming, sedimentation) and particle size variations. *(Mengual et al., 1999)* **[1]**

Zeta potential measurements of a diluted suspension were made by electrophoresis with a Zetasizer 3000 apparatus (Malvern Instruments).
Furthermore, pH measurements were made with a standard MeterLab Radiometer analytical PHM210 pH-meter and a combined pH electrode PHC3001-8 which is especially designed for aqueous suspensions.

The size of the suspended particles was measured by two different ways: correlation photon spectroscopy and acoustic spectroscopy.
The correlation photon spectroscopy allows measuring size below the limit of the static light diffusion and diffraction methods (≈ 50 nm). For this study, a Zêtasizer Nano S (Malvern Instruments) was used. The principle of this apparatus is based on the Stokes-Einstein law which gives the Brownian diffusion coefficient of the particles according to their size and the physical properties of the medium. The retrodiffused light (angle of 173°) is detected and permits to determine the particle size distribution of the suspensions.

The size distribution of nanoparticles suspended in liquids is a critical parameter in a multitude of industries and applications. Particle size analysis of concentrated systems using conventional light scattering methods often requires severe dilution. Uncertainties arise due to the unknown behaviour of such dense dispersions during dilution. Another current question is how representative the sample is. So a better understanding of aggregation phenomena would result if measurements were done in true processing conditions with respect to solid content and hydrodynamic conditions.

Sound waves interact in a similar manner to light waves but have the advantage that they can travel through concentrated suspensions and emulsions. Ultrasonic attenuation spectroscopy is capable for examining the concentrated or optically opaque systems without any dilution. Such in-situ characterization of concentrated systems makes the acoustic method very useful because it does not need to modify the dispersion state of the suspending particles.

In this work, we have access to the commercial acoustic spectrometer Ultrasizer (Malvern Instruments, United Kingdom). Particle size analysis using acoustic spectroscopy consists of:

- Predicting attenuation and velocity spectra by mathematical modelling for any particle size distribution (PSD) and volume concentration,
- Measuring attenuation and velocity spectra,
- Inverting the mathematical model to extract both the PSD and the volume concentration from the measured spectra.

The Ultrasizer measures the acoustic attenuation spectrum of the sample over the frequency range of 1-160 MHz. The range used for a given measurement depends on the attenuation characteristics of the samples (particles size, solid content).
The interaction of ultrasound waves with particles has been comprehensively described through a complete mathematical framework which accurately predicts the attenuation spectrum of any suspension. A rigorous but complex model has been published by Epstein and Carhart *(1953)* **[2]** and Allegra and Hawley *(1972)* **[3]**, which predicts the scattering of an acoustic plane wave by a sphere of a given size.
When a sound wave passes through a suspension, changes occur to the wave as well as to the two phases of the particulate medium. A particle presents a discontinuity to sound propagation and the wave scatters with a redistribution of the acoustic energy throughout the volume before being detected at the receiver (scattering and diffraction losses). In addition, absorption phenomena occur when particles move relative to the suspending medium and the mechanical energy degrades into heat (viscous losses) and temperature differences develop between phases with mechanical energy going again into heat (thermal losses).
Epstein and Carhart *(1953)* and Allegra and Hawley *(1972)* have shown that any of these attenuation phenomena can be accurately characterized through fundamental equations based on the laws of conservation of mass, energy, and momentum, the thermodynamic equations of state, and stress-strain relations for isotropic elastic solids or viscous, by formulating the Wave Equations which describe the interaction between the sound wave and the particles.

2.3 Aggregation experiments

Aggregation experiments were carried out in the Ultrasizer batch cell. The tank used has a specific geometry (*Figure 3)*. It is a water jacketed agitated vessel of 470 mL capacity. The stirrer, a three-bladed impeller, was located very near to the bottom of the tank. The stirring speed was fixed at 600 rpm. The experimental set-up shown in *Figure 4* also includes a thermostatic bath.
440 mL of a 0.8 M sodium chloride solution was firstly poured into the tank and stirred. When the desired operating temperature (25°C) was reached, 11 mL of Klebosol 30R50 was added instantaneously to obtain the desired solid concentration.
The attenuation spectrum versus frequency was measured after different periods of time.

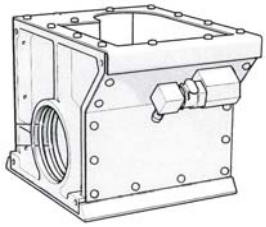

Figure 3: batch cell of the Ultrasizer

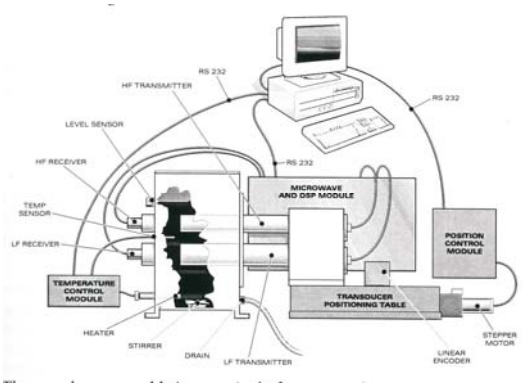

Figure 4: Experimental set-up

A measure of the attenuation of the medium was done first to determine the equation of the attenuation in the medium versus frequency. The physical properties concerning liquid and solid phases are summarized in *Table 1*.

	Silica	aqueous solution of NaCl (0.8 M)
Density ($kg.m^{-3}$)	$2.20\ 10^{3}$	$9.9524\ 10^{2}$
Sound speed ($m.s^{-1}$)	$5.96\ 10^{3}$	$1.4970\ 10^{3}$
Thermal dilatation ($°C^{-1}$)	$1.56\ 10^{-6}$	$2.5677\ 10^{-4}$
Thermal conductivity ($J.m^{-1}.s^{-1}.°C^{-1}$)	1.37	$5.9525\ 10^{-1}$
Heat capacity ($J.kg^{-1}.°C^{-1}$)	$7.42\ 10^{2}$	$4.1785\ 10^{3}$
Shear rigidity ($N.m^{-2}$)	$3.13\ 10^{10}$	
Viscosity (Po)		$9.0300\ 10^{-3}$
Attenuation coefficient - factor ($dB.inch^{-1}$)	$1.46\ 10^{-3}$	$2.00\ 10^{-1}$
Attenuation coefficient - exponent	2.00	1.976

Table 1: Physical properties of silica and 0,8M aqueous sodium chloride solution

3. RESULTS AND DISCUSSION

3.1 Characterization of initial suspensions

3.1.1 Physicochemical stability

The pH of the solution has a strong influence on the stability of colloidal silica suspensions. Indeed, the gelation rate is very high for pH 4-5. However, below this critical zone of pH, and around the isoelectric point (pH ~ 2), the suspension is stabilized by hydrogen bonds that are formed between the silica particles and the dispersed phase. Above this pH, and more particularly for pH>8, the suspension is stabilized by electrostatic repulsions. The initial silica suspension has a solid content of 30 % wt. and a pH of 8.97. Additionally, the stability of this suspension is strengthened by sodium ions that adsorb on the silanol groups (Si-OH), which increase the charge of the particle surfaces and increase the range of the electrostatic repulsion forces. *Figure 5* shows the evolution of pH versus the solid content of the suspension.

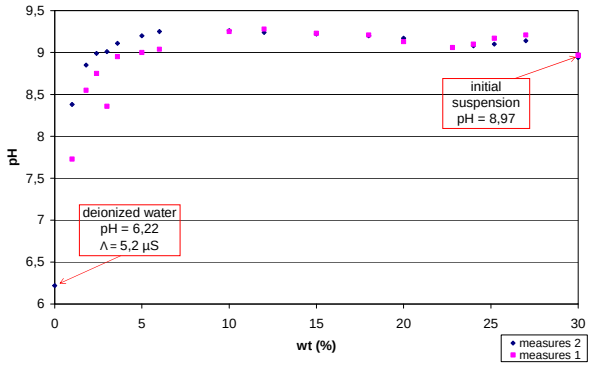

Figure 5 : Evolution of pH versus solid content of Klebosol 30R50

Diluting the suspension until 1 wt. %, the pH of the suspension does not fluctuate a lot and remains between 7.73 and 9.25.

The zeta potential of a very diluted Klebosol suspension is ξ = - 56.1 mV. That corroborates the stabilization of the silica suspension by electrostatic repulsions.

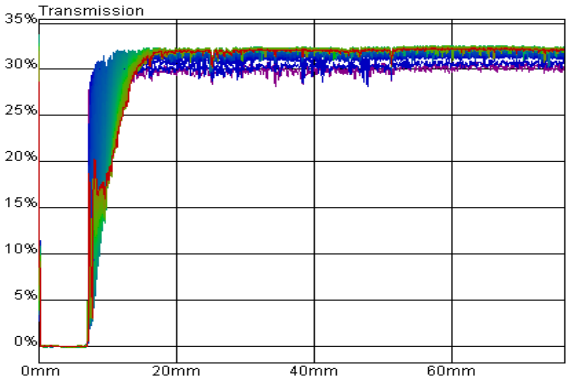

Figure 6a: Diffuse transmitance of Klebosol 30R50 30 % wt.

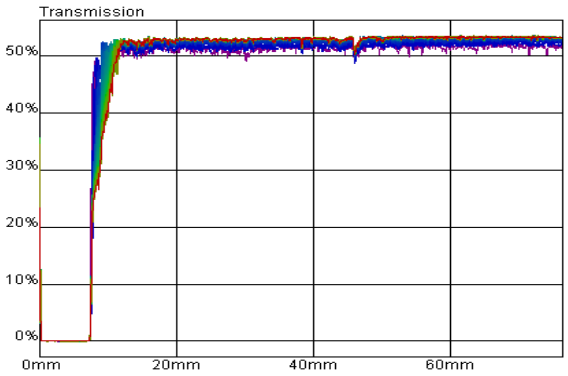

Figure 6b: Diffuse transmitance of Klebosol 30R50 3 % wt.

The stability of two Klebosol 30R50 suspensions having different solid contents was measured analyzing the transmitted and backscattered light fluxes by the dispersions. *Figures 6a* and *6b* report the transmission profiles versus the cell height of the two suspensions measured each 40 min during approximately 5 days and a half. Those profiles are regular on the whole cell height and remain invariant during the measure. Therefore, the silica suspension remains stable and homogeneous in this range of concentration. Thus, the homogeneity of the suspension is not affected by major destabilization phenomena such as particle migration (creaming, sedimentation), particle size variation or aggregation (coalescence, flocculation).

3.1.2 Particle sizing

Photons correlation spectroscopy

For very diluted suspension (wt.<1%), the mean size measured by photon correlation spectroscopy with the Zetasizer NanoS is about d=85.3 nm and is almost constant for the different concentrations (*Figure 7*) (reproducibility ~1%). This is in good agreement with the

observations made using scanning electronic microscopy. There is an almost linear decrease of the mean size measured when the mass concentration is higher than 1wt %. Two phenomena could explain this trend : the multiple scattering of the wave due to the excessive concentration of particles and/or a modification of the structural factor due to the interaction between particles *(Xu, 2000)* **[4]**. Thus, 1 wt % appears to be the limit concentration to obtain a correct analysis with this apparatus concerning Klebosol 30R50.
Figure 8 shows the particle size distributions measured for the concentration lower than 1% wt. It represents the size distributions calculated by the software with the partial list square method.

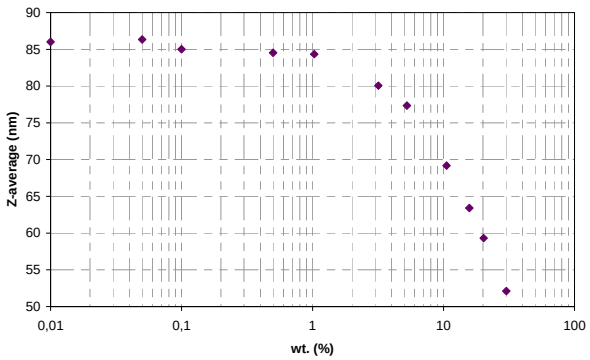

Figure 7: Mean diameter of the suspending particles of the Klebosol 30R50 versus concentration

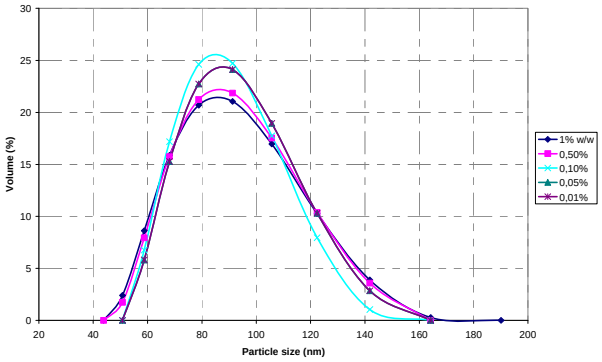

Figure 8: Particle size distributions of different Klebosol 30R50 suspensions measured with the Zêtasizer NanoS

Acoustic Spectroscopy
The Ultrasizer measures the attenuation of the ultrasonic wave through the suspension for different frequencies. However, it is more pertinent to consider the excess of attenuation due only to the silica particles in the medium and not to the intrinsic attenuation of each phase. The excess of attenuation, α_e, is:

$$\alpha_e = \alpha_t - c\alpha_{pd} - (1-c)\alpha_{pc} \qquad (2)$$

were α_t is the total attenuation, α_{pd} the attenuation of the dispersed phase, α_{pc} the attenuation of the continuous phase and c the volume concentration of the dispersed phase.
The equation of the excess of attenuation function versus the frequency, f, is determined from the attenuation spectrum of water and doing the hypothesis that the attenuation of the solid phase is negligible compared with the attenuation of the liquid phase:

$$\alpha_e(f) = \alpha_t - (1-c)(0{,}0047 f^2 - 0{,}0083 f) \qquad (3)$$

On *Figure 9*, it can be seen that for different concentrations of Klebosol 30R50, the attenuation spectra are parallel (reproducibility ~ 1.5%). The trend of the curves is characteristic of the visco-inertial behaviour of the suspensions.

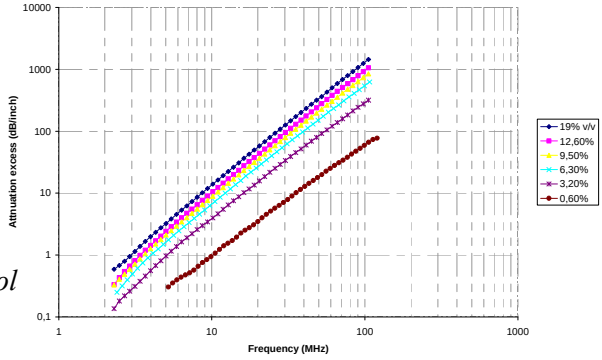

Figure 9: Excess attenuation spectra of Klebosol 30R50 versus frequency for different concentrations

In theory, the attenuation is proportional to the concentration of the suspended particles and moreover, when the visco-inertial effects are predominant, the attenuation is also proportional

to the wave frequency. Then, normalizing the spectra by the frequency and the concentration, the curves would be superimposed. But the normalized spectra (*Figure 10*) do not coincide (the distance between two curves goes from 3 to 20 %). The trend of these curves highlights the existence of the multiple scattering of the acoustic wave in the suspension that modifies the behaviour of the wave. Multiple scattering is increased at higher concentrations. That is why for higher concentrations the curves are almost linear while for the more diluted suspensions, the curves are more curved.
To take into account the multiple scattering of the wave through the suspension, a correction factor was determined in such a way the curves be superimposed. Then, the modified data were used to determine the particle size distributions corresponding to each spectrum. The results are reported in *Figure 11*. It can be seen that the distributions obtained are in good agreement with the results gave by the microscopy and the photons correlation spectroscopy.

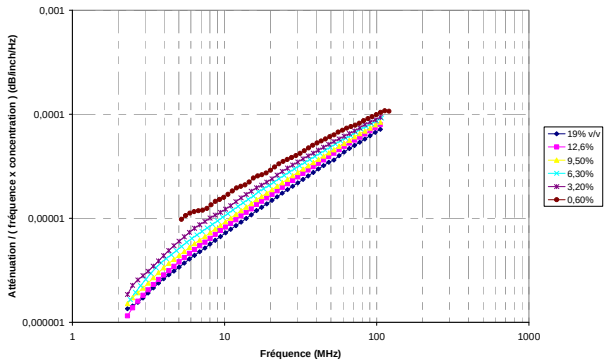

Figure 10: Excess attenuation spectra of Klebosol 30R50 normalized by the frequency and the volume concentration for different concentrations

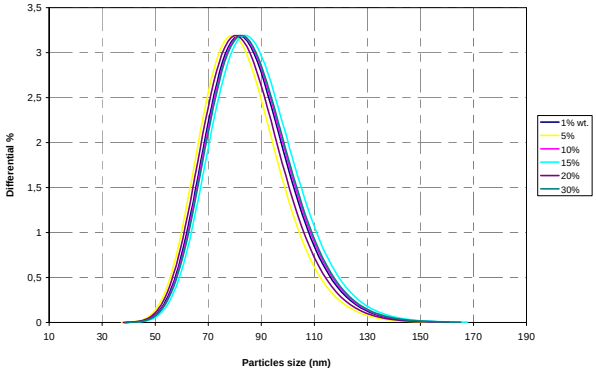

Figure 11: Particles size distributions of different Klebosol 30R50 suspensions measured with the Ultrasizer

3.2 Aggregation kinetics

The silica aggregation process was analyzed for given operational parameters (electrolyte concentration, silica concentration, temperature and stirring speed).
The Ultrasizer is used to quantify the change in size of the suspending particles as a function of time. *Figure 12* presents the evolution of the attenuation spectra recorded each 30 min during 8 hours during the aggregation of Klebosol 30R50 colloidal silica 1% wt. The other parameters are the same as in section 2. The spectra shown on *Figure 13* were obtained normalizing the previous ones by the frequency and the volume concentration ($\Phi = 0.63\%$)

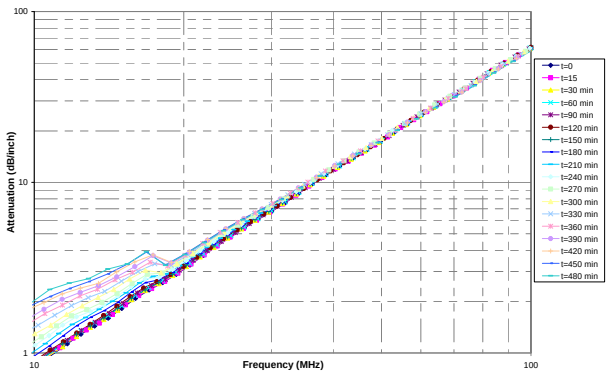

Figure 12: Attenuation spectra of Klebosol 30R50 during the aggregation process

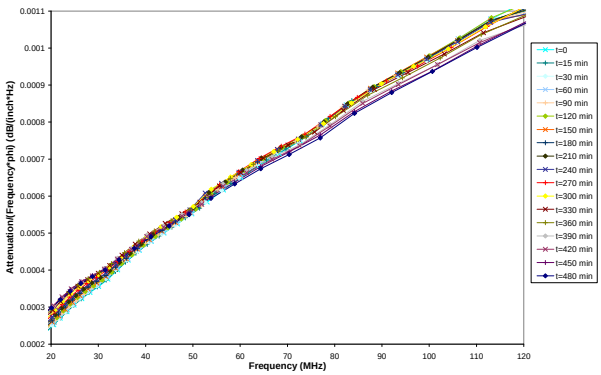

Figure 13: Attenuation spectra during the aggregation process normalized by the frequency and the volume concentration

For times between 0 and 150 min, the spectra are quite similar, indicating that the particle dispersion is not undergoing important destabilization by aggregation. At further times, distinct changes in the spectra are observed: there is an increase in attenuation at low frequencies and a decrease at high frequencies (the gradient of the curves decreases). It can also be concluded that the aggregation process is almost completed within 8 hours (480 min) because the spectra are not still evolving.

Taking into account the multiple scattering of the ultrasonic wave through the suspension, the particle size distributions of the suspension during the destabilization is shown in *Figure 14a.* The aggregation of particles is illustrated by the shift of the distribution towards the largest sizes. At the beginning ($t = 0^+$), a few minutes after the addition of the silica suspension in the sodium chloride solution, the monomodal log-normal curve of the particle size distribution has a mean size of 80 nm. This is in very good agreement with the results obtained for the characterization of the initial suspension. Until t = 240 min, the mean size does not change a lot (it increases from 80 nm to 100 nm) but the geometric deviation increases, as shown on *Figure 14b* where it can be seen that the width of the distribution is increasing. An important change in size as aggregation proceeds is seen once the process time exceeded 270 min: the distribution becomes bimodal. There are two populations: one of about 90 nm (primary particles) which becomes narrower (the particles of this size are less and less numerous) and another one of about 500-700 nm which becomes larger (the aggregates of this size are more and more numerous) at the same time. Later, for t > 360 min, the particle population seems to have three modes: the later two and another one of about 10 µm but the Ultrasizer software is not able to draw a trimodal distribution.

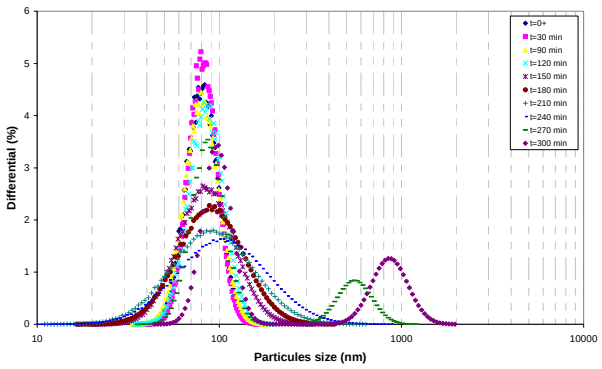

Figure 14a: Differential particle size distributions during the aggregation of Klebosol 30R50 (wt. 1%) by sodium chloride solution (0,8M) for 0+< t <300 min.

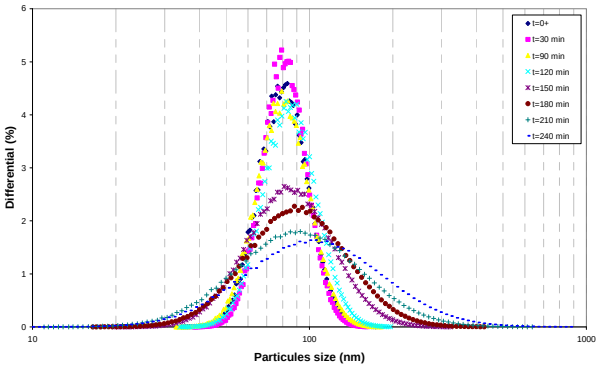

Figure 14b: Differential particle size distributions during the aggregation of Klebosol 30R50 (wt. 1%) by sodium chloride solution (0,8M) for 0+< t <240 min.

From these results, it can be supposed that the silica aggregation process is the succession of two aggregation stages probably corresponding to two distinct mechanisms: the perikinetic aggregation and the orthokinetic aggregation. First, the collisions between primary particles of 80 nm are brought about by a slow perikinetic mechanism for particle sizes smaller than 100nm leading to a slow increase of the width of the distribution from the primary particle size towards the larger ones. This stage is followed by a rapid orthokinetic mechanism for the coarse particles resulting in the apparition of large aggregates that form a second and probably a third population until about 10 µm.
The perikinetic aggregation is relatively slow (4 hours in the conditions of this experiment) because the motions of the small particles are brought about by diffusion and the repulsive colloidal interactions increase the stability of the suspension, which reduces the collision frequency. But during the orthokinetic aggregation (about 1h30), the collisions of coarse

aggregates result from the fluid motion and then, the collision frequency is higher because the particles overcome easily the potential barrier as a result of their relative motion *(Schaer et al., 2001)***[5].**

4. CONCLUSIONS

In this study, the aggregation of colloidal silica is observed in absence of any other phenomena such as nucleation or particle growth. Various techniques (multiple light scattering, photons correlation spectroscopy, acoustic spectroscopy) were used to characterize the properties of concentrated suspensions of nanoparticles.
Based on the acoustic spectrometry, the evolution of the attenuation spectra and of the calculated particle size distributions during a destabilization process showed the existence of two stages of aggregation having different kinetics: a slow perikinetic aggregation of small primary particles (until about 100 nm) and a fast orthokinetic aggregation of larger aggregates (until more than 10 μm).

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