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Aggregation of concentrated colloidal silica dispersions in a stirred tank

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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 physico-chemical interactions and hydrodynamic forces. This study is focused on the analysis of the behaviour of colloidal silica in dense suspensions subjected to hydrodynamic forces in conditions of destabilization.

A colloidal silica suspension of particles with an initial size of about 80 nm was used. The silica suspension concentration was varied between 3 and 20% of weight. The phenomenon of aggregation was observed in the absence of any other process such as precipitation and the destabilization of the colloidal suspensions was obtained by adding sodium chloride salt.

Various techniques of characterization of the particle size (acoustic spectroscopy, laser diffraction) and of the physico-chemical properties of the suspensions were used allowing defining the silica dispersion properties (suspension stability, particle size, pH).

The experiments were proceeded in a batch agitated vessel. They were made in order to observe the influence of different parameters (silica concentration, temperature, agitation speed) on the behaviour of the suspended particles.

The evolution of the particle size distributions versus time during the processes of aggregation was particularly followed on line by acoustic spectroscopy in dense conditions. Samples were also analyzed after an appropriate dilution by laser diffraction. The results show the different stages of the silica aggregation process whose kinetic rates depend either on physico-chemical or hydrodynamics parameters. They allow understanding the mechanisms of the aggregation process under flowing conditions.

KEYWORDS: Aggregation, colloidal silica, dense suspensions, laser diffraction, acoustic spectroscopy, characterization on-line.

I. INTRODUCTION

The success of nanoparticles is due to the industrial interest for many applications of this type of particles. But the usual properties of 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 stability of the suspensions depends on the forces which control the movement of the particles. It can be the result of the relative movement of the particles by diffusion (Brownian movement) or under the effects of an external force (shearing by agitation or flow) or be controlled by the gravitational and/or repulsive interparticle interactions (Israelachvili, 1992) [1] The objective of this study is to analyze the process of aggregation of concentrated suspensions of nanoparticles placed under conditions of flow (shearing, transport) identical to those met in real processes using suitable methods of characterization that allow a reliable analysis of the particle size distribution in dense medium.

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 both respect to solid content and hydrodynamic conditions.

II. EXPERIMENTAL

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 2.37 g/ml) and its specific surface around $50\text{m}^2/\text{g}$. Silica particles are spherical and have a diameter of about 80 nm (cf *Figure 1*). Deionised water (pH~6 and $\Lambda\sim 5\text{-}7\ \mu\text{S}$) was used to prepare the diluted suspensions.

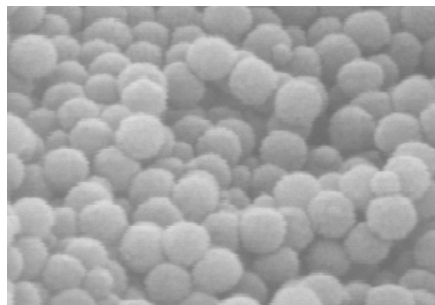


Figure 1: SEM photography of Klebosol 30R50 (x 62000)

The stability of the different silica suspensions was first measured. Using dynamic diffusion of light, and with measurements of pH and zeta potential, it was established that the silica suspensions remain stable and homogeneous in the range of concentration used ($3\% < \text{wt.} <$

20%). 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). (Tourbin et al., 2005) [2]

For this study, the size of the suspended particles was measured by two different ways: laser diffraction and acoustic spectroscopy.

Laser diffraction is a well-known technique that will not be described here. A Mastersizer 2000 (Malvern Instruments) was used to analyze the diluted samples.

Acoustic spectroscopy is a much less known technique. 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 had access to the commercial acoustic spectrometer Ultrasizer (Malvern Instruments). 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 (particle 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) [3] and Allegra and Hawley (1972) [4], 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 and Allegra and Hawley 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.

The size of the particles suspended in the initial suspension was verified before beginning the aggregation process. By laser diffraction, the mean size is about 80 nm considering a number distribution which is coherent with SEM observations, and about 112 nm for a volume distribution. The size measured by acoustic spectroscopy in terms of volume distribution give results in a good agreement as it is shown in *Figure 2*. Remember that the analysis performed using the Ultrasizer are in dense conditions whereas they are done in very dilute conditions using Mastersizer 2000.

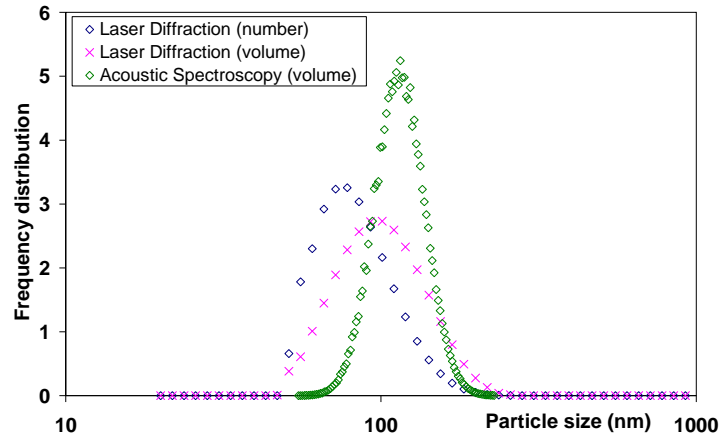


Figure 2: Comparison of Volume and Number frequency distribution measured by laser diffraction and acoustic spectroscopy. Suspension of a 10 % wt. suspension

Aggregation experiments were carried out in a standard water jacketed batch agitated vessel of a capacity of 1L. The suspension is stirred with a A310 axial flow impeller (Lightnin). The experimental set-up also includes a thermostatic bath.

600 mL of a 2 M sodium chloride solution was firstly poured into the tank and stirred in such a way the final concentration of salt is 0.8 M. When the desired operating temperature was reached, 900 mL of a suspension of colloidal silica at a chosen concentration was added as instantaneously as possible to obtain the desired solid concentration.

The suspension was continuously recycled from the stirred batch reactor through the flow cell of the acoustic spectrometer with a peristaltic pump (Masterflex) that allows on-line size analysis. However, the effect of the pump on the aggregates needed to be considered. The main criterion for determining the best pump and flowrate was minimum shear on the aggregates. As a result, a peristaltic pump was chosen in preference to other types of pumps. Moreover, the pump was placed downstream of the Ultrasizer, allowing the aggregates to be sampled before passing through the pump. A suitable pump flowrate that would provide minimum shear to the aggregates was selected.

The attenuation spectrum versus frequency was measured after different periods of time.

Then the evolution of the particle size distributions versus time during the processes of aggregation was then followed on-line by acoustic spectroscopy in dense conditions. Samples were also analyzed after an appropriate dilution by laser diffraction in order to compare the size distributions in dense and diluted conditions.

III. RESULTS AND DISCUSSION

The silica aggregation process was analyzed for given operational parameters: electrolyte concentration, silica concentration, temperature and stirring speed.

The different experiments that were carried out are summarized in *Table 1*.

Table 1: Parameters of the experiments of destabilization of the silica suspensions by sodium chloride

Experiment	[SiO ₂] (% wt.)	[NaCl] (mol.L ⁻¹)	Temperature (°C)	Stirring speed
1	3	0.8	25	450
2	6	0.8	25	450
3	10	0.8	25	450
4	20	0.8	25	450
5	20	0.8	12	450
6	20	0.8	65	450
7	20	0.8	25	1120
8	20	0.8	25	690

Analysis of the sample – Evolution of particle size distribution during the destabilization

The Ultrasizer is used to quantify the change in size of the suspending particles on-line of the process as a function of time. For example, the evolution of the attenuation spectra recorded each 30 min during 8 hours during the aggregation of Klebosol 30R50 colloidal silica at 6% wt is presented on *Figure 3*.

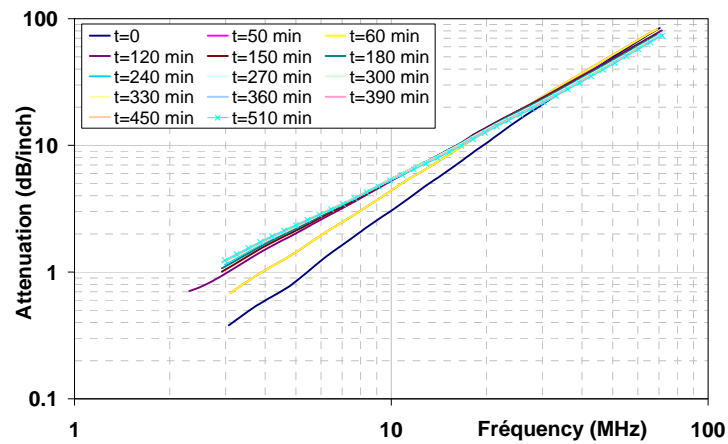


Figure 3: Attenuation spectra during the aggregation of a 6% wt. silica suspension (Exp 2).

For times between 0 and 60 min, the spectra are quite similar, indicating that the particle dispersion is not undergoing important destabilization by aggregation. At further times, a significant change in the spectra is observed: the gradient of the curves decreases. It can also be supposed that the aggregation process is almost completed within 8 hours because the spectra do not evolve anymore.

Taking into account the multiple scattering of the ultrasonic wave through the suspension, the particle size distributions of the suspension during the destabilization were calculated (Tourbin et al., 2005) [2]. The preliminary studies had shown that the results of the analysis of granulometry of aggregated suspension of Klebosol by acoustic spectroscopy and by laser diffraction are in a good agreement. For experiment n°1, the results are represented on *Figures 4 and 5*.

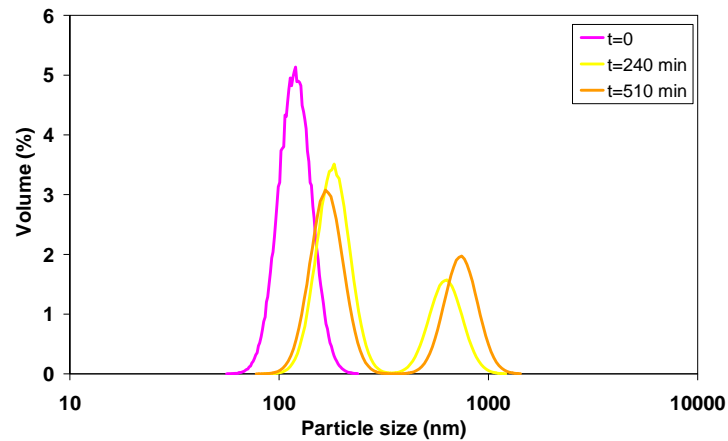


Figure 4: Particle size distribution measured by acoustic spectroscopy in dense conditions on-line of the aggregation process. $[\text{SiO}_2]=6\%$ wt./ $[\text{NaCl}]=0.8$ M/ $T=25^\circ\text{C}$ /stirring speed=450 rpm (Exp 2)

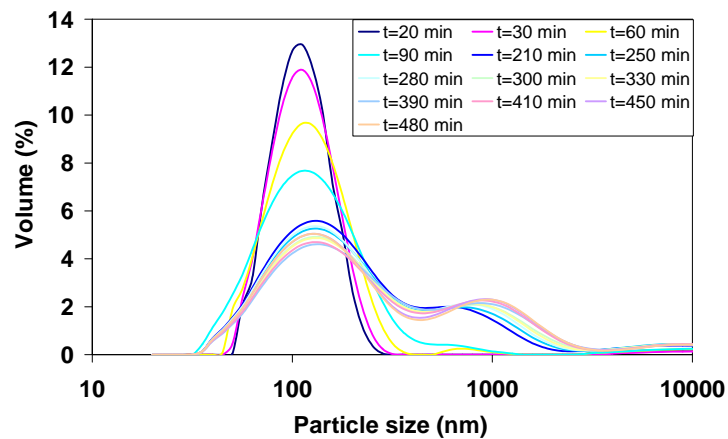


Figure 5: Particle size distribution measured by laser diffraction. Diluted suspensions of samples taken during the aggregation process. $[\text{SiO}_2]=6\%$ wt./ $[\text{NaCl}]=0.8$ M/ $T=25^\circ\text{C}$ /stirring speed=450 rpm (Exp 2)

The aggregation of particles is illustrated by the shift of the distribution towards the largest sizes. At the beginning ($t = 0^+$), the monomodal log-normal curve of the particle size distribution has a mean size of 112 nm. Until about $t = 135$ min, the mean size does not change a lot but the geometric deviation increases (the width of the distribution is increasing). An important change in size as aggregation proceeds is seen once the process time exceeded 150 min: the distribution becomes bimodal. There are two populations: one of about 120 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.

From these results, it can be supposed that the silica aggregation process is the succession of at least two aggregation stages probably corresponding to two distinct mechanisms. It corresponds to what some authors named the two stages of perikinetic aggregation: first, a slow one, and then a fast one. First, the collisions between primary particles of 80 nm are brought about by a slow perikinetic mechanism for particle sizes smaller than 100 nm 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 mechanism for the coarse particles resulting in the apparition of large aggregates that form a second population of about 1 μm .

This passage of a slow phase of aggregation to a fast one can be explained by the increase of the frequency of the collisions between particles when the aggregates start to grow (cf *Figure 6*)

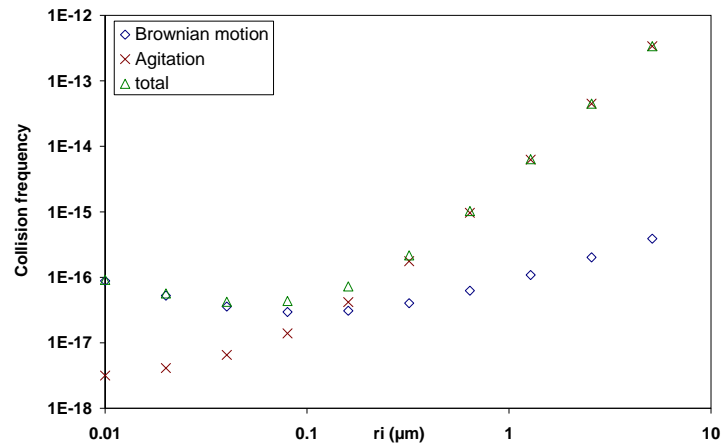


Figure 6: Collision frequency for collisions between a particle of a diameter of $r_j=100$ nm and another particle of diameter of $10 \text{ nm} < r_i < 10 \mu\text{m}$. $T=25^\circ\text{C}$ /stirring speed=450 rpm

The first stage is relatively slow because the motion of the small particles is brought about by diffusion (Brownian motion). Thus, when the suspension begins to be constituted by primary particles and aggregates, the frequency of collision increases and the aggregation becomes faster. Indeed, during the second stage, the collisions result from the fluid motion (principally by agitation) 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].

Effect of particle concentration on aggregation kinetics (Experiments 1, 2 and 4)

To compare the evolution of the particle size distribution according to the silica concentration, the results are shown in terms of the evolution of the modes of the distribution on *Figure 7* and in terms of the evolution of the ratio w_2/w_1 on *Figure 8* with

$$\frac{w_2}{w_1} = \frac{\text{volume percentage of the second mode (peak of aggregates)}}{\text{volume percentage of the first mode (peak of primary particles)}}$$

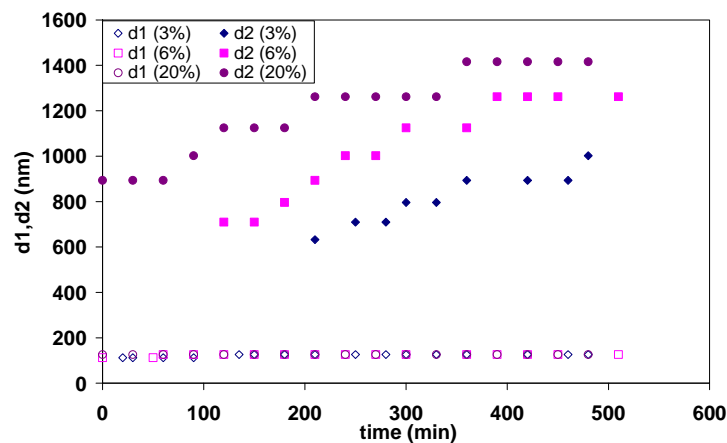


Figure 7: Comparison of the evolution of the modes (d_1 =peak of primary particles and d_2 =peak of aggregates) of the particle size distribution for the experiments n°1, 2 and 4.

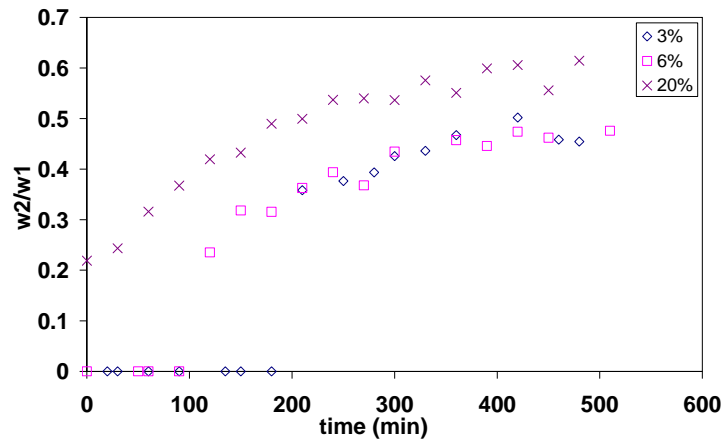


Figure 8: Comparison of the evolution of the ration w_2/w_1 of the particle size distribution for the experiments n°1, 2 and 4.

It can be observed that the silica concentration has an influence on the kinetics of aggregation of colloidal silica. Indeed, from the comparison of the results for the three experiments it results that the higher the silica concentration is, the faster the first phase of aggregation and the larger the aggregates final size is.

This result is not surprising considering the formalism introduced by Smoluchowski (1917) [6] :

$$\text{number of collisions} = \beta(i, j) n_i n_j$$

which expresses the number of collisions between two particles of sizes r_i and r_j as a function of $\beta(i, j)$ the kernel of agglomeration, n_i and n_j the concentrations of particles i and j .

Effect of temperature on aggregation kinetics (Experiments 4, 5, and 6)

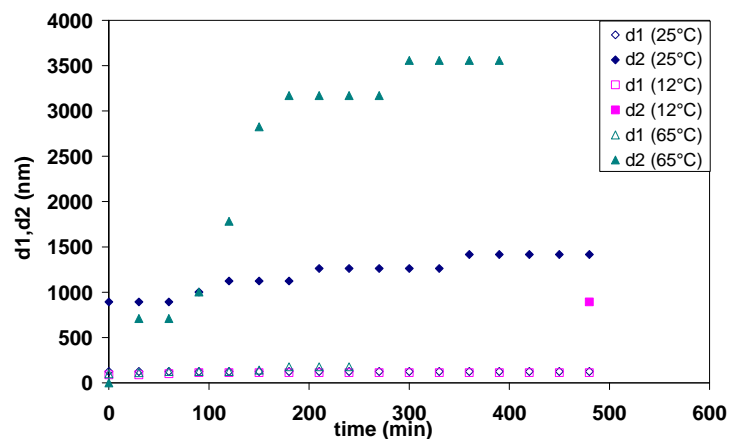


Figure 9: Comparison of the evolution of the modes of the particle size distribution for the experiments n°4, 5, and 6.

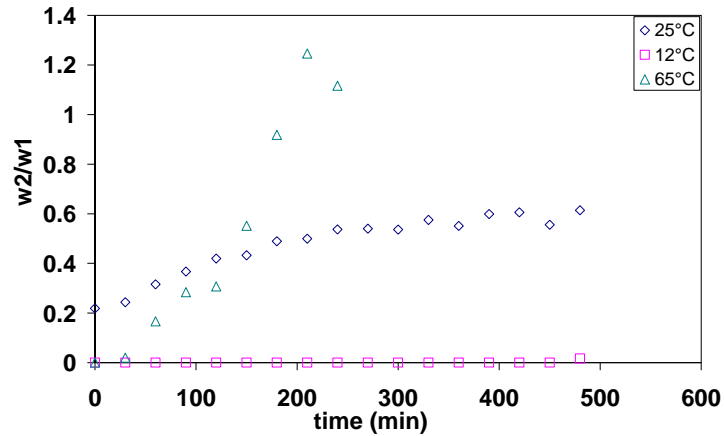


Figure 10: Comparison of the evolution of the ration w_2/w_1 of the particle size distribution for the experiments n°4, 5, and 6.

At $T=12^\circ\text{C}$, the aggregation of silica is relatively slow. Indeed, the distribution of particle size evolves and moves to the biggest size (d_{50} changes from 102 nm to 124 nm) but remains monomodal. At $T=25^\circ\text{C}$, the distribution quickly becomes bimodal and continues to evolve towards the biggest sizes. At $T=65^\circ\text{C}$, the aggregation is even faster. As previously, the distribution quickly becomes bimodal and continues to evolve towards the biggest size. Finally, the collisions between primary particles and aggregates become so important that after 240 min of aggregation, there is no more primary particle and the suspension contains only aggregates. (cf Figure 11)

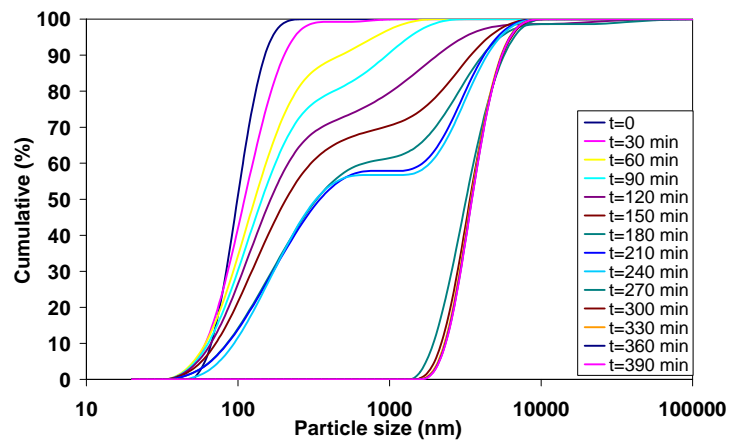


Figure 11: Cumulated particle size distribution measured by laser diffraction. $[\text{SiO}_2]=20\%$ wt./ $[\text{NaCl}]=0.8\text{ M}$ / $T=65^\circ\text{C}$ /stirring speed=450 rpm (Exp 6)

The temperature has also a very great influence on the kinetics of colloidal aggregation of silica. Indeed, those three experiments (exp 4, 5, and 6) show that the higher the temperature is, more the first phase of aggregation goes fast (the aggregates are formed faster) and more the aggregates final size is large.

Indeed, the temperature influences the diffusion of the particles, i.e. the first phase of aggregation where the collisions are a function of the Brownian motion of the particles which is characterized by the Stokes-Einstein equation

$$D = \frac{k_B T}{3\pi\eta d}$$

with k_B the Boltzmann constant, T the temperature, η the viscosity of the fluid et d the particles diameter.

The coefficient of Brownian diffusion is thus directly a function of the temperature which also affects the value of the suspension viscosity.

Effect of stirring speed on aggregation kinetics (Experiments 4, 7 and 8)

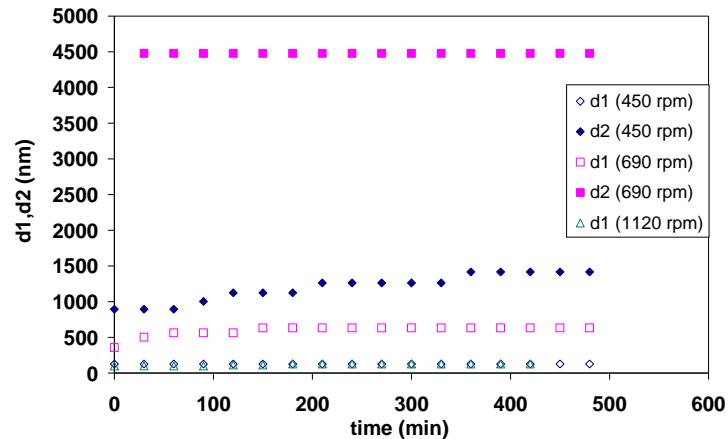


Figure 12: Comparison of the evolution of the modes of the particle size distribution for the experiments n°4, 7 and 8.

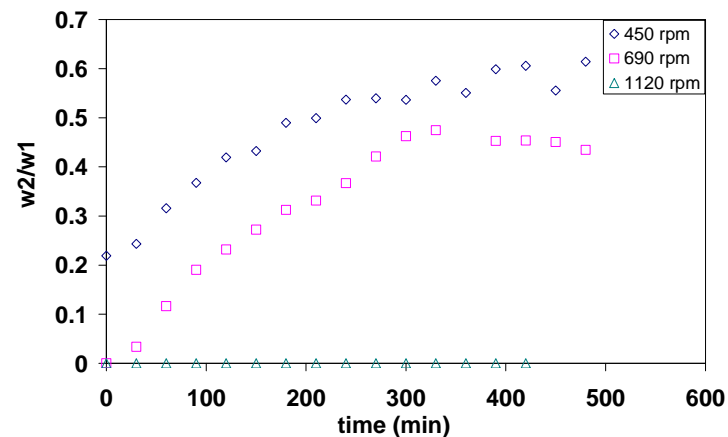


Figure 13: Comparison of the evolution of the ration w_2/w_1 of the particle size distribution for the experiments n°4, 7, and 8.

For a stirring speed of 450 rpm ($Re = 28673$), the particle size distribution quickly becomes bimodal and continues to evolve towards the biggest sizes. For a stirring speed of 690 rpm ($Re = 43965$), the maximum size is higher than previously, but at the final time, there are less aggregates and more primary particles. For a stirring speed of 1120 rpm ($Re = 71363$), the distribution remains monomodal during the process.

It can be supposed that the evolutions of the aggregates size and of the mass concentration are the consequences of two contradictory phenomena: the increase of the frequency of collision due to the increase of the agitation, that would explain the increase of the aggregates size from the experiment n°4 to the experiment n°7 ; and the decrease of the efficiency of collisions due to the increase of the agitation (van der Ven and Mason, 1977) [7] or the breakage of the aggregates as soon as they are formed, that would explain the decrease of the mass concentration of the peak of aggregates when the agitation increases.

IV. CONCLUSIONS

In this study, the aggregation of colloidal silica is observed in absence of any other phenomena such as nucleation or particle growth. Two techniques were used to characterize the properties of concentrated suspensions of nanoparticles on-line (acoustic spectroscopy) and off-line of the process (single light scattering).

The follow-up of the particle size distributions during the destabilization process showed the existence of at least two stages of aggregation having different kinetics: a slow perikinetic aggregation of small primary particles (until about 100 nm) and a faster perikinetic one of larger aggregates (until more than 10 μm).

The influence of various operational parameters is highlighted by those experiments. It was observed that an increase of one of the physicochemical parameters of the process, like the concentration of silica or the temperature, enhances the kinetics of the first stage aggregation of silica. On the contrary, the stirring speed, which is a hydrodynamic parameter, has no influence on the evolution of the particle size distribution during the first stage of the aggregation process, but influences the final size and the final number of particles.

V. ACKNOWLEDGEMENTS

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