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INFLUENCE OF NON- SETTING CONDITIONS ON AGGREGATION OF DILUTED SOLIDS IN LIQUID PHASE

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Abstract. We present here the main results of an experimental study of aggregation which was performed on two silica granular samples: one is naturally hydrophilic; the other has been made hydrophobic by superficial grafting of hydrophobic groups. Aggregation is studied in water-ethanol mixtures of variable compositions and followed by in situ turbidimetry at different stirring rates. The aggregation behaviours of the two samples are quite different. Aggregates of hydrophilic particles are small and fragile whereas aggregates of hydrophobic particles are large and particularly solid. Interpretation of these differences is presented; it is based on several elements: modelling of hydrophobic interaction and of aggregate morphology, modelling of the aggregate optical properties and determination of the aggregation and fragmentation rates. Essential modification introduced by non-setting consists of the formation of gas bridges around contact points between particles in aggregates.

INTRODUCTION

Aggregation of hydrophilic particles in stirred liquid media can be considered as a relatively well understood process in spite of the variety and complexity of its aspects: physico-chemical, hydrodynamic, morphological [1]; on the contrary, little is known about aggregation of hydrophobic particles in aqueous media and more generally about the aggregate structure and properties. This case is met in several industrial situations: suspension, sedimentation and flotation of hydrophobic powders in aqueous media of course, however also when solid particles are not wetted by liquid media, for instance, alumina inclusions in liquid steel baths [2].

A large number of experimental works indeed have definitely proved the existence of very strong long range attractive forces between hydrophobic surfaces in water [3-4]. This hydrophobic interaction was quantified from direct force measurements and proved to be, in most cases, much larger than the van der Waals forces. Several of the experimental works mention the existence of gas bridges between particles in close interaction [4-6]. In a recent theoretical work [7], we show that hydrophobic particles are likely covered by a gas layer which invades their superficial porosity; we prove too that this gas layer may play an essential part both in the aggregate formation and fragmentation.

To our knowledge, no systematic study of hydrophobic aggregation exists. The aim of this paper is to present a compared experimental study of aggregation of two silica samples coming from the same lot: one is naturally hydrophilic; the other has been made hydrophobic by surface chemical processing. The results will be then interpreted in reference with classical aggregation models [1,8-9] and with new theoretical considerations [7].

EXPERIMENTAL PART

1. Materials and methods

Original solid samples consist of monodisperse silica spheres (0.5 μm and 1.5 μm in diameter, *Geltech Inc* products). They are poorly soluble in water and can be made hydrophobic by grafting of carbon chains. Grafting procedure involves an hydroxylation process which produces highly reactive surface silanol (-SiOH) groups, then a setting step with a N,N-Dimethyloctadecylaminosilane solution; this results in a surface silanisation reaction, i.e. the grafting of a carbon chain via a strong Si-O-Si bond. Both silica particles, processed or unprocessed, have a zero point charge pH of 3.2.

Aggregation is studied in water-ethanol solutions of variable composition because hydrophobicity (or equivalently non-wetting) varies with the ethanol ratio. Wetting of a solid is characterized by the contact angle of a liquid drop put on its surface. Perfect wetting corresponds to a zero angle whereas non-wetting begins for angles higher than 90°. For our hydrophobized silica, contact angle value is given in Table 1. Starting from 125° in pure water, it decreases with ethanol addition; non-wetting conditions vanish beyond 15% volume ratio in ethanol.

Table 1. Contact angle versus ethanol volume content in ethanol-water mixture

EtOH (%)	0	3.45	5	10	15	25
Contact angle (°)	125	118	116	105	90	67

Aggregation is studied in a double jacketed 4-baffled 1.45 L pyrex vessel. This reactor is provided with a watertight cover so that it can be completely filled with liquid, avoiding in this the presence of a free interface which could entrap hydrophobic particles. Agitation is ensured by a four bladed 45° Teflon impeller. Temperature is kept constant at 25.00 °C. The reactor is fitted with an optical system to measure in situ the suspension turbidity in the wavelength range 350 nm-800 nm. Details can be found in [10].

Each aggregation experiment consists of the following steps:

- i) preliminary dispersion by ultrasounds of 0.246 g of solid sample in an ethanol-rich small volume;
- ii) filling-up of the reactor with the ethanol-water solution;
- iii) injection of the silica suspension and destabilization by nitric acid addition (pH = 2.4). This pH value is very close to the zero point charge and allows aggregation to take place at significant rate;
- iv) after this injection, aggregation starts and can be followed by continuous in situ turbidity measurements [8-9].

2. Principle of exploitation of the experimental data

Light scattering by solid particles (here aggregates) in suspension results in extinction of an incident light beam of wavelength λ_0 , the intensity $I_0(\lambda_0)$ of which is reduced down to value $I(\lambda_0)$ after crossing of an optical path of length L_{opt} . Turbidity τ , which expresses this extinction phenomenon, is defined by:

$$\tau(\lambda_0) = \frac{1}{L_{opt}} \ln \frac{I_0(\lambda_0)}{I(\lambda_0)} \quad (1)$$

τ depends on mean diameter d_p , particle density function f according to the integral:

$$\tau(\lambda_0) = \int_0^\infty C_{ext} d_p f(d_p) dd_p \quad (2)$$

Particle extinction cross-section C_{ext} is derived from the Mie theory [11]; its calculation is relatively easy for spherical, compact, or large particles, however much more delicate for small, non compact aggregates [12].

With our experimental system, turbidity variation with time is available over a whole aggregation experiment for several wavelengths. Moreover from dynamic models of the process and morphological and physical models of the aggregates, density function $f(d_p)$, thus turbidity can be calculated at any time [8-9]. From comparison between experimental and predicted values, the most relevant models can be selected and their unknown parameters determined. From a more qualitative point of view, turbidity $\tau(t)$ plot shape can be analysed from its main characteristics: initial slope, which is globally proportional to the aggregation rate, final plateau height, which is significant of dynamic equilibrium between aggregation and fragmentation (see Fig. 1 for instance).

3. Experimental results

3.1. Stirring rate influence on aggregation of hydrophilic silica

Stirring rate has a multiple influence on aggregation: collision frequency increase, capture efficiency decrease, aggregate fragmentation increase.

Figure 1 shows aggregation of $0.5 \mu\text{m}$ non processed (hydrophilic) silica at different stirring rate values. Turbidity increases with time. For $1.5 \mu\text{m}$ particles, however, turbidity decreases [10]. This behaviour difference is due to light scattering properties which vary a lot in the investigated size range. From a more quantitative point of view, aggregation is relatively slow, particularly at low stirring rate (low initial slope values) and produces small aggregates, particularly at high stirring rate (low variation of turbidity between initial value and final plateau). These elements will be integrated later on in a global model.

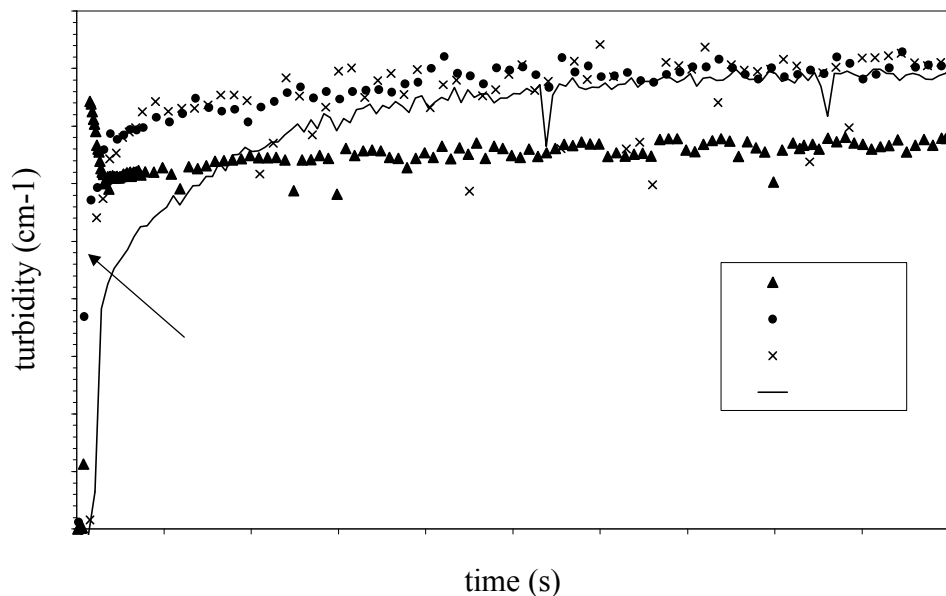


Figure 1. Influence of stirring rate on $0.5 \mu\text{m}$ hydrophilic silica aggregation

3.2. Stirring rate influence on aggregation of hydrophobic silica

Figure 2 shows aggregation of $0.5 \mu\text{m}$ hydrophobic silica at different stirring rates. Turbidity decreases contrary to what has been observed previously. This change points to a modification of the aggregate scattering properties probably due to the presence of gas bridges. The same behaviour is observed for $1.5 \mu\text{m}$ particles. The stirring rate effects are globally the same as for hydrophilic silica, however, aggregation is much more rapid and large agglomerates are formed as indicated by the low final level of turbidity.

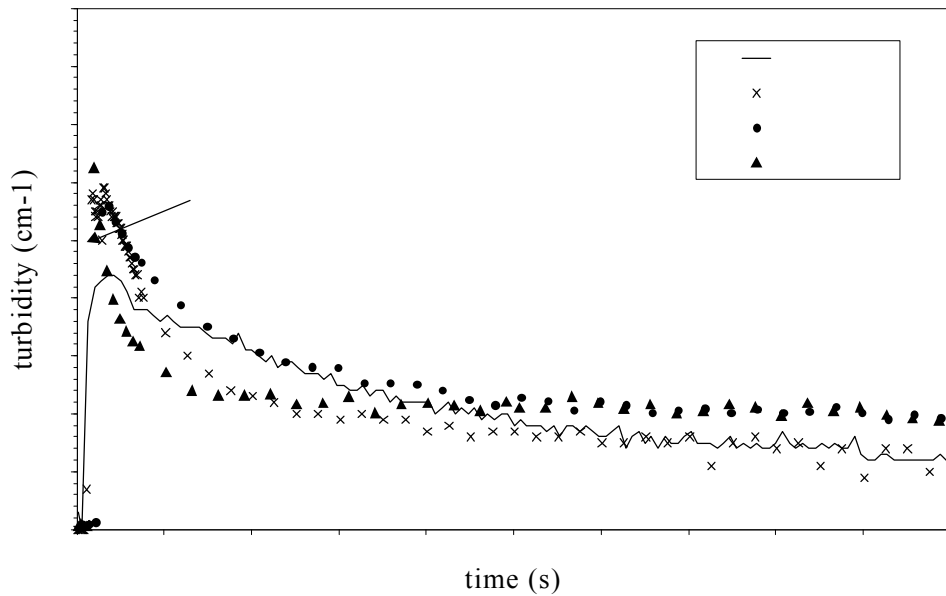


Figure 2. Influence of stirring rate on 0.5 μm hydrophobic silica aggregation

3.3. Influence of the liquid phase composition

Analysis of the turbidity curves in water-ethanol solutions is delicate, because of the turbidity value offset due to the change in the medium refractive index. In the case of hydrophilic silica, they have the same aspect whatever the composition. In the case of hydrophobic silica, effect of ethanol content is complex (Figure 3). However, after correction, it seems that in all cases, presence of ethanol decreases the aggregation rate.

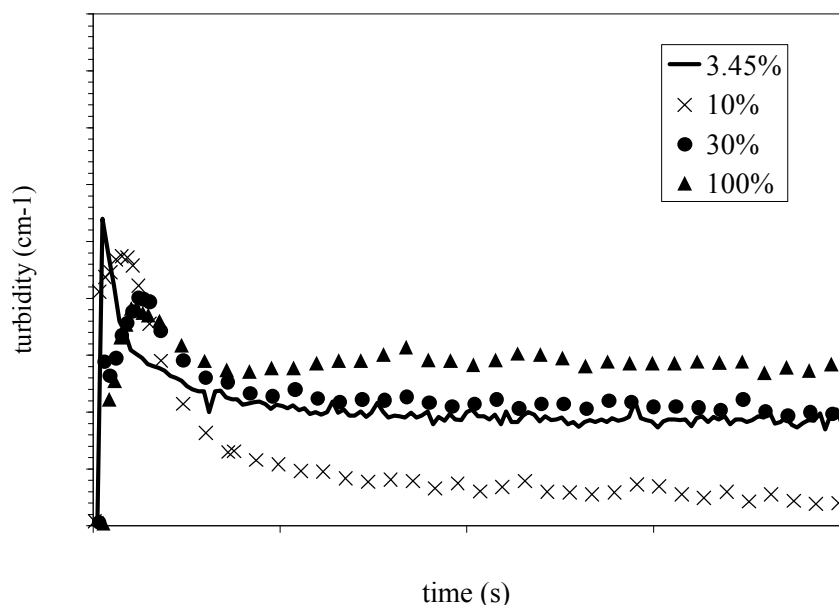


Figure 3. Effect of ethanol volume content on hydrophobic silica aggregate

3.4. Aggregate size and morphology

Photographs of aggregates withdrawn from the medium at late stages of aggregation of 1.5 μm particles confirm the presence of small relatively ramified aggregates in the case of hydrophilic silica and of enormous aggregates in the case of hydrophobic silica (Figure 4).

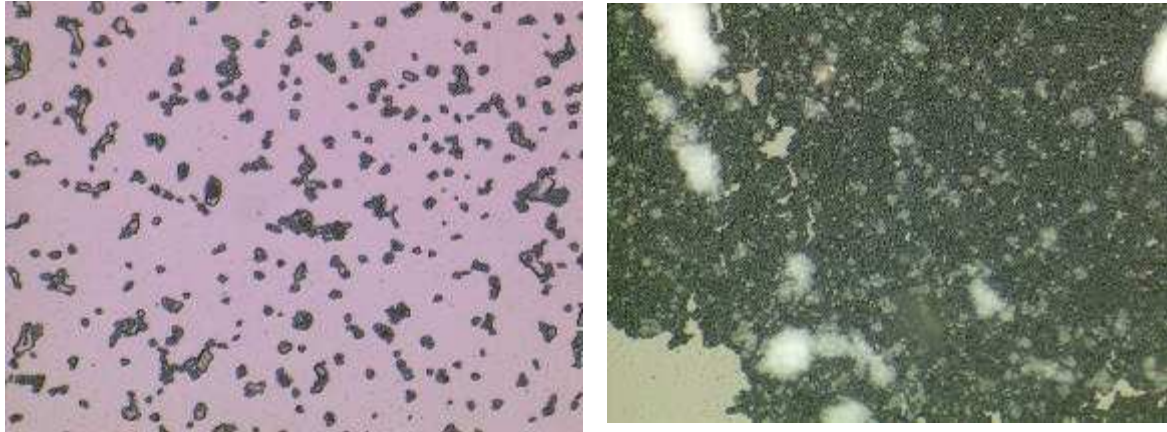


Figure 4. Photographs of 1.5 μm silica particle aggregates (left side: hydrophilic particles; right: hydrophobic particles)

Results interpretation requires on one hand model of hydrophilic silica aggregation, on the other hand understanding of the specific elements brought by hydrophoby.

THEORY

1. Basic elements of modeling

From a general point of view, aggregation of hydrophilic silica is expected to follow the classical theory of turbulent aggregation [13]. However, some attention should be given to the small size and morphology of the aggregates which are indeed proved to be ramified and consist in a few tens of particles at the maximum [10; 12]. Classical models, either hydrodynamic or optical, however were conceived for large aggregates and based on quasi-fractal morphology. For instance, the concept of fractal dimension cannot be rigorously kept without modification for the smallest aggregates. However, this convenient tool for describing and modelling ramified objects can be generalised for all the aggregate sizes. One of us [12] introduced indeed the notion of *local fractal dimension* to represent the aggregates morphology down to a few particles. Thanks to this generalization, procedures established for large objects can be applied over the whole range of aggregate size. Moreover, Gruy [12] developed original calculation of the aggregate extinction cross-section C_{ext} . In these conditions, results concerning hydrophilic silica aggregation can be interpreted using the modified models. Fractal dimension of the aggregates ranges between 2.4 and 2.5 and may vary with their size.

In [7], we proved that when solid particles are immersed in a non-wetting liquid, gas or vapour spontaneously fills the pores or the surface anfractuosités (Figure 5). This results in a partial or total coverage of the solid surface with a gas layer. Consequences are multiple:

- i) when two particles get in contact, their mutual gas pockets can merge, creating a gas bridge which ensures strong cohesion between them (Figure 6);
- ii) prior to the contact, presence of bubbles at the particle surface may give rise to an additional static attractive force; this force, which is called *Bjerknes force* [14] has a hydrodynamic origin and is due to coupled thermal vibrations of the bubbles. Ruckenstein [14] proposes a calculation procedure based on dimensional and experimental considerations, however does not obtain quantitative determinations. We recently re-visited this problem [7], using another approach and correcting some errors. We obtained the order of magnitude of the Bjerknes force and concluded that in several cases they were not necessarily higher than the van der Waals force as Ruckenstein claimed.

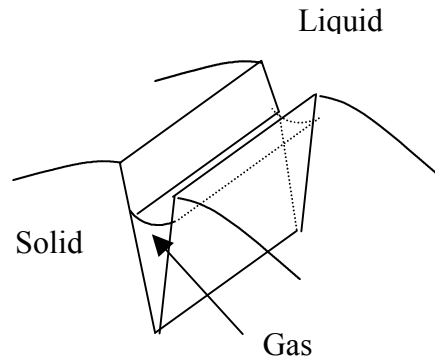


Figure 5. Gas cavity in a crevice in a pore

iii) existence of a gas-liquid interface (instead of a solid-liquid interface) modifies too the boundary conditions, thus the particle motion in the liquid phase (violation of the no-slip condition); in particular, when two particles or aggregates are in close approach, the liquid layer between them should be evacuated. This may result in a repulsive force which reduces the collision rate by a *capture efficiency coefficient* lower than one. In case of non-wetting, we re-calculated the capture efficiency coefficient [7] and proved it was slightly higher than in case of wetting, whatever the interaction force (van der Waals or Ruckenstein-like) thus aggregation rate is increased.

iv) the main consequence of non-wetting, however, concerns the fragmentation of the aggregates; hydrophilic particle aggregates, indeed, have a weak cohesion, because of the low value of the van der Waals forces which are responsible for their cohesion; in case of hydrophobic particles, on the contrary, gas bridges between particles ensure very strong cohesion forces and considerably reduce the fragmentation possibilities.

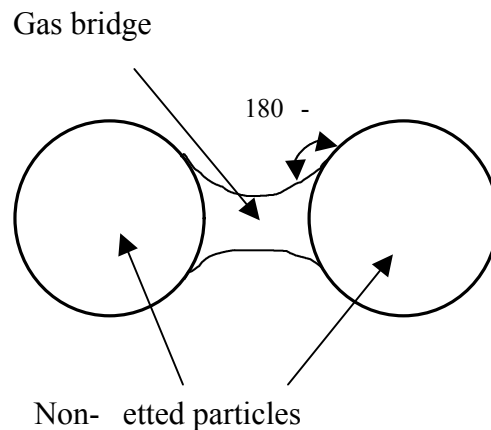


Figure 6. Gas bridge between solid particles in non-wetting liquid

2. Next theoretical aspects

In the text above, we often refer to the presence of gaseous bridges between hydrophobic particles and we attribute to this particularity most of the new behaviours observed in hydrophobic aggregation. This deserves to be verified because observation of the samples is difficult and not conclusive. One of our subjects of interest concerns the new optical properties of the aggregates and their consequences on turbidity.

2.1. Light scattering by hydrophobic silica aggregates

Refractive indices of silica, water and gases are respectively 1.44, 1.34 and 1.0. Scattering properties of particles in a medium mainly depends on the index contrast between the media

and on the particle size. Presence of gas (air or vapour) in an aggregate may considerably change this contrast and be responsible for the behaviour modification e noted in Figures 1 and 2. Calculation of the scattering properties of a silica-water-air aggregate requires assumptions on the three phase location. The two cases which have been envisaged - homogeneous density in the porous particle or surrounding thin layer [10]- give us similar results. Particle extinction section is reduced as expected and gas proportion is found to be equal up to 0.3, which could correspond to a uniform external layer of 0.05 μm in thickness.

2.2. Simulation of turbidity time evolution

Basic simulation equation is the well-known partial derivative equation of Smoluchowski [13]. In case of hydrophilic aggregation, fragmentation is envisaged. Agreement with experimental turbidity plots is good for fractal dimension of 2.4 (Figure 7). At 200 rpm, the predicted maximum particle number in the aggregates is 68, whereas experiment gives 64 [15]. In case of hydrophobic aggregation, fragmentation is no considered. Fractal dimension is found to be higher (2.7). This is consistent with the more compact observed aggregates. Aggregates can contain several hundreds of particles. Agreement between experimental and theoretical plots is still good as shown in Figure 8 for stirring rate of 200 rpm.

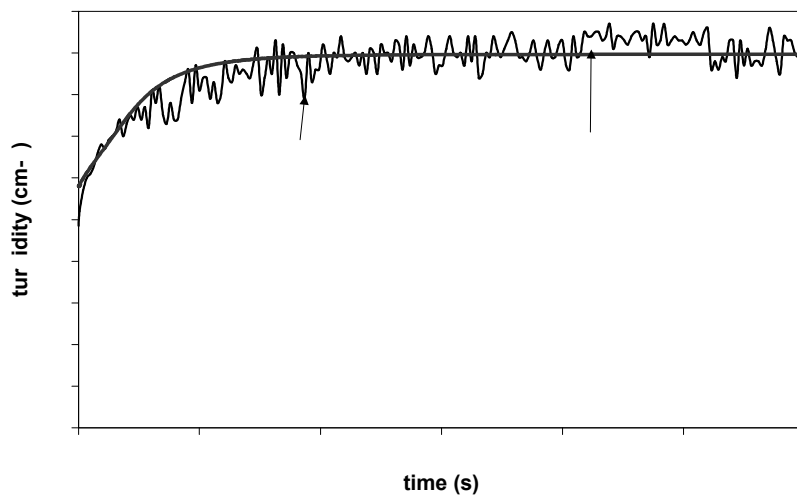


Figure 7. Turbidity variation with time (experimental and simulated) during aggregation of hydrophilic $0.5 \mu\text{m}$ silica particles.

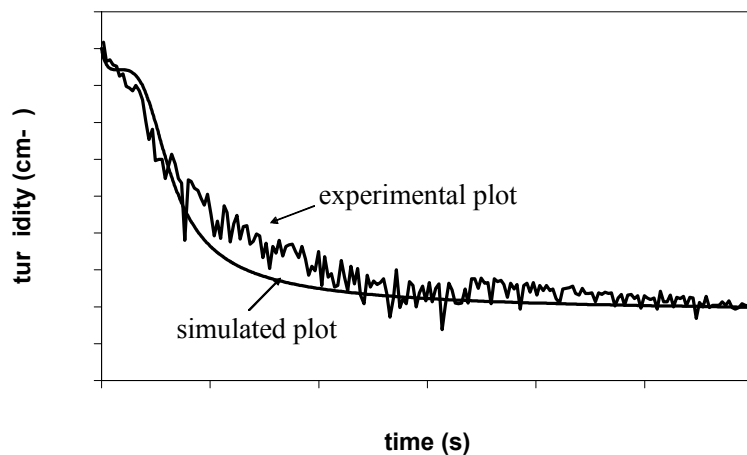


Figure 8. Turbidity variation with time (experimental and simulated) during aggregation of hydrophobic $0.5 \mu\text{m}$ silica particles.

CONCLUSION

In this work, we emphasize the main consequences of non-wetting on solid particle aggregation in stirred liquid media. In case of non-wetting, very large and resistant aggregates are formed. The presence of gas bridges between particles is at the origin of the cohesion of the hydrophobic aggregates. Influence of non-wetting exists on other aggregation characteristics (interaction forces, capture efficiency), however is less significant. Presence of gas in the aggregates also affects their optical properties; this is an important detail, knowing that optical methods are the most widespread particle sizing techniques.

The application field of this study is not restricted to the only systems of hydrophobic solid particles in water, whatever its importance, relatively, for instance to transport, stirring, sedimentation, flotation. Recently we were faced to the problem of aggregation of alumina inclusions in molten steel baths [2]. Alumina is not wetted by steel and observations prove that very large ramified clusters can be formed and heavily affect the mechanical properties of the metal if they are not eliminated at early stages of the process. Present models as well as analogy with hydrophobic aggregation can provide with information about the conditions of formation of these clusters and on their location in the industrial facilities, so that elimination procedures can be operated with more efficiency.

REFERENCES

- [1] De Boer G.B.J., Hoedemakers G.F.M., Thoenes D., Chem. Eng. Sci. 67 (1992), 301.
- [2] Cournil M., Gruy F., Gardin P., Saint-Raymond H., Phys. Stat. Sol.(A), 189 (2002), 159-68.
- [3] Yaminsky S., Yushchenko S., Amelina E.A., E.D. Shchukin E.D., J. Colloid and Interf. Sci. 96 (1983), 301.
- [4] Parker, J.L., Claesson P.M., Attard P., J. Phys. Chem., 98 (1994), 8468.
- [5] Yushchenko, S., Yaminsky S., Shchukin E.D., J. Colloid and Interf. Sci. 96 (1983), 307.
- [6] Yakubov, G.E., Butt H.J., Vinogradova, O.L., J. Phys. Chem., 104 (2000), 3407.
- [7] Cournil, M., Gruy F., Cugniet P. Gardin P., Saint-Raymond H., J. Colloid and Interf. Sci., (2003) submitted.
- [8] Saint-Raymond, H., Gruy F., Cournil M., J. Colloid and Interf. Sci., 202 (1998), 238.
- [9] Tontrup C., Gruy F., Cournil M., J. Coll. Inter. Sci., 229 (2000), 511-525.
- [10] Cugniet P., PhD Dissertation, (2003), Etude de l'agrégation de particules solides en milieu non mouillant. Interprétation et modélisation, Ecole des Mines de Saint-Etienne (France).
- [11] van de Hulst H.C., Light Scattering by Small Particles (1957) Wiley, New York.
- [12] Gruy, F., J. Colloid and Interf. Sci., 237 (2001), 28.
- [13] Kusters, K.A., Bijers J.G., Thoenes, D., Chem. Eng. Sci. 52 (1997), 107.
- [14] Ruckenstein, E, J. Colloid Interface Sci., 188 (1997), 218-223.
- [15] Cournil M., Gruy F., Cugniet, P., Congrès Français de Génie des Procédés (2003), Saint-Nazaire, submitted.