The On-Line Optical Investigation of Concentrated Dispersions in Precipitation and Grinding Processes

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Abstract

The present work reports new progress in the development of a multiple light scattering technique for investigating calcium carbonate precipitation and grinding processes. The optical analyser Turbiscan was used for the on-line analysis of light transmission and backscattering from a concentrated calcium carbonate dispersion. From a multiple scattering model based on the photon diffusion approximation, the size and mean refractive index of crystals or nuclei agglomerates are derived from measurements of the backscattered light flux. The time evolution of the particle mean diameter was determined with the on-line Turbiscan during the grinding process. In the precipitation process, the nucleation, growth and agglomeration of fine particles were investigated using this instrument. The crystal or nuclei agglomerate sizes derived from light flux measurements are compared with direct size determination by means of scanning electron microscopy. The multiple scattering technique was found to be highly sensitive to operating conditions (feed flow rate, calcium carbonate volume fraction, reactant concentration and stirring rate), and proved to be a powerful way of controlling precipitation or grinding processes and of optimising operating time.

Introduction

Optical techniques for the measurement of particle sizes and concentrations are usually carried out by elastic light scattering or diffractometry. Unfortunately, industrial and laboratory applications may require the use of optical diagnosis in densely laden flows for which multiple scattering phenomena are significant. Indeed, concentrated solid liquid dispersions such as food, detergents or pharmaceuticals are frequently encountered in industrial situations.

The aim of the present paper is to report new progress in the development of a measurement technique for studying precipitation and grinding processes. Solid liquid dispersions are often generated in an agitated batch vessel, for instance by precipitation. Sometimes, a more energetic dispersive action is needed when size reduction of particles is carried out. The control of precipitation and wet milling processes is of great interest for industrial applications.

Physico-chemical and processing conditions strongly influence the macroscopic behaviour of concentrated dispersions. Both physico-chemical and hydrodynamic interactions between particles determine densely laden flows. As a consequence, dispersions display non-Newtonian features and specific flow properties resulting from changes in the microstructure when increasing the shear stress [1]. However, microrheological models relating the dispersion viscosity and the aggregate mean size involve several structure parameters (packing concentration, fractal dimension and rupture parameter of aggregates) [1]. On the other hand, simple light scattering methods usually used for particle sizing require prior sampling and dilution that may change the macroscopic properties of the dispersion.

Recently, direct techniques were developed to characterise the on-line and in-line properties of concentrated dispersions in a non-intrusive and non-denatur-
Ultrasonic spectrometry techniques provide advantages for on-line particle size analyses, particularly the ability to operate on undiluted and optically opaque media. The technique consists in propagating ultrasonic waves of variable frequency through the particulate system and measuring the frequency dependence of the attenuation to derive particle size [2-5]. The ultrasonic velocity method and the electroacoustic technique can also be used for particle size characterisation in concentrated systems. The ultrasonic velocity method consists in measuring the transit time of pulsed multiple frequency ultrasonic waves propagating through a medium [6]. In the electroacoustic method, an alternating electric field causes the electrically charged particles to move back and forth generating sound waves. Zeta potential and particle size are derived from the analysis of sound waves in relation to particle motions [7].

Multiple light scattering methods represent an alternative to acoustic spectrometry techniques for the characterisation of densely laden flows. In the multiple scattering regime, the transport mean free path representative of particle size can indeed be derived from the analysis of the light flux distribution in the incoherent backscattered spot light [8-10]. The present work concerns the study of calcium carbonate precipitation and grinding with an on-line optical device (Turbiscan On-Line instrument) that analyses multiple light scattered from a concentrated dispersion. Calcium carbonate is a soluble salt widely used in industry as a filler or a basic raw material in the manufacture of paint, coating, talc, adhesive, as well as in water treatment processes. Concentrated suspensions of calcium carbonate were produced by batch precipitation and the size reduction of a commercial calcite was carried out in a continuous stirred bead mill. During the grinding process, the analyser was used to characterise changes in particle size. During the precipitation process, the nucleation, growth and agglomeration of fine particles were investigated with the optical instrument. The size and mean refractive index of particles or nuclei agglomerates are derived from measurements of the backscattered light flux on the basis of a multiple light scattering model by Snabre et al. [8,9].

**Multiple light scattering**

Multiple light scattering methods are increasingly used to characterise concentrated dispersed media such as suspensions or emulsions. One considers the interaction of a focused light beam (light wavelength $\lambda$, polarisation effects are ignored) with particles of diameter $d$ randomly distributed in a fluid. Incident photons undergo multiple scattering events before absorption, backscattering or transmission through the sample. In the weak and multiple light scattering regime ($d > \lambda$), interference effects are averaged out over the photon mean path $\lambda$ and the photon diffusion approximation can be used because of the randomisation of scattered waves [11]. Monte Carlo simulations and statistical models are then suitable for predicting the spatial distribution of multiply scattered photons in the backscattered spot light [8].

**Conservative multiple light scattering**

In the framework of the diffusion approximation, the characteristic lengths involved in conservative multiple light scattering (no light absorption phenomena) are the photon mean path $\lambda$ and the transport mean path $\lambda^*$, which are dependent upon the physical properties of the scattering medium (refractive index $n$ of suspending fluid, refractive index $n_p$ of particles, particle mean diameter $d$ and particle volume fraction $\phi$). The photon mean path $\lambda$ is the average distance between two scattering events in the medium. All information about the initial direction of a wandering photon is further lost over the transport mean path $\lambda^*$, which represents a decorrelation length between the direction of photon propagation and the incident direction. The scattering medium geometry and the transport mean path $\lambda^*$ determine the photon path length distribution in the medium. For a random distribution of scatterers, the path lengths $\lambda$ and $\lambda^*$ are related to the particle mean diameter $d$ and the particle volume fraction $\phi$ through the relations [8]:

$$\lambda = \frac{2d}{3\phi Q_1}, \quad \lambda^* = \frac{\lambda}{1-g} = \frac{2d}{3\phi(1-g)Q_1} \quad (1)$$

where $Q_1(n_p/n) d$ is the scattering efficiency (ratio of total scattering cross-section and geometrical cross-section $\pi d^2/4$ of a particle). The asymmetry parameter $g(n_p/n, d)$ represents the average cosine of scattering angles from a single particle and describes the anisotropy of the scattering diagram ($g=0$ for isotropic Rayleigh scatterers and $0.5 < g < 1$ for Mie scatterers of sizes larger than the light wavelength). The optical parameters $Q_1$ and $g$ may be determined from the Mie theory. For large non-spherical particles ($d > \lambda$), both the scattering efficiency and the asymmetry parameter no longer depend upon scatterer size. The mean diameter representative of scattering phenomena is the surface mean diameter or Sauter diameter:

**References**
When illuminating the scattering medium with a focused beam, the normalised surface light flux $F(r)$ in the centre and outer regions of the backscattered spot light obey the scaling relations [8]:

$$ F(r) = (1-B) 0.03 \left( \frac{\lambda^*}{r} \right)^{1.4} \text{ for } r < 4 \lambda^* $$

$$ F(r) = (1-B) \frac{\lambda^*}{\pi r^3} \text{ for } r > 4 \lambda^* $$

where $r$ is the radial distance from the centre of the spot light and $B$ accounts for boundary reflections at air/wall and liquid/wall interfaces ($B=0.2$ for an aqueous suspension in a cylindrical glass tube [9,10]).

**Turbiscan On-Line measurements**

The Turbiscan On-Line device for the size characterisation of dispersed media is developed and sold by Formulaction (France). This device usually allows the characterisation of dispersions with a particle volume fraction to 70% and a particle surface mean diameter ranging from ten or so nanometres to a few millimetres, depending on the optical properties of the medium. A near-infrared focused LED ($\lambda=850$ nm) illuminates the scattering medium flowing in a cylindrical glass tube (fig. 1) [9]. A transmission (detection angle $\theta=0$) and a backscattering detector (detection angle $\theta=135^\circ$) of small aperture and rectangular cross-section (width $dl$ and height $dh << dl$) detect both the transmitted and multiply backscattered light flux (fig. 1). The transmission level $T(\lambda)$ involves the tube radius $R$ and the photon mean path $\lambda$. The integration of the normalised surface light flux $F(r)$ over the detection area $\delta S=dh \, dl$ further gives the backscattering level $BS(\lambda^*)$ or diffuse reflectance measured by the sensor:

$$ BS(\lambda^*) = \frac{\int_{\delta S} F(r, \lambda^*) ds}{\int_{\delta S} F_{r}(r, \lambda^*) ds} $$

where $F_r$ is the light flux backscattered from a reference suspension (polystyrene spheres with diameter $d_0=0.3 \, \mu m$, particle volume fraction $\phi_0=10\%$ and reference transport path $\lambda^*_0=70 \, \mu m$). From a numerical inversion of relation (4), the photon free path $\lambda$ or transport free path $\lambda^*$ are derived from the transmission rate $T(\lambda)$ or the diffuse reflectance $BS(\lambda^*)$. For known particle volume fractions, the Mie Theory then gives an estimate of the surface mean diameter $d$ of scatterers [9].

Both experiments with polystyrene spheres (refractive index $n_p=1.59$) and Monte Carlo simulations prove the model [9]. Indeed, the relation (4) describes the volume fraction dependence of the diffuse reflectance $BS(\phi)$ for suspensions of polystyrene spheres [9]. In the concentrated regime, independent scattering results in a continuous increase of the diffuse reflectance $BS$ with particle volume fraction. However, departure from independent scattering occurs in concentrated dispersions of small particles ($\phi > 10\%$ and $d < \lambda$) where the increase in correlation among particles induces short-scale interference of the scattered waves [11]. Dependent scattering effects cause an increase of the transport path length $\lambda^*$ and a decrease of the diffuse reflectance $BS$ [10-12]. For non-absorbing Rayleigh scatterers ($d << \lambda$), the Percus-Yevick approximation for the pair distribution function gives an analytical expression of the transport mean path $\lambda^*(d, \phi)$ in the dependent scattering regime [5,12]:

$$ \lambda^* = \frac{2d}{3(1-\phi)Q_i - (1+2\phi)^2} \text{ for } d < \lambda $$

**Calcite crystals**

Preliminary experiments were performed with calcium carbonate particles and compared with the predictions of the scattering model. Three crystalline forms for calcium carbonate are reported in the literature [13,14]: rhombic (calcite), spherical (vaterite) and needle-like (aragonite) particles. Precipitated pure calcite (>99%, Merck) corresponding to the rhombic form of the calcium carbonate is considered in this section. Electron microscopy observations show compact calcite crystals of a mean size around 10 $\mu m$ and
larger open agglomerates (fig. 2).

The calcium carbonate volume fraction dependence of the backscattering level $BS(\phi)$ was investigated with the Turbiscan optical analyser. Experiments were performed in a batch well-stirred reactor. A peristaltic pump allows the suspension circulation at a constant flow rate ($Q=40$ l/h) through the optical analyser. The backscattering level of the suspension was measured for particle volume fraction up to 25%. A higher particle volume fraction results in unstable flows and poorly reproducible experiments for calcite aqueous suspensions without a dispersing agent.

Figure 3 shows the experimental and theoretical dependence of the transmission and backscattering levels upon the particle volume fraction $\phi$ for calcium carbonate aqueous suspension. In the diluted regime ($\phi<\phi_c$), the transmission level $T(\phi)$ decreases exponentially with particle volume fraction. The strong diffuse reflectance $BS$ in the diluted regime results from the dominant boundary reflections on the inner tube interface. In the concentrated regime ($\phi>\phi_c$), the transmission level $T(\phi)$ becomes negligible and the diffuse reflectance $BS(\phi)$ increases with particle volume fraction as a result of independent scattering representative of scatterers larger than the light wavelength. The agglomeration of large and compact calcite particles weakly changes the scattering area per unit volume. As a consequence, transmission and backscattering levels are mainly sensitive to calcite crystals since light waves cannot resolve the structure of large agglomerates. Considering a refractive index $n_p=1.52$ for calcite rhombic crystals [15], the scattering model describes experimental data (fig. 3) for an average calcite crystal diameter $d=9\ \mu m$ and is in good agreement with electron microscopy observations (fig. 2). Because of multiple scattering phenomena and photon randomisation, the model remains suitable for describing the diffuse reflectance of a dense collection of irregularly shaped and polydispersed compact calcite crystals.

The scattering model was used to determine the calcite crystal diameter dependence of the backscattering level $BS$ for a particle volume fraction ranging from 4% up to 14% (fig. 4). In the case of Rayleigh scatterers smaller than the wavelength (nearly isotropic scattering), the diffuse reflectance $BS$ increases with particle surface mean diameter. On the other hand, the anisotropic forward scattering of light from calcite crystals larger than the wavelength results in a decrease of the backscattering level with

![Fig. 2](image2.png)  
**Fig. 2** Microphotograph of (unground) rhombic calcite particles.

![Fig. 3](image3.png)  
**Fig. 3** Theoretical (full lines) and experimental backscattering ($\bullet$) or transmission ($\circ$) levels versus particle volume fraction for calcite aqueous suspensions. Mean refractive index $n_p=1.52$, $d_h=500\ \mu m$ and $\lambda^*=70\ \mu m$. Particle surface mean diameter $d=9\ \mu m$.

![Fig. 4](image4.png)  
**Fig. 4** Theoretical backscattering level $BS$ versus particle surface mean diameter $d$ for particle volume fraction $\phi=4\%$, $\phi=8.4\%$ and $\phi=13.7\%$. Mean refractive index of the agglomerates $n_p=1.52$, $d_h=500\ \mu m$ and $\lambda^*=70\ \mu m$. Closed symbols ($\bullet$) show experimental backscattering levels.
Backscattering level measurements and theoretical predictions show a reasonable agreement for a calcite crystal surface mean size $d = 9 \mu m$ and particle volume fractions in the range from 4% up to 14% (black symbols in fig. 4). These results show the ability of the multiple scattering model to describe the backscattering level of concentrated aqueous suspensions of calcium carbonate. Multiple light scattering is especially sensitive to the surface mean size of calcite crystals and is weakly influenced by agglomeration phenomena since crystals are larger than the light wavelength. In the following sections, the optical device is used to study changes in particle diameter or volume fraction during calcium carbonate precipitation and grinding processes. Experimental transmission or backscattering levels are interpreted within the framework of the scattering model.

**Experimental set-up**

**Experimental set-up for grinding runs**

Wet grinding of calcium carbonate was performed in a laboratory stirred bead mill (Drais Pearl Mill PML-V/H, 0.8 litre in capacity). The mill consists of a cylindrical grinding chamber agitated with four discs mounted on a driven shaft (fig. 5). About 80% of the chamber volume is filled with grinding zirconium beads (bead density 2300 kg/m$^3$) ranging from 400 to 600 $\mu m$ in size. The stirring rate was kept constant at 2130 rpm. During the grinding runs, the beads are kept in the chamber by using a separating gap, which permits a continuous mill discharge. Cooling water circulating from a thermostatic bath through the mill jacket prevents overheating of the grinding chamber.

Grinding runs were performed initially with calcium carbonate particles suspended in distilled water without a dispersing agent for weight fractions of particles ranging from 10% to 30% (i.e. particle volume fraction $4% < \phi < 14\%$). Then, more dense suspensions (60 wt.% equivalent to 35.6 vol.%) were used adding a dispersing agent (sodium polyacrylate). Under these conditions, the suspensions remain macroscopically homogeneous and can be pumped from a well-stirred reactor so that no settling occurs. A peristaltic pump circulates the calcium carbonate suspension from the feeding tank to both the grinding chamber and the optical analyser placed on-line at the outlet of the mill. In that case, direct measurements on the whole outlet flow were performed. A second feed reactor containing distilled water was used to clean the installation before each experiment.

**Experimental set-up for precipitation runs**

Calcium carbonate precipitation is realised by mixing a carbonate-salt aqueous solution with a calcium-salt solution. Batch experiments for calcium carbonate precipitation were performed in a well-stirred 1.2-litre crystalliser. Figure 6 shows a schematic diagram of the experimental set-up. Cooling water circulating from a thermostatic bath through the reactor jacket is used to maintain a constant temperature $T_R = 21^\circ C$ in the reactor. Equimolar solutions of calcium nitrate and sodium carbonate were added to get the desired calcium and carbonate ion concentration in the reactor.

The time evolution of calcium carbonate precipitation was then followed with the optical analyser by measuring the time variation of the backscattering level $BS$. For this purpose, a peristaltic pump circulates the suspension at a constant flow rate $Q = 30 l/h$ through the cylindrical cell of the optical analyser.
Results

Grinding experiments without sodium polyacrylate

At the beginning of an experiment, a precise amount of calcium carbonate particles was injected into the feed reactor previously filled with distilled water to prepare a suspension of known particle volume fraction. Water from the second feed reactor circulates first through the installation. After a few minutes, the calcium carbonate suspension was pumped to the mill at a controlled flow rate. The flow rate can be changed by adjusting the peristaltic pump without stopping the flow during an experiment. The grinding process was followed with the Turbiscan On-Line by measuring the time variations of the backscattering level $BS(t)$. Samples were further taken during grinding experiments to determine the flow rate and the suspension density. Calcium carbonate particles were visualised by scanning electron microscopy at the beginning and the end of each experiment (fig. 2 and fig. 7). Rhombic calcite crystal agglomerates as well as irregularly shaped fragments were always observed (fig. 7). X-ray analysis shows no polymorphism transformation during the wet grinding of calcite particles.

The experimental conditions regarding the calcite volume fraction $\phi$, the feed flow rate $Q$ and the mean residence time $\tau=V/Q$ of particles in the reactor of volume $V=400 \text{ ml}$ are listed in table 1.

For the calcium carbonate volume fraction $\phi > 4\%$, the suspension flowing in the cylindrical tube of the optical analyser is optically thick and only the backscattering level was analysed since the transmission level becomes negligible. Figure 8 shows time variations of the backscattering level $BS(t)$ for a calcium carbonate volume fraction $\phi=13.7\%$ and a feed flow rate $Q=22.2 \text{ l/h}$. The mill was initially filled with water. The diffuse reflectance $BS(t)$ increases sharply as the process starts before stabilising at $BS=92.4\%$ after a few hundred seconds with signal fluctuations less than 0.2%.

Influence of flow rate

Figure 9 shows the time variation of the backscattering level when gradually increasing the feed flow rate for a calcium carbonate volume fraction $\phi=13.7\%$.

| Experiment | G1 | G2 | G3 | G4 | G5 | G6 |
|------------|----|----|----|----|----|----|
| $\phi$ (%) | 4  | 4  | 8.4| 8.4| 13.7| 13.7|
| $Q$ (l/h) | 21.2| 45.6| 45.6| 22.6| 47.5| 20.4|
| $\tau$ (s) | 67.9| 31.6| 30.8| 63.7| 30.3| 70.6|
| $r$ (s) | 19.8| 72.7| 46.2| 63.2| 74.0| 20.0|

Table 1 Operating conditions during the wet grinding process without additive

![Image](https://example.com/image.png)
At a constant flow rate $Q=20.4$ l/h, the backscattering level first reaches a steady level $BS=92.3\%$ (fig. 9(a)). After a steep flow rate increase from 20.4 to 47.5 l/h, the rise in the backscattering stationary level indicates larger particles (fig. 3) as a result of a reduced mean residence time of particles in the reactor and a weaker efficiency of the grinding process. The backscattering stationary level increases with feed flow rate $20 < Q < 72$ l/h and is representative of independent scattering from particles larger than the light wavelength. Figure 9 further shows the reversibility of the experiments since an identical backscattering stationary level is observed when the flow rate is reduced to the initial value $Q=20.4$ l/h (fig. 9 (a) BS=92.3\% and (b) BS=92.2\%). The reproducibility of the experiments was verified since differences in the backscattering levels never exceed 0.2\% for identical hydrodynamic conditions.

**Influence of calcium carbonate volume fraction**

In this section, the effect of the particle volume fraction on the grinding efficiency is analysed. Figure 10 shows the backscattering curves $BS(t)$ for the calcium carbonate volume fraction $\phi=4\%$, $\phi=8.4\%$ and $\phi=13.7\%$. For identical flow rate conditions, the backscattering stationary level increases with particle volume fraction, which indicates a reduced grinding efficiency at high solids concentrations.

The effect of the solids concentration on the grinding efficiency mainly depends on the solids mechanical properties and operating conditions. Concerning the grinding of limestone, experiments from Kwade et al. [16] showed that more mechanical energy is required to achieve a similar product fineness at very low limestone concentrations since the grinding probability of a particle becomes negligible. At intermediate solids concentrations, the grinding efficiency rises because of a higher presence probability of particles near the stressed region. For high solids concentrations and at constant rate of supplied mechanical energy, particle crowding reduces again the fragmentation rate and the grinding efficiency. Moreover, part of the mechanical energy is lost in viscous dissipation energy because of the viscosity increase of the suspension. In the case of calcium carbonate grinding, a higher fineness is achieved as the particle volume fraction decreases. The higher the solids concentration, the shorter is the interparticle distance, and the aggregation phenomenon in the absence of a dispersing agent is promoted, leading to an increase of the viscosity.

**Grinding experiments with sodium polyacrylate**

A dispersing agent was used to obtain denser calcium carbonate suspensions which were pumpable and able to flow in the grinding set-up pipes. Sodium polyacrylate is one of the most frequently used additives in the grinding of calcite, and prevents the aggregation phenomenon which takes place during the size reduction process and decreases the viscosity of the ground suspensions [17]. Grinding experiments were performed at a particle volume fraction of 35.6\% (60 wt.\%) using sodium polyacrylate (molecular weight 5100 g/mol) at a concentration of 1 wt.\% relative to calcite dry matter. Figure 11 shows the time evolution of the backscattering level $BS(t)$ for two feed flow rates $Q=7$ l/h and $Q=32$ l/h. As previously observed, the signal first increases sharply and then reaches a stationary level after a variable time depending on the flow rate. As expected, the $BS$ values obtained are higher ($BS=97.5\%$ for $Q=7$ l/h i.e. $\tau=206$ s and $BS=95.3\%$ for $Q=32$ l/h i.e. $\tau=45$ s) than those corresponding to lower volume fractions (see fig. 10).

The optical system can also be used to determine the delay time $\tau^*$ necessary to reach a steady state when starting the process or changing the feeding conditions.

Hydrodynamic conditions in the grinding chamber (solids concentration and stirring rate) strongly influence the time interval $\tau^*$. For the present experiments, this delay time necessary to reach a backscattering stationary level ranges between 50 and 300 s and indeed varies as the inverse of feed flow rate. However, $\tau^*$ is always shorter than the time interval $\tau^*=4-5\tau$ usually considered in a grinding process, where $\tau$ is the mean residence time $\tau=V/Q$.
Fig. 10 Time dependence of the backscattering level $BS(t)$ for different initial calcium carbonate volume fractions $\phi=4\%$, $\phi=8.4\%$ and $\phi=13.7\%$ and variable feed flow rates.

[18]. A possible explanation is the small size of the laboratory grinding chamber (0.8 l) whose hydrodynamic behaviour can be assimilated with a good approximation to that of a perfect mixed reactor [19].

Precipitation experiments

The stirred reactor is first filled up with distilled water and the temperature is kept constant at 21°C. After a few minutes, the first reactant (sodium carbonate solution) is introduced into the reactor. Several minutes later, an equimolar calcium nitrate solution is added and the precipitation process starts immediately because of the high reactant concentrations ranging from 0.1 mol/l up to 0.4 mol/l. The time evolution of the backscattering level $BS$ is recorded with the Turbiscan On-Line during the precipitation process.

Samples were taken from the reactor with a syringe during the precipitation process. A few drops of hydrochloric acid were added rapidly to the filtrated solution to stop calcium carbonate precipitation. The samples were dried at room temperature and characterised by scanning electron microscopy. The calcium concentration in the reactor was further determined by sample proportioning. The effects of reactant concentration $c$ and stirring rate $\omega$ on the precipitation process were studied. The experimental conditions are shown in table 2.

For high reactant concentrations $c > 0.1$ mol/l, precipitation occurs instantaneously as soon as a few drops of nitrate calcium solution are introduced into the sodium carbonate solution. The turbulent mixing time $t_m = 7.3(D_r/\dot{e})^{1/3}$ is about six seconds where $D_r$ is the reactor diameter and $\dot{e}$ the viscous dissipation rate per unit mass of stirred suspension [20]. As a consequence, calcium carbonate precipitation takes place before complete mixing and a viscous gelatinous reaction product is formed during the first seconds of the precipitation process in agreement with reported

Fig. 11 Time dependence of the backscattering level $BS(t)$ for calcium carbonate volume fraction $\phi=35.6\%$ (adding dispersant agent) at two different feed flow rates: $Q=32$ l/h (a) and $Q=71$ l/h (b).

Table 2 Operating conditions during the precipitation runs ($T_R=21$°C)

| Experiment | P1 | P2 | P3 | P4 | P5 | P6 | P7 | P8 | P9 | P10 |
|------------|----|----|----|----|----|----|----|----|----|-----|
| $c$ (mol/l) | 0.1 | 0.1 | 0.15 | 0.15 | 0.2 | 0.3 | 0.3 | 0.4 | 0.3 | 0.3 |
| $\omega$ (rpm) | 710 | 710 | 710 | 710 | 710 | 710 | 710 | 1000 | 500 |
observations from S. Kabasci [14].

Figure 12 shows the time evolution of the backscattering level $BS(t)$ for a reactant concentration $c=0.3$ mol/l and a stirring rate $\omega=500$ rpm. The optically transparent aqueous carbonate salt solution displays a high backscattering level because of internal reflections (fig. 12a). The introduction of the calcium nitrate reactant induces an instantaneous calcium carbonate precipitation and a steep decrease of the backscattering level as the scattering medium becomes optically thick. The backscattering level further rapidly increases before reaching a stationary level after a delay time of about 500 seconds.

The backscattering curves $BS(t)$ indeed show several stages just after reactant introduction and calcium carbonate precipitation (fig. 12b). On a short time scale $t<10s$, the backscattering level increases steeply in relation to the nucleation phase since the crystal concentration rises and the medium scatters the incident light more strongly. During the nucleation phase, the observed decrease of the backscattering level (fig. 12b) probably results from the mixing of the gelatinous reaction product. The nucleation phase can be considered complete after a few seconds as confirmed by sample proportioning during the precipitation process. After the nucleation phase, the nuclei species form spherical agglomerates and then the backscattering level $BS(t)$ displays a bell-shaped variation and a further decrease before reaching a stationary level after a few minutes (fig. 12b). For similar operating conditions, the experiments are reproducible and the signal deviation remains less than 1% (fig. 13).

During the course of experiments, the calcium ion concentration remaining in the solution was determined and the particles were further visualised by scanning electron microscopy (fig. 14). Spherical vaterite crystals (agglomerates of nuclei) and porous

![Fig. 12](image1.png)

**Fig. 12** Time dependence of the backscattering level $BS(t)$ for initial reactant concentration $c=0.3$ mol/l ($T_R=21^\circ$C, $\omega=500$ rpm) and time $t<1000$ s (a) or $150<s<t<400$ s (b).

![Fig. 13](image2.png)

**Fig. 13** Time dependence of the backscattering level $BS(t)$ for initial reactant concentration $c=0.15$ mol/l or $c=0.3$ mol/l ($T_R=21^\circ$C, $\omega=710$ rpm).

![Fig. 14](image3.png)

**Fig. 14** Microphotograph of agglomerates of spherical vaterite crystals formed at time $t=60s$. 
Large aggregates were always observed briefly during calcium carbonate precipitation.

For a given nuclei and crystal concentration, the scattering model predicts a maximum backscattering level for agglomerates of a size close to the light wavelength $\lambda = 0.85 \mu m$ (see fig. 4). Therefore, the bell-shaped backscattering curves $BS(t)$ probably reflect the formation of nuclei agglomerates which are larger than the wavelength in agreement with electron microscopy visualisation (fig. 14). Nuclei agglomerates can further stick and form large open structures or aggregates. Over a long time scale, the light wave cannot resolve the internal structure of large porous aggregates made of sub-units larger than the wavelength, and multiple light scattering becomes mainly sensitive to nuclei agglomerating.

**Influence of reactant concentration**

Figure 15 shows the backscattering curves $BS(t)$ for reactant concentrations ranging from 0.1 mol/l up to 0.4 mol/l. As a consequence of mixing phenomena during the nucleation phase and formation of a gelatious phase, the backscattering curves $BS(t)$ display a first oscillation (more pronounced for the high reactant concentration $c=0.4$ mol/l) a few seconds after precipitation starts. During nucleation and agglomeration phases, the scattering behaviour and the maximum backscattering level increases with the reactant concentration since more nuclei are formed in the reactor (fig. 15). The optical signal $BS(t)$ further displays time oscillations near the maximum backscattering level except for the weakest reactant concentration $c=0.1$ mol/l.

Nuclei agglomeration promotes the formation of porous agglomerates which trap some liquid solution. One may thus expect calcium carbonate precipitation within nuclei agglomerates and a delayed compaction of structures. Size increase to above one micron lowers the backscattering level while the compaction of agglomerates results in a higher average refractive index and stronger scattering phenomena. Therefore, the observed oscillations near the maximum backscattering level probably results from the competition between growth and compaction of nuclei agglomerates. Indeed, the signal oscillation is more intense and occurs earlier in time when increasing the reactant concentration because high ionic concentrations promote the calcium carbonate precipitation within nuclei agglomerates. A small reactant concentration $c=0.1$ mol/l prevents the compaction of nuclei agglomerates and then the backscattering peak is no longer observed (fig. 15).

**Influence of stirring rate**

Calcium carbonate precipitation was performed under different flow conditions in the stirred reactor. For stirring rates in the range from 500 rpm to 710 rpm, the flow conditions have no significant influence upon the backscattering curves $BS(t)$ (fig. 16). On the other hand, a high stirring rate $\omega=1000$ rpm greatly changes the scattering behaviour during the first minute. High shear gradients delay the nucleation phase and the growth of nuclei agglomerates. Over longer times $t > 1$ min, the flow conditions have less influence both on the growth and the compaction of nuclei agglomerates. However, the backscattering stationary level is somewhat lower under strong stirring conditions.
Discussion

Grinding experiments

For a known calcium carbonate volume fraction, the time evolution of particle surface mean diameter can be determined from the measurement of the backscattering level during the grinding process. Figure 17 shows the particle volume fraction dependence on the surface mean particle diameter for backscattering stationary levels displayed in figure 10 (experiments without additive). The surface mean particle diameter increases with calcium carbonate volume fraction and with the feed flow rate (i.e. reducing the mean residence time) because of the lower grinding efficiency. Whatever the operating conditions, the surface mean diameter of the ground particles always remain larger than the light wavelength \( \lambda = 850 \text{ nm} \), as confirmed by electron microscopy analysis of samples. One can further expect precise values of the average size of particles because of the high sensitivity of the backscattering level upon scatterer diameter for calcite crystals larger than the wavelength (fig. 4).

During grinding experiments, changes in the feeding rate significantly affect the backscattered light detected by the on-line optical sensor at the outlet of the mill. Thus, the optical device can be used to adjust the flow rate and control the grinding process. However, the on-line control of particle size from measurement of the backscattering level requires knowledge of the particle volume fraction. Indeed, the backscattering level is dependent both upon particle fineness and solid concentration. The analysis of the transient behaviour of multiple light scattering phenomena further gives information about the delay time required to reach steady state and can also be used to optimise the operating time during grinding processes.

Precipitation experiments

Precipitation experiments can be analysed on the basis of the multiple scattering model. In the framework of a mean field approximation, porous nuclei agglomerates trap some liquid which reduces the mean refractive index of scatterers. Since the nucleation phase only takes a few seconds, a constant nuclei volume fraction is further assumed. Sample proportioning indeed indicates a roughly constant particle volume fraction after about 20 seconds. However, the mean refractive index of nuclei agglomerates appears to increase during particle growth as a result of carbonate calcium precipitation within agglomerates. Figure 18 shows the particle diameter dependence of the backscattering level \( BS(d, \phi) \) for a mean refractive index \( n_p = 1.475 \) (a) or \( n_p = 1.51 \) (b).

For an experimental particle volume fraction \( 0.3\% < \phi < 1.6\% \) and a mean refractive index \( n_p = 1.475 \), the mean field scattering model predicts the maximum values of the backscattering level \( BS(\phi) \) (figs. 15 and 18a) very well. When compared to the refractive index \( n_p = 1.52 \) of calcite crystals at wavelength \( \lambda = 0.65 \text{ \textmu m} \) [15], a mean refractive index \( n_p = 1.475 \) indicates the formation of porous nuclei agglomerates.

During the first stage of the precipitation process, the rise of the backscattering level from an initial value \( BS = 20\% \) (fig. 15) corresponds both to the nucleation phase and the growth of agglomerates from nuclei of initial size \( d = 0.15 \text{ \textmu m} \). The limited backscattering level variation at a low particle volume fraction \( \phi = 0.38\% \) results both from internal reflections and weak light scattering from diluted suspensions (fig. 15).

The scattering model considers monosized particles, and the theoretical backscattering level then displays an oscillating behaviour for particles of a size close to the light wavelength, because of interference effects (fig. 18). For polydispersed agglomerates formed during batch precipitation, the observed oscillation in the scattering behaviour cannot be a result of interference effects but is rather the result of a restructuration process of nuclei agglomerates as discussed above.

In a second stage, the growth of nuclei agglomerates beyond the light wavelength leads to a decrease of the backscattering level in agreement with experiments (figs. 15 and 18a). Light scattering phenomena then become mainly sensitive to the porous nuclei agglomerates and cannot resolve the structure of aggregates larger than the light wavelength. In the framework of the mean field scattering model and for a refractive index \( n_p = 1.475 \), the experimental back-
scattering stationary values $BS(\phi)$ give a nuclei agglomerate size of about 1.3 $\mu$m (closed symbols in fig. 18a). However, electron microscopy analyses of spherical vaterite crystals indicate larger agglomerates of the size 1 $\mu$m < $d$ < 20 $\mu$m. At the end of the precipitation process, one can expect a larger mean refractive index because of calcium carbonate precipitation within the agglomerates. A refractive index $n_p = 1.51$ indeed enhances the backscattering level and then the scattering model predicts agglomerates of characteristic size $d = 5$ $\mu$m (closed symbols in fig. 18b) in better agreement with electron microscopy observations.

According to these results, the optical instrument is suitable for analysing precipitation processes. A rapid nucleation phase is followed by the formation of nuclei agglomerates and open aggregates after a few minutes. The time analysis of the backscattering curves shows crystal growth and a compaction process of the agglomerates. A mean field multiple scattering model predicts porous nuclei agglomerates with a mean refractive index $1.47 < n_p < 1.51$ and average size increasing from 0.15 $\mu$m up to 5 $\mu$m. Rapid stirring of the solution in the batch reactor was further shown to delay both nucleation and agglomeration phases during the first minute. The mean field scattering model proposed here assumes monosized homogeneous particles and neglects the multi-scale structure of porous and polydispersed agglomerates. Despite crude approximations, the model reasonably describes carbonate calcium precipitation in a batch reactor, because the statistical spatial distribution of multiply scattered photons mainly involves an average transport length depending on the mean scattering properties of nuclei agglomerates.

Conclusion

On-line optical experiments were performed with the Turbiscan On-Line to study concentrated calcium carbonate suspensions. The optical device is suitable for analysing calcium carbonate precipitation and grinding processes. During the continuous wet grinding process, the particle volume fraction remains constant and the particle average size was derived from the measurement of the backscattering level. In the case of calcium carbonate precipitation, assuming that the nucleation step lasts only a few seconds, a constant nuclei volume fraction for the agglomeration step was then considered. Moreover, porous nuclei agglomerates were considered as homogeneous spheres (mean field approximation). Despite crude approximations, the multiple scattering model reasonably describes the precipitation process and predicts nuclei agglomerate size in good agreement with electron microscopy observations. As a conclusion, the Turbiscan On-Line is well suited to analyse changes in particle diameter or volume fraction and estimate the optical properties of scatterers.

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Nomenclature

| Symbol | Description                          | Unit |
|--------|--------------------------------------|------|
| BS     | Backscattering level                 | %    |
| c      | Reactant concentration               | mol/l|
| d      | Average particle diameter            | m    |
| d<s>   | Polystyrene sphere diameter          | m    |
| dh     | Detector height                      | m    |
| dl     | Detector width                       | m    |
| D<s>   | Batch reactor diameter               | m    |
| g      | Asymmetry parameter                  |      |
| n<inf> | Fluid refractive index               |      |
| n<sup>p</sup> | Particle refractive index         |      |
| Q      | Feed flow rate                       | 1/h  |
| Q<s>   | Scattering efficiency factor         |      |
| t      | Time                                 | s    |
| T      | Transmission level                   | %    |
| t<inf> | Turbulent mixing time                | s    |
| T<inf> | Reactor temperature                  | °C   |
| V      | Volume of the grinding chamber       | m³   |
| ε      | Viscous dissipation energy per unit  |      |

| Description                                                                                                      |
|-----------------------------------------------------------------------------------------------------------------|
| mass of stirred suspension                                                                                       |
| J/kg                                                                                                            |
| φ                                                                                                               |
| Particle volume fraction                                                                                         |
| %                                                                                                               |
| φ<inf>                                                                                                          |
| Critical particle volume fraction                                                                                |
| %                                                                                                               |
| λ                                                                                                               |
| Photon mean path                                                                                                 |
| m                                                                                                               |
| λ<inf>                                                                                                          |
| Photon transport path                                                                                            |
| m                                                                                                               |
| Λ                                                                                                               |
| Light wavelength                                                                                                |
| m                                                                                                               |
| τ<inf>                                                                                                          |
| Delay time                                                                                                      |
| s                                                                                                               |
| ω                                                                                                               |
| Reactor stirring rate                                                                                            |
| rpm                                                                                                             |

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