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# Production of a Highly Concentrated $CaCO_3$ Suspension by Cross-Flow Microfiltration in the Presence of a Dispersant

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**Abstract:** This article presents the study of the cross-flow microfiltration of an aqueous calcium carbonate suspension in the presence of dispersant in order to obtain the highly concentrated retentate. In the absence of a dispersant, the cross-flow microfiltration with cylindrical ceramic membrane permitted to increase the $CaCO_3$ suspension concentration from 27 to 36.5%. The retentate concentration is increased markedly in the presence of the dispersant (up to 70%). In the presence of the dispersant, the productivity of cross-flow microfiltration of $CaCO_3$ suspension is almost 30% higher than the productivity of dead-end microfiltration of this suspension at the same pressure of 1 bar. However, the permeate contamination by the dispersant could not be avoided and a subsequent separation must be provided to purify the permeate.

**Keywords:** Highly concentrated suspensions, cross-flow filtration, dispersant, plugging

## INTRODUCTION

Highly loaded suspensions are made up of large aggregates owing to attraction forces or Van der Waals forces between particles. This leads to a high suspension viscosity. For decreasing of suspension viscosity and enhancing its

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fluidity, the aggregation of particles must be prevented. Indeed, the fluidity of concentrated mineral suspensions is highly desired in the industry. It is required in many practical applications, such as ceramic processing or paper coating (1, 2). For example, highly concentrated suspensions of calcium carbonate (72–75 wt.%) are widely used in the paper industry for paper coating, which improves the paper gloss and printability, brightness, and whiteness.

Concentrated mineral suspensions tend to form flocs and agglomerates. To avoid their formation and break the existing agglomerates, special chemical agents such as surfactants, wetting agents, or dispersants should be added (3).

Nowadays different techniques are used to prepare highly loaded suspensions. It consists either in rehydration of powders (colloidal processing) or in dehydration of diluted suspensions both in the presence of the dispersant (4, 5, 6). Nevertheless, the dehydration remains the standard technique to produce mineral suspensions up to 75 wt.%. It involves a thermal dehydration (spray drying to evaporate excess water) (7) that consumes a considerable amount of energy. The mechanical dehydration by pressure filtration (70–74 wt.%), followed by filter cake redispersion in the presence of dispersants (8) constitutes an alternative non-thermal method. However, a high energy consumption is still required in order to redisperse a formed filter cake, as well as special equipment like jaw crushers and blade mixers (9), so that, in order to reduce the global energy consumption, many patents (10, 11, 12) advised to proceed first mechanically to obtain a partly dehydrated suspension. This suspension can then be dehydrated by evaporating the excess water and maintaining its fluidity by adding dispersants.

Other methods involving only mechanical dehydration have been proposed in several patents or works to concentrate suspensions (9, 13, 14, 15). Suspensions are then deflocculated by dispersants before filtration. However, this technique has some drawbacks. Deflocculation implies the production of fine mineral particles that tend to clog the filter cloth and penetrate the filtrate. These particles lead to a higher specific cake resistance thereby complicating the filtration process. Additionally, a filtrate contamination may occur due to the release of non-attached dispersant molecules. They may pass through the filter medium to the aqueous filtrate. Husson et al. (16) have proposed a precoat filtration process with a batch filter-press to avoid these drawbacks. Its particularity is the formation of a first precoat layer using a flocculated suspension without dispersant. This precoat is able to retain the non-fixed dispersant molecules presented in a second filtered suspension that is a chemically deflocculated suspension (DS). By this way the precoat can be dispersed, without any dispersant release into the filtrate. Modelling has also been carried out in (17, 18) to determine the thickness of this precoat. The second filtration with DS achieves the cake formation and consolidation. However, the filter cake fluidity is only obtained after a supplementary stage of cake homogenization by a mechanical agitation. This extra stage and the impossibility to work continuously with a filter-press, have encouraged the research of a continuous process. The cross-flow microfiltration is actually a technique to think of. In the present article we study this new process and compare it with the already mentioned precoated batch filtration.

## Action of Dispersants

The required flowability of the charged mineral suspensions is often obtained with chemical agents. These chemical agents are ionic or non ionic products such as polymers. Their function is to disaggregate large formations of particles, called flocs, into separated fine particles establishing solid-liquid dispersions. These dispersions are to be maintained stable, so that an electrostatic barrier or a steric stabilization is required. For the electrostatic barrier, ionic dispersants are mainly used, while for the steric stabilization non-ionic dispersants are widely used (19).

Mineral acids derived dispersants are the simplest charged type. Other major types are phosphates, silicates, borates, and aluminates. The second group of charged dispersants is related to surfactants. Its action strongly depends on their alkyl chain length. Their chain length is related to their viscosity and their steric characteristics. Alkyl sulfates and sulfonates are the most utilized.

The third group of charged dispersant comprises of organic polyacid salt dispersants made of polymerized acrylic and maleic acid, and mixtures. This last type of dispersant has been used in the current study.

# EXPERIMENTAL PROCEDURES

## Experimental Apparatus

A schematic representation of the experimental apparatus is shown in Fig. 1. It comprises an agitated tank with the suspension, and a cross-flow microfiltration membrane. The double walled tank possesses a water refrigeration system. This system enables to maintain a constant temperature near 17°C. A peristaltic pump (Masterlfex 7529–00), is used for suspension and retentate circulation through the system. Masterflex plastic tubing is also used for constituting the rest of the loop. A balance PM 6000 (Mettler-Toledo, France) is used, with the corresponding computer, to obtain all the information about permeate punctual flow and its mass at each moment. Pressure gauges are placed to facilitate head loss calculations. The ceramic membrane system is cylindrical and has an average pore diameter of 0.8 microns. Its sectional area (perpendicular to the solution/retentate flow) is $3.40 \cdot 10^{-5}\,\mathrm{m}^2$. The total filtration area is $3.86 \cdot 10^{-3}\,\mathrm{m}^2$. Since the

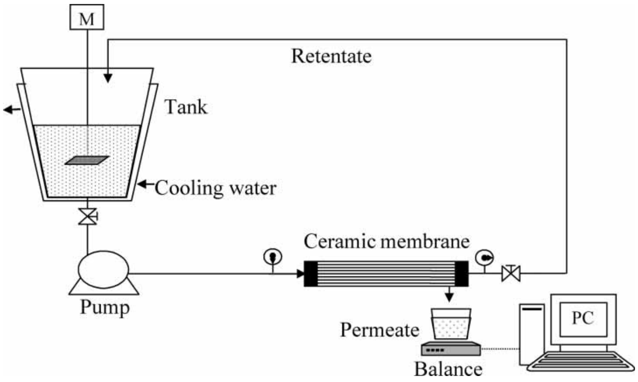

*Figure 1.* Experimental apparatus.

permeate flow is negligible in comparison to the retentate flow, a linear pressure profile is assumed along the membrane and the transmembrane pressure (TMP) is defined by Eq. (1),

$$TMP = \left[\frac{P_{in} + P_{out}}{2}\right] - P_{atm} \tag{1}$$

$P_{in}$ and $P_{out}$ are respectively the inlet and outlet membrane manometric pressures and $P_{atm}$ is assumed to be the atmospheric pressure (1 bar). After that, the membrane resistance, $R_m$, was calculated from Eq. (2),

$$R_m = \frac{TMP}{\mu f_p} A_m \tag{2}$$

where $\mu$ is the water viscosity calculated at 17°C (21), $f_p$ is the permeate flow rate and $A_m$ represents the total filtration area. This experimental approach to assess the membrane resistance gave then a value $R_m = 2.8 \cdot 10^{10}\ \mathrm{m}^{-1}$.

The suspension of calcium carbonate was provided by OMYA France. It has a solid content of approximately 27 wt% and an average particles size of 1.81 μm (measured by a laser granulometer Malvern mastersizer X, Malvern Instruments S.A.). The calcium carbonate density, measured by helium picnometry, was $2.83\ \mathrm{g} \cdot \mathrm{cm}^{-3}$.

The dispersant supplied by COATEX France, referenced DV 834, was a sodium polyacrylate. The retentate dryness was determined with an infrared desiccator SMO 01 (Scaltec Instruments, Germany). A conductimeter HI 8820 N (Hanna Instruments, Portugal) was used to measure the permeate electrical conductivity. The permeate turbidity was measured by a turbidimeter FSC 402 (Mettler-Toledo, France). Finally, the rheological characteristics (viscosity, shear stress) of the concentrated suspension (retentate), were analyzed by a computer controlled viscosimeter VT 550 (HAAKE).

### Methods

Three types of filtration experiments were realized: without dispersant, with initial dispersant addition, and with delayed dispersant addition.

In all experiments the suspension is placed in the agitated tank (Fig. 1) to be pumped through the filtration system. When the operation is started, the pump head supply is settled to have an average retentate velocity of $1\ \mathrm{m \cdot s^{-1}}$. This corresponded to an average manometric pressure of 1 bar. The permeate is collected in the membrane carter and is released in the permeate outlet. The computer linked to the balance, assured determination of the permeate cumulative mass rate. The retentate concentration is subsequently calculated during the experiment.

The experiments were performed at several dispersant concentrations, which varied from 0.5 to 2.5 wt.%. The mixture was previously subjected to an agitation at 120 rpm for 10 min. The filtration experiments ended either because of plugging problems or when the desired retentate concentration was reached. When it was a plugging problem, the membrane was disassembled to be cleaned by water or diluted nitric acid. At the end of the experiments, the retentate stored in the tank was unloaded and analyzed. It was observed that the retentate had the same aspect that the filter cake produced by the dead-end batch filtration with homogenization (for same solid content) and remained in a fluid state.

### Material Balance

The material balance gives the values of retentate mass ($M_{l,t}$) and retentate mass concentration ($w_t$) depending on the permeate cumulative mass ($M_{p,t}$),

$$M_{l,t} = M_{l,o} - M_{p,t} \tag{3}$$

$$w_t = \frac{M_s}{M_s + M_{l,t}} \tag{4}$$

where $M_{l,o}$ is the initial mass of liquid in suspension, $M_{l,o} = M_o - M_s$, $M_o$ is the initial mass of suspension, $M_S$ is the mass of solid particles, $M_S = M_o w_o$, and $w_o$ is the initial solid content of suspension. The calculated values of $w_t$ were correlated with the desiccation analysis. Errors were less than 2%.

## RESULTS AND DISCUSSION

### Filtration without Dispersant

These experiments were carried out to examine the behavior of the system while filtering a suspension of aggregated particles. The cross-flow microfiltration was proceeded up to the system plugging by deposited particles.

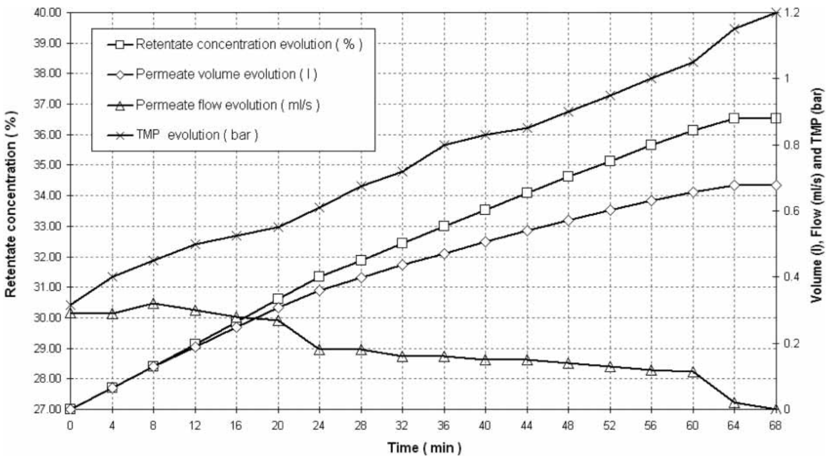

***Figure 2.*** Evolution of an experimentation without dispersant.

As shown in Fig. 2, the permeate volume and retentate concentration continuously increase up to some threshold values corresponding to the system plugging. The TMP elevation and the permeate flow rate decreasing indicate the growing filter cake thickness and resistance. The maximal concentration, which was attained by cross-flow microfiltration of deflocculated calcium carbonate suspension, was approximately 36.5% wt after 64 minutes of filtration (Fig. 2).

## Initial Addition of Dispersant

As can be seen from Fig. 3, the permeate flow rate was not decreased with dispersant addition and even somewhat increased when 1% of dispersant was added. Two regions can be distinguished on the curves of the permeate flow rate. At the start of the operation, the cake thickness growth resulting in a rapid decrease of the permeate flow rate. Generally, this step of cross–flow filtration is considered similar to the dead end filtration and the Carman-Ruth equation of standard filtration may be applied (17). In the second region the permeate flow rate decreases slowly and approaches to zero. However, the addition of the 1% of the dispersant prolongs the duration of cross–flow microfiltration.

This is confirmed by the fitting of experimental data using the Ruth-Carman equation expressed in the following form (Eq. 5) (17).

$$\frac{t}{V} = \frac{\mu\alpha C_o}{2TMP_{Am}^2 V + \frac{\mu R_m}{TMP_{Am}},} \tag{5}$$

where $\alpha$ represents the specific resistance of the cake deposited on the membrane surface, $C_0$ is the suspension concentration, $V$ is the volume of permeate, and $t$ is

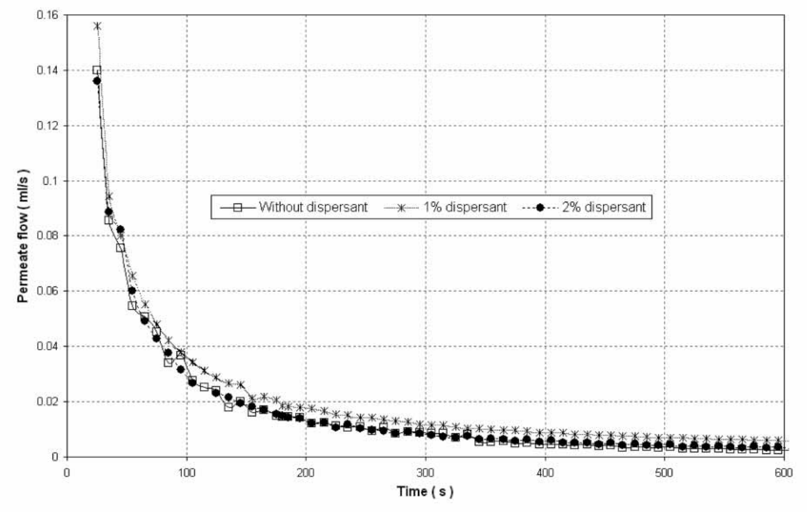

*Figure 3.* Dispersant concentration effects on filtrate flow.

the filtration time. The data presented in Fig. 4, can be fitted by a straight line in coordinates $t/V$ vs. $V$ during the first step of cross–flow filtration in the absence and in the presence of the dispersant. Such behavior is similar to the dead end filtration and shows that both the cake specific resistance $\alpha$ and the suspension concentration $C_0$ do not change importantly at the start of the operation. Nearly the same value of $\alpha \approx 1.12\ 10^{13}$ m/kg has been found from the slope of the straight line at the start of the cross-flow filtration in the absence of and in the presence of the dispersant. Vorobiev et al. (17) carried out the dead end filtration tests with identical calcium carbonate suspension in the presence of the dispersant and found that the increase of the dispersant concentration to 0.1 wt.% slightly decreases the specific cake resistance and the increase of dispersant over 0.1 wt% resulted in the formation of the cake with higher specific resistance. The specific resistance that is found in our experiments is at least twice higher than the values found by Vorobiev et al. for the dead end filtration. This result can be explained by the fact that in cross-flow filtration the formed cake is mostly constituted of the fine particles. For example, Chellam and Wiesner (20), using glass particles ranging in size from 1 to 25 μm, reported that large particles were absent from the cake obtained in cross-flow filtration. They also observed that specific resistances of cake formed during cross-flow filtration were much larger (by a factor ranging from 5 to 132) than those of cakes formed from the feed suspension. This result also corroborates with the work of Ould-Dris et al. (21) showed that the distribution spectrum of the particles in the cake is clearly shifted towards the smaller sizes in cross flow filtration. As can also be seen from Fig. 4, the curves in coordinates $t/V$ vs. $V$ deviate noticeably from the straight line after the starting period. However,

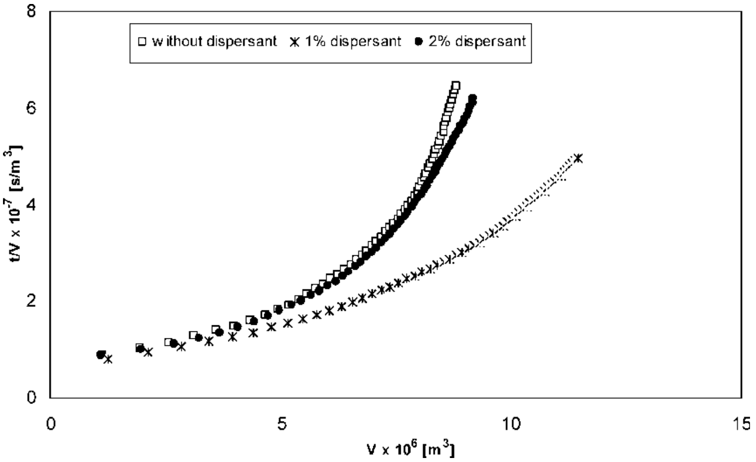

*Figure 4.* Comparison of the transient cross flow filtration with the Ruth equation.

the operation can be more effective with a smaller quantity of added dispersant (1% wt), when the slope of experimental $t/V - V$ curve changes less, and the additional quantity of the permeate can be obtained (Fig. 4).

## Delayed Addition of Dispersant

This part of the study has a double purpose: 1) to investigate the specific effect of the dispersant on cake formation/evolution, 2) to avoid the permeate contamination by dispersant. To achieve both objectives, the dispersant addition was delayed.

Fig. 5 shows that the addition of the dispersant during cross-flow microfiltration leads to the short-time decrease of TMP and cake resistance $R_c$ calculated as

$$R_r = \frac{TMPA_m}{f_p \mu} - R_m \tag{6}$$

This phenomenon may be due to the weakening of contacts between the cake particles induced by the dispersant and detachment of some particles (aggregates) from the cake. However, with the following continuation of cross-flow microfiltration, the TMP and the cake resistance increase again identically to the process in the absence of the dispersant (Fig. 2). The second objective was to avoid the permeate contamination by the dispersant. The idea was to simulate the precoat formation in dead-end filtration proposed in (18). To this purpose, a dispersant free precoat was formed. This precoat had the unique function to retain the dispersant. Unfortunately, the conductimetry analysis indicates a significant release of dispersant to the permeate.

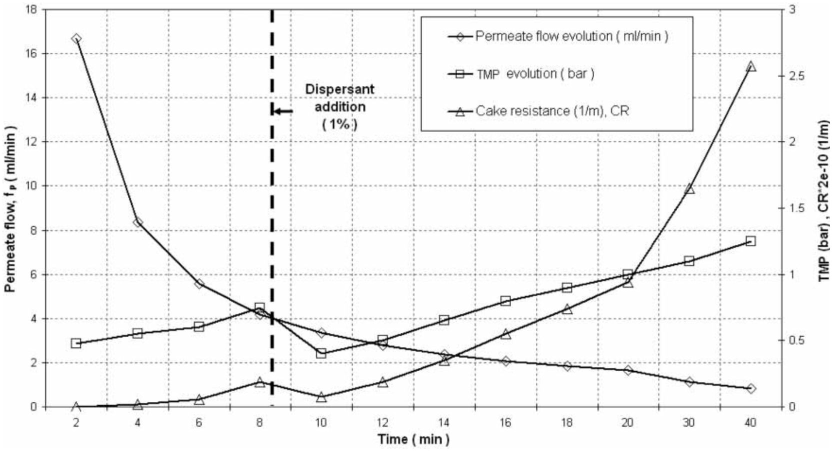

*Figure 5.* Experimentation with dispersant free precoat formation.

## Process Optimization

Once the dispersant effects and plugging problems are cleared, the process was optimized. Concerning the retentate, the objective was to achieve the maximum dryness with the minimal viscosity. The evolution of retentate dryness as a function of dispersant concentration can be observed in Fig. 6.

As shown in Fig. 6, the dispersant addition allows the dryness increasing from 36.5% (suspension free of dispersant) to about 70% (for 1.8% of added dispersant). It has to be noticed that these results are comparable with those of

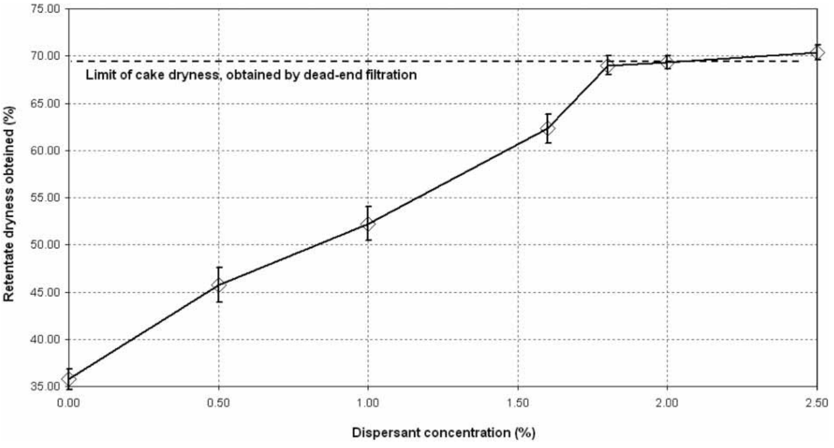

*Figure 6.* Maximal achievable retentate dryness versus dispersant concentration.

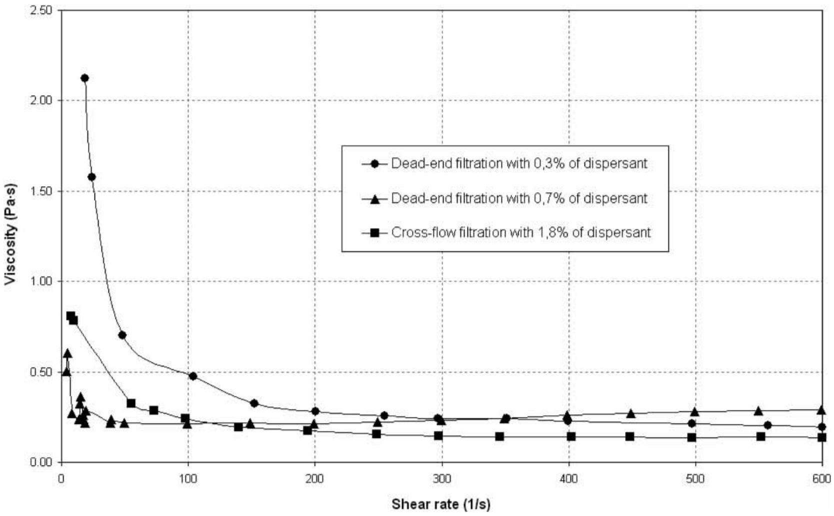

***Figure 7.*** Dead-end and cross flow filtration rheological behaviour comparison.

dead-end filtration, obtained after the cake homogenization (17, 18). The dispersant concentration needed is however higher than in dead end filtration and for the time being, there is no solution to avoid the permeate contamination by dispersant in the cross-flow process.

To estimate the performance of both processes, the viscosity of the retentate obtained in cross-flow filtration was compared to the viscosity of a homogenized cake, obtained in dead end filtration (Fig. 7).

As can be seen from Fig. 7, the concentrated suspensions of $CaCO_3$ obtained by cross-flow and dead end processes show the shear thinning behavior. For studied suspensions, the viscosity is less than 0.5 Pa.s for shear rates between 100 and 600 $s^{-1}$. All three suspensions are easily handled or pumped. The following pictures (Fig. 8) denote the liquidity of the obtained retentate.

***Figure 8.*** Pictures of the obtained cross-flow filtration retentate; 1.8 wt% DV834; 68.9 wt% dryness.

***Table 1.*** Comparison of cross-flow microfiltration productivity against dead-end's one

| Cross-flow microfiltration (1 bar) | Dead-end batch microfiltration (1 bar) | Dead-end batch microfiltration (5 bar) |
|---|---|---|
| 21 kg/m$^2$·h | 16 kg/m$^2$·h | 48 kg/m$^2$·h |

### Filtration Time and Production Rates

Filtration time is directly related to the process productivity. Time is obviously an important item when comparing dead-end and cross-flow microfiltration. Table 1 displays the approximate productivity of each process. This productivity represents the quantity of concentrated suspension (68–70% w/w), obtained in one hour per one square meter of filtration area.

Derived from Table 1, the productivity in cross-flow microfiltration is almost 30% higher than in dead-end batch microfiltration, for the same average filtration pressure (1 bar). Moreover, it should be noted that the cross-flow process runs continuously. Dead-end microfiltration implies cycles comprising cake discharging and filter chamber re-assembling (for filter-presses). Additionally, the cake homogenization should be accomplished separately in case of dead-end microfiltration. Therefore, it is assumable that the productivity of the cross-flow filtration process is high enough to consider it as a good alternative to the dead-end one.

## CONCLUSIONS

The results of this investigation confirm the feasibility of concentrating the calcium carbonate suspension by a membrane cross-flow microfiltration in the presence of the dispersant. The dispersant enhances the fluidity of concentrated retentate and helps to avoid the plugging problems. The productivity of the continuous cross-flow process is higher comparatively with a batch process realized at the same pressure.

Dryness of the retentate obtained with this alternative process is comparable to the dryness of the cake obtained in dead-end microfiltration process (~70 wt.%). Such high dryness can be obtained with a suspension fluidity similar to that obtained with the dead-end microfiltration process.

This investigation shows the results of an early development stage, so that, technical problems have still to be resolved. Permeate contamination by dispersant could not be avoided and a subsequent separation must be provided to purify the permeate. The quantity of added dispersant should also be minimized.

## SYMBOLS

| | |
|---|---|
| $DS$ | Deflocculated suspension |
| wt.% | Mass fraction or dryness |
| $TMP$ | Average transmembrane pressure (bar) |
| $P_{in}$ | Membrane inlet pressure (bar) |
| $P_{out}$ | Membrane outlet pressure (bar) |
| $P_{atm}$ | Atmosferic pressure (bar) |
| $R_m$ | Membrane resistance ($m^{-1}$) |
| $\mu$ | Viscosity ($Pa \cdot s$) |
| $f_p$ | Permeate flow ($m^3 \cdot s^{-1}$) |
| $A_m$ | Membrane filtration surface |
| $M_s$ | Solid's mass in suspension (g) |
| $M_o$ | Initial mass of suspension (g) |
| $w_o$ | Initial suspension dryness (wt.%) |
| $M_{l,o}$ | Initial mass of liquid in suspension (g) |
| $M_{l,t}$ | Liquid mass in function of time (g) |
| $M_{p,t}$ | Permeated mass of liquid in function of time (g) |
| $t$ | Time (s) |
| $\alpha$ | Deposition layer, cake specific resistance (m/kg) |
| $CR$ | Percolation resistance offered by the cake and the membrane clogging ($m^{-1}$) |

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