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Flocculation of PCC filler in papermaking: Influence of the particle characteristics

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Abstract
The influence of precipitated calcium carbonate (PCC) characteristics on the flocculation process and flocs structure was investigated in the presence of a linear, high molecular weight, cationic polyacrylamide of high charge density. For that, a commercial PCC sample was used, either as supplied (original PCC) or after a washing process (treated PCC). The PCC samples were characterised, and the flocculation process, for different flocculant concentrations, was monitored using the light diffraction scattering technique (LDS). Flocs structure was evaluated by determining the mass fractal dimension of the flocs. It was found that the particle size of the original PCC was larger than that of the PCC submitted to the cleaning process. As a consequence, the optimum flocculant dosage was lower for the original PCC than for the treated PCC. Despite the kinetics of flocculation being independent of the differences in the PCC samples, the flocs compactness at the end of flocculation was higher in the case of the original PCC, resulting in more resistant flocs to shearing. The results showed that the PCC characteristics affect mainly the optimum flocculant dosage, the flocs structure and, thus, the flocs resistance and their reflocculation capability.

Keywords: Cationic polyacrylamide; Flocculation; Laser diffraction scattering; Mass fractal dimension; Precipitated calcium carbonate (PCC); Reflocculation

1. Introduction
In the last decade precipitated calcium carbonate (PCC) is gaining preference in relation to ground calcium carbonate (GCC) as filler in the papermaking industry (Chapnerkar, 2004). The PCC production process requires, however, the use of several additives in order to control particle size, shape and surface characteristics and, therefore, the flocculation process and the flocs characteristics, which are critical for adequate retention of the filler during web formation, are also influenced by the presence and properties of such additives (Vanerek et al., 2000; Suty et al., 1996). Indeed, the performance of the polyelectrolytes used as retention aids can be considerably reduced because the flocculation mechanism and, thus, the evolved flocs characteristics depend on the size and surface properties of the PCC particles.

In addition, it is known that the flocculation process is influenced by the flocculant characteristics and concentration (Williams et al., 1992; Berlin et al., 1997; Bremmell et al., 1998; Blanco et al., 2002a). For instance, many studies show that the flocculation mechanism is much dependent on the polymer charge density (Bremmell et al., 1998; Blanco et al., 2005). For very high molecular weights, as the charge density of the polymer increases the bridging mechanism becomes less significant and both the patching and the bridging mechanisms can occur simultaneously (Swerin et al., 1997; Biggs et al., 2000; Blanco et al., 2002a; Rasteiro et al., 2008). Generally, the degree of flocculation and reflocculation (which affect the flocs characteristics, namely their mechanical resistance, and, as a consequence, play an outstanding role on the retention and dewatering process (Peng and Williams, 1994; Shin et al., 1997; Norell et al., 1999; Yoon and Deng, 2004)), depend on the type of predominant flocculation mechanism. The flocs produced by a patching mechanism are more compact and thus more resistant to shear forces (Norell et al., 1999), and reflocculation is also better performed (Norell et al., 1999; Blanco et al., 2002b). The patching bonds are less degraded by shear forces and are more easily re-established after break-
In the case of flocs produced by the bridging mechanism, shear forces cause some polymer degradation and, therefore, the flocs reform only partially and, simultaneously, the aggregate structure is compacted to denser forms by shear-induced reorganization (Spicer et al., 1998). As a consequence, the flocs produced by deflocculation are smaller but stronger than the original ones except when the floculant is in excess (Rasteiro et al., 2008). Therefore, in order to improve the retention of PCC in sheet formation it is important to understand which flocculation mechanisms dominate.

Flocculant concentration not only affects the flocculation mechanism but also the deflocculation and reflocculation processes. Recent studies proved that for lower flocculant concentrations the flocs grow faster and reach a stable size more rapidly (Rasteiro et al., 2008). The "optimum" flocculant concentration corresponds to the largest flocs size obtained at the equilibrium between break-up and formation of flocs. For flocculant concentrations higher than the optimum, the floc size decreases due to electrostatic repulsion or to steric stabilization (Blanco et al., 2002a).

In this paper, the effect of commercial PCC characteristics on flocculation, deflocculation and reflocculation is investigated as a function of flocculant dosage and shear force intensity, at a laboratory scale. The experiments were performed using two PCC samples, one as supplied by the manufacturer and the other after removing most of the additives present at the surface of the original particles. Flocculation was carried out in the presence of a high molecular weight CPAM (cationic polyacrylamide) with very high charge density. The light diffraction scattering (LDS) technique was used to monitor flocculation, deflocculation and reflocculation by measuring the floc size distribution with flocculation time (ISO 13320-1, 1999; Rasteiro et al., 2008). The flocs compactness was also evaluated by extracting, from the scattering pattern, the mass fractal dimension of the flocs \( d_f \) (Teixeira, 1988).

2. Materials and methods

In order to perform the flocculation tests, a commercial scalenohedral PCC suspension was used in this study, either as supplied or after a washing process that altered both the aggregation of the mineral particles and their surface properties. For that, the supplied original PCC particles were suspended in distilled water and the suspension stocked during several days as an attempt to remove most of the chemicals, distinct of calcium carbonate and resulting from the additives used in the PCC production, that are present at the particles surface. Then, the water was removed and the PCC dried to obtain a dry powder. In this work, the commercial PCC and the PCC obtained after the cleaning process are referred to as "original PCC" and "treated PCC", respectively. Working PCC suspensions of both original and treated PCC particles were prepared at 1% (w/w) in distilled water and, in order to obtain a good dispersion of the particles, the suspensions were first magnetically stirred at 600 rpm for 40 min and then submitted to sonication at 50 kHz during 15 min. However, probably due to the presence of much more chemicals, the suspension of original PCC has to be stirred for 3 more hours, before use, to obtain a stable PCC suspension which did not change with time.

For both the original and the treated particles, the mean size of the particle aggregates before flocculation was determined by the LDS technique (Malvern Masterziser 2000, Malvern Instruments) and the zeta potential at the particles surface was measured using the Zetasizer NanoZS equipment (Malvern Instruments). Besides, the two PCC samples were also analyzed in terms of the chemical composition through FTIR spectroscopy and atomic absorption spectroscopy.

The flocculant used in this study was a cationic linear dimethylamino-ethyl-acrylate polyacrylamide with a molecular weight around 7.2 \( \times 10^6 \) g/mol and 80% (w/w) of charged groups (Alpine-Floc, BHWM (AQUA+TECH Specialties, S.A.)). For the experiments, a stock solution of BHWM prepared at 0.05% (w/w) in distilled water was diluted, when necessary. Dilutions had to be prepared daily.

To avoid undesirable interferences in the flocculation process, the water conductivity was also controlled and kept in the range from 5 to 8 \( \mu \text{S/cm} \).

The flocculation of the PCC particles was followed by measuring the evolution of the aggregates size, using the aforementioned LDS technique (Rasteiro et al., 2007, 2008). A volume of PCC suspension, prepared as before, was added to 700 mL of distilled water in the equipment vessel until 30% obscuration was observed, and the tests were carried out setting the pump speed to 1400 rpm. With LDS, the obscuration must be kept within certain limits, always above 5% and, ideally, below 20%, in order to obtain a good signal. Indeed, as recently demonstrated, the obscuration is a good control parameter to assess the signal quality and when the obscuration is too low the validity of the results is not guaranteed (Rasteiro et al., 2007). Since the obscuration decreases during the flocculation test, due to the reduction of the number of scattering entities, it was decided to start the tests with an obscuration of 30% with the objective of obtaining, at the end of flocculation, an obscuration higher than 5%.

Tests were conducted at different flocculant concentrations for the two PCC samples. The particle size of PCC was always measured at the start of the test, before adding the flocculant to the suspension. After that, predetermined amounts of flocculant were added at once and the floc size distribution was measured every minute during 14 min, i.e., until the floc size distribution seemed to stabilize. In this study, the optimum flocculant concentration is considered as the one leading to larger flocs after the stabilization period. From the scattering pattern used to determine particle size, it is also possible, with this technique, to monitor the mass fractal dimension of the floc, \( d_f \), during the tests (Teixeira, 1988).

Floc resistance was evaluated using sonication as the source of shearing. The flocs were submitted to sonication directly in the LDS equipment during 30 s at 10 kHz and at 20 kHz. After sonication, the reflocculation process was initiated and followed during a subsequent period of 14 min.

3. Results and discussion

3.1. Characterization of the two PCC samples

The results of the physical and chemical characterization of both PCC samples before the addition of flocculant are summarized in Tables 1 and 2 and Figs. 1 and 2. As can be seen in Table 1, the volume weighted median size (\( d_{50} \)) of the original PCC particles is much larger than that of the treated PCC particles (3.5 and 0.5 \( \mu \text{m} \), respectively) and the corresponding size distribution is also different. In fact, as revealed by the scanning electron microscopy images of Fig. 3, the original
Table 1 – Characteristics of the original and treated PCC particles

<table>
<thead>
<tr>
<th></th>
<th>pH</th>
<th>dp50 (μm)</th>
<th>dF</th>
<th>ζ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original PCC</td>
<td>8.2</td>
<td>3.5</td>
<td>2.4</td>
<td>1.6</td>
</tr>
<tr>
<td>Treated PCC</td>
<td>7.5</td>
<td>0.5</td>
<td>3</td>
<td>−27</td>
</tr>
</tbody>
</table>

dp50, volume weighted median diameter; dF, mass fractal dimension; ζ, zeta potential.

Table 2 – The results of the chemical analysis of the original and treated PCC particles by atomic absorption spectroscopy

<table>
<thead>
<tr>
<th></th>
<th>Ca</th>
<th>Mg</th>
<th>Na</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original PCC</td>
<td>818.70</td>
<td>1.939</td>
<td>0.376</td>
<td>0.115</td>
</tr>
<tr>
<td>Treated PCC</td>
<td>862.16</td>
<td>1.874</td>
<td>0.955</td>
<td>0.366</td>
</tr>
</tbody>
</table>

Fig. 1 – Particles size distribution of the original and treated commercial PCC.

PCC has more and larger aggregates than the PCC submitted to treatment, even after sonication, though many small particles can also be seen. Therefore, the respective median diameter, weighted in volume, is larger. Furthermore, the mass fractal dimension (dF) of the original PCC particles is 2.4 whereas the one of the treated PCC particles is 3, indicating that the former is mainly constituted of aggregates, while in the suspension of washed PCC the primary particles are the dominant ones. In fact, the aggregates of the treated PCC that appear in the SEM image of Fig. 3(b), look as very loose aggregates of individual particles, which are easily dispersed in suspension. These differences are most probably a result of the removal of some chemicals adsorbed at the surface of the original particles, which change the surface charge of the particles and consequently their tendency to aggregation. This fact is proved by the values of the zeta potential (ζ, Table 1)—the lower absolute value of the zeta potential for the original particles reveal that they are more prone to aggregation.

The removal of some chemicals during the washing process is confirmed by the results of the chemical analysis that was carried out. In fact, although having identical FTIR spectra (Fig. 2), typical of calcium carbonate, the original and the treated PCC particles are, chemically, slightly different, as demonstrated by the variation of the percentage of the sodium, potassium and calcium (Table 2).

3.2. Flocculation tests

The aforementioned differences between the original and the treated PCC samples, in terms of particle size, aggregation, zeta potential and chemical composition affected substantially their flocculation behaviour, as shown by the flocculation tests. In order to evaluate the performance of the flocculant, flocculation was processed by adding the flocculant all at once and by following the time course of the process. Figs. 4 and 5 show the evolution with time of the median size of the flocs (dp50) for original and treated PCC, respectively. For each PCC it is possible to identify the optimum flocculant dosage leading to larger flocs at the end of the stabilization period. In the case of the original PCC the optimum flocculant dosage measured is 2 mg/g (mg of flocculant/g of PCC) while for the treated PCC it is 10 mg/g. As expected, much less amount of flocculant is required for the original PCC. Since the particles are larger, the number of particles per unit volume is smaller and, thus, the particle surface area for the polymer to be adsorbed is lower. Moreover, since the zeta potential of original PCC is closer to zero than the zeta potential of treated PCC, the amount of flocculant required for charge neutralization is very low.

From a kinetic point of view, the characteristics of the PCC do not affect the process significantly when we compare the kinetic curves for the optimum flocculant dosages. This result is expected since, according to other findings, the flocculation kinetics is mainly dependent on the flocculant characteristics and on the flocculation mechanisms involved (Rasteiro et al., 2008). With the flocculant BHMW, which compared to other commercial flocculants has a high molecular weight and a very high charge density, the patching and the bridging mechanisms occur simultaneously but, due to a competition effect, as the flocculant concentration increases the adsorption rate decreases and aggregation of particles proceeds increasingly by the patching mechanism (Rasteiro et al., 2008). So, for both samples at the optimum flocculant concentration, patching
must be the dominant mechanism. For higher concentrations, the kinetics is too slow and flocculation can even be prevented due to excess of flocculant around the particles.

Although the optimal amounts of flocculant required by the two types of PCC are significantly different, the maximum aggregate sizes are similar in both cases: 50 μm for the original PCC (Fig. 4) and 55 μm for the treated PCC (Fig. 5). Moreover, in both cases, the particle size distribution at the end of flocculation is identical for the optimum flocculant dosage (Fig. 6). However, the flocs at the end of flocculation are significantly different in terms of fractal dimensions, as reported in Tables 3 and 4. The higher mass fractal dimension of the flocs obtained from original PCC is indicative of a denser flocs structure and corresponds to more PCC particles per floc. In fact, for the original PCC, each starting particle was already an aggregate. Tables 3 and 4 also show that the mass fractal
dimension values increase with the flocculant concentration, corresponding to an increasing predominance of the patching mechanism, which produces denser flocs (as demonstrated in a previous study (Rasteiro et al., 2008)). For the treated PCC, $d_F$ is higher for 2 mg/g of flocculant, but this is perhaps due to the fact that, for such a low concentration, flocculation is quite reduced.

3.3. Deflocculation and reflocculation tests

At the end of the flocculation process the flocs were submitted to sonication at 10 and 20 kHz in order to break them and to study the eventual subsequent reflocculation. The evolution with time of the median flocs size during deflocculation at 10 kHz and reflocculation is shown in Figs. 7 and 8 for the original PCC and the treated PCC, respectively. Since, the flocs corresponding to the treated PCC are more open (lower fractal dimension), as mentioned before, they are weaker and less resistant to shearing actions. Naturally, when sonication is made at 20 kHz the break-up of flocs is more extensive.

The percentage of the flocs break-up has been computed as the ratio of the difference between the initial and the final flocs size after shearing and the size of the flocs at the end of flocculation. Moreover, the extension of reflocculation was evaluated by the ratio of the difference between the flocs size after reflocculation and after shearing and the flocs size after shearing.

The resistance of the flocs of the treated PCC is more dependent on the flocculant concentration than in the case of the original PCC. This must be related to the fact that the final flocs size is also more dependent on flocculant concentration when treated PCC is used. Larger flocs are more susceptible to breakage. Once again, this is the result of the differences in the initial characteristics of the PCC particles (the original PCC particles are already quite compact aggregates of smaller particles).

For both PCC samples reflocculation increases with the flocculant concentration and is also more extensive in the case of the treated PCC (Tables 5 and 6). Due to floc fragmentation, free particle surface where the flocculant polymer can be adsorbed again is created. The higher the concentration of the flocculant the higher the number of bonds that can be established between fragments, thus intensifying the degree of reflocculation. In general, reflocculation is higher for the treated PCC flocs. Since much more polymer is required to flocculate the treated PCC, more broken bonds at the end of the shearing action are available to be restored in the reflocculation process. Moreover, since breakage is higher for the treated PCC flocs more free particle surface for polymer re-adsorption is available in this case.

The mass fractal dimension at the end of reflocculation is higher than before breakage and is higher for the lowest concentrations (see Tables 3 and 4). In fact, when the polymer is not in excess, reflocculation can only occur through bonds that have been partially degraded, and aggregation corresponds to particles reorganization which results in denser flocs. On the contrary, when the polymer is in excess, the particles reorganization is more difficult because extra polymer chains are free to create new bonds leading to flocs more similar to the original ones. Moreover, when comparing the reflocculated aggregates produced with the two PCC samples, those corresponding to the original PCC are more compact (higher fractal dimension), again, in accordance with what has been discussed before.

4. Conclusions

This study confirms that the presence of additives in suspensions of commercial PCC, namely at the surface of the particles, greatly affects their flocculation process and the resulting flocs structure. The knowledge of the flocs characteristics, particularly the flocs size, mechanical strength,
structure and reflocculation capabilities, is essential in order to ensure the adequate quality when PCC is used as filler in the papermaking industry.

The results show that the initial particle size distribution of the filler is an important parameter to define the optimum flocculant concentration. As the filler particle size increases a lower amount of flocculant is necessary to reach the optimum flocculant dosage. The zeta potential is also a parameter to consider: as the absolute value of the charge at the particle surface decreases, the amount of flocculant to reach the optimum flocculant dosage decreases as well.

The kinetics of the flocculation process is not much influenced by the PCC characteristics. However, the flocs structure and thus the flocs compactness are affected by PCC characteristics such as initial particle size and charge. Indeed, larger particles originate denser flocs with higher mass fractal dimensions at the end of flocculation, and therefore, more resistant to shear forces. It may be that if the initial particles of the filler are already dense aggregates of finer particles, the resistance of the final flocs can increase. The break-up of flocs is not so pronounced in this case but, on the other hand, a lower reflocculation capability exists. After reflocculation, the flocs produced with the larger PCC particles continue to have mass fractal dimensions higher than the flocs produced with the smaller PCC particles. It must be stressed, however, that, in general, flocs become more compact after breakage and reflocculation.

A careful evaluation of the properties of the final flocs and of how they correlate with the characteristics of the initial PCC particles (size, shape and surface properties) is of most importance to the control of filler retention in paper production. Thus, in summary, the study conducted alerts us for the need to examine carefully the handling and addition strategy of the PCC used in the flocculation stage, in paper production, since it can alter, dramatically, the characteristics of the PCC particles, and consequently influence the flocculation process itself.

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