Effect of Water Cationic Content on flocculation, flocs resistance and reflocculation capacity of PCC induced by polyelectrolytes

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ABSTRACT

In papermaking, mill water closure may result in a significant increase of inorganic salts in the white water. The effect of these contaminants on the performance of retention aids was evaluated, in this study, through flocculation of Precipitated Calcium Carbonate (PCC) with three very high molecular weight cationic polyacrylamides (C-PAM) of medium charge density and with different degrees of branching. Furthermore, flocs resistance and reflocculation capacity was also investigated when

1

different types of shear forces were applied. Tests were carried out in distilled water and in industrial water containing a high concentration of cationic compounds. The flocculation, deflocculation and reflocculation processes were monitored by evaluating particle size distribution using a light diffraction spectroscopy technique. Additionally to the effect of the cationic content of the medium, the influence of the flocculant dosage and degree of polymer branching were also studied. The effect of these parameters on the flocs structure was estimated by determining both the mass fractal dimension and the scattering exponent of the aggregates. The results show that the presence of inorganic salts affects significantly the performance of the polyelectrolytes. The flocculation kinetics is faster but the required flocculant dosage is higher when the suspending medium is industrial water. The cationic entities affect also the flocs structure because they reduce the reconformation of the polymer during flocculation. Additionally, in industrial water, flocs become more resistant and this effect is more pronounced as the flocculant branching decreases. In the case of the linear polymer, this effect is not so obvious because reconformation is less pronounced due to its molecular structure. Reflocculation capacity of flocs is very reduced both in distilled and industrial water.

INTRODUCTION

In papermaking, polyelectrolytes are widely used as retention aids.[1-4] The efficiency of these polymeric additives depends on several factors namely flocculant characteristics (structure, molecular weight, charge density and concentration), characteristics of the suspended particles (size and charge density), characteristics of the suspending medium (pH, conductivity and ionic charge) and contact time and turbulence intensity, among others.[2,3,5]

It is well reported in the literature that the charge density of the polyelectrolyte and its structure are factors that significantly affect flocculation because they determine conformation of the polymer when adsorbed on the particle surface.[5,6] In the case of high molecular weight C-PAM (cationic polyacrylamides) of medium charge density, studies prove that flocculation occurs by the bridging

2

mechanism.[4,7,8] The polymer concentration is also an important parameter since the rate of adsorption depends on the amount of polymer that reaches the particle surface.[9] Tadros (2005) proposed the "diffusion-controlled adsorption kinetics model", stating that adsorption dominates when the surface concentration of polymer is lower than the equilibrium concentration, whereas desorption is the ruling phenomena when the surface concentration is higher than the equilibrium concentration.[9] La Mer and Healy (1963) have shown that when flocculation occurs by the bridging mechanism the equilibrium concentration is reached when the polymer surface coverage is 50%.[10] Moreover, a repulsion effect between particles can coexist due to the excess of polymer concentration.[1,7]

Concerning the suspending medium, many studies demonstrated that the presence of electrolytes can affect the performance of the retention aid.[8,11-14] For example, Hulkko and Deng (1999) found that single C-PAM systems and microparticle retention aids systems were significantly affected by the increase of electrolyte concentration due to the salting-out effect.[12] Studies performed by Stemme and co-workers (1999) have also indicated that the increase of the ionic strength affects the performance of the microparticle retention aids systems.[8] More recently, Stoll and Chodanowski (2002) have shown the influence of the polymer chain stiffness and of the ionic concentration on polymer adsorption by using Monte Carlo simulations.[13] They found that better adsorption of the polymer was promoted by decreasing the chain stiffness or by decreasing the ionic concentration.[13] In these cases, high concentrations of dissolved inorganic compounds may affect the conformation of the polymer chain due to the salting-out effect thus reducing the polymer's bridging capability.[12] Consequently, these changes in polymer conformation result in alterations in the flocs characteristics and flocculation kinetics. Additionally, Vanerek and co-workers (2000) observed that the impurities of the water (anionic substances) affect the surface charge of the precipitated calcium carbonate (PCC).[15] These impurities can adsorb on the PCC surface that becomes more negative.[15]

Since the closure of the process water circuits results in a significant increase of the inorganic salts in water,[12] it is essential to know how this cationic content affects the flocculation process and, thus, the retention capacity of the flocculant. However, the effect of electrolytes on flocculation has been mainly

studied on the performance of retention aids systems with linear polymers. Since the polymer structure is a factor that affects both flocculation and flocs characteristics it is also interesting to study the effect of the ionic strength on branched polymers performance.

Additionally, flocculated suspensions are normally submitted to high shear forces (shear rate higher than 1000 s^{-1}) in the wet end of a paper machine where turbulence is high to favor formation of the paper sheet.[16] Under these shear conditions, the initial flocs are usually broken up but the suspension can partially reflocculate when the shear forces decrease.[17] Resistance of flocs and reflocculation capacity depend also on the flocculants characteristics. Indeed, the strength of flocs depends on the nature of the interactions between particles and on the flocs density,[18,19] and reflocculation depends on the predominant flocculation mechanism.[7,20] Since the reflocculated suspension is involved in the sheet formation stage, it is essential to understand both the flocculation and reflocculation processes to optimize and control the industrial process.

Recent studies have shown that Light Diffraction Spectroscopy (LDS) is a useful and powerful technique to monitor the dynamics of flocculation and to evaluate the effect of the flocculant characteristics and dosage.[21,22] In another paper, it was also demonstrated that this technique can be used to evaluate the deflocculation and reflocculation processes, when flocs are submitted to mechanical forces (sonication) or to hydrodynamic shearing.[23] Furthermore, LDS not only allows the determination of the aggregate mean size and size distribution, but gives also the mass fractal dimension of the flocs, d_F.[4,24] This mass fractal dimension provides a mean of expressing the degree to which primary particles fill the space within the nominal volume occupied by an aggregate: for solid non-porous particles $d_F = 3$ and for porous particles $1 < d_F < 3$.[24] In addition, when aggregate restructuring occurs the aggregate structure is no longer fractal. Restructuring takes place at large length scales and information about flocs structure is provided by the so called scattering exponent, SE, that is also determined from the scattering pattern.[24] Biggs *et al.* (2000) indicate that scattering patterns at small length scale refer to the scattered light from primary aggregates whereas at large length scale they correspond to the light scattered from secondary aggregates that resulted from the aggregation of the primary ones.[4] It is, therefore, a

convenient parameter to characterize the density of the flocs.[24] It is well known that flocculation kinetics is influenced by the fractal nature of the aggregates since the collision radius depends on the fractal dimension of the floc[25] thus, fractal dimension has to be taken into consideration when analyzing and modeling the flocculation process.

The aim of this study is to understand the effect of the ionic content of the suspending medium on the flocculation process, namely on the flocculation kinetics and floc structure (through d_F and SE determination). Furthermore, the effect of the water ionic content on flocs resistance and reflocculation capacity was investigated. Flocculation, deflocculation and reflocculation studies were performed in distilled and in industrial waters, varying flocculant dosage and flocculant branching. The first part of this paper presents the results obtained in distilled water. In the second part of the paper, results obtained in industrial water were gathered and were compared with those obtained in distilled water. In addition, the effect of the polymer concentration and of the polymer branching were discussed for both distilled and industrial water tests.

In all the tests, the LDS technique was used to study the flocculation, deflocculation and reflocculation processes. Additionally, zeta potential measurements have been carried out as the flocculation progressed, since a variation in this parameter gives an indication of polymer reconformation, as mentioned by several authors.[5,26,27] Here, only results for the flocculation of PCC in the presence of three high molecular weight and medium charge density (50%) cationic polyacrylamides with different degrees of branching will be presented.

MATERIALS AND METHOD

Materials

The industrial PCC suspensions were prepared at 1 % (w/w) in distilled water and in industrial water (white water from the industrial plant).

The suspension was firstly agitated using magnetic stirring and then submitted to sonication at 50 kHz during 15 minutes to obtain a good dispersion of the PCC particles. The pH of the PCC suspension in these conditions was 7.5, the median size of the particles was 0.5 μm and the zeta potential of the particles was -30 mV in distilled water and -37 mV in industrial water.

Three new C-PAM emulsions of very high molecular weight, developed and supplied by AQUA+TECH, were used in this study: i) Alpine-Floc[TM] E1, a linear polyacrylamide with a molecular weight around 1.2×10^7 g/mol and 50% (w/w) of groups charged; ii) Alpine-Floc[TM] E1+, a low branched polyacrylamide with a molecular weight around 1.3×10^7 g/mol and 50% (w/w) of groups charged; iii) Alpine-Floc[TM] E1++++, a highly branched polyacrylamide with a molecular weight of 1.2×10^7 g/mol and 50% (w/w) of groups charged. The cationic monomer in all the polymers is dimethylamino ethyl acrylate. Flocculant solutions were prepared daily with distilled water at 0.1% (w/w).

Flocculation tests were performed both in distilled water and in industrial water. Before use, the suspended material of the industrial white water were removed by microfiltration. The main quantifiable difference is the ionic content of both the distilled and the industrial waters and, consequently, the value of the conductivity (see Table 1). The ionic content was determined by Atomic Absorption Spectroscopy (AAS) and by ion chromatography.

Methods

The flocculation of the PCC particles was monitored by measuring the size of the aggregates by light diffraction scattering (LDS) in a Malvern Mastersizer 2000 (Malvern Instruments). The 1% (w/w) PCC suspension was diluted with water to a concentration of 0.05% (w/w) corresponding to 70% obscuration. The obscuration should be kept around 20% for good signal quality. However, since obscuration decreases during the flocculation test due to particle aggregation, it is necessary to start the tests with a higher obscuration value, as demonstrated in previous studies,[22] to guarantee that at the end

of flocculation the obscuration is always above 5% (below this value the signal quality starts to be poor).

The same methodology described in previous papers was used to study flocculation, deflocculation and reflocculation, both in distilled and industrial water.[22,23]

Both flocculants were tested with different concentrations close to the optimum dosage as determined by the pre-screening methodology developed by Blanco.[28] The size of the PCC particles was measured before the addition of the flocculant to the suspension. For the studies of flocculation dynamics, the flocculant was added at once and the flocs size was measured every minute during 14 minutes (at this time the flocs size was stabilized).

The flocs resistance was evaluated using two different types of shear forces. The first approach was to submit the flocs to sonication at 20 kHz during 30 seconds. This mechanical shear force was directly applied to the suspension in the LDS dispersion unit, after flocculation. The second method involved the application of hydrodynamic shear forces during one minute by increasing the recirculating peristaltic pump speed in the equipment from 1400 rpm to 2200 rpm, which corresponds to increasing the shear rate in the flow tubes from 312 s^{-1} to 708 s^{-1}, respectively. After shearing tests, the shear force was restored to the initial value to allow for the reflocculation process to take place, which was then monitored during 5 minutes.

The mass fractal dimension of the flocs during the flocculation process and at the end of reflocculation was also computed from the scattering pattern used to determine particle size. The individual particles could be considered to follow the Rayleigh-Gans-Debye approximation (particles smaller than 1.0 μm and refractive index 1.572).[24] Since secondary aggregates resulting from the aggregation of primary aggregates can be formed, the so called scattering exponent,[24] corresponding to the region of the larger scattering aggregates (lower diffraction angles), was also computed from the scattering pattern.

The zeta potential of the flocs was also measured in the course of flocculation, using the Zetasizer NanoZS equipment (Malvern Instruments), at three moments: one minute after the addition of the flocculant, 7 minutes after the addition of the flocculant and at the end of flocculation (14 minutes).

RESULTS AND DISCUSSION

Experiments with distilled water

The time evolution of the PCC median floc size in distilled water is illustrated in Figures 1 to 3 for E1, E1+ and E1++++ respectively, for different concentrations (mg of polymer/g of PCC). It can be observed that the floc size increases with time up to a maximum and decreases, thereafter, due to aggregate restructuring. It was demonstrated in a previous study that for flocculants of medium charge density the flocculation occurs mainly by the bridging mechanism.[22] Therefore, after adsorbing at the particle surface, the polymer chains start to re-arrange, resulting in aggregate re-conformation and decrease in the flocs size, as observed also by others authors. [29-31] This decrease is more notorious for the optimum concentrations of each polymer, respectively 4 mg E1/g PCC, 12 mg E1+/g PCC and 8 mg E1++++/g PCC (Figures 1 to 3). When the polyelectrolyte was in excess the flocculation kinetics was much slower due to the diffusion barrier and to the repulsive forces. Consequently, aggregates had enough time to reach a stable configuration during the aggregation step and no or little reconformation occurred.

Additionally, reconformation is less evident in the cases of both the linear (E1) and the highly branched polymer (E1++++). In fact, for the linear polymer (E1), flocculation kinetics was faster and, moreover, the amount of polymer necessary to perform flocculation was lower (Figure 1). During the first seconds the polymer adsorbed at the particle surface in a flat configuration and, under these conditions, the polymer chain had less space for reconformation than in the case of the branched polymers (Figures 2 and 3). For the highly branched E1++++, the radius of gyration of the polymer (size of the polymer chain) is smaller and reconformation becomes also more difficult.[4,32]

8

Furthermore, the polymer structure also affected the flocs size at the maximum in the flocculation curve. The linear polymer (E1) produced smaller flocs than flocs produced with the branched polymers. The larger flocs were produced by the low branched polymer (E1+). A linear relationship between the flocs size and the polymers branching degree does not exist probably due to the reasons explained before (kinetics and polymer conformation). It is reasonable to assume that flocs size and polymer structure must be related. Therefore, since the linear polymer adsorbs in a flatter configuration at the particle surface, the space between particles is small and smaller flocs are obtained. In the case of the highly branched polymer, the space between particles is also small but now due to the smaller polymer radius of gyration. That is, there are different factors related with the polymer characteristics that condition the flocs size.

The influence of the polymer structure on both the flocculation kinetics and the flocs structure is confirmed by the mass fractal dimension and scattering exponent values. The values of the mass fractal dimension (d_F), that correspond to the structural characteristics of the primary flocs, and of the scattering exponent (SE), related to the secondary aggregates, are presented in Table 2. In all tables, results for the optimum dosage are highlighted in grey background. The first conclusion is that the polymer concentration affected the fractal dimension and the scattering exponent in the same way. In general, for the optimum flocculant dosage, flocs are less compact (d_F and SE are smaller) at the maximum in the kinetic curve where flocs produced are larger. Flocs at the end of flocculation are more compact (d_F and SE are higher) than at the maximum in the kinetic curve due to restructuring of polymer chains, but the compactness decreases as the polymer concentration increases.

The trends detected in Table 2 reinforce the conclusion that the degree of branching of the polymer affected the flocculation process and the flocs structure. Indeed, comparing results obtained for the optimum flocculant dosage, both the mass fractal dimension and scattering exponent at the maximum in the kinetic curve indicate that flocs produced with E1 and E1++++ have a denser structure. This agrees with what was observed before in relation with flocs size. Moreover, the larger E1++++ flocs have got a more open structure than flocs produced with E1 (d_F and SE are lower for E1++++ than for E1).

At the end of flocculation, the differences in the d_F values are small probably due to flocs restructuring. However, comparing results for the corresponding optimum flocculant dosage, the scattering exponent value is higher for flocs produced with E1+ and lower for flocs produced with E1++++. Furthermore, the increase in d_F and SE during flocculation is small for both E1 and E1++++. These two facts confirm that the polymer reconformation was less extensive in the case of E1 and E1++++. Additionally, in the case of E1++++ the flocs structure is much more open at the maximum in the kinetics curve than for E1 and, thus, the degree of flocculant reconformation was not enough to reach the same degree of compactness at the end of flocculation, as that obtained with E1.

The decay of the zeta potential values during flocculation in distilled water, as shown in Figure 4a, for the three flocculants, is also an indication of the polymer chains restructuring. This agrees with findings of others authors [5,26,27] and is most certainly due to the rearrangement of polymer chains that leads to a stronger attachment of the positive sections to the particles and, thus, leaves less free positive branches.

Regarding the different values for the optimal concentration for the three polymers, the larger difference can be found between the linear and the branched polyelectrolytes. In fact, as mentioned before, the linear polymer tends to acquire a flatter configuration on the particles surface, and thus coverage is obtained with a smaller dosage of polymer. In the case of both E1+ and E1++++ the dosage necessary is higher, being smaller for E1++++ than for E1+. The higher number of branches in the chain of E1++++, though giving rise to a lower radius of gyration, renders the charged sections of the chain more accessible to the particles, and therefore leads to an easier attachment of the polymer to the particles. This is why the dosage is lower than the one of E1+. Even being bridging also the predominant mechanism the E1++++ polymer chains do not protrude so much from the particle surface and tend to have again a flatter configuration than the one occurring with E1+. This agrees with the more open structure of the E1+ aggregates, at the maximum of the kinetics curve as discussed above.

With regard to the breakage tests, it is evident in Figures 5 and 6 that the flocs size rapidly decreases when they are submitted to sonication. Breakage of flocs indicates that the polymer chains detach from the particles surface resulting in rupture of bonds between the particles in the aggregate. The break-up

10

by sonication of the flocs formed with both E1+ and E1++++ was not much dependent on the flocculant concentration, as shown in Table 3. However, the degree of branching seemed to affect the floc resistance. In fact, flocs produced with E1+ and E1++++ offered the same resistance to sonication but were less resistant than flocs produced with E1. This fact does not correlate well with the d_F and SE values calculated at the end of the flocculation process. Size seems to be the factor that most affects the resistance to breakage, since the main difference between the three polymers, at the end of flocculation, is on the flocs sizes (Figures 1 to 3). The flocs sizes of aggregates produced with E1+ and E1++++ are similar, while flocs produced with E1 reached a much smaller size. Consequently, as the flocs size increases, flocs resistance decreases.

The reflocculation degree of the flocs was very small or practically inexistent whatever the flocculants used. Figures 5 and 6 show the reflocculation behavior for E1 and E1+ respectively. In fact, as described before, the predominant flocculation mechanism with E1, E1+ and E1++++ is by bridging. Flocs formed by bridging mechanism are strong; however, if they breakup the polymer degrades and the reflocculation process becomes more difficult.[16,33,34] As described in the literature,[16,33,34] the original polymer bonds are not able to reform to their previous extent, and, moreover, the polymer chains at the particle surface reconform, increasing coverage of the surface and inhibiting reflocculation with fresh polymer. Regarding the flocs structure at the end of reflocculation, it is difficult to detect significant differences with flocculant concentration due to the small reflocculation capacity (Table 4). Nevertheless, d_F values of reflocculated flocs are slightly higher than before breakage. This indicates a more compact structure of the reflocculated flocs. Reflocculated flocs structure followed the same trend as described for flocs structure at the end of flocculation, i.e., flocs produced with the highly branched polymer are slightly less compact upon reflocculation.

The results of Table 3 show also that the resistance of aggregates submitted to increasing hydrodynamic shearing forces was not dependent on the flocculant concentration, following the same trend as detected when sonication was applied. Nevertheless, the decrease in the flocs size under hydrodynamic shearing was less notorious than under sonication (Figures 5 and 6). As described in a

previous study, [23] flocs size decrease during deflocculation when the pump speed increases must be due to flocs erosion, while sonication promotes flocs fragmentation, which explains the different degree of breakage for the two cases. Additionally, neither the branching nor the floc size seemed to affect floc resistance in the case of hydrodynamic shearing.

Reflocculation of hydrodynamically sheared flocs was also practically inexistent (Figures 5 and 6). The bonds that break during shearing refer to the detachment of very small particles and do not lead to reflocculation.[23]

At the end of reflocculation (Table 4), similar conclusions can be made concerning the structure of reflocculated flocs that were broken by either sonication or hydrodynamic shear. However, when the hydrodynamically sheared flocs were reflocculated the change in d_F (before and after breakage) was not so pronounced as for the sonicated ones.

Experiments with Industrial Water.

Similar flocculation tests were conducted using industrial water as the suspending medium. The results are shown in Figures 7 to 9 for E1, E1+ and E1++++, respectively. The kinetics of the flocculation process in industrial water followed a pattern that was similar to the pattern of the flocculation in distilled water, though slightly faster in the industrial white water. In fact, it is known that the thickness of the double layer surrounding the particle surface depends upon the concentration of ions in solution and can be calculated from the ionic strength of the medium: the higher the ionic strength, the more compressed the double layer becomes. Therefore, the thickness of the double layer of the PCC particles was reduced due to the high cationic content of the white water and this contributed also to the flocculation of the PCC particles. Flocculation, though being mainly due to bridging, is facilitated by the decrease of the repulsive forces and this is why velocity is slightly higher.

Moreover, with industrial water, restructuring was less effective when using E1+ and E1++++ since the flocs size decreased less. This can be explained by a salting-out effect caused by the high cationic content of the industrial water; the polymer adopted a more coiled structure and, thus, the capability for

reconformation was reduced.[12,14,35] In fact, the zeta potential did not decrease during flocculation (Figure 4b), therefore confirming the reduction of the polymer reconformation capability as explained previously. The polymer chain of E1 was also affected by the salting-out effect but the flocs size decrease during flocculation was slightly more pronounced than in distilled water (Figures 1 and 7). Considering that the polymer chain adopts a more coiled structure in the presence of salts, chains of E1 in industrial water have a similar behavior as E1+ in distilled water, i.e., becomes more flexible. Moreover, before the maximum in the kinetic curve, due to the very fast adsorption of this polymer at particle surface particles did not have enough time to reach stable positions. As a result, there was enough space for restructuring of the polymer chain to occur afterwards, with the consequent decrease in flocs size as observed in Figure 7. At the maximum in kinetic curves, there are still polymer tails and loops at the particle surface and certainly because of that the zeta potential did not decay during flocculation (Figure 4b).

For flocculation tests in industrial water, higher polymer dosages were, in general, required in agreement with the lower zeta potential of the PCC particles (Figure 4). As observed by Vanerek and co-workers (2000), since the industrial water contains more contaminants, the surface charge of the PCC particles in industrial water is more negative than in distilled water and thus more polymer is necessary to neutralize those charges.[15] Studies performed by Shubin and Linse (1997) and Stoll and Chodanowski (2002) have shown that polymer adsorption is promoted by decreasing the salt concentration.[13,14] Consequently, in industrial water, a larger amount of polyelectrolyte was needed to obtain the same particle surface coverage with the polymer. The optimum flocculant dosage for E1+ continued to be higher than for E1++++ and again was the lowest for E1 (35 mg/g, 30 mg/g and 20 mg/g, respectively). It is interesting to note that some tests made with a "simulated industrial water" (distilled water to which exactly the same cations as in the industrial water were added) did not show the same trends as with the real industrial water. So, what is determinant for the results is the higher negative charge of the PCC particles in the white water.

The high cationic content of the industrial water also alters the effect of branching of the polymer in the flocs characteristics. The flocs obtained in distilled water with E1+ are in general larger while in industrial water the opposite happens. E1++++ is less affected by the salting-out effect than E1+ due to its smaller gyration radius. Concerning E1, the polymer has a more coiled and flexible structure, leading to higher distances between particles and resulting in larger flocs than in distilled water.

These effects are also reflected in the fractal dimension and scattering exponent values shown in Table 5. For the optimum concentrations, the structures of flocs produced by E1+ and E1++++, at the maximum in the kinetic curve, are denser in industrial water than in distilled water as a result of the more coiled structure adopted by the polymers. Furthermore, these differences are again less pronounced for E1++++. For E1, the high decrease of the SE value from distilled to industrial water indicated that flocs structure became more open in industrial water. Indeed, as explained before, the salting-out effect allows an increase of the polymer chain flexibility and thus produces larger flocs with a more open structure than in distilled water. This difference is more evident for the secondary aggregates (by comparison of the SE values) since secondary aggregates were still very loose due to the very fast aggregation kinetics in industrial water.

At the end of flocculation, the behavior is very different from that observed in distilled water. Indeed, in distilled water both primary and secondary flocs have a denser structure at the end of flocculation than at the maximum in the kinetic curve, due to flocs restructuring. In industrial water, the secondary aggregates are effectively denser at the end of flocculation but primary aggregates become slightly less compact. Reconformation occurs mainly at the secondary aggregates level because primary aggregates were already quite compact at the maximum of the kinetic curve.

Despite these differences in the flocs structure, similar trends were observed in distilled and in industrial waters concerning to the flocculant concentration. As the flocculant concentration increases the mass fractal dimension and the scattering exponent decrease.

The effect of sonication and of pump speed on flocs resistance in industrial water is similar to the one observed in distilled water (Figures 5 and 6, Tables 6 and 7). Results in Tables 3 and 6 show that the

resistance of flocs produced with E1 and E1++++ is similar in both waters when comparing values obtained for the optimum dosages. However, for the optimum dosage, the flocs produced with E1+ are more resistant in industrial water than in distilled water. Here again, the flocculant branching seemed to have little effect on flocs resistance because the flocs structure at the end of flocculation is similar (Table 5). As in distilled water, it is the flocs size that most affects the flocs resistance. This explains the higher resistance of flocs produced with E1+ which are smaller in size. Flocs produced in industrial water became generally more compact after breakage similarly to those produced in distilled water, mainly when breakage occurred by sonication (Table 7). The secondary aggregates are more compact in industrial than in distilled water (Tables 4 and 7). When the breakage resulted from hydrodynamic shearing (erosion mechanism) the densification was almost negligible.

CONCLUSIONS

The results obtained demonstrate that the degree of flocculant branching and the cationic character of the suspending medium affect significantly the flocculation process and the flocs structure.

Independently of the suspending medium, the optimum flocculant dosage increases as the flocculant branching increases but for the very high branched polymer the optimum dosage slightly decreases.

In distilled water, restructuring of flocs is very high, while, in industrial water, the presence of cationic compounds causes a more coiled structure of the polymer chain reducing its reconformation capability.

Moreover, the high cationic content of the industrial water enhances the flocculation kinetics. Nevertheless, the optimum flocculant dosage becomes higher in industrial water due, again, to the more coiled conformation of the polymer and the presence of contaminants.

Aggregates' structure is dependent on the flocculant branching and on the cationic content of the suspending medium. For the branched polymers and in distilled water, flocs at the maximum in the kinetic curve are larger and less compact as the flocculant branching decreases. The flocs produced with

the linear polymer are the densest and the smallest. At the end of flocculation, flocs are denser than at the maximum in kinetic curve.

In industrial water, flocs at the maximum in the kinetic curve are more compact than in distilled water. This is less pronounced for the more branched flocculant which is less affected by the cationic content of the water. For this flocculant, flocs at the maximum in the kinetics curve are also larger than in distilled water. Furthermore, for the linear polymer and in industrial water, the more coiled configuration of the polymer results in larger and less compact flocs.

At the end of flocculation and in industrial water, there is a distinction between the structure of primary and secondary flocs. Secondary aggregates continue to be denser than those produced at the maximum in the kinetics curve. Nevertheless, primary flocs become slightly less compact indicating that the reconformation of the polymer chain, after the aggregation stage, is reduced in industrial water.

The resistance of flocs is mainly dependent on the flocs size before break up. As the flocs size increases the resistance of flocs decreases. Since flocculation kinetics and flocs size depend on the flocculant characteristics and on the suspending medium, the resistance of flocs also depends on the flocculant characteristics and on the suspending medium.

It can be concluded that highly branched flocculants are less affected by the water cationic content in all the stages, flocculation and break up, thus leading to similar flocs structures independently of the suspending medium.

As a final comment, it is important to stress that when screening flocculants performance and optimizing flocculant dosage for industrial purposes, it is essential to take into account the characteristics of the suspending medium. So, the common practice of using distilled water for the screening tests may lead to erroneous conclusions.

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17

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List of Tables

Table 1. Characterization of distilled and industrial waters.

Water	Ionic content (mg/L)								Conductivity (μS/cm)	pH
	Na^+	Ca^{2+}	Mg^{2+}	Al^{3+}	K^+	Cl^-	SO_4^{2-}	Br^-		
Distilled	0.27	0.27	0.027	-	0.27	-	-	-	4-8	6.4
Industrial	87	23	5.4	0.18	2.9	62	17	3.8	569	7.7

Table 2. Flocs fractal dimension and scattering exponent (distilled water)*.

Flocculant	Concentration (mg/g)	Maximum in the kinetic curve		End of flocculation	
		d_F	SE	d_F	SE
	2	1.45	2.19	1.54	2.55
E1	4	1.33	2.36	1.54	2.47
	8	1.48	2.48	1.51	2.55
	8	1.36	2.05	1.59	2.51
E1+	12	1.13	1.37	1.54	2.56
	25	1.20	2.03	1.31	2.09
	6	1.53	1.74	1.57	2.45
E1++++	8	1.46	1.61	1.52	2.33
	10	1.31	1.97	1.49	2.37

* grey lines refer to the optimum flocculant dosage

Table 3. Flocs break up percentages (distilled water).*

Flocculant	Concentration (mg/g)	Break up (%)	
		20 kHz	2200 rpm
E1	4	39	17
	8	43	17
E1+	12	78	17
	25	77	18
E1++++	8	77	19
	10	65	18

* grey lines refer to the optimum flocculant dosage

Table 4. Flocs fractal dimension and scattering exponent after 5 min of reflocculation (distilled water).*

Flocculant	Concentration (mg/g)	20 kHz		2200 rpm	
		d_F	SE	d_F	SE
E1	4	1.65	2.48	1.61	2.37
	8	1.65	2.51	1.59	2.51
E1+	12	1.60	2.55	1.62	2.56
	25	1.52	2.57	1.43	2.29
E1++++	8	1.75	2.28	1.57	2.29
	10	1.62	2.26	1.59	2.40

* grey lines refer to the optimum flocculant dosage

Table 5. Flocs fractal dimension and scattering exponent (industrial water).*

Flocculant	Concentration (mg/g)	Maximum in the kinetic curve		End of flocculation	
		d_F	SE	d_F	SE
E1	8	1.51	2.47	1.48	2.66
	20	1.40	1.45	1.37	2.64
	25	1.42	1.66	1.17	2.62
E1+	25	1.47	2.12	1.38	2.61
	35	1.45	1.98	1.27	2.60
	40	1.29	1.84	1.06	2.57
E1++++	10	1.44	2.45	1.43	2.60
	30	1.53	1.75	1.30	2.57
	35	1.33	2.26	1.23	2.58

* grey lines refer to the optimum flocculant dosage

Table 6. Flocs break up percentages (industrial water).*

Flocculant	Concentration (mg/g)	Break up (%)	
		20 kHz	2200 rpm
E1	8	40	16
	20	55	5
E1+	25	31	17
	35	40	9
E1++++	10	36	18
	30	60	12

* grey lines refer to the optimum flocculant dosage

Table 7. Flocs fractal dimension and scattering exponent after 5 min of reflocculation (industrial water).*

Flocculant	Concentration (mg/g)	20 kHz		2200 rpm	
		d_F	SE	d_F	SE
E1	8	1.50	2.66	1.52	2.66
	20	1.45	2.65	1.37	2.69
E1+	25	1.46	2.62	1.41	2.68
	35	1.45	2.59	1.23	2.65
E1++++	10	1.51	2.63	1.48	2.62
	30	1.49	2.59	1.30	2.64

* grey lines refer to the optimum flocculant dosage
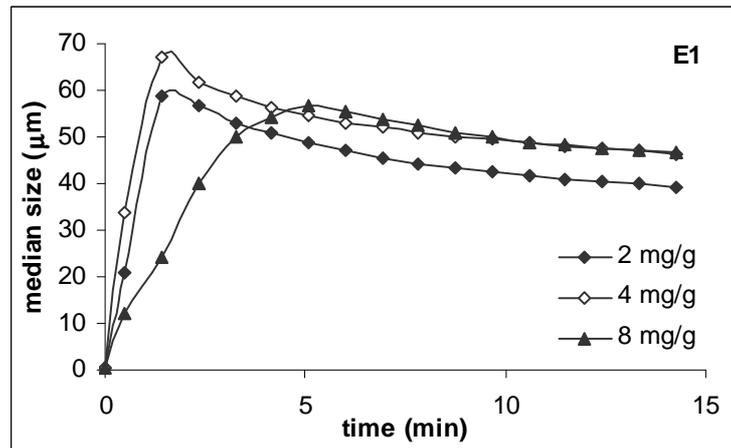
Figure 1. Evolution of the flocs median size during flocculation in distilled water (E1).
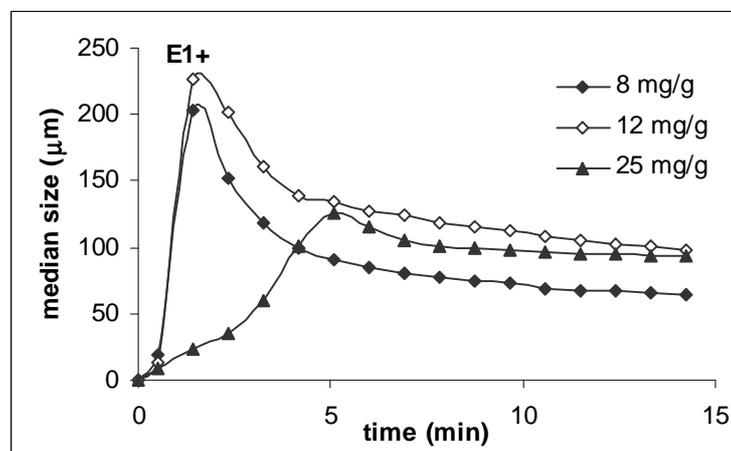
Figure 2. Evolution of the flocs median size during flocculation in distilled water (E1+).
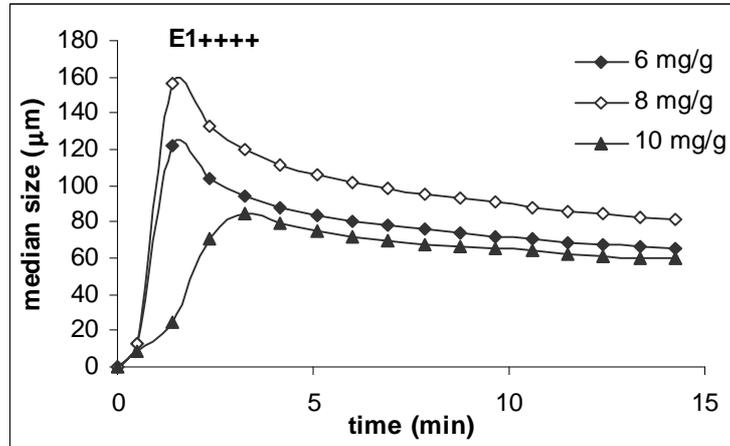
Figure 3. Evolution of the flocs median size during flocculation in distilled water (E1++++).
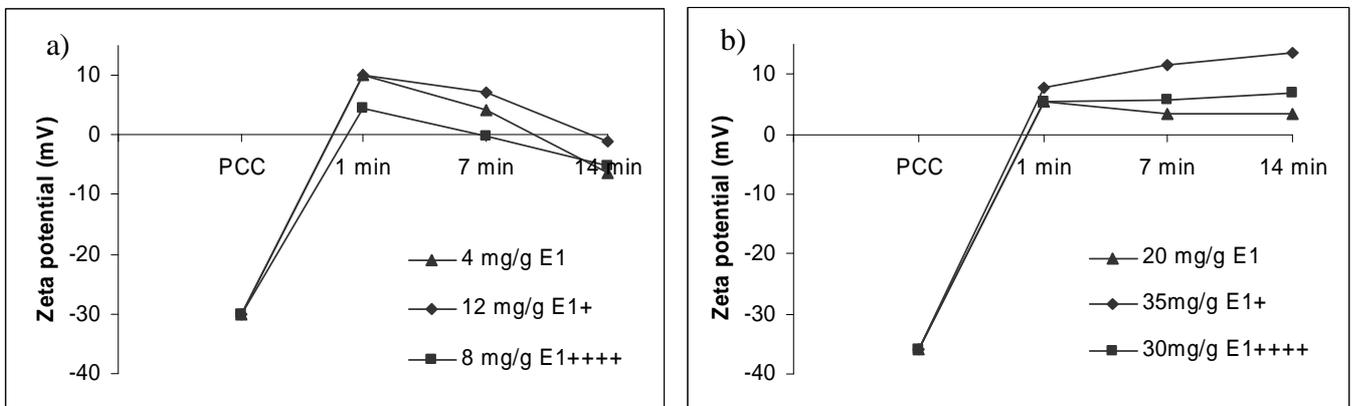
Figure 4. Zeta potential for PCC and for the optimum flocculant dosage at 1, 7 and 14 minutes after

flocculant addition in (a) distilled and in (b) industrial water.
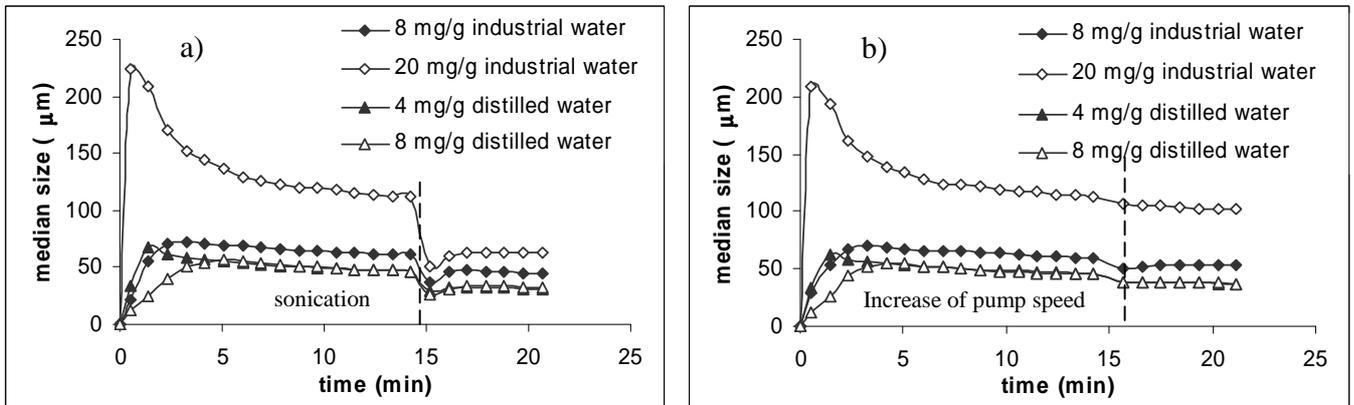
Figure 5. Flocculation with E1, deflocculation and reflocculation after a) sonication and b) increase of

the pump speed (distilled and industrial water).
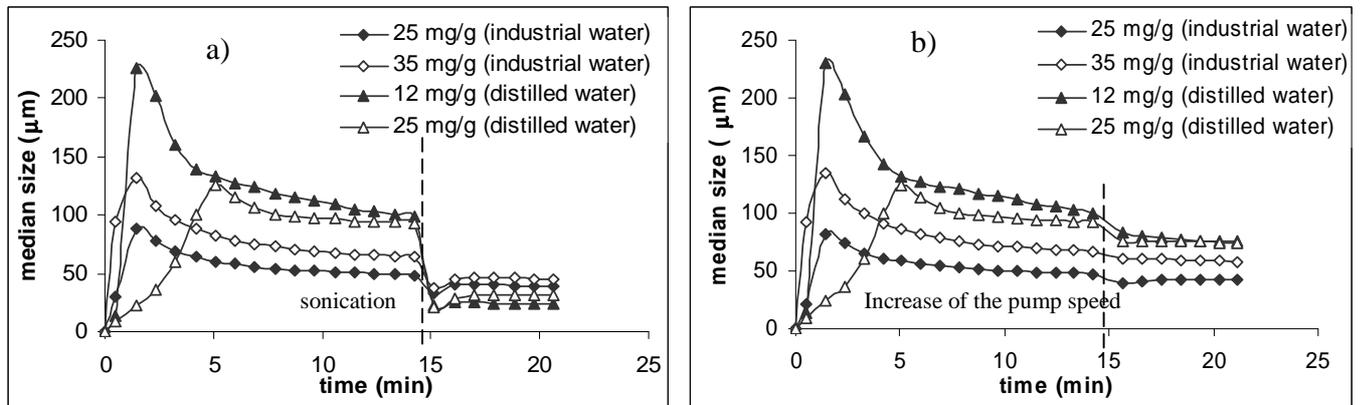
Figure 6. Flocculation with E1+, deflocculation and reflocculation after a) sonication and b) increase of

the pump speed (distilled and industrial water).
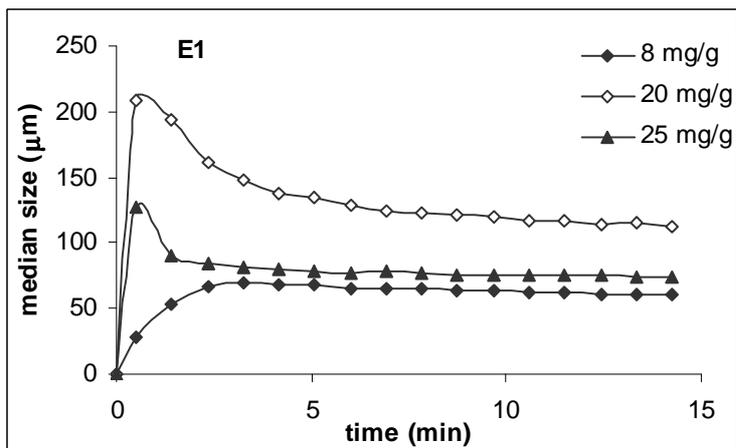
Figure 7. Evolution of the flocs median size during flocculation in industrial water (E1).
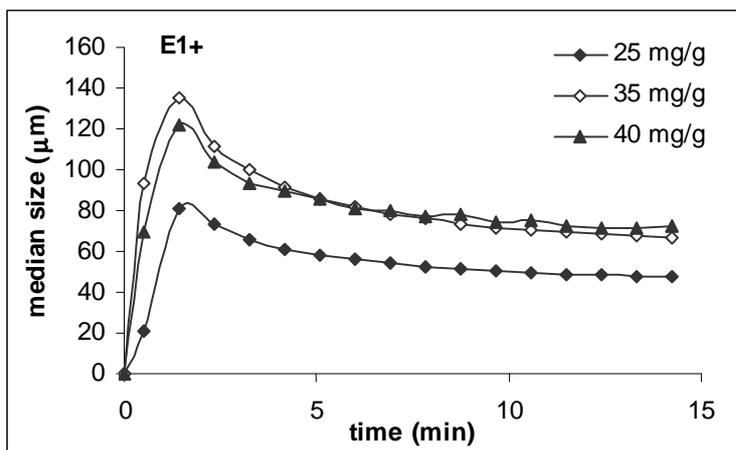

Figure 8. Evolution of the flocs median size during flocculation in industrial water (E1+).
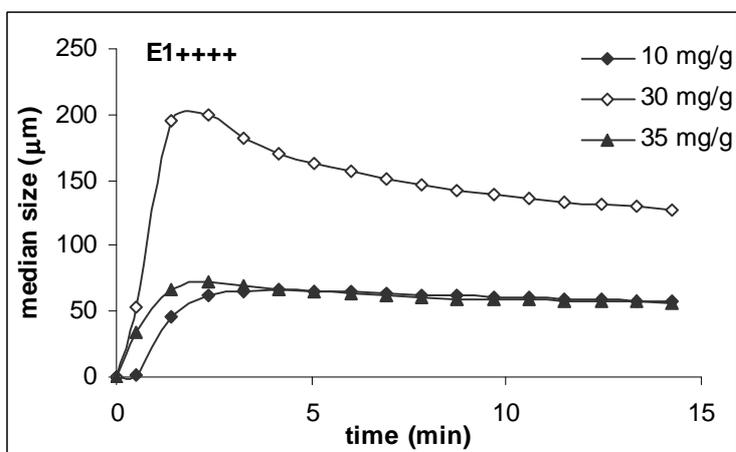

Figure 9. Evolution of the flocs median size during flocculation in industrial water (E1++++).