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# Flocculation kinetics of precipitated calcium carbonate 

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#### Abstract

When the percentage of filler in paper is increased, the optical properties are improved and the production cost lowered. However, fillers weaken paper strength by decreasing the fibre-fibre bonded area. Little is known about the optimum filler floc size or filler floc properties to allow developing optimum paper characteristics. Consequently, the kinetics of aggregation of scalenohedral precipitated calcium carbonate (PCC) filler was studied using various polymers (flocculants, coagulants and dry strength agents). The sodium salt of partially hydrolysed polyvinyl formamide copolymerized with acrylic acid (PVFA/NaAA) or C-starch lead to floc sizes, less sensitive to dosage within a certain range. Results from stability ratios correlate with PCC particle size. The change in particle size measured by photometric dispersion analysis (PDA) correlates well with the change in PCC particle size measured by light scattering/diffraction. Kinetic calculations show the orthokinetic aggregation times to be consistent with the experimental PDA results. The main uncertainty in the orthokinetic times is estimating the effective shear rate. It is proposed that the bridging surface area of PCC particles, the area which can form bonds between PCC particles or aggregates, should be used to study the kinetics of PCC aggregation, and not the total or projected surface area. In polymer induced aggregation, the PCC particle size increases to a plateau value with increasing polymer dosage. Two regions are most pronounced for C-PAM, PVFA/NaAA and A-starch. Region I corresponds to bridging flocculation. Region II is where the particle size reaches a plateau, and not the expected maximum predicted by classical polymer bridging theory or charge neutralisation theory, likely because of a competition between particle aggregation and polymer adsorption.


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## 1. Introduction

The rate of change in the pulp and paper industry is increasing, and additives, other than cellulose fibre, have become essential in making paper. Fillers are the most significant portion of these additives, in terms of weight percent. Typical filler additions range from $3 \%$ to $30 \%$ [1], and can even reach $38 \%$ for certain supercalendered papers [2]. Fillers are insoluble solid particles, added to the papermaking furnish to improve paper sheet optical properties and reduce production costs. While most fillers are naturally occurring minerals, others are manufactured chemically [2]. From the wide selection of fillers on the market, the most common are [1]: kaolin clay, calcium carbonate, titanium dioxide, talc, silica, and silicate. These fillers are divided into two categories: (1) fillers (mineral fillers) that are cheaper than fibre (regular and delaminated clays, natural calcium carbonates, chalk, precipitated calcium

[^1]carbonates and talc) and (2) specialty fillers, more expensive than fibre, for specific purposes (titanium dioxide, precipitated silica, silicates, as well as structured clays) [1]. Fillers can be added to a pulp furnish prior to the headbox, or applied as a coating to the surface of the sheet once formed. Each type of filler has specific characteristics, and fulfills particular functions, however, their role in the pulp and paper industry can be summarized by [1]: (1) to reduce production cost (fibre substitution); (2) to improve optical properties (opacity, brightness); (3) to improve printability; (4) to improve sheet formation; (5) to improve smoothness; and (6) to improve dimensional stability. However, fillers may have unwanted side effects [3]: (1) they reduce mechanical strength (interference with interfibre bonding); (2) they cause abrasion (on wires, blades and printing plates); (3) they impair retention (increase of retention aid dosage); (4) they increase two-sidedness; (5) they reduce stiffness; (6) they increase dusting tendency; (7) they increase the quantity of deposits in the paper machine system; and (8) they require a more complex white water recirculation loop. Some fillers are more detrimental to paper strength than others. When compared at constant total area of filler per mass of paper, the burst strength follows the trend clay $>$ talc $>$ GCC [3]. In a related study, ground calcium carbonate (GCC) and precipitated calcium carbon-
ate (PCC) showed similar strength effects [4] whereas, at a subtler level, it seems that prismatic PCC is less detrimental to strength than scalenohedral PCC [5,6]. PCC is produced in scalenohedral, rhombohedral, and needle shaped or aragonite structures: scalenohedral PCC is the most widely used in papermaking.

For a particular filler type, the smallest size fillers have the most detrimental effect on paper strength $[3,7,8]$ at a constant loading level ( g filler/g fibre). The size distribution within the sheet is unlikely to equal the original size distribution of the filler dispersion. Average particle size, density, size distribution, and aggregate size, are as important as individual particle size, for their effects on paper properties [8]. Interestingly, Bown [8] studied sheet properties with $20 \%$ filler content, using chalk and kaolin having particle sizes from less than $1-12 \mu \mathrm{~m}$, and found that the effect of aggregating the kaolin produced either a rigid, open structure (calcined kaolin) or a flexible, compressible structure (strongly flocculated kaolin) [8]. Recent studies showed the filler distribution in paper sheets to be irregular in the $z$ (thickness) direction [9-11]. This reflects the influences of paper machine design, operational conditions, drainage and wet end chemistry, etc. on the paper quality.

Some authors $[3,12]$ suggest that fillers weaken paper by lowering the fibre-fibre bonded area. While this is the basis of all existing hypotheses of filler-induced paper strength loss, there is little direct evidence to support the concept [3]. If the contribution of filler is removed, the density of most papers decreases with increasing filler content, suggesting less fibre-fibre bonding [3,12]. It is possible that filler particles act as flaws causing local areas of stress, which initiate sheet failure [3]. Lindström et al. [13] showed how the stress concentration level (as determined by life length (Zhurkov approach) measurements) in filled papers (using common clay) decreases when cationic starch is added. Tanaka et al. [12] showed the addition of potato starch improves the strength properties without changing the structure of paper, made solely from kraft pulp, while beating or addition of filler changes the structure. Beazley and Petereit [14] published the most widely quoted model for filler strength effects. van de Ven et al. [15] have shown that filling wet paper, with the use of secondary headbox, decreases the strength of the paper with filler concentration as occurs with conventional paper.

Fillers often form aggregates well before sheet formation, especially in the short circulation loop [16]. These aggregates are weak
and can be broken by shear [17]. Filler aggregation has been studied from the perspective of aggregation prior to being injected in the pulp furnish [18], and to a much smaller extent within the papermaking process. Mill trials, using starch for PCC aggregation, and prior to the addition of PCC in pulp, has also helped to reduce linting and dusting [19]. Lindström and Floren [4] showed the effect of cationic starch wet end addition on sheet consolidation to be larger the smaller the filler particle size. Modgi et al. [19] showed potato and tapioca starches aggregated PCC in distilled and de-ionised water (DDW) at 25 and $50^{\circ} \mathrm{C}$ and process water (PW) at $50^{\circ} \mathrm{C}$. Tapioca starch gave the highest rate of aggregation and aggregate size [19].

Macromolecules adsorbed onto particle surfaces may either stabilize or destabilize the colloidal particle dispersion. The behaviour will depend on the degree of surface coverage, molecular weight, charge density, type of polymer, and polymer state. For partially covered surfaces, the already adsorbed polymer on a given particle may attach to the bare surface on another particle forming particle-particle bridges (bridging flocculation) [20-23]. The bridging flocculation rate is a function of the degree of surface coverage. The classical work of LaMer and Healy [24] predicts a maximum flocculation rate at half coverage. Fleer and Lyklema [25] and Gregory [23] reported that each suspended particle was only partly covered by polyelectrolyte at the point of maximum agglomeration.

Papermaker strategies are to increase the strength of paper at a similar filler level, or an increased filler level, while maintaining paper strength. It can be suggested that increased filler in paper, with filler aggregation, but without affecting paper strength is caused by two effects: (1) a decrease in apparent surface area of the filler particles and (2) a drop in the number of discrete filler particles. Filler aggregation could also increase filler retention by mechanical entrapment.

This paper studies the kinetics of PCC aggregation before adding PCC to the wet end of a paper machine. Various polymers (Table 1) were evaluated for their ability to aggregate PCC and to find the chemistry and conditions that induce an optimum PCC floc size during papermaking. PCC aggregation was studied using particle size measurement, photometric dispersion analysis (PDA), scanning electron microscopy (SEM) and light microscopy. Kinetic calculations were performed to theoretically validate the experimental results.

Table 1
Characteristics of the chemical compounds.

| Product | Commercial name | Charge density (equiv./kg dry) | Description |
| :---: | :---: | :---: | :---: |
| Cationic potato starch (C-starch) | EmCat C3 (AKP Canada) | +0.48 | 0.3\% nitrogen |
| Anionic potato carboxymethyl starch (A-starch) | EmCoat CMS 60 (AKP Canada) | -0.92 | Amylose/amylopectine 20:80\%, degree of substitution $=0.1, \mathrm{Mw} \approx 5 \mathrm{MDa}$ |
| Cationic polyacrylamide (C-PAM) | Percol 292 (Ciba Specialty Chemicals) | +1.1 | Linear flocculant, $\mathrm{Mw} \approx 1 \mathrm{MDa}$ |
| Anionic polyacrylamide (A-PAM) | LPM 1475 (Ciba Specialty Chemicals) | -2.6 (pH 7.0), -3.7 (pH 9.0) | Linear flocculant, $\mathrm{Mw} \approx 3.65$ millions, iodine value of $8-10$, substitution: 50 mole\% |
| Poly(ethylene oxide) (PEO) | Oxicol (Ciba Specialty Chemicals) | Nonionic | $\mathrm{Mw} \approx 6 \mathrm{MDa}$ |
| PEO cofactor | Oxirez (Ciba Specialty Chemicals) | Anionic | Sulphone type resin |
| PVFA/NaAA | Catiofast PR 8236 (BASF) | Amphoteric - 1.2 (pH 9.0) | Sodium salt of partially hydrolysed polyvinyl formamide copolymerized with acrylic acid $\mathrm{Mw} \approx 0.6 \mathrm{MDa}$ (Fig. 3) |
| Glyoxalated-PAM (PAM-glyoxal) | Baystrength 2000 (Lanxess, now Kemira) | +0.48 | $\mathrm{Mw} \approx 20-100 \mathrm{kDa}$ |
| Cationic polyacrylamide (C-PAM) | Raisabond 7815 (Ciba Specialty) Chemicals | +3.5 | Dry strength resin, cross-linked polymer, iodine value: 1.5 , substitution: 35 mole\% given by the acryloxethyltrimethyl ammonium chloride |
| Polyamine (Pam) | Catiofast 8153 (BASF) | +9.9 ( pH 4.7 ), +8.6 ( pH 8.9 ) | Coagulant, quaternary polyamine, $\mathrm{Mw} \approx 50 \mathrm{kDa}$ |
| Polyethylenimine (PEI) | Polysciences Inc. | +13.1 (pH 7.0), +5.5 (pH 9.0) | $\mathrm{Mw} \approx 70 \mathrm{kDa}$ |



- PCC-Average, 04/21/06 09:53:19

Fig. 1. Particle size distribution of PCC.

## 2. Materials and methods

### 2.1. Chemicals

### 2.1.1. PCC

Precipitated calcium carbonate, Albacar-HO from Mineral Technology inc., with a weak negative charge density of -1.3 mequiv./ kg (ionic charge of the slurry: $-272 \mu$ equiv./L), was used. The charge density was measured for a $20.9 \%$ suspension of PCC sampled from the satellite production plant, without dilution. pH of the PCC suspension was 9.0. Pure PCC is positively charged [26], as confirmed by molecular modelling calculations [27], but turns negative upon dilution by adsorbing impurities, even in distilled water, because of the small surface area of dilute PCC [26]. It also turns negative in process water. No dispersant was added to the PCC sampled from the satellite production plant, but it was originally prepared with the satellite plant process water, resulting in slightly negative
particles. The average particle size, measured by static light scattering/diffraction, is $4.4 \mu \mathrm{~m}$ (Fig. 1). Measurements with and without ultrasound gave very similar PCC particle sizes.

Because these results were higher than measured by sedimentation $(1.43 \mu \mathrm{~m})$, SEM was performed to validate them. The SEM pictures used one drop of stirred $20.9 \%$ PCC suspension, diluted to $1 / 1000$ to ensure discrete particles. Results showed the PCC particles to be irregular in shape, having lots of asperities, within the same size range as measured by SLS (Figs. 1 and 2). The experimental total specific surface area (SSA), measured by nitrogen adsorption, was reported to be $13.95 \pm 0.70 \mathrm{~m}^{2} / \mathrm{g}$ PCC by the supplier (2-year average).

### 2.1.2. Polymers

The polymers used to flocculate PCC are in Table 1, together with their charge density and other properties. For all commercial dry polymers, including PEO, fresh solutions were prepared the day of experiment. Starches were cooked at $95^{\circ} \mathrm{C}$ for 45 min at $2 \%(\mathrm{w} / \mathrm{w})$ solids. After the cooking time, the starches were diluted with water and kept warm $\left(40-45^{\circ} \mathrm{C}\right)$ during the experimental work. All other polymers were dissolved using de-ionised water.

### 2.1.3. Film formation with PCC and polymers

A glass plate coating technique was used to screen the different chemistries. The polymer was added in 200 g of filler suspension, $20.9 \%$ weight, and agitated at 800 rpm for $0.5-1.0 \mathrm{~min}$. A thin film of about $100 \mu \mathrm{~m}$ was coated on the surface of the horizontal glass plate, which was then inclined and let to dry. While the fillers were aggregating, the challenge is to generate a uniform opaque thin film.

### 2.1.4. Adsorption isotherm

The adsorption isotherms were measured to determine the maximum amount of polymer adsorbed on the slightly negative PCC.


Fig. 2. SEM images of PCC particles in the original commercial $20.9 \%$ suspension.


Fig. 3. Molecular structure of the sodium salt form of partially hydrolysed polyvinyl formamide copolymerized with acrylic acid (PVFA/NaAA).

Results were expressed in terms of adsorbed polymer as a function of the amount of polymer added instead of polymer in the solution. Two different chemistries were evaluated using: (a) sodium salt of partially hydrolysed PVFA/NaAA, an amphoteric polymer (Table 1 and Fig. 3), and (b) cationic potato starch, because it is commonly used in papermaking processes (Table 1).

The adsorption isotherm was measured at room temperature by solution depletion: 120 g of a $20.9 \%$ PCC suspension was placed in a $200-\mathrm{mL}$ beaker; the appropriate amount of polymer was injected in the beaker; 1 min of agitation; the PCC-polymer suspension was transferred into two centrifuge tubes and rotated at a speed of 2330 rpm for 5 min . The polyelectrolyte concentration in the supernatant was titrated using a Mütek PCD 03 Particle Charge Detector, and the amount of polymer adsorbed on PCC was calculated. The PVFA/NaAA was titrated using poly-diallyl-dimethyl-ammonium chloride poly(DADMAC), having a molecular weight of about 107 kDa . The cationic starch was titrated with polyvinyl sulphonated potassium salt (PVSK). This procedure was repeated for various polymer dosages until a plateau was observed, which equals the maximum amount of polymer that can be adsorbed on PCC ( $\Gamma_{\max }$ ). A blank experiment was performed using identical conditions, without PCC, to measure the charge density of the polymer under these specific conditions.

Fig. 4 shows that both chemistries result in a high affinity type adsorption isotherm, indicated by the observation that the adsorbed equals the amount added up to about $5 \mathrm{mg} / \mathrm{g}$ of PCC, with a maximum amount of adsorbed polymer of: $\Gamma_{\max } \approx 7 \mathrm{mg} / \mathrm{g} \mathrm{PCC}$. The $\Gamma_{\text {max }}$ of PVFA/NaAA on PCC was found to be identical to that determined in an external laboratory, using photometric titration (UV-vis spectrophotometer) method (Ref: BASF, Germany).

Although the chemistry differs, polyethyleneimine (PEI) has been shown to adsorb on GCC and PCC and the adsorption


Fig. 4. Adsorption isotherms of PVFA/NaAA and cationic starch on PCC expressed as polymer adsorbed as a function of polymer added. For both polymers, the maximum amount adsorbed ( $\Gamma_{\max }$ ) is about $7 \mathrm{mg} / \mathrm{g} \mathrm{PCC}$. The straight line shows $100 \%$ adsorption.


Fig. 5. Experimental set up for the photometric dispersion analysis (PDA) experiments. The shear in the suspension can be controlled by stirring and in the tube by the peristaltic pump (flow rate).
isotherms, after 1 h of equilibration, gave $\Gamma_{\text {max }}$ in the range of $4-10 \mathrm{mg} \mathrm{PEI} / \mathrm{g}$ of PCC, depending on the particle size, surface area, and electrophoretic mobility [28]. The results from Fig. 4 are within this range.

### 2.2. Particle size analysis (static light scattering/diffraction)

Particle size analyses were performed using a Malvern Mastersizer instrument equipped with a Hydro 2000S wet dispersion accessory (A). This instrument uses the Frauenhofer diffraction and Mie scattering theories to calculate the particle size. A refractive index of 1.607 was used for PCC. Results for PCC and PCC/polymer systems are an average of five measurements, with a stirring rate of 1925 rpm and no ultrasound.

### 2.3. PDA

### 2.3.1. Aggregation

Changes in the state of PCC aggregation were monitored by a Photometric Dispersion Analyzer (PDA 2000 Rank Brothers, Cambridge, UK) $[29,30]$. The PCC suspension was pumped from the outlet of a 1-L beaker through a transparent 3 mm diameter tubing into the photocell of the PDA, which monitors the fluctuations in intensity of transmitted light (Fig. 5). The experimental apparatus has a recirculation loop to allow measurements of the flocculation kinetics.

The transmitted light intensity has two major components: $\bar{V}$ which represents the average transmitted light intensity and a much smaller component $\left(V_{r m s}\right)$ defined as the standard deviation around the mean signal. The $V_{r m s}$ increases considerably as particles aggregate, whereas the aggregation only slightly changes $\bar{V}$. Therefore a significant increase in the ratio $(R)$ is a clear indication of particle aggregation (Fig. 6), with $R$ defined as:
$R=\frac{V_{r m s}}{\bar{V}}$
For dilute systems, $R$ varies linearly with the square root of the concentration, and for polydisperse systems $R$ is approximately linear with the particle radius, $a[29,30]$ :
$R \cong C N^{1 / 2} a$
where $N$ is the number of particles per unit volume, and $C$ a constant.
The initial aggregation rates, for the two PVFA/NaAA dosages are nearly identical (Fig. 6). The initial slopes are related to the flocculation efficiencies or stability ratios. The stability ratio $W$ for a


Fig. 6. Change in apparent particle size of PCC (ratio $R$ ) as a function of time for 1.25 and 5 mg of PVFA/NaAA/g of PCC. PCC aggregation starts almost immediately after polymer injection. The maximum aggregation rate for a specific chemical dosage $\left(k_{i}\right)$ is given by the initial slope of the $R$ vs. time relationship.
particular aggregation rate $k_{i}$, is [31]:
$W=\frac{k_{\text {fast }}}{k_{i}} \cong \frac{(d R / d t)_{\text {fast }}}{(d R / d t)_{i}}$
where $k_{\text {fast }}$ is the fastest rate of aggregation described by $\log W=0$ : when $\log W=\infty$ the suspension is stable. Stability ratio ( $\log W$ ) curves were determined using the following method. The total suspension volume was 1 L . The suspension was stirred at 300 rpm using a three-blade propeller, 6.5 cm of diameter. The concentration of PCC was $2000 \mathrm{mg} / \mathrm{L}$. Flow rates, controlled with a peristaltic pump and a recirculation loop, were $\sim 200-300 \mathrm{~mL} / \mathrm{min}$. No salt was added. Prior to polymer addition, the signal (ratio) was stable over time showing that the PCC suspension was stable. Since $k_{i}$ is proportional to the flocculation efficiency $\alpha, W \cong 1 / \alpha$.

The flocculation efficiency determines the fractal dimension of aggregates: high efficiency leads to open flocs, while low efficiency leads to more dense flocs because the particles can penetrate the flocs before being captured [32-39]. However, the flocculation efficiencies $(\alpha)$ for PVFA/NaAA ( 1.25 and $5 \mathrm{mg} / \mathrm{g}$ PCC) are the same and consequently a similar fractal dimension should be expected.

The plateau amplitude ( $\Delta R$ ) (Fig. 6), can be correlated with the particle size obtained from other experimental methods, such as light scattering. The amplitude $\Delta R\left(R_{\text {plateau }}-R_{\text {base line }}\right)$ of the original PDA curves was plotted as a function of the experimental change in particle size measured by SLS/diffraction, for PVFA/NaAA and C-starch polymers (Fig. 7). The correlations are good ( $r^{2}=0.9149$ and 0.9675 , respectively). Moreover, Fig. 7 shows different slopes for PVFA/NaAA and C-starch, implying different PCC floc structures, which scatter light differently. Also variation in flow rate can affect the particles orientation distribution, which also would change the slope.

Knowing the amplitude $(\Delta R)$, the slope $\left(\cong C N^{1 / 2}\right.$ ) and results from Fig. 7, it is possible to calculate the particle size as a function of time (Fig. 11).

## 3. Results

### 3.1. Particle size analysis

Numerous chemistries trigger PCC aggregation, but few polymers induce the desired degree of aggregation. For example, the flocculants: PEO/cofactor, A-PAM and C-PAM retention aid systems, are very cost effective in inducing PCC aggregation, but they


Fig. 7. Steady state PDA amplitudes, expressed as $\Delta R$, as a function of the change of PCC particle size, as measured by static light scattering/diffraction. Data from Fig. 12, below, were used to plot the above graph. The fitted lines were forced to go through the origin (zero).
have a disadvantage of creating very large aggregates at high polymer dosage (Fig. 8). However, the dry strength agents: C-PAM, glyoxalated-PAM and the polyamine coagulant (Pam) do not significantly induce filler aggregation. Similar to other systems [40,41], neither PEO nor cofactor alone, without salt, induce PCC aggregation. PCC aggregates induced by PVFA/NaAA and C-starch have floc sizes less sensitive to dosage in region I (Fig. 8). In addition, considering that both contribute to the dry strength of paper, these are robust systems which are suitable for papermaking. Modgi et al. [19] reported that for corn and potato starches, beyond a starch dosage of $40 \mathrm{mg} / \mathrm{g}$ of PCC, further aggregation is still possible. However, for tapioca starch, with a higher molecular weight and cationicity, PCC aggregate size is a maximum at concentration of $32 \mathrm{mg} / \mathrm{g}$ of PCC [19]. For papermaking, the particle size and size distribution have to be controlled and adjusted to an optimum value which has not been determined within the scope of this work. Because cost is a limiting parameter, a correct balance, between aggregate size and cost, has to be chosen for each type of paper.

The mechanisms behind filler aggregation are not fully understood, but polymer bridging through electrostatic interactions is


Fig. 8. Particle size as a function of polymer dosage. All experiments were performed using 2000 ppm of PCC suspensions, room temperature and no added salt. The cofactor:PEO ratio, 4.5:1, was constant for all PEO dosages. Inset: regions I and II for C-PAM flocculation curve.
one possibility. In this work, the aggregation of the negatively charged PCC particles (probably due to impurities from the process water) is induced by the positively charged polyelectrolyte, such as C-PAM and C-starch. Interestingly, anionic polyacrylamide (A-PAM) strongly induces PCC aggregation possibly through polymer bridging, while anionic starch (A-starch) only slightly aggregates PCC, even at 5 or $10 \mathrm{mg} / \mathrm{g}$ of PCC. These results are not surprising because it has been reported that polymers adsorb on surfaces regardless of charges [42]. The enthalpic driving forces for the adsorption of polymers (and small molecules) on surfaces take many forms [42]. Moreover, PVFA/NaAA, which is amphoteric, also aggregates PCC. PEI is not shown because it acts as a stabiliser for PCC, as observed by Vanerek et al. [43].

The present results may be divided into two regions (see inset Fig. 8, I and II) which are most pronounced for C-PAM, PVFA/NaAA and A-starch. Region I corresponds to bridging flocculation and region II is where the particle size reaches a plateau. Bridging theory would predict a maximum flocculation at intermediate polymer dosage which is not observed in this work. The same flocculation behaviour was observed with PCC and identical C-PAM (Fig. 5, Ref. [26]). A likely explanation of our results is that aggregates form before the particles get fully coated. Further coating does not break up particles, but prevent further aggregation. One question still remains: the competition between aggregation and polymer adsorption explains why particles aggregate at excess polymer and why aggregation stops. It does not explain why aggregation stops at low polymer concentrations. Perhaps at low concentrations the bonds are weaker and there is a dynamic equilibrium between floc formation and break-up. This equilibrium is absent at high polymer dosages, because otherwise it would lead to restabilisation. At low dosage of polymer (region I), PEO/cofactor and C-starch which are known to cluster [ $41,44,45$ ], gave faster flocculation rates and larger flocs because the polymer clusters enlarge the effective polymer size leading to larger flocs. The A-PAM is highly charged and gives strong flocs, likely due to the binding of the carboxylic groups of the A-PAM with the calcium ions on the surface of the $\mathrm{CaCO}_{3}$ particles, possibly removing anionic impurities from the surface. PAM-glyoxal, C-PAM (dry strength), and polyamine cause little or no flocculation, because they have very low molecular weight and act as dispersants similar as PEI. It is of interest to note that for CPAM the onset of the plateau (Fig. 8) occurs at a dosage similar the ones used in industrial applications.

The observation that PCC behaves differently when exposed to different chemistries is seen in Fig. 9: these differences give different film properties. Fig. 8 shows that PVFA/NaAA aggregates PCC and Fig. 9 (middle-left) shows it is possible to obtain a cohesive film. Tears are unsuitable because they reflect discontinuities in the film (middle-right of Fig. 9). The sample on the right of Fig. 9 should be interpreted with caution because it was slightly wet.

## 3.2. $P D A$

### 3.2.1. Effect of salt

Before studying PCC aggregation induced by polymers any further, it is necessary to determine whether only salt induces flocculation. $\mathrm{CaCl}_{2}$ was selected because $\mathrm{Ca}^{2+}$ is one of the most probable free calcium salts in papermaking. Fig. 10 shows that salt $\left(\mathrm{CaCl}_{2}\right)$ concentrations, ranging from 0.02 to 0.1 M , do not induce PCC aggregation, implying that the aggregation observed in Fig. 8 is induced by the polymers, and not by salts. One experiment was performed with C-starch to show that the system was properly functioning (Fig. 10). Suty et al. [28] reported that salt $\left(\mathrm{CaCl}_{2}\right)$ destabilizes GCC. They showed that the critical coagulation concentration (CCC) was about $0.02 \mathrm{M} \mathrm{CaCl}_{2}$. GCC is normally dispersed with a negatively charged dispersant, which probably explains their results. However, SLS, SEM and PDA results show that $\mathrm{CaCl}_{2}$ does


Fig. 9. Films ( $100 \mu \mathrm{~m}$ ) of: (left) PCC; (middle-left) PCC + PVFA/NaAA; (middle-right) PCC + A-PAM; and (right) PCC + PVFA/NaAA + A-PAM, on glass plates. Anionic polyacrylamide (A-PAM) is highly charged.
not induce PCC aggregation for the PCC sample used in this study. We speculate that the studied PCC, which has a low charge density (low surface charge), is sterically stabilized by adsorbed impurities from the process water of the satellite production plant. Alternatively calcium adsorption can reverse the charge of PCC, resulting in stable positively charged particles. This charge reversal has been observed by streaming potential measurements.

### 3.2.2. Calculated particle size from PDA results

Fig. 11 shows the calculated particle size as a function of time. This provides more details than the original PDA curves. No induction period was observed for PCC aggregation as seen for microcrystalline cellulose flocculation using PEO/cofactor chemistry $[40,41]$, i.e. PCC aggregation starts almost immediately after polymer injection. The initial slopes $\left(k_{i}\right)$ after polymer injection represent the initial flocculation rates.

Fig. 12 shows that the particle size measured by SLS/diffraction, as a function of polymer dosage, correlates very well with the amplitude $(\Delta R)$ of the original PDA curves for PVFA/NaAA and Cstarch. Interestingly, the particle size plateaus at a dosage close


Fig. 10. Apparent particle size $(R)$ of PCC as a function of time and for different added $\mathrm{CaCl}_{2}$ concentrations. PCC concentration was 2000 ppm for all experiments. This PCC does not contain dispersing agent. Salt concentrations reported in this graph do not include salts that might have been present in the original commercial PCC suspension.


Fig. 11. Calculated particle size of PCC as a function of time for 5 mg of PVFA/NaAA or C-starch $/ \mathrm{g}$ PCC. The calculated particle size was estimated from the amplitude of the ratio ( $\Delta R$ ): Eq. (2) and Fig. 7. No salt was added.
to $\Gamma_{\text {max }}^{p c}: \approx 7 \mathrm{mg} / \mathrm{g}$ of PCC that were experimentally measured for both chemistries (Figs. 4 and 12). Most likely, full coverage prevents further aggregation.

### 3.2.3. Stability ratio from PDA results

For most of the polymers shown in Fig. 8, the original PDA curves were used to build the stability ratio $(\log W)$ curves (Fig. 13). Results show that the stability ratios obtained from the original PDA curves, parallel the results obtained from SLS/diffraction (Fig. 8). The largest PCC aggregates correlate with the fastest kinetics. The maximum floc size results from a dynamic equilibrium between flocculation and floc break-up. Hence, for the present systems a higher flocculation rate correlates with higher bond strength. The PEO/cofactor chemistry gave the fastest PCC aggregation rate, defined as $k_{\text {fast }}$. Consequently, the value of $k_{\text {fast }}$ obtained at 5 mg PEO $/ \mathrm{g}$ of PCC was used as the reference aggregation rate, to which the aggregation rate $k_{i}$ of PCC, using other polymers, was compared (Fig. 13). The PAM-glyoxal gave the lowest aggregation rate, consistent with the results in Fig. 8. For the PVFA/NaAA/PCC system, there is no significant difference in the initial flocculation rates, between 1.25 mg and $5 \mathrm{mg} / \mathrm{g} \mathrm{PCC} ,\mathrm{also} \mathrm{consistent} \mathrm{with} \mathrm{the} \mathrm{results} \mathrm{in} \mathrm{Figs}$.6 and 8.


Fig. 12. Change in particle size measured by SLS/diffraction and change in amplitude ( $\Delta R$ ) of the PDA plot as a function of PVFA/NaAA and C-starch dosage.


Fig. 13. Stability ratio $(\log W)$ as a function of polymer dosage. All experiments were performed using 2000 ppm of PCC suspensions, room temperature and no added salt. The fastest aggregation rate, $k_{\text {fast }}$, obtained from the 5 mg PEO/cofactor/g of PCC system, was used as the reference aggregation rate to compare the performance of the above chemicals on the same basis.

### 3.3. Kinetic calculations

To theoretically investigate the results, kinetic calculations were performed using the same experimental conditions and value of $\Gamma_{\max }$ obtained from the adsorption isotherm in Fig. 4. Because the maximum amount of polymer adsorbed on PCC $\left(\Gamma_{\max }^{p c}\right)$ is $\approx 7 \mathrm{mg} / \mathrm{g}$ PCC, and the total SSA of PCC particles is $13.95 \pm 0.70 \mathrm{~m}^{2} / \mathrm{g} \mathrm{PCC}$, half coverage is when the concentration of PVFA/NaAA $\cong 0.25 \mathrm{mg} / \mathrm{m}^{2}$ PCC. The kinetics of adsorption of PVFA/NaAA onto PCC was calculated for perikinetic (diffusion controlled) and orthokinetic (shear induced) interactions, while the PCC aggregation is considered orthokinetic (shear induced). All experiments were at room temperature; therefore the kinetic calculations were performed at $25^{\circ} \mathrm{C}$. The kinetics of polymer adsorption can be modelled by Langmuir kinetics, which are characterized by an initial linear increase of the fractional surface coverage with time, followed by a nonlinear approach to an equilibrium plateau [46,47]. The adsorption time $\tau_{\text {ads }}^{p c}$ is the time at which the slope of the initial linear increase intersects the plateau value.

The aggregation time ( $\tau_{a g g}^{c c}$ ) is the time needed to reduce the number of PCC particles by half. These calculations take into account the attachment rate only. Although the initial rate does not give the complete picture, and detachment rate is not considered, nevertheless these calculations have been shown to be useful in numerous applications [43,48-53].

### 3.3.1. Diffusion controlled interactions

Adsorption of polymer, modelled as a small spherical particles depositing on PCC. The initial polymer adsorption kinetics is controlled by mass transfer to the surface and thus a polymer behaves much like a small particle being transported to the surface by diffusion and/or flow [21,46]. For diffusion controlled (perikinetic) collisions of unequal diameter spheres, the Smoluchowski rate constant ( $k_{s m}$ ) can be calculated from [54]:
$k_{s m}=\frac{2 k T}{3 \eta} \frac{\left(a_{1}+a_{2}\right)^{2}}{a_{1} a_{2}}$
where $k$ is the Boltzmann constant, $T$ is the absolute temperature, $a_{1}$ and $a_{2}$ are the radii of the polymer and PCC, respectively, and $\eta$ is the viscosity of the medium. The adsorption time of polymer on

Table 2
Theoretical predictions of PCC aggregation and polymer adsorption times ${ }^{\text {a }}$.

| PVFA $/ \mathrm{NaAA}\left(\mathrm{mg} \mathrm{L}^{-1}\right)$ | PCC $\left(\mathrm{mg} \mathrm{L}^{-1}\right)$ | PVFA/NaAA $(\mathrm{mg} / \mathrm{g} \mathrm{PCC})$ | $\tau_{a d s}^{p c}(\mathrm{~s})$ perikinetic | $\tau_{a d s}^{p c}(\mathrm{~s})$ orthokinetic | $n_{o}^{p c}$ | $\tau_{a g g}^{c c}(\mathrm{~s})$ orthokinetic |
| :--- | :--- | :--- | :--- | ---: | :--- | :--- |
| 20 | 1580 | 12.7 | $22(412)$ | $13(210)$ | $34(1.81)$ | 129 |
| 10 | 1780 | 5.6 | $43(827)$ | $28(475)$ | $15(0.8)$ | 115 |
| 2 | 1940 | 1.0 | $216(4337)$ | $138(2713)$ | $3(0.14)$ | 105 |
| 1 | 1960 | 0.5 | $433(8418)$ | $273(5319)$ | $1(0.07)$ | 104 |

${ }^{\text {a }}$ Calculated from the projected surface area $\left(0.52 \mathrm{~m}^{2} / \mathrm{g} \mathrm{PCC}\right)$; values in brackets were calculated from the experimental $\Gamma_{\max }^{p c}(\approx 7 \mathrm{mg}$ PVFA/NaAA/g PCC).
$\operatorname{PCC}\left(\tau_{a d s}^{p c}\right)$ can be estimated [54] from Eq. (5):
$\tau_{a d s}^{p c}=\frac{1}{\alpha_{a d s}^{p c} k_{s m} n_{c} n_{o}^{p c}}$
where $\alpha_{\text {ads }}^{p c}$ is the adsorption efficiency of the polymer on PCC, assumed to be $1, n_{c}$ is the number of PCC particles per unit volume and $n_{o}^{p c}$ is the amount of polymer initially present in the suspension relative to the total amount of polymer that can be adsorbed on PCC, which can be estimated from:
$n_{o}^{p c}=\frac{c_{p o l}}{4 \pi a^{2} n_{c} \Gamma_{\max }}$
where $c_{p o l}$ the polymer concentration and $\Gamma_{\max }$ the maximum amount of polymer that can be adsorbed on PCC particles.

### 3.3.2. Shear induced interactions

Aggregation of PCC particles was treated as shear-induced collisions of equal diameter spheres. From Smoluchowski's theory the half-time aggregation rate constant $\left(k_{s m}\right)$ can be calculated according to Eq. (7), assuming a uniform shear [54]:
$k_{s m}=\frac{16}{3} G a^{3}$
where $G$ is the velocity gradient or shear rate, and $a$ is the radius of the discrete PCC particle. The radius of PCC is $2.2 \mu \mathrm{~m}$. The shear rate is estimated to be $10 \mathrm{~s}^{-1}$ [55]. The PCC aggregation time ( $\tau_{\text {agg }}^{c c}$ ), defined as the time required to reduce the number of PCC particles by one half at equilibrium aggregation, can be estimated as [54]:
$\tau_{a g g}^{c c}=\frac{1}{\alpha_{a g g}^{c c} k_{s m} n_{c}}$
where $\alpha_{a g g}^{c c}$ is the aggregation efficiency, defined as the ratio of the number of collisions leading to aggregation to the total number of collisions [54], $\alpha_{\text {agg }}^{c c}$ is assumed to be equal to 1 .

From the above equations and previous experimental results, the kinetics calculations are summarized for different PVFA/NaAA/PCC systems (Table 2).

The orthokinetic aggregation times are consistent with the experimental PDA results (Table 2 and Fig. 11). The main uncer-
tainty in these orthokinetic times is the estimate of the effective shear rate under the experimental conditions.

The situation is actually more complex because the theoretical adsorption time is needed to fully adsorb a specific dosage of polymer on PCC surface $\left(\tau_{a d s}^{p c}\right)$. Table 2 shows that the adsorption time of the PVFA/NaAA on PCC increases as the PVFA/NaAA concentration decreases. Table 2 shows that the dimensionless $n_{o}^{p c}$, which is the PVFA/NaAA concentration relative to the maximum amount of PVFA/NaAA that can be adsorbed on the available PCC surface area, differs significantly depending on whether it is calculated from the projected surface area ( $S_{\text {proj }}$ ) or the experimental $\Gamma_{\max }^{p c}$ (values in brackets). This has a drastic effect on the polymer adsorption time. Since the diffusion controlled interactions (perikinetic) apply to polymers and small fillers, and discrete PCC particles and aggregates are relatively large, it became necessary to consider the shear induced interactions (orthokinetic) as well. Results show that perikinetic adsorption times are about 1.6-2 times longer than those for the orthokinetic interactions (Table 2). Considering the size of PCC, results from shear-induced orthokinetic calculations are probably more reliable. The kinetics of PCC aggregation is most likely related to polymer adsorbed on the top of the surface asperities of each PCC particle. The bridging surface area $\left(S_{\text {Bridg }}\right)$, defined as the area that really plays a role during PCC aggregation, is lower than the projected surface area ( $S_{\text {proj }} \approx 0.52 \mathrm{~m}^{2} / \mathrm{g}$ ) and consequently much smaller than the total SSA measured by nitrogen adsorption; $13.95 \pm 0.70 \mathrm{~m}^{2} / \mathrm{g} \mathrm{PCC}$. The bridging surface area is ill defined (Fig. 14) and depends on the morphology of the PCC particles and on the polymer molecular weight and structure. For example, branched high molecular weight polymer will adsorb differently on this type of PCC than linear lower molecular weight polymer, such as PVFA/NaAA, which will occupy more surface than starch which is bigger and branched, partly due to the amylopectin which is about $80 \%$ ( $\mathrm{w} / \mathrm{w}$ ) of the starch [45,56]. This explains the differences observed in Fig. 8 where the polymers behave differently because they affect the PCC bridging surface area differently due to the different molecular weight (size) and state of dissolution (clusters, entanglements).

Consequently, the experimental total specific surface area measured by nitrogen adsorption cannot be used because a large


Fig. 14. PCC particle from Fig. 2 (bottom left). Structure of PCC particle (diameter of about $4 \mu \mathrm{~m}$ ) (left and right are mirror images). The speculated bridging surface area (light grey) is more accessible to polymer than that inside the asperities. The light grey color of the pigment (colored with MGI Photosuite program) is the highest surface elevation, the medium grey color, a little bit deeper and the dark grey color, the valley. The background was erased with Adobe Photoshop. This SEM image's contrast depends on the tilt and orientation of the detector.


Fig. 15. The above cartoon based on observed floc structure shows the interactions between two PCC particles coated with polymers (darker areas indicate adsorbed polymer). Top: classical bridging or charge neutralisation flocculation, and bottom: additional polymer absorption results in higher coverage of the external and internal surface and prevents further aggregation due to (electro)steric repulsion.
amount of polymer is buried inside the asperities and not effective for aggregation. In other words, the top of the surface asperities (bridging surface) is the critical surface for PCC aggregation. As long as there is enough polymers to glue the tips, aggregation can occur (Fig. 15). More polymers can penetrate inside the PCC but the initial flocculation kinetics is determined by the amount of polymer on the external surface.

## 4. Concluding remarks

The kinetics of PCC aggregation was studied using static light scattering/diffraction, PDA, and SEM. Kinetic calculations were performed to theoretically validate the experimental PCC aggregation times. PCC aggregates induced by PVFA/NaAA or cationic starch (Cstarch) are less sensitive to dosage within a certain range. Both flocculants, PEO/cofactor and C-PAM, gave higher flocculation rates and larger floc sizes making them useful, for process water clarification. The change in particle size measured by PDA correlates well with the change in PCC particle size measured by SLS/diffraction. Using the amplitude ( $\Delta R$ ) from the PDA experiments (equation $\left.\Delta R \cong C N^{1 / 2} \Delta a\right)$ and results from Fig. 7 it was possible to estimate the PCC particle size as a function of time. For the present system, results from stability ratios correlate well with the change in particle size measured by SLS as a function of dosage.

During polymer induced flocculation, the particle size increases from its initial value to a plateau value. The results are divided into two regions (inset of Fig. 8: I and II) which are most pronounced for C-PAM, PVFA/NaAA and A-starch. Region I corresponds to bridging flocculation and region II, the particle size reaches a plateau, instead of a maximum, as expected from the classical polymer bridging theory or charge neutralisation theory. A likely explanation is that aggregates form before the particles get fully coated. Further coat-
ing does not break up particles, but prevent further aggregation. PEO/cofactor, which is known to cluster, gave faster flocculation rate and larger flocs; because the polymer cluster enlarge the effective polymer size leading to larger flocs. The A-PAM is highly charged and gives strong flocs due to strong binding to PCC. PAM-glyoxal, C-PAM (dry strength), and polyamine cause little or no flocculation, because they act as dispersants, similar to PEI.

Kinetic calculations show that the orthokinetic aggregation times agree with the experimental PDA results. The main uncertainty in these orthokinetic times is the estimate of the effective shear rate. The situation is actually more complex: the theoretical absorption time to fully absorb a specific dosage of polymer on PCC surface $\left(\tau_{\text {ads }}^{p c}\right)$ is required. The available surface area differs significantly, depending on whether it is theoretically calculated from the projected surface area, or from the total surface area determined from the experimental $\Gamma_{\text {max }}^{p c}$. These different surface areas translate into different adsorption times for the bridging, projected and total surface areas.

Finally, it is suggested that the bridging surface area, defined as the area that can form bonds between PCC particles or aggregates, the top of the asperities (accessible surface), is the critical surface for PCC aggregation.

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