

Retention of PCC and GCC fillers on chemical pulp fines surfaces

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ABSTRACT: We studied the retention of precipitated and ground calcium carbonate fillers (PCC and GCC, respectively) on chemical pulp fines surfaces by measuring the amounts of adsorbed fillers on the surfaces of the primary and secondary fines and long fiber fractions of eucalyptus pulp in the presence of a polymeric flocculant (CPAM). The mechanism of filler particle retention and adsorption on fines surfaces was clarified in more detail by measuring the kinetics of PCC adsorption in the absence of flocculant. The results showed that the primary and secondary fines fractions adsorb more PCC and GCC fillers on their surfaces (per gram of pulp) than the long fiber fraction in both the absence and presence of flocculants. In the absence of flocculants the adsorption of PCC both on fines and on the fiber fractions follows Langmuir kinetics, implying that the adsorption is in dynamic equilibrium with filler detachment and the maximum possible amount of filler that can be adsorbed corresponds to the monolayer coverage of particles. At low flocculant doses, i.e., doses that are relevant to papermaking, the fines fractions adsorb significantly more filler than the fiber fractions. In this case, their high surface charge density promotes CPAM adsorption onto fines, which in turn increases the adsorption of fillers to the fines surfaces through polymer bridges.

Application: Our results show papermakers how different chemical pulp fines fractions can influence retention of calcium carbonate fillers.

The retention of fillers significantly influences filtration-based separation operations in papermaking. Both the sheet forming process in the paper machine and various separation processes such as solids recovery from the circulation water involve the attachment of small particles, including mineral fillers, to the fiber network during filtration. Since filler retention by mechanical entrapment is poor, retention is closely associated with the ability of the various pulp fractions to adsorb fillers on their surfaces through colloidal interactions. The influence of organic pulp fines fractions on filler retention is of particular interest because the fines contribute significantly to particle adsorption in the stock due to their high external surface area. In turn, they are better retained in the fiber network than are individual filler particles.

The fines in chemical pulps are either a) primary fines consisting of wood cells and other material that is initially present in the pulp before beating or b) secondary fines generated during beating. The secondary fines contain fiber fragments and more fibrillar and lamellar material originating from the fiber cell wall [1–3]. The physical and chemical properties of these fines fractions, such as their accessible surface area, surface chemical composition, and surface charge density, differ significantly from those of long fibers [4–6]. The ability of these fines to interact with and adsorb other components also differs from that of fibers [7]. Nevertheless, earlier investigations studied the adsorption and retention of fillers on the long fiber fraction and therefore the effect of different fines fractions on total filler retention in chemical pulps is not yet completely clear.

Our aim was to clarify the effects of different chemical pulp fines on the retention of precipitated and ground calcium carbonate fillers (PCC and GCC, respectively). To do so, we measured the amounts of fillers adsorbed on the surfaces of primary and secondary fines and long fiber fractions of eucalyptus pulp in the presence of a polymeric flocculant (CPAM) by following the concentration of unadsorbed filler particles in a stirred beaker in terms of turbidity. We clarified the mechanism of filler particle retention and adsorption on fines surfaces by modeling PCC adsorption as a function of time in the absence of flocculant using the Langmuir theory. The experimental observations on PCC adsorption were compared with values given by the modified Langmuir adsorption equation.

THEORETICAL

The Langmuir theory was developed for the adsorption of gases on surfaces [8] and later modified for the adsorption of small particles on fibers by Alince et al. [9], and was used to model the adsorption kinetics of a PCC filler on fines and fiber surfaces in the absence of flocculants. The experiments were conducted only with a positively charged PCC that has a natural attraction for anionic wood material, contrary to the negatively charged GCC, which would not have been adsorbed on pulp without flocculants. According to the Langmuir kinetics, filler deposition consists of competing processes of adsorption and detachment, which are characterized by the adsorption and detachment rate constants, k_a and k_d , respectively, and the equilibrium constant $K (=k_a/k_d)$. The maximum possible amount of filler that can be adsorbed, $\Gamma_{\max}$ (g/g), corresponds to monolayer coverage of particles over the fiber sur-

faces. In Eq. 1, the fractional coverage of surfaces by filler, θ ($= \Gamma/\Gamma_{\max}$, where Γ is the amount of filler deposited, in g/g), at time t is defined as:

$$\frac{d\theta}{dt} = k_a(\beta - \theta)(1 - \theta) - k_d\theta \quad (1)$$

in which $\beta = c_o/\Gamma_{\max}$, where c_o is the initial concentration of filler particles in g/g. The solution to Eq. (1) is [10]:

$$\theta = \frac{2\beta(\lambda - 1) + \theta_0(A(1 - \lambda) + B(\lambda + 1))}{A(\lambda - 1) + B(\lambda + 1) + \theta_0(1 - \lambda)} \quad (2)$$

where θ_0 is the fractional coverage, θ , at time $t = 0$, and λ , A and B are given as:

$$\lambda = e^{Bk_a t}$$

$$A = K + \beta + 1 \text{ and}$$

$$B = ((\beta - 1)^2 + 2K(\beta + 1) + K^2)^{1/2}.$$

The adsorption rate constant k_a can be obtained by a best fit of Eq. 2 to the experimental points, and the deposition rate constant from the equilibrium constant K , obtained from Eq. 1 under steady state conditions, i.e. $d\theta/dt = 0$.

EXPERIMENTAL

Materials

Bleached eucalyptus (*E. globulus*) chemical pulp obtained in dry laboratory form was disintegrated in deionized water, beaten in a PFI mill (3000 revs) according to EN ISO 5264-2:2002 standard, and fractionated onto the primary and secondary fines fractions and the long fiber fraction using a dynamic drainage jar (DDJ) equipped with a 76- μ m opening (200-mesh) stainless steel wire mesh. We carried out the separation at a consistency of 1 g/dm³ and an agitation speed of 800 rpm. We separated the primary fines fraction from the disintegrated pulp before beating and took the secondary fines fraction from the primary fines-free pulp after beating. The long fiber fraction was left after separating out the secondary fines. All the pulp fractions were treated with acid (0.01 M HCl) before the experiments in order to remove metal ions and were then converted to sodium form by treatment

with NaHCO₃ (0.001 M) at pH 9.5 (pH adjusted with 0.1 M NaOH solution). We washed the samples with deionized water until their conductivity was less than 5 μ S/cm using Schleicher & Schuell No. 604 and Macherey Nagel No. 617 filter papers.

We analyzed the particles in the fines fractions with an image analyzer that classified them individually into fibrillar and non-fibrillar particles and ray cells and measured their apparent mass proportions [11]. Electron spectroscopy for chemical analysis (ESCA, AXIS 165 spectrometer by Kratos Analytical, Chestnut Ridge, New York) was used to measure the surface content of lignin, extractives, and carbohydrates in the pulp fractions [12]. The total and surface charges of the fractions were measured by polyelectrolyte titration [13] using poly(1,5-dimethyl-1,5-diazaundecamethylene) bromide (Polybrene, Sigma-Aldrich Chemie GmbH, Taufkirchen, Germany) for the total charge and poly(dimethyldiallylammonium) chloride (PolyDADMAC, Ciba Specialty Chemicals Ltd., Basel, Switzerland) for the surface charge. The average weighted length and width of the long fibers, as determined with a Metso FiberLab analyzer, were 0.80 mm and 15.9 μ m, respectively. The Canadian standard freeness (CSF) value of the fibers measured according to TAPPI 227 om-99 "Freeness of pulp (Canadian Standard Method)" was 410 ml. **Table I** shows the properties of the pulp fractions.

GCC and PCC with a scalenohedral crystal shape, both supplied in the form of a water slurry with a solid content of about 20%, were used as mineral fillers. The particle size obtained from a Sedigraph (D50 value) and the surface area of the filler particles (BET) as given by the manufacturer, were 2.4 μ m and 8.0 m²/g for PCC and 2.0 μ m and 2.3 m²/g for GCC, respectively. The zeta potentials and electrophoretic mobilities of the fillers, measured with a Coulter Delsa 440 Doppler electrophoretic light scatter analyzer, were +7.5 mV and 0.60 μ m²/Vcm², respectively, for PCC and -25.0 mV and -2.0 μ m²/Vcm² for GCC.

The CPAM used as a polymeric flocculant had a molecular weight of 7 $\times$ 10⁶ g/mol and a charge density of 1 meq/g. We prepared the stock solution of polymer (5 g/dm³) by mixing polymer granules into deionized water and stirring at 200 rpm for 90 min. The stock solution was diluted to 5 mg/dm³ before use.

Measurement of filler adsorption

Adsorption of filler particles onto the fines and long fiber fractions was followed by measurement of the concentration of unadsorbed filler particles in a beaker (stirred at 175 rpm),

Pulp fraction	Particle content (% w/w)		Surface composition (%)			Charge properties (μ g/g)	
	Fibrils	Ray cells	Lignin	Extractives	Carbohydrates	Total charge	Surface charge
Fiber	–	–	<1	<1	99	86.8	11.5
Primary fines	9	8	7	8	85	84.4	14.3
Seconodary fines	17	3	3	5	92	75.3	15.7

I. Properties of the fines and fiber fractions.

with turbidity measured using a Hach Ratio/XR Turbidimeter. First, we measured the deposition of PCC on the pulp fractions as a function of time in the absence of flocculant and then we obtained an equilibrium amount of adsorbed PCC and GCC fillers as a function of the flocculant (CPAM) dosage.

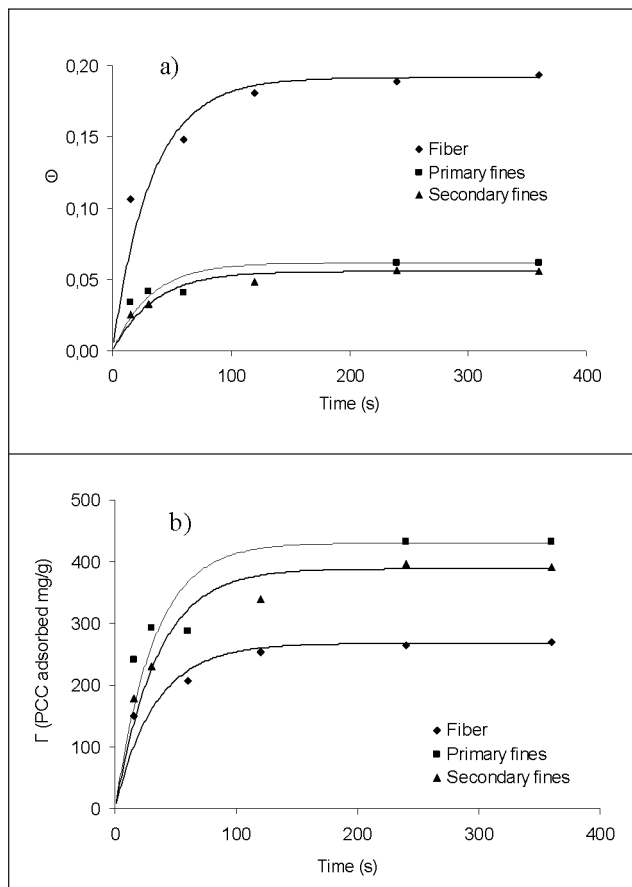
The experiments consisted of adding 6 mg of filler to 10 mg of fibers or fines suspended in a solution of deionised water containing 10 mM of NaCl and 1 mM of NaHCO₃ as background electrolytes, followed by the addition of the polymer. We measured the kinetics of PCC adsorption in deionized water without electrolytes. The total volume of each suspension was 100 cm³. Unadsorbed filler particles were then separated from the suspension up to 240 s after the start of the experiment or when the filler adsorption equilibrium was reached (360 s). Filtering a portion of the suspension through a screen while being stirred allowed unadsorbed fillers to pass through but retained wood materials and adsorbed filler. The smallest, colloidal-size fraction of the fines, which might have passed through the screen, had already been removed from the pulp during pretreatment. In addition, the large filler aggregates were screened from the filler suspension. We used a calibration line for turbidity versus filler concentration (correlation constant R² = 0.99) to determine the amount of filler in the filtrate [14].

RESULTS AND DISCUSSION

Kinetics in the absence of flocculants

Figure 1 shows the adsorption of PCC filler on primary fines, secondary fines, and long fibers as a function of time. Both the fractional coverage of fines and fibers by PCC and the amount of PCC adsorbed in mg/g are presented. PCC, which has a positive surface charge that arises from the preferential sorption of Ca²⁺ ions originating from the partial dissolving of CaCO₃ in water, adsorbs on both anionic fines and fibers in the absence of flocculants. However, the amount of adsorbed PCC in mg/g was significantly higher with the fines fractions than with the fiber fraction, despite the fractional surface coverage, i.e. $\Gamma/\Gamma_{\max}$, which was much lower with fines due to their high external surface area and thus high $\Gamma_{\max}$ value. The steady-state amount of adsorbed PCC, Γ_{∞} (Γ as $t \rightarrow \infty$), for an initial filler concentration of 600 mg/g was 270 mg/g for fibers, which is close to the value of 280 mg/g presented earlier [15].

The primary fines adsorbed slightly more PCC than did the secondary fines, despite their larger size [1] and smaller accessible surface area for particle adsorption. The steady-state amounts of adsorbed PCC were 430 mg/g for primary fines and 400 mg/g for secondary fines. The similarity may be due to the removal of the smallest particles from the fines fractions during pretreatment. Because the particle size distributions of the primary and secondary fines fractions were similar, the small particles which were initially abundant, particularly in secondary fines [1], were lacking. This was also supported by particle size measurements conducted with a laser diffraction particle size analyzer (Beckman Coulter LS 13 320).



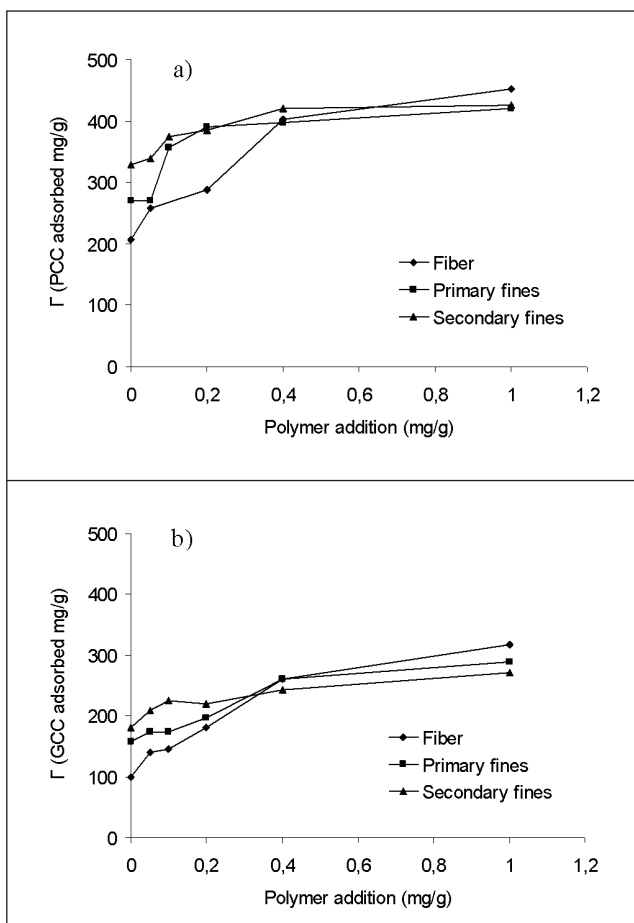
1. Adsorption of PCC filler particles as a function of time in the absence of flocculants and electrolytes: (a) Fractional coverage of fines and fibers by PCC and (b) amount of PCC adsorbed, in mg/g. The points are experimental observations and the solid lines are calculated from the modified Langmuir equation (Eq. 2).

Theoretical curves for PCC adsorption on fines and fiber surfaces were obtained from the modified Langmuir equation (Eq. 2) using the values for K and k_a that gave a best-fit value for the experimental points (Fig. 1 and **Table II**). The value of $\Gamma_{\max}$ for the fiber fraction was obtained from Fimbel and Siffert [16]; $\Gamma_{\max}$ for the fines was calculated from this value taking into account that the specific surface area of chemical pulp fines is about five times greater than that of fibers [17]. The results showed that the adsorption of PCC on both fibers and fines was in good agreement with the Langmuir kinetic model. Visible observations also provided evidence that cationic PCC flocculated some fines to larger aggregates, but we presumed this did not significantly affect the accessible surface area of fines and or the adsorption kinetics of PCC.

We observed adsorption of PCC to be in dynamic equilib-

Pulp fraction	k_a (s ⁻¹)	k_d (s ⁻¹)	K	$\Gamma_{\max}$ (g/g)
Fiber	0.014	0.014	1.0	1.4
Primary fines	0.011	0.020	1.7	7.0
Secondary fines	0.010	0.020	2.0	7.0

II. Kinetics of PCC adsorption on fiber and fines fractions.



2. Adsorption of (a) PCC and (b) GCC filler particles on fines and fiber fractions as a function of CPAM dosage (filler dosage 600 mg/g, background electrolytes 10 mM of NaCl and 1 mM of NaHCO_3).

rium with the filler detachment, as the plateau amount of adsorbed PCC was less than the amount of filler added. That, in turn, was significantly lower than the amount required for monolayer coverage, i.e., $\Gamma_\infty < c_0 < \Gamma_{\text{max}}$. The detachment rate constant, which was inversely proportional to the bond strength [10], was higher for the fines than for the fibers, despite fines having a higher surface charge (Table I), which was expected to promote PCC attachment to the surfaces.

Retention in the presence of flocculant

Figure 2 shows the adsorption of PCC and GCC fillers (600 mg/g dosage) onto the pulp fractions in the presence of a flocculant (CPAM) as a function of the flocculant dosage. The amounts of fillers adsorbed were measured after 360 s, when equilibrium in the adsorption was reached. Although the CPAM also promoted some flocculation among the filler particles, it was previously observed to have only a minor effect on the retention of fillers [18]. Both fines fractions retained more filler than did the long fibers at low polymer doses (i.e., doses that are relevant to papermaking) and the plateau level of filler adsorption was reached at a dosage of about 0.4 mg/g, which is close to the value of 0.5 mg/g reported previously [19]. The amount of PCC adsorbed to the fines at doses below

0.3 mg/g was about 35% higher than that for the fiber fraction.

The driving force for adsorption and flocculation by CPAM is the charge interaction (electrosorption) between the polymer segments and the surface charges. That can be characterized by the adsorption enthalpy per segment X_s , which consists of a nonelectrostatic contribution X_s^0 and an electrostatic contribution X_s^{el} , i.e. $X_s = X_s^0 + X_s^{\text{el}}$ [20]. The difference in the amount of adsorbed fillers between the fines and fibers may be related to the differences between X_s parameters, and particularly the differences between X_s^{el} parameters, since the surface charge density of the fines was higher than those of fibers [21]. Thus the high surface charge density of the fines promoted CPAM adsorption, which in turn promoted adsorption between the fillers and the fines surfaces through polymer bridges.

At higher polymer dosages equal amounts of filler were adsorbed on both the fines and fibers, while at a polymer dosage of 1 mg/g the fiber fraction adsorbed more filler than both the primary or secondary fines. CPAM not only promotes filler adsorption but also flocculates the fines and fibers. Thus, filler particles were attached particularly inside the voluminous fiber flocs, which increased their retention to the fiber fraction.

In the absence and presence of a flocculant, the amount of adsorbed filler was measured to be higher for PCC than for GCC. That finding was consistent with previous results reported [22] and was caused by the positive surface charge of PCC, which itself promotes its adsorption to anionic pulp material by electrostatic interaction [23]. GCC, on the other hand, was negatively charged which reduced its adsorption. The amount of PCC adsorbed in the absence of flocculant and electrolytes was almost equal (Fig. 1) to that of the optimal flocculant dosage in the presence of electrolytes (Fig 2). In the absence of a flocculant the PCC was adsorbed to the anionic pulp material due to the electrostatic interaction. In the presence of flocculants and electrolytes PCC was adsorbed mainly due to a bridging action of the CPAM, since the electrolytes screened the electrostatic interaction between PCC and the pulp material and reduced its promoting effect on PCC adsorption.

CONCLUSIONS

Primary and secondary fines fractions of eucalyptus chemical pulp adsorbed more PCC and GCC fillers (per gram of pulp fraction) than long fiber fraction in both the absence and presence of flocculants. In the absence of flocculants the adsorption of PCC both on fines and fiber fractions followed Langmuir kinetic model. That finding implies that the adsorption was in dynamic equilibrium with filler detachment and that the maximum possible amount of filler which can be adsorbed corresponded to monolayer coverage of particles. At low flocculant (CPAM) doses, fines fractions adsorbed significantly more fillers than fiber fractions due to their high surface area and charge density. That promoted CPAM adsorption onto fines, which in turn increase the adsorption of fillers onto fines surfaces through polymer bridges. **TJ**

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INSIGHTS FROM THE AUTHORS

We were particularly interested in the influence of organic pulp fines fractions on filler retention because the fines contribute significantly to particle adsorption in the stock due to their high external surface area. In turn, they are better retained in the fiber network than are individual filler particles. Earlier studies were concerned with the deposition of fillers on only the long fiber fraction. In earlier work, we demonstrated that mechanical pulp fines have a unique effect on filler retention. This work shows that the fines of the chemical pulp contribute filler retention more than corresponding fiber fraction.

We found it interesting that fillers tend to interact with pulp components and deposit on their surfaces rather than form large flocs among each other. Therefore, fines have an especially important role in filler retention. The results of our work show how retention of calcium carbonate fillers might be influ-



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enced by different chemical pulp fines fractions.

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