Effect of PCC filler on dewatering of fiber suspension

HENRIKKI LIIMATAINEN, SIRPA KOKKO, PÄIVI ROUSU, AND JOUKO NIINIMÄKI

ABSTRACT: The effect of precipitated calcium carbonate (PCC) paper filler on water removal from pine, eucalyptus, and birch kraft pulps was investigated in the vacuum filtration process by measuring average specific filtration resistances (SFRs). PCC reduced the filtration resistance of beaten pulps, that is, increased water removal, in a lab-scale process. This result, which contradicts previous findings with other fillers, is thought to be related both to the high porosity of scalenohedral PCC and, as proved here, to the cationic surface charge of PCC particles, which promotes particle deposition on anionic fibers and reduces the specific surface area of the stock. The responses of pulps to PCC addition varied, and a correlation between SFR and the zeta potential of the fibers was observed.

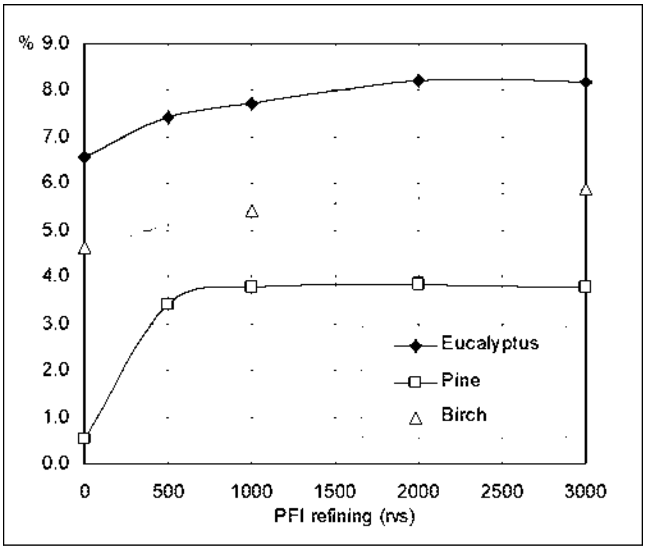
Application: This study demonstrates the effect of cationic PCC filler on dewatering of chemical pulps and shows how the surface charge of fibers affects water removal of pulps containing PCC. The cationically-charged PCC particles, by attaching to the fibers by electrostatic attraction and reducing total surface area, can improve dewatering efficiency.

Filtration is an important unit process in papermaking. Both the sheet forming process on the papermachine and various separation processes such as fiber recovery by disk savealls are based on the filtration of suspensions containing pulp and additives. Filtration performance is characterized by water removal efficiency, which, in turn, depends on the properties of the pulp suspension components. In particular, small particles with high surface area tend to plug the filter cake and reduce dewatering efficiency.

The properties of wood-based materials (individual fibers, primary fines, and especially secondary fines) play a significant role in drainage. Fiber morphology affects drainage, but the most important factors, such as fiber swelling and conformability, are related to internal fibrillation. The significant properties of fines are their morphology and particle size distribution. These properties are, in turn, related to the fundamental properties of materials: specific surface area and specific volume.

In addition to the wood material, mineral fillers significantly affect drainage. The filler type, size, and shape affect dewatering [1], but the chemical composition of the surface affects the surface charge and thus has a significant effect on particle behavior in the fiber network. This is due to the fact that small particles (0.1-10 μm) tend to attach to the filter cake mainly through chemical interactions. The importance of other retention mechanisms, such as filtration or mechanical entrapment, is usually minor for these particles [2].

The chemical interactions originate from short-distance van der Waals attractive forces and repulsive or attractive electrostatic forces. In the filtration of charged particles, the interaction is mainly controlled by electrostatic forces, which depend on the surface charge of the components. Most of the fillers used in papermaking carry a negative charge, and therefore their interaction with anionic fibers is repulsive. Consequently, polyelectrolytes are needed to promote the retention of anionic fillers on the fibers and facilitate drainage of the stock by preventing the fillers from forming a dense layer close to the filter media. Cationic polyacrylamides (C-PAMs), for instance, are commonly used to flocculate particles onto pulp fibers and to increase both retention and water removal.



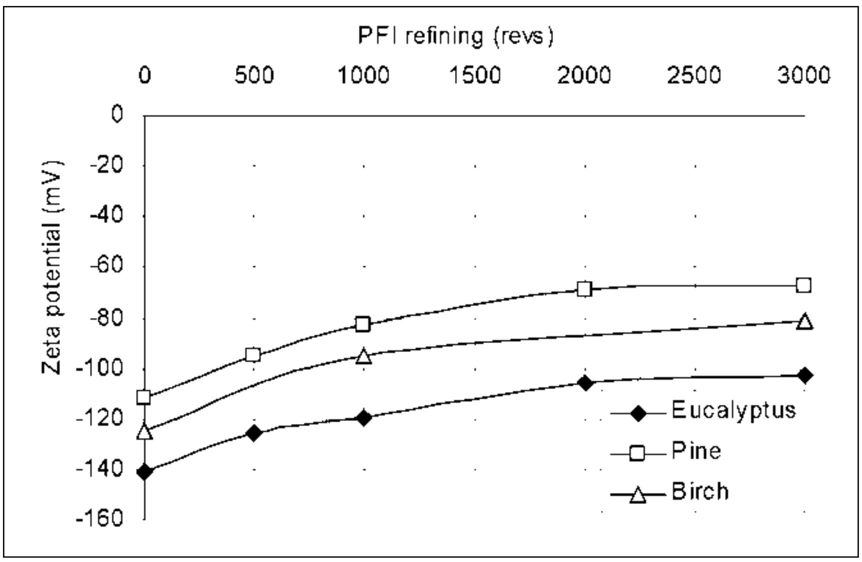
1. Percent fines in the pulps.

Unlike most fillers, precipitated calcium carbonate (PCC) filler, a synthetic calcium carbonate mineral used in neutral papermaking, is positively charged in its native form. The positive

Sample	Length (l)	Width	Coarseness	Bendability[1]	Total charge	CSF
(PFI revs)	(mm)	(µm)	(mg/m)		(µmol/g)	(mL)
Eucalyptus						
0	0.76	18.5	90.2	2.0	-79	496
500	0.76	18.7	112.2	3.3	-60	–
1000	0.77	19.1	104.4	3.8	-87	–
2000	0.78	19.5	79.0	4.2	-82	–
3000	0.77	19.7	86.2	4.1	-87	–
Birch						
0	0.92	21.6	105.0	4.4	-65	535
1000	0.96	22.5	100.7	5.2	-67	–
3000	0.96	23.7	96.0	6.1	-73	–
Pine						
0	2.00	30.0	380.6	5.3	-47	657
500	2.07	30.3	328.9	3.9	-47	–
1000	2.20	31.0	192.5	6.5	–	–
2000	2.11	31.3	249.0	5.4	-47	–
3000	2.18	31.9	190.3	5.9	-45	–

1. Bendability of length fraction 0.5-1.2 mm.

I. Fiber properties.



2. Zeta potentials of the pulps as a function of beating.

surface charge of PCC particles arises from the preferential sorption of Ca^{2+} ions originating from partial dissolution of $CaCO_3$ in water onto the surface of the filler. The cationic charge associated with calcium carbonate is reported to increase filler deposition on the fiber surfaces [3,4], but little published material is available on the effect of cationic PCC fillers on the water removal efficiency of stock.

In this study, cake filtration of softwood and hardwood kraft pulps containing precipitated calcium carbonate was investigated by measuring the specific filtration resistance (SFR) in vacuum filtration. The objective was to characterize the effect of PCC filler on pulp dewatering, in order to understand the behavior of fine particles in the filtration process. In particular, the response of different pulp types to PCC addition was clarified.

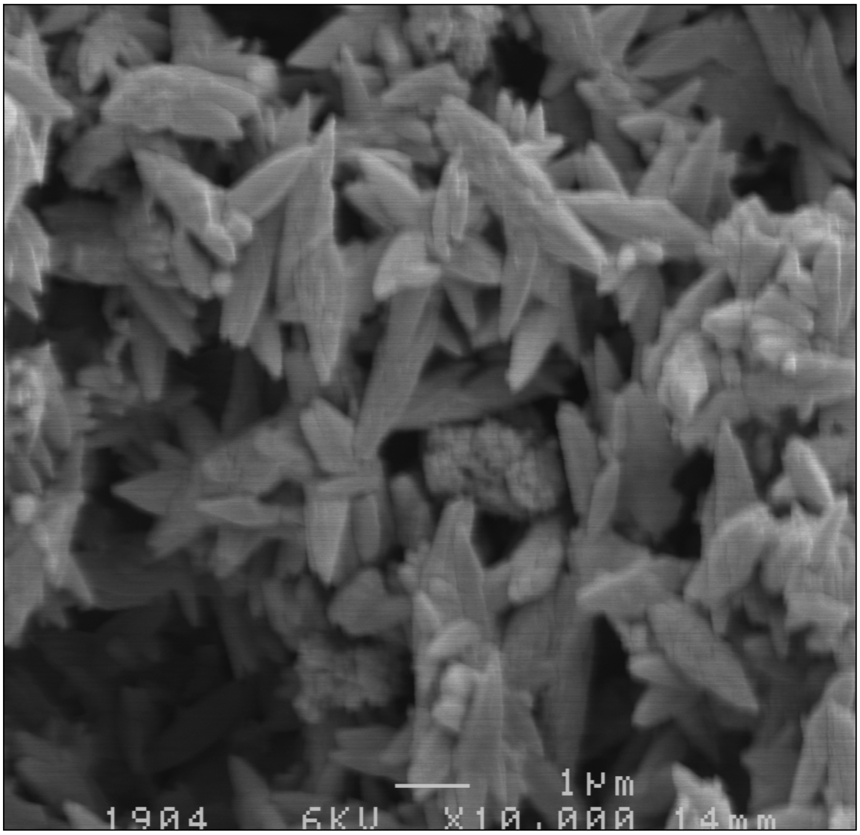
MATERIALS

Pulps

Bleached eucalyptus (*E. globulus*), birch (*Betula verrucosa*), and pine (*Pinus sylvestris*) chemical pulps were obtained in dry lap form. Pulps were disintegrated in deionized water and beaten in a PFI mill according to EN ISO 5264-2:2002 [5]. The properties of the pulps were analyzed with an L&W STFI Fibermaster image analyzer (**Table I**). A Bauer-McNett classifier was used to measure the fines content (P200) (**Fig. 1**). The charge properties were characterized with methylene blue sorption for the total charge [6, 7] (Table I) and zeta potential (**Fig. 2**) with Mütek SZP-06 for the surface charge. The zeta potential measurement was based on detection of the streaming potential of the sample.

Filler

PCC filler with scalenohedral (cigar-shaped) crystals was supplied in the form of a water slurry with a solids content of



3. SEM micrograph of the PCC filler.

20%. The particle size obtained from a Sedigraph (D_{50} value) and the surface area of the filler particles (BET) as given by the manufacturer were 2.4 µm and 8 m^2/g, respectively. The volume statistics mean particle size, measured with a laser diffraction particle size analyzer (Beckman Coulter LS 13 320), was 3.9 µm. The measured value for the zeta potential was +7.5 mV and for electrophoretic mobility 0.60 $\mu m s^{-1}$/ $V cm^{-1}$. The Coulter Delsa 440 (Doppler Electrophoretic Light Scatter Analyzer) was used for these determinations. A scanning electron micrograph of filler particles is presented in **Fig. 3**.

METHODOLOGY

Filtration experiments

In the first phase, the specific filtration resistances of pure pulps were measured in order to characterize the filtration behavior of the fibers. In the second phase, the PCC filler was added to the pulps and the changes in dewatering were observed. Average specific filtration resistances were calculated after 18 seconds of filtration based on Eq. (1): where

$$\frac{1}{A}\frac{dV}{dt} = \frac{\Delta p}{\mu\left(\alpha_{av}\frac{W}{A} + R\right)} \quad (1)$$

dV/dt = volumetric flow rate of the filtrate, m^3/s
A = filtration area, m^2
Δp = pressure difference across the fibrous mat and wire, Pa
μ = viscosity of the filtrate, Pa s
α_{av} = average specific filtration resistance of the filter cake, m/kg
W = mass of solids retained, kg
R = filtration resistance of the wire, m^{-1}.

A detailed method for determining the SFR is presented in Wakeman and Tarleton[8]. The effect of particle retention is taken into account in the values presented here. The relative standard deviation (RSD) of the measurement was less than 5.5%.

The SFR measurements were carried out with unbeaten and beaten pulps and pulps with PCC filler. The PCC was added to the pulp slurry with gentle stirring for two minutes. Under these conditions, the adsorption of $CaCO_3$ will reach equilibrium within 30 s [9]. The experiments were performed at the natural pH of a PCC and pulp mixture (8.5-9.0) and a conductivity of about 130 µS/cm. Some additional measurements were carried out at pH 7 to confirm the results. The fiber consistency of the pulp slurries was 1.7% and the amount of filler was 50% of the dry fiber weight. As the filtration resistance is a function of consistency, the experiments were confirmed by using the same total dry matter content for pure pulps and slurries containing PCC.

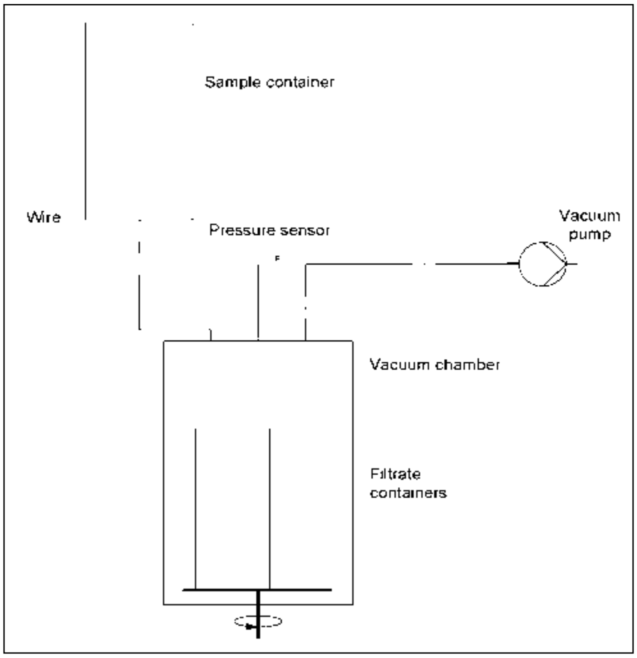
The vacuum filtrations were carried out by filtering the pulp slurries through a wire (open area 16%; 0.20 mm monofilament) under a constant pressure difference (18 kPa) at room temperature. The experimental setup of the apparatus is shown in **Fig. 4**. The fluid was drained without fiber mat formation at the beginning of the experiment, but a filter cake started to form on the wire in the course of time, and the thickening of the fiber network began to change into cake filtration. The total filtration time varied from 30 to 170 s depending on the dewatering properties of the slurry.

In addition to SFRs, generally used drainage indicators, Schopper-Riegler (SR) and Canadian standard freeness (CSF), were measured for the pulps according to EN ISO 5267-1:2000 [10] and TAPPI 227 om-99 [11] (**Fig. 5** and Table I), respectively. These methods differ significantly from the SFR method, however, in that they measure drainage at the very beginning of filtration.

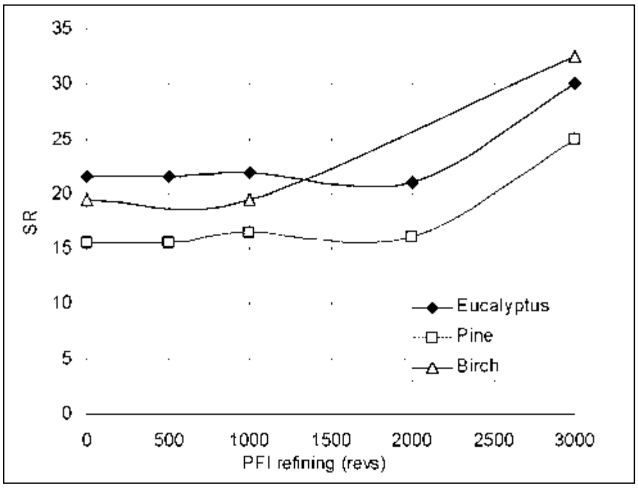
RESULTS

SFR of pure pulps

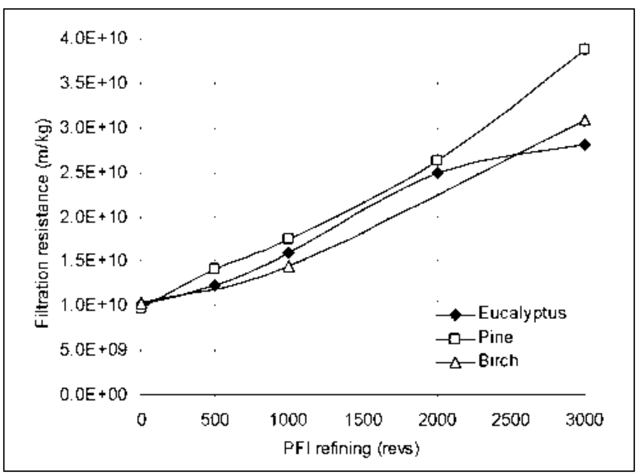
The SFRs of the pure pulps are shown in **Fig. 6**. Despite the differences in fiber properties, the SFRs of the unbeaten pulps were similar. For the beaten pulps, the filtration resistances started to vary as the degree of beating increased. The eucalyptus and birch pulps, with shorter av-



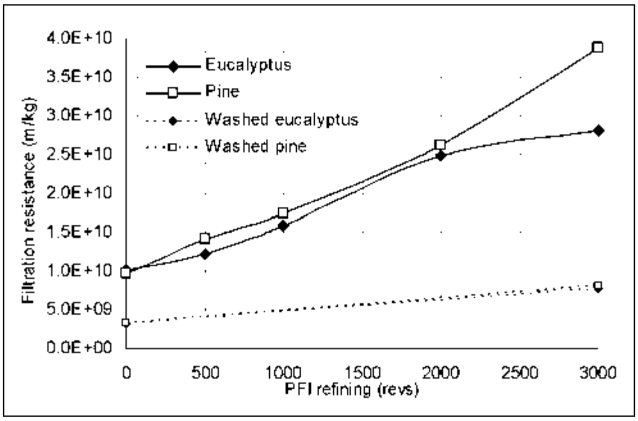
4. Experimental apparatus for vacuum filtration.



5. SR values of pulps as a function of beating.



6. Filtration resistance of pure kraft pulps.



7. SFR for untreated washed (fines-free) pulps.

erage fiber lengths than the pine pulp, were expected to have a higher SFR, because the short fibers could form a denser fiber cake. However, fiber length had no effect for unbeaten pulps. The lowest dewatering efficiency among the beaten pulps was for pine pulp, which has the highest average fiber length. This finding was also confirmed by another laboratory.

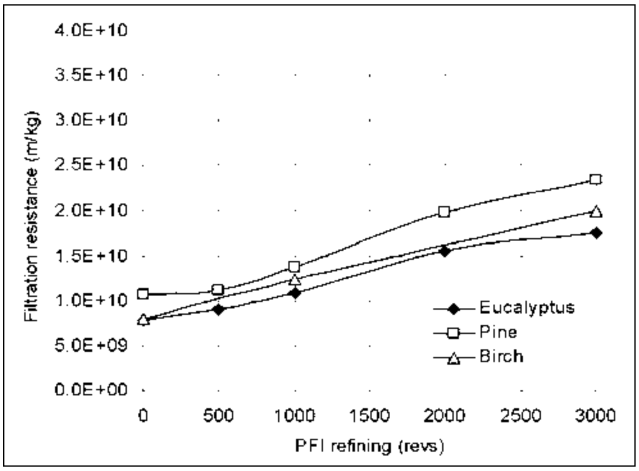
Contrary to the SFR results, the Schopper-Riegler (SR) and CSF values correlated with average fiber length (Fig. 5 and Table I). Eucalyptus pulp, which had the lowest fiber length, had the highest SR number and the lowest CSF value. Differences in SR and CSF values were already observed among the unbeaten pulps. The SR values increased slowly relative to the SFRs when the pulps were beaten.

The fiber properties measured for the pulps (Table I) showed that beating increased the width and flexibility of the fibers and reduced their coarseness. Average fiber length was unchanged for the eucalyptus and birch pulps, but a slight increase was observed for the pine pulp. The percent fines (Fig. 1) increased significantly for the pine pulp when the pulp was beaten (from 0.5% to 3.8%), compared to an increase of about 1.5 percentage points for the eucalyptus and birch pulps. The SR values of the pulps followed the relative order of the percent fines in each pulp, but the SFRs of the various pulp types did not show any direct correlation with percent fines.

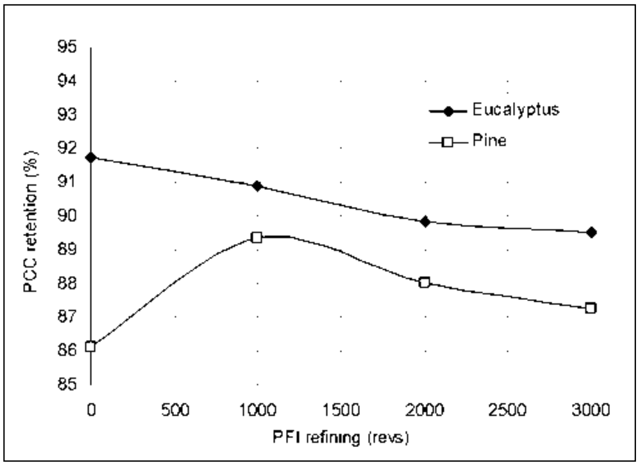
The influence of fiber fines on filtration resistance was illustrated using pine and eucalyptus pulps from which the fines had been removed by washing with a Bauer-McNett apparatus using a 200-mesh screen. The SFRs of the original and fines-free samples are shown in **Fig. 7**. The filtration resistances of the pulps decreased significantly when the fines were removed. The results show that pine and eucalyptus pulps are similar in their water removal behavior when the fines have been removed.

Effect of PCC on filtration resistance

The SFR values for the pulps containing PCC filler are shown in **Fig. 8**. Compared with the SFRs for pure pulps (Fig. 6), the filtration resistances of beaten pulps decreased. It was expected that these resistances would increase, because the small particle size would increase the surface area of the stock. In addition, the relative order of SFR values changed



8. Filtration resistance of pulps containing PCC filler.

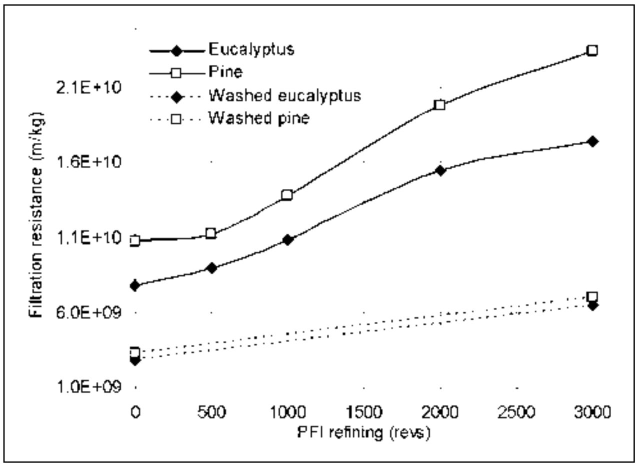


9. Retention of PCC in eucalyptus and pine pulps in the DDJ.

when the PCC was added. Whereas for pure pulps the highest water removal efficiency values, that is, the lowest SFR values, had been for birch, the lowest SFR values after the PCC addition were measured for eucalyptus.

The retention of PCC on fibers of different surface charge was illustrated in a dynamic drainage jar (DDJ) where retention is controlled by colloidal interactions instead of by mechanical entrapment or particle filtration [12,13]. The values obtained for the eucalyptus and pine pulps are shown in **Fig. 9**. Higher retention was measured for eucalyptus pulp than for pine pulp.

The effect of fines on water removal in pulps containing PCC was demonstrated using fines-free pine and eucalyptus pulps, the SFRs for which are shown in **Fig. 10**. The removal of anionic fines reduced the SFR.



10. SFRs for washed and untreated pulps with PCC.

DISCUSSION

SFR of pure pulps

The SFRs of pure pulps were greatly influenced by the fines fraction. Removal of the fines caused a significant decrease in filtration resistances and led to similar water removal behavior among the various pulps. The secondary fines, i.e., the fines fraction produced during beating, had an especially significant effect on filtration resistance [14]. Fines have a very high specific surface area relative to fibers and plug the pores of the filter cake efficiently. In addition, the anionic surface charge on the fines and fibers prevents both efficient sorption of fines onto the fibers and homoflocculation of the fines fraction. The result is an electrostatic stabilization that allows the dispersed fines material to penetrate the fiber network and become concentrated at the bottom of the cake.

The average filtration resistance increased within each pulp type as the amount of fines increased, although no direct correlation between the SFR of a pulp type and the amount of fines was observed. This finding indicates that other fiber properties also play a significant role in drainage. Fiber flexibility could partly explain the dewatering behavior of the pulps, since the compressibility of the cake increases with greater fiber flexibility, and the cake porosity and permeability diminish. Pine pulp, which had the highest flexibility, also had the highest SFR. Increased fiber width could have the opposite effect on fiber cake structure, as the porosity of the fiber network increases with fiber diameter [15]. Fiber length proved to have only a minor effect on drainage. Earlier results published by Mantar et al. [16] and Pires [17] also demonstrate that the filtration resistance of hardwood and softwood chemical pulps does not necessarily change systematically with average fiber length when different pulp types are compared.

The increase in SFR values as a function of beating also demonstrates the differences in beatability among pulps. The properties of softwood pulps develop faster than those of hardwood pulps. For example, the fines content of pine pulp increases markedly with beating, especially at the beginning. As a result, the filtration resistance of pine pulp was higher than that of either birch or eucalyptus pulps with the same degree of beating.

The water removal efficiency of the pulps as characterized by SFR differed from that based on SR freeness in the standard test, in terms of both their rank order of water removal efficiency and their responses to beating. As also stated by Springer et al. [18], SFR seems to be more sensitive in describing the flow resistance of beaten pulps (the curvature in Fig. 6 is greater than in Fig. 5 at a low level of beating). The difference in behavior between SFR and SR in vacuum experiments is probably related to the fact that SR measures the drainage rate at the beginning of the water removal process, whereas SFR describes the average drainage rate after a longer period (18 s).

Effect of PCC on filtration resistance

Anionic fillers had been previously observed [1] to increase the SFR of pulp. Due to electrostatic repulsion, the filler particles remain largely unattached to fibers and plug the filter cake. PCC is positively charged, however, and an attraction therefore exists between the fibers and filler particles. The results obtained here indicate that the deposition of filler particles on fibers due to attractive interaction was strong enough to reduce the surface area of the fiber suspension and to increase water removal. Thus, the decrease in SFR might be associated with the fact that when the part of the pulp containing dispersed anionic fines is replaced with cationic PCC, the total surface area decreases. In addition, the grade of PCC used here had a high porosity, which promotes water removal from the stock.

Furthermore, our findings suggest that fiber-PCC filler attraction and the SFR of the stock depend on pulp quality, because there are differences in the response to PCC addition. Some of these differences may be associated with structural properties, but mechanical entrapment of dispersed filler particles on fibers has been shown to be of only minor importance in filler attachment [2]. Comparison of the SFRs of the pulps with the zeta potential of the fibers (Figs. 8 and 2) shows that the water removal efficiency of pulps containing PCC correlates with the surface charge of the fibers. For pure fibers, no correlation exists. In addition, it was shown in the DDJ retention experiments that the higher zeta potential of eucalyptus fibers, compared to pine fibers, resulted in stronger interaction and better filler retention. These findings support the assumption that the electrostatic fiber-filler interaction described by the charge on fibers increases the deposition of PCC on fibers and reduces plugging of the filter cake. This means not only better retention, but also higher fluid permeability.

In addition to direct sorption of PCC onto fibers, flocculation of fiber fines and filler particles may significantly influence SFR. Davison [19] has reported that the fines and clay particles form free flocs, and these filler-fines flocs could become entrapped in the fiber cake more readily than individual particles and reduce fluid permeability to a lesser degree. The results obtained here show that the differences in SFR between pine and eucalyptus pulps are smaller for fines-free pulps than for the original pulps (Fig. 10). This suggests that fines-filler interaction has an important effect on drainage.

CONCLUSIONS

Most of the fillers used in papermaking carry a negative charge, which prevents

AUTHOR INSIGHTS

Unlike ground calcium carbonate (GCC) and most other anionic fillers, PCC has a natural attraction to anionic fibers due to its cationic surface charge. The cationic surface is reported to increase the retention of PCC, but little published material is available on the effect of PCC on water removal efficiency of stock. Increased retention often means that water removal is reduced, which is harmful to paper production.

In contrast to previous findings with other fillers, our results show that PCC reduces the filtration resistance of pulps, that is, it increases water removal. This result is thought to be related to the cationic surface charge of PCC particles, which promotes particle sorption on anionic fibers and reduces the specific surface area of the stock. In addition, our results show that the sorption of PCC particles increases and filtration resistance decreases when the anionic charge of the fibers increases.

However, real papermaking stock contains many heterogeneous components, including anionic impurities which could sorb onto the surfaces of particles and fibers and modify the interaction between cationic fillers and anionic fibers. In addition, the highly turbulent conditions on the papermachine make it necessary to use retention agents also for cationic fillers despite their natural attraction for fibers.

This study shows how cationic PCC filler can be used in mills to improve the dewatering behavior of chemical pulps, as well as improving our understanding of the filler-fiber interactions involved.

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particle deposition on the fibers and facilitate the plugging of the fiber cake in filtration processes. This plugging of the cake detracts from dewatering of the fiber-filler suspension. However, cationically-charged PCC particles attach efficiently to the fibers by attractive electrostatic forces, and this deposition reduces the total surface area of the stock and increases the dewatering efficiency, thereby reducing the SFR of the suspension. When the anionic charge of the fibers increases, the deposition of PCC particles increases and filtration resistance decreases. **TJ**

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