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FILLER AND FINES RETENTION IN PAPERMAKING

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ABSTRACT

On a paper machine the retention of fillers and fines during the first pass can be very different from the retention during a subsequent pass, because fillers and fines have much more time to interact in the short circulation loop than during the period between the injection of a retention aid and the forming section of the machine. Also in the short circulation loop reconformation of adsorbed polymer can occur, often reducing the flocculation efficiency of the polymer and interfering with subsequent adsorption. Thus for a meaningful modeling of retention on a paper machine first pass retention and second pass retention should be distinguished. Retention of fillers and fines can result from deposition on fibers, either freely suspended in the papermaking suspension or immobilized in the forming sheet, or by capturing fines and filler aggregates in the sheet by mechanical entrapment. Aggregates are more likely to be formed in the short circulation loop than on the paper machine. Effects of retention aids, detachment from fibers and the importance of polymer transfer are discussed.

1. INTRODUCTION

Incorporation of fillers and fines in a sheet of paper increases many of the paper properties, such as strength and optical properties. For many papers incorporating fillers also reduces costs. On a paper machine with an effective short recirculation loop, the amount of fines and fillers ending up in the final sheet is nearly independent of what is commonly called "first pass retention" of fines and fillers, because at steady state operation all fines and added fillers end up in the sheet. First pass retention is a misnomer, since it is an average, steady state, retention of fines and fillers, some of which may have passed through the machine several times. True first pass retention can be very different from second pass retention (i.e. the fraction of particles retained when passing through the forming section for a second time). To distinguish between the retention of particles which pass through the forming section for the first time, second time etc, we will reserve the term first pass retention (FPR) for fines and fillers which are retained when passing for the first time through the forming section, second pass retention (SPR), for those particles which pass through the forming section for a second time, third pass retention (TPR) when passing for the third time, etc. As to the average steady state retention, we will refer to this as wet end retention (WER, usually referred to as first pass retention). WER determines how many fines and fillers are being recirculated in the short circulation loop. High concentrations of fines and fillers in the circulation loop can cause problems, such as filler and fines deposition on the wall of the loop and holding tanks, increased difficulty in pumping the whitewater around, increased foaming, loss of fines and fillers when holding tanks overflow, etc. Thus, for economic reasons there exists an optimal fines and filler retention: at a low WER the costs of operating and maintaining the short recirculating loop are higher, whereas at high WER the cost of retention aid systems are higher. Also the drainage will be affected by the composition of the furnish in the headbox, which is different for different WER values. This affects runnability and possibly machine speed. The properties of the paper are also affected by wet end retention, because fines and fillers can aggregate within the short loop and end up in the paper as aggregates instead of single particles. They can also interact with other non-retained material, such as sizing, and strength agents. Also fines and fillers can be "poisoned", making retention in subsequent passes very difficult. Differences in drainage can affect paper uniformity. Thus in all likelihood, there also exists an optimum WER at which paper properties are optimum, which can be different from the optimum WER based on economic considerations only. Thus the prevailing trend in trying to maximize WER is not warranted. Instead one should look for an optimum WER, at which economic and paper properties concerns are balanced.

Fillers and fines can be incorporated in a forming sheet by five related mechanisms:

(i) By deposition on fibers suspended in the papermaking furnish, in the headbox, slice, or in the drainage section prior to reaching the dryline.
(ii) By deposition on fibers which are incorporated in the forming sheet (during drainage).
(iii) By homoflocculation of fillers and fines and subsequent entrapment of filler and fines aggregates in the sheet.
(iv) By heteroflocculation of fines and fillers and subsequent entrapment of aggregates in the forming sheet.
(v) By deposition of fillers on fines which are subsequently captured in the forming sheet (so-called "piggy-back riding").

The deposition of fillers or fines on fibers can be in the form of individual particles or, when they are unstable, in the form of aggregates.

All five mechanisms involve deposition and/or flocculation, usually induced by retention aids. For optimum performance, retention aids must be selective, i.e. they must induce desirable flocculation processes and prevent undesirable ones (such as fiber flocculation). Whether interactions are desirable or undesirable often depends on the final paper product one wants to make. For instance, if one wants to incorporate as much filler as possible (e.g. to reduce costs), flocculating the fillers and capturing them in the pores of the forming sheet is a good strategy. If, on the other hand, one wants to optimize the optical properties of the paper, the deposition of well-dispersed particles is preferable and flocculation of fillers is to be avoided.

2. DEPOSITION OF FILLERS AND FINES ON FIBERS

(a) Kinetics of deposition and detachment

Deposition of fillers and fines on fibers can be fairly well described by Langmuir kinetics [1]:

$$\frac{d\theta}{dt} = k_1(n_o - 1)(1 - \theta) - k_2\theta \tag{1}$$

The fractional coverage, θ, of fibers by particles depends on the deposition rate (first term on rhs) and on the detachment rate (second term of rhs). The initial concentration of particles (fillers or fines), n_o, is expressed in dimensionless form (relative to monolayer coverage). The deposition rate constant can be expressed as

$$k_1 = \alpha_d k_{fast} \tag{2}$$

and the detachment rate constant as

$$k_2 = k_2^o e^{-E/kT} \tag{3}$$

Equations (2) and (3) show that the rate constants can be decomposed in factors that depend mainly on hydrodynamic conditions (k_{fast} and k_2^o) and factors that depend on physicochemical conditions (the deposition efficiency α_d and the bond strength E). The deposition efficiency α_d is determined by the colloidal forces acting between the fibers and the fillers. The major forces are van der Waals attractive forces, electrostatic forces, bridging forces and steric repulsive forces. For repulsive electrostatic fiber-filler interactions, α_d is a strong function of ionic strength. At low salt concentrations $\alpha_d \approx 0$, whereas above a critical salt concentration, referred to as CDC, (critical deposition concentration), $\alpha_d \approx 1$. The ionic strength of process water varies from mill to mill. Typical conductivities of white water correspond to equivalent 1–1 salt concentrations in the range 1–10 mM [2]. CDCs are often within this range. Thus for industrial conditions in some process waters the filler deposition efficiency $\alpha_d \approx 0$, whereas in others $\alpha_d \approx 1$. In whitewaters containing large concentrations of bivalent ions (such as Ca^{2+}), usually $\alpha_d \approx 1$.

In the presence of retention aids, α_d and E become time-dependent. E.g. α_d may vary from 0 before the addition of a retention aid to 1 after the addition. The change from 0 to 1 occurs on the time scale of polymer adsorption. Similarly, E can vary from a weak bond to a strong bond in the same time period.

We have shown earlier [3] that k_{fast} is a strong function of the ratio a/R, a being the radius of a filler particle and R that of a fiber. The rate constant k_{fast} increases with a/R, the reason being that large fillers can approach fibers to shorter distances where van der Waals attractive forces are larger. This size-dependence of k_1 is important when fillers flocculate and deposit as aggregates on pulp fibers. Since aggregates are much larger than single particles, they deposit on fibers with a larger initial rate. An example is given in Figure 1, which shows the deposition on fibers of single well-dispersed clay particles and that of clay aggregates. As can be seen, the clay aggregates deposit with a much larger rate.

Other factors that influence the deposition kinetics are fiber fibrillation and

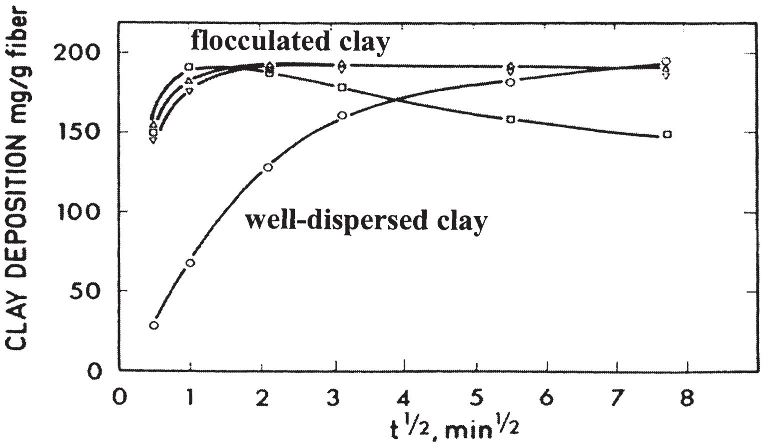

Figure 1 Deposition of clay on fibers as a function of time. Slow paddle stirring. $C_F = 0.1$ %. (after [4]). The initial deposition for aggregates (induced by pH or cationic flocculant) is much higher than for well-dispersed clay particles. Deposition is shown as $t^{1/2}$ for convenience only, allowing short and long time data to fit on the same graph.

the formation of fiber flocs. When a filler or fines particle collides with a fiber floc, it can deposit on fibers which are located on the surface of the floc, or it can enter the interior of the floc. When they enter a floc, they could conceivably deposit on a fiber surface within the floc, however this is unlikely to happen, because flocs break up well before a filler particle that has entered the floc deposits on its interior. It can be shown that the rate constant for deposition on fiber flocs (proportional to nN_{fl}, n being the number of fibers per floc and N_{fl} the number concentration of fiber flocs) is similar to that for the deposition on dispersed fibers (proportional to the number concentration of fibers) and thus the deposition on the outside surface of a floc occurs at a similar rate as deposition on dispersed fibers.

Of more importance is fiber fibrillation, which affects the effective volume of a fiber, thus increasing k_1, and the surface area available for deposition, thus decreasing n_o. The deposition kinetics is governed by the product k_1n_o which probably increases somewhat with fibrillation. Fibrillation also has a strong effect on particle detachment. Detachment of fillers from fibrils is more difficult than detachment from the main body of the fibers. Because particles are subject to fluctuating hydrodynamic forces, particle-fiber bonds are randomly being compressed and stretched. Only during stretching can detachment take place. Because fibrils are flexible and mobile, they can adjust to fluctuating forces by moving along with the flow. This reduces the time the bonds are stretched, thus minimizing detachment. Hence the detachment rate constant k_2 for a fibrillated fiber is expected to be smaller than for a smooth fiber. That fillers stick stronger to fibrils than to fibers has been observed experimentally [5].

(b) Filler retention in the absence of retention aids

In the absence of retention aids fillers can deposit on fibers either when the fibers and fillers are oppositely charged, or when they have the same charge but the salt concentration is above the CDC. An example of positive PCC depositing on negative fibers is shown in Figure 2. From the best fit to Equation (1) one obtains $k_1 = 1.4.10^{-2}s^{-1}$ and $k_2 = 1.1.10^{-3}s^{-1}$. The deposition rate is in fair agreement with the fast shear-induced deposition rate, i.e.$\alpha_d = 1$ [6].

The low detachment rate deduced from Figure 2 is not typical of papermaking conditions. At papermaking conditions one expects detachment rate constants to be very large, because k_2^0 increases steeply with shear rate. Thus even when the deposition rates are high ($\alpha_d \approx 1$), no appreciable filler retention occurs in papermaking in the absence of retention aids, since the bond strength E is too weak to withstand the shear forces. The reason why the bond

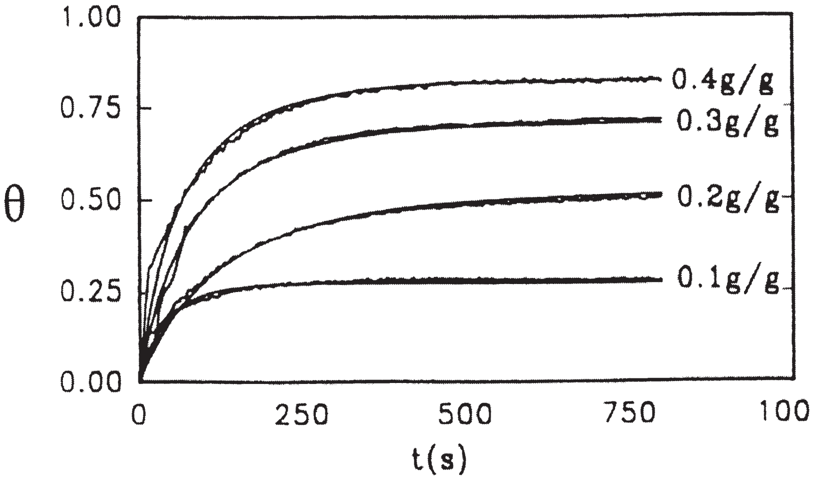

Figure 2 Kinetics of deposition of positively charged PCC (precipitated calcium carbonate) on negatively charged pulp fibers, for various PCC dosages indicated in the figure. pH=9.5 (after [6]).

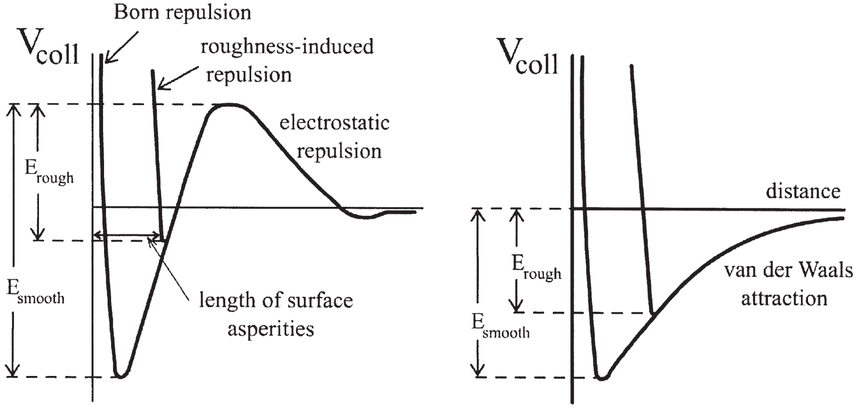

Figure 3 Weakening of the fiber-filler bond due to fiber surface roughness. (a) electrostatic repulsion between fiber and filler (left), (b) absence of electrostatic repulsion (right).

strength is weak is the surface roughness of the fibers, which prevents close fiber-filler contact. Schematic diagrams for the interaction energy, V_{coll}, between a fiber and a filler are shown in Figure 3, which includes a "steric" force arising from surface roughness. It can be seen that the energy minimum in which a filler particle is captured on rough fibers, E_{rough}, is much smaller than the minimum for smooth fibers, E_{smooth} (in which case the minimum is determined by the Born repulsion).

From this argument it follows that in many cases the role of the retention aid is not to induce deposition, but to ensure that the bond strength between a filler and a fiber is strong enough to withstand the large shear forces acting on the particles.

(c) Deposition by charge modification

(i) Effective charge model

We can modify the surface charge of fibers, fines and fillers by adsorption of highly charged polyelectrolytes, such as PEI (polyethylene imine), pDADMAC (polydiallyldimethylammonium chloride), high charge density C-PAM (cationic polyacrylamide) or other polymers (such as e.g. polypropylene imine (PPI) dendrimers [7]). These polyelectrolytes initially (at low dosages) reduce the electrostatic repulsion between fibers and fillers and subsequently (at high dosages) reverse the charge and create electrostatic repulsion between

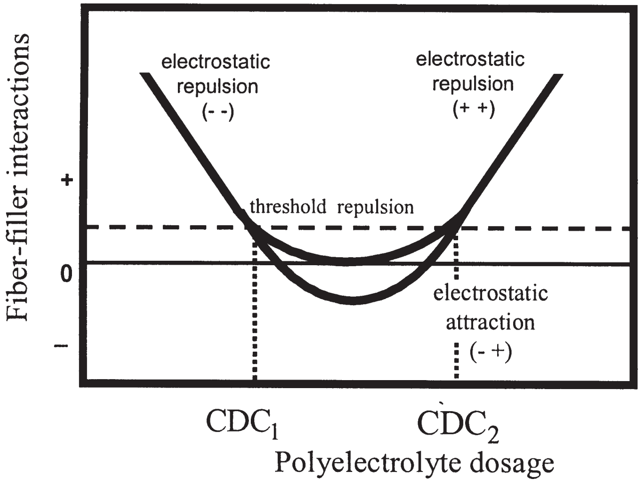

Figure 4 Fiber-filler interaction as a function of polyelectrolyte dosage. (1) fiber and filler charge change in an identical manner (top curve), (2) charge of fibers is reversed prior to that of the fillers (or vice versa) (bottom curve).

positive surfaces. Thus these polyelectrolytes cause deposition only within a certain concentration range, as shown schematically in Figure 4 (between CDC_1 and CDC_2).

If fibers and fillers change their charge in a similar manner, the electrostatic interaction between them becomes zero when the particles reach their point of zero charge and increases afterwards. More realistically, the polyelectrolyte adsorbs on the fibers and the fillers with a different rate and one of the components becomes positive before the other, resulting in electrostatic attraction. Deposition occurs when the repulsion between the fibers and the fillers is below a certain threshold value, determined by the height of the energy barrier. This height determines whether or not the shear can push particles over the barrier into the primary minimum (cf. e.g. Figure 3). Thus no deposition occurs below a certain polyelectrolyte concentration (CDC_1) and above a second polyelectrolyte concentration (CDC_2).

To induce filler deposition on fibers, one can either pretreat the fibers or the fillers, or one can add the polymer to the fiber-filler mixture. Pretreatment leads to either positive fillers or positive fibers, whereas for polymer addition, the charges on the particles are dictated by the kinetics of polyelectrolyte adsorption. At high shear conditions on a paper machine, polyelectrolytes adsorb preferentially (i.e. faster) on fibers and thus this situation is similar as pretreating the fibers. At low shear, e.g. in the mixing chest, polyelectrolytes will adsorb on both fibers and fillers, with a preference for fillers if their concentration and thus their surface area is sufficiently large.

Polyelectrolyte dosages are usually less than a monolayer coverage (i.e. $n_o < 1$) and thus polyelectrolyte addition (to the mixture) leads to partially coated fibers with a net positive charge. The surface of the fiber can be thought of as a surface of negative charge dotted with (highly charged) positive patches. The fillers will remain negatively charged, since little polyelectrolyte adsorbs on them. A filler particle in the vicinity of a partially coated fiber will experience a fluctuating force, randomly fluctuating between attractive and repulsive, depending on how close it is to positive or bare (negative) patches. On average the force will be attractive, since the net charge on the fiber is positive. Since fillers orbit a fiber prior to deposition (as they are in a flow regime similar to the region of closed trajectories), this net attractive force will cause the fillers to be on an approach trajectory, eventually landing on a positive patch. Thus fibers partially coated by polyelectrolytes behave very similar as fibers with a uniformly distributed charge with the same average charge density.

The deposition of fillers on fibers in suspensions of pretreated fibers or fillers is again described by Langmuir kinetics. The same applies to suspensions to which polyelectrolytes are added to the mixture at high shear, since polyelectrolyte adsorption on fibers is shear-induced. The detachment rate increases with shear much more than the deposition rate, resulting in less filler retention at high shear.

(ii) Role of zeta-potentials

The zeta-potential has been postulated to be the controlling parameter in filler retention, as well in a number of other phenomena [8–10]. Optimum filler retention is assumed to occur when the zeta-potential is (close to) zero. A problem with this assumption is that a papermaking suspension contains many different zeta-potentials, all of which are functions of time after polyelectrolyte addition. Measurement of a single papermaking furnish zeta-potential, (e.g. with an a.c. streaming current device) are difficult to interpret. Usually one adds polyelectrolyte till the “average” zeta-potential is zero. However, this potential reflects the potential of the wall of the device on which polyelectrolytes, fillers, fines, etc. have adsorbed. If some of these components adsorb preferentially, their contribution will heavily skew the observed value.

Since the deposition of fillers on fibers induced by highly charged polyelectrolytes is driven by electrostatic forces, it makes sense to measure the zeta-potentials of the individual components, or alternatively, the distribution in zeta-potentials. Modern zeta-potential instruments can provide this information. For fiber-filler interactions, the important parameters are the zeta-potentials of fibers and fillers (ζ_1 and ζ_2), or what really counts their product $\zeta_1\zeta_2$, and the ionic strength (or more precisely the double layer thickness). These parameters determine the height of the energy barrier, which controls the deposition efficiency. Notice that when $\zeta_1 = 0$ or $\zeta_2 = 0$ the repulsive force is zero, despite the fact that the "average" zeta-potential could be large (either negative or positive). The energy barrier controls the threshold repulsion shown in Figure 4. For a given salt concentration the product $\zeta_1\zeta_2$ must be below a critical value. It is not necessary that $\zeta_1 = \zeta_2 = 0$. Obviously when $\zeta_1 > 0$ and $\zeta_2 < 0$ (or vice versa), the product $\zeta_1\zeta_2$ is negative and filler deposition always occurs. Zeta-potentials have nothing to say how polyelectrolytes affect the bond strength, equally important in filler retention.

(d) Deposition by polymer bridging

(i) Heteroflocculation

Polymer bridging between fibers and fillers takes place when neutral polymers or low charge density polyelectrolytes adsorb on the surface of the particles. When polymer adsorbs both on the fibers and the fillers, thus linking them together, filler deposition on fibers can be considered an example of heteroflocculation by macromolecular bridging. Examples of bridging molecules are PEO (polyethylene oxide), N-PAM (neutral polyacrylamide), low charge density C-PAM and A-PAM (anionic polyacrylamide) and starch. Some water soluble polysaccharides present in the whitewater could conceivably bridge particles, but since they have a low affinity for fibers, their bond strength is expected to be weak. Besides single macromolecules, also association complexes can act as bridging agents, such as PEO-cofactor complexes [11] and complexes between low charge density C-PAM and anionic dissolved substances [12].

When added close to the headbox at less than monolayer concentrations ($n_o < 1$), polymer addition will result in partially coated fibers (i.e. with a fractional coverage $\theta < 1$) and almost bare fillers. Since (most) fillers will only deposit on polymer patches, the deposition efficiency will be given by

$$\alpha_d = \theta \tag{4}$$

For flat particles (such as clays) and/or thick polymer patches, the deposition efficiency is expected to be even higher. When polymer is present on both the fibers (with coverage θ_1) and on the fillers (with coverage θ_2), the deposition efficiency equals

$$\alpha_d = (1 - \theta_1)\theta_2 + (1 - \theta_2)\theta_1 \tag{5}$$

which, like Equation (4) can be modified for fillers with different geometries. Notice that for large dosages of polymer, θ_1 and θ_2 approach 1, resulting in $\alpha_d = 0$ and thus flocculation no longer occurs due to steric repulsion.

Equations (4,5) apply when the polymer layer thickness δ_p exceeds the thickness δ_{el} over which electrostatic repulsion acts between fibers and fillers. (As an approximation we can equate δ_{el} with $2\kappa^{-1}$, $1/\kappa$ being the Debye length, but δ_{el} depends on the surface charge density of the fibers and fillers as well). Hence polymer bridging is more efficient for high molecular weight polymers which adsorb as thick patches. Another reason why high molecular weight polymers are preferred is that they lead to stronger bonds for two reasons: (i) more polymer segments are in contact with the fiber and filler at any given time and (ii) the probability of breaking the polymer bond is reduced. A fiber in turbulent flow is subject to a fluctuating flow field in which the flow components can change randomly from compressional flow to extensional flow. When a fiber-filler bond is compressed no breakage occurs, whereas when such a bond is stretched in extensional flow, breakage might occur, depending on the magnitude of the flow and the duration of the extensional flow. Breakage is most likely to occur when the bond is fully stretched. Since it takes longer to fully stretch a high molecular weight polymer, the probability of breakage is reduced: before the bond can stretch fully, usually the flow is changed to a compressional mode, thus avoiding bond breakage. Finally, high molecular weight polymers can increase the fast deposition rate constant, k_{fast}, by intercepting particles at larger distances of approach.

As examples we will discuss the deposition of fillers and fines on fibers by two commonly used bridging agents: low charge density C-PAM and PEO/cofactor complexes.

Polymer bridging by LCD (low charge density) C-PAM is given in Figure 5, which shows the results of $CaCO_3$ (either precipitated, PCC, or ground, GCC, without dispersants) deposition on fibers. As can be seen, the extent of deposition is very insensitive to polymer dosage.

The reason is that steric repulsion is not dominant, since van der Waals attractive forces continue to play a major role. The interaction energy between a fiber and a filler in the presence of a LCD polyelectrolyte is shown schematically in Figure 6. The van der Waals energy is calculated according to the theory of sphere-wall interactions, whereas the repulsive steric (or electrosteric) energy is expected to become large at a distance twice the

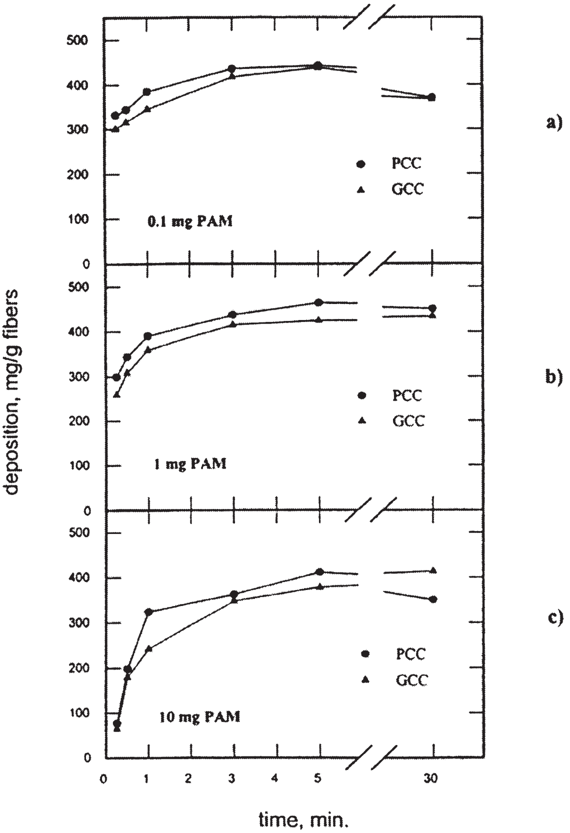

Figure 5 Deposition of PCC and pure GCC (without anionic dispersant) on fibers induced by LCD C-PAM as a function of time for various C-PAM dosages indicated in the figure (after [13]).

polymer layer thickness, estimated as 100 nm. It can be seen that for such systems the depth of the energy minimum can be several kT (thermal energy) units, sufficiently deep to keep particles captured.

To study fines deposition on fibers in isolation, one can separate the fines from the long fiber fraction, treat each fraction separately and add them together. An example is shown in Figure 7, where C-PAM coated fibers are added to bare fines. It can be seen that deposition occurs, followed by detachment.

The initial deposition rate closely follows the predictions of shear-induced

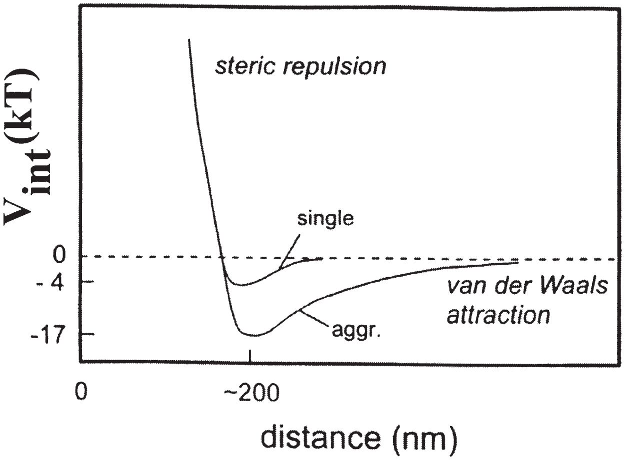

Figure 6 Estimated interaction energy between PCC fillers and pulp fibers coated by LCD C-PAM. Fillers can deposit either as single particles or as small aggregates. (after [13]).

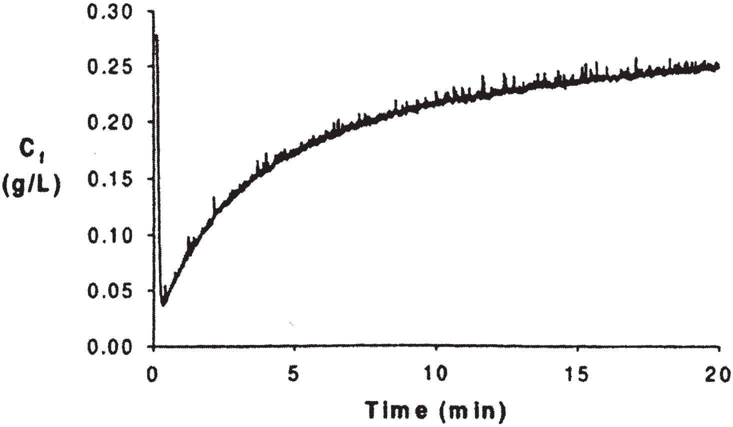

Figure 7 Fines deposition on C-PAM coated fibers, followed by fines detachment (after [14]). During the initial few seconds the concentration of dispersed (non-deposited) fines decreases, due to deposition on fibers, whereas afterwards fines leave the fibers and the concentration of dispersed fines increases.

Table 1 Efficiency of fines deposition on fibers[a]

System	α_d
1.bare fiber – bare fines	0
2.coated fibers – bare fines	1
3.bare fibers – coated fines	1.8
4.bare fibers – depleted fines	0.8
5.bare fibers – fines with transferred polymer	0
6.fibers with transferred polymer – bare fines	0.6
7.depleted fibers – fines with transferred polymer	0
8.coated fibers – coated fines	fast

note[a]: mechanical fibers and fines, treated with C-PAM (after [14])

deposition [14, 15] (Smoluchowski kinetics). Different pretreatments of fibers and fines can lead to different deposition efficiencies, as can be seen from Table 1. Besides experiments with bare and fully coated fibers and fines, fines and fibers were also separated after a deposition experiment, resulting in polymer transfer from fibers to fines and fibers with less than full coverage, referred to in the table as "depleted". Vice versa, one can obtain depleted fines and fibers with transferred polymer.

The deposition efficiencies α_d in Table 1 are expressed relative to the deposition of bare fines on fully coated fibers. For case 3, $\alpha_d > 1$, likely because treating fines with C-PAM leads to fines flocculation (see below) and larger particles (or flocs) deposit on fibers with a larger rate than small particles (cf. Figure 1). When C-PAM is transferred from coated fines to fibers and the depleted fines are added to fresh bare fibers, deposition is again rapid, with an efficiency of 80% (case 4). For depleted fines the surface coverage θ_2 (of polymer on fines) is less than 1, resulting in a somewhat reduced deposition rate. When fibers with transferred C-PAM are added to bare fines (case 6), again a rather rapid deposition occurs with an efficiency of 60%, because the surface coverage θ_1 (of polymer on fibers) is less than 1. When both fibers and fines have polymer on their surface (either transferred or depleted) no deposition occurs, implying that electrostatic repulsion between fibers and fines prevents polymer bridging between polymer patches and bare patches. When both fibers and fines are fully coated by C-PAM, this electrostatic repulsion is eliminated and the adsorption layers are not sufficiently thick to prevent deposition by van der Waals attraction.

Next we discuss the macromolecular bridging by PEO and cofactor retention aids. An example is presented in Figure 8, which shows the deposition of

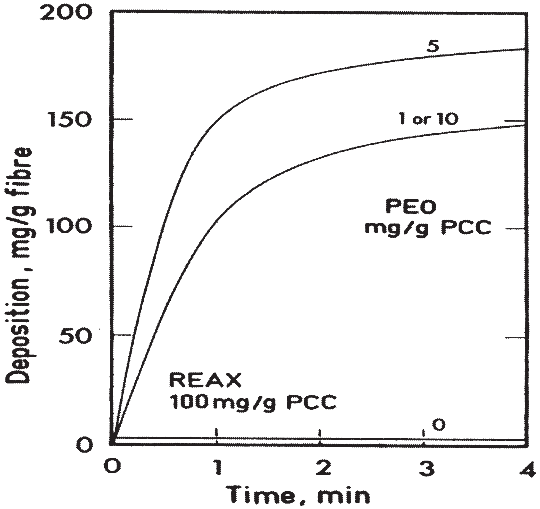

Figure 8 Deposition of PCC on pulp fibers as a function of time for various PEO dosages indicated in the figure. [SKL or REAX]=100 mg/g fiber. (after [16]).

PCC particles on fibers by PEO-SKL (sulfonated kraft lignin) complexes. It has been shown that PEO-cofactor retention aids deposit fillers on fibers by the process of association-induced polymer bridging [11, 16]. PEO by itself does not adsorb on most fibers but PEO-cofactor complexes do and thus are able to bridge fibers and fillers. It can be seen that in the absence of PEO no deposition occurs, since SKL adsorbs on PCC and makes the particles negative, thus preventing deposition on negative fibers. Optimum deposition occurs at a PEO dosage of 5 mg/g, at which fibers and fillers are partially coated. Increasing the PEO dosage beyond the optimum dosage results in reduced deposition as predicted by Equation (8). Thus PCC deposition on fibers induced by PEO-SKL is fully consistent with the mechanism of macromolecular bridging by PEO-SKL complexes.

For mechanical pulps polymer adsorption on fines occurs simultaneously with adsorption on fibers, since fiber and fines volume fractions are comparable, while for chemical pulps more polymer ends up on the fibers than on the fines. That for TMP pulps these processes occur simultaneously can be seen from Figure 9, which shows the changes in light absorbance taking place after a PEO-cofactor retention aid system is added to a TMP fiber/fines suspension. The initial increase in absorbance is likely due to fines flocculation, whereas the decrease is due to deposition of fines on fibers. The deposited

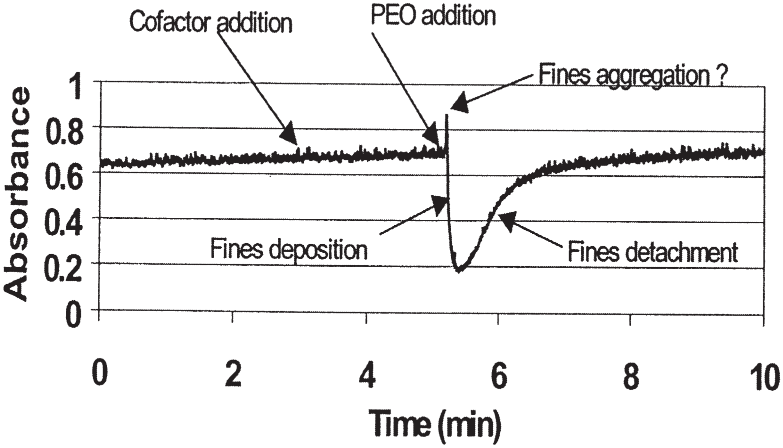

Figure 9 Fines deposition on fibers induced by a PEO-cofactor retention aid system, as deduced from the absorbance of the supernatant. The initial spike after PEO addition is likely due to fines flocculation. (after [21]).

fines are slowly released again, possibly due to PEO flattening (similar as for clay) or to polymer transfer (see below). The state of PEO dissolution also strongly affects fines deposition, since entangled PEO molecules are more effective bridging agents than disentangled ones [17–20].

(ii) The role of zeta-potentials

Because neutral polymers and LCD polyelectrolytes function by macromolecular bridging, the zeta-potential has little effect on the deposition efficiency. Optimum dosages are not determined by the point of zero charge, but by the condition $\alpha_d = 1$, corresponding to a monolayer of polymer on either the fibers or the fillers or, when polymer adsorbs equally on fibers and fillers, when $\theta_1 = \theta_2 = 1/2$ (and $\alpha_d = 1/2$). The zeta-potential has some effect when interactions between bare surfaces can also lead to deposition, in which case

$$\alpha_d = \alpha_b (1 - \theta_1)(1 - \theta_2) + (1 - \theta_1)\theta_2 + (1 - \theta_2)\theta_1 \tag{6}$$

where α_b is the efficiency at which bare fillers deposit on bare fiber. By reducing the zeta-potential to (near) zero, α_b can be increased from zero to one. However, changing the zeta-potential requires another additive, such as e.g. a polyelectrolyte. These additional additives can interact with the polymeric retention aid and reduce its efficiency. When anionic DCS interfere with LCD polyelectrolytes, their neutralization with a HCD (high charge density) polyelectrolyte (an ATC, an anionic trash collector) prior to the addition of the LCD (low charge density) bridging polyelectrolyte could increase its efficiency.

3 RETENTION BY DUAL POLYMERIC AND MICROPARTICULATE RETENTION AID SYSTEMS

It has been shown on experimental and real paper machines that dual polymeric and microparticulate retention aid systems can improve retention and reduce chemical costs as compared to single component retention aids. Few fundamental studies on filler deposition induced by these systems are reported in the literature. Various reasons for the efficiency of dual polymeric retention aid systems have been put forward [5]. Here we mention the two most important ones: (i) Fiber-filler bonds with 2 polymers are stronger than single polymer bonds. Denoting a cationic polyelectrolyte by CPEL and an anionic one by APEL, we can say that fiber-CPEL-APEL-CPEL-filler bonds are stronger than fiber-CPEL-filler bonds. The same applies to fines. The reason could be that the dual system has a larger effective molecular weight and that CPELs can be used with a high affinity for the fibers and fillers. Thus both the fiber-CPEL bond and the CPEL-APEL bonds are strong. (ii) Dual polymeric systems offer more control, since one polymer can be added early and one late in the papermaking process. This allows optimum time for CPEL adsorption prior to APEL bridging. The time delay between cationic and anionic polyelectrolyte additions has a strong effect for low CPEL dosages, likely due to CPEL transfer and subsequent reconformation and flattening. When adding CPEL and APEL together (no delay), CPEL-APEL complexes form prior to CPEL adsorption on fibers, thus reducing the bridging efficiency.

The same is true for microparticulate systems [12, 15, 22–24]. For instance in the C-PAM/bentonite system, the fiber-CPEL-montmorillonite-CPEL-filler bond is much stronger than the fiber-CPEL-filler bond. (Montmorillonite is the major component of bentonite). Moreover with microparticulate systems one has the same control as with dual polymeric systems: one component (usually CPEL) is added first and the second component (usually montmorillonite, bentonite or silica) is added later. An example of filler deposition of PCC fillers on fibers induced by a microparticulate retention aid system is shown in Figure 10. Initially 200 mg of PCC are added to 1 g of fiber and the suspension is sheared at 1500 rpm. Next (after 30 s) C-PAM is

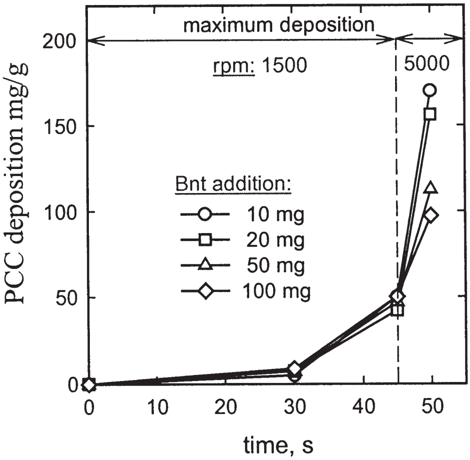

Figure 10 Deposition of PCC on pulp fibers. At 30 s, C-PAM is added and at 45 s the shear is increased and bentonite is added at various dosages indicated in the figure (after [12, 23]).

added and PCC deposition on fibers takes place. To simulate the increase of shear on a paper machine, where a pulp suspension passes through a screen and fan pump, the shear is increased to 5000 rpm and at the same time bentonite is added. This results in a tremendous increase in PCC deposition. Since the detachment rate increases with shear more than the deposition rate, this result indicates that bentonite creates very strong bonds between fibers and PCC fillers. Deposition is optimum at a bentonite dosage of 10 mg/g, corresponding to about 4 stacks of montmorillonite plates.

4 FILLER AND FINES DETACHMENT FROM FIBERS AND POLYMER TRANSFER

Particle detachment from fibers can have a large effect on fines and filler retention. When particle deposition is caused by polymers or polyelectrolytes, particle detachment can be accompanied by polymer (or polyelectrolyte) transfer. Fillers and fines with transferred polymer can flocculate, resulting in the incorporation of aggregates in the sheet. Polymer transfer can be the fastest way for polymer to adsorb on particles, especially for fillers, because polymer adsorption on fibers is usually faster than adsorption on fillers under high shear conditions. Also the rate of particle deposition on fibers is faster than polymer adsorption on fillers [1]. If the filler detachment rate is faster than the polymer adsorption rate (on the fillers), then fillers acquire polymer faster by polymer transfer than by direct adsorption. For mechanical fines polymer adsorption is similar as for fibers, because fines concentrations in the headbox are comparable to fiber concentrations. Thus such fines acquire polymer both by direct adsorption and by transfer.

An example of fines detachment was already shown in Figure 7, where a short period of fines deposition was followed by 20 minutes of detachment. Equation (1) predicts that fines deposition should increase gradually till a plateau is reached, at which time a dynamical equilibrium between deposition and detachment is established. The observation in Figure 7 shows that either the detachment rate "constant" k_2 is increasing with time, or the deposition rate "constant" k_1 is decreasing with time (or both). The explanation is that fines pick up C-PAM from the fibers when they detach, resulting in positive fines (as concluded from electrophoretic mobility measurements [24]), which deposit with a much lower rate on the positive fibers. Fines detachment was also seen in Figure 9, where an alternative explanation is the flattening of adsorbed PEO molecules, resulting in weaker polymer bridges, because of increased electrostatic repulsion at shorter fiber-fines separations.

Polymer transfer has been observed in a number of experimental systems [24–26]. Usually the transfer is not complete and an equilibrium distribution is established, with some polymer residing on the fibers and some on the fillers (or fines). This distribution is determined by the relative affinities of the polymer for the fibers and fillers and their respective surface areas. Prior to reaching an equilibrium distribution, kinetic factors play a major role in the polymer redistribution. Besides polymer transfer, also polymer breakage and polymer rearrangement can lead to a time dependence of the deposition and detachment rate constants. For highly charged polyelectrolytes which act by charge modification, the precise polymer configuration has less effect than for neutral polymers which function by bridging. In papermaking polymer transfer can be minimized by adding the polymer close to the headbox. Also the rupture of polymer chains might occur, but this is more likely to happen during detachment of larger particles, such as fines.

The amount of polymer transfer can be estimated from the apparent detachment rate, k_{app}, seen e.g. in Figure 7. For coated fibers and bare fines, and defining the time of maximum fines deposition as $t = 0$, fines detachment can be approximately described by:

$$\theta \approx e^{-k_{app}t} \tag{7}$$

The time-dependence of the deposition rate constant can be described by a time-dependence of the deposition efficiency α_d, according to Equation (5), in which now θ_1 and θ_2 depend on time, due to polymer transfer. Their changes with time are related, because the total polymer concentration is constant. Denoting the surface area of the fibers by A_1 and that of the fines (or fillers) by A_2 and assuming all polymer is adsorbed, then

$$\frac{d\theta_1}{dt} = -\frac{A_1}{A_2}\frac{d\theta_2}{dt} \tag{8}$$

Moreover, the number of polymers adsorbed on fibers, n_p, (per unit volume) is expected to change as

$$\frac{dn_p}{dt} = -m\frac{dM}{dt} \tag{9}$$

where M is the number of fines leaving the fibers (per unit volume) and m the number of polymer molecules transferred during a single detachment; m is defined as positive if polymer is transferred from fibers to fines and negative if polymer is transferred from fines to fibers. Since $dM / dt = k_2N_f$, Equation (9) can be written as

$$\frac{d\theta_1}{dt} = -m\frac{N_f^{max}}{n_p^{max}}k_2\theta = -\beta k_2\theta \tag{10}$$

Here N_f^{max} is the maximum number of fines that can deposit on a fiber (as a monolayer) and n_p^{max} the maximum number of polymer molecules that can adsorb on a fiber. Assuming cylindrical fines of radius a_f and length L_f and polymers of radius a_p, the ratio β/m equals

$$\frac{N_f^{max}}{n_p^{max}} \approx \frac{\pi a_p^2}{2a_fL_f} \tag{11}$$

Estimating a_f from the specific surface area ($11\ m^2 / g$) yields $a_f = 0.1\ \mu m$. Assuming $L_f = 100\ \mu m$, results, for 100 nm size polymer, in $N_f^{max}/n_p^{max} \approx 10^{-4}$. Substituting Equation (7) into Equation (10) and integrating yields for the change in polymer coverage on the fibers:

$$\Delta\theta_1 \approx -\beta\frac{k_2}{k_{app}} \tag{12}$$

Experimental values are [24]: $\Delta\theta_1 = 0.8$, $k_2 = 8\ \text{min}^{-1}$ and $k_{app} = 0.2\ \text{min}^{-1}$ and thus $\beta \approx 0.02$, or equivalently, $m \approx 200$. Although a rough estimate, this argument suggests that on average a few hundred polymer molecules are transferred from fibers to fines, each time a fines particle detaches itself from a fiber. This large number is due to the large contact area between fibers and adsorbed fines.

Polymer transfer does not necessarily reduce the deposition efficiency. If polymer were to transfer from fibers to fillers, the deposition efficiency would change from θ_1^F to θ_2^f, the coverage on fibers and fillers (or fines) respectively, provided the amount of polymer is less than needed for a monolayer on fillers. If $A_2 < A_1$, $\theta_1^F > \theta_2^f$ and thus the efficiency has increased during polymer transfer. In general, defining $N = N_1 + N_2$, N_1 and N_2 being the number of molecules on fibers and fillers, and expressing the deposition efficiency (cf. Equation (8)) in terms of the polymer transfer $x = N_2 / N_1$ yields

$$\alpha_d = \theta_1^F + (\theta_2^f - \theta_1^F - 2\theta_1^F\theta_2^f)x + 2\theta_1^F\theta_2^f x^2 \tag{13}$$

which is valid for $x < A_2/NA_1$. Notice that $\theta_2^f > 1$ when more polymer is present than needed for a monolayer coverage on fillers. When the polymer transfer reaches A_2/NA_1, then $\theta_2 = 1$ and no further transfer is possible. When $A_2 > NA_1$, all polymer can transfer. Depending on the values of θ_1^F and θ_2^f, the deposition efficiency can increase or decrease during polymer transfer.

Equations (10–13) describe the transfer of polymer when no polymer degradation (or cleavage) occurs. Polymer cleavage has been observed during deposition and detachment of fillers from fibers[27] and deduced from fines detachment experiments [24]. Although polymer degradation certainly can happen, it is not obvious that it occurs during filler or fines detachment from fibers. The degradation could also happen when a polymer chain bridges two fibers which subsequently separate. The cleaved polymer can afterwards be transferred to fillers or fines. The polymer transfer coefficient (proportional to m), was found to increase with shear for C-PAM bridges and to be independent of salt concentration [24]. It was speculated that this was due to polymer cleavage. Other possible explanations are the stretching of polymer bridges by shear, leading to less polymer-surface contact points, and the screening of both C-PAM – fiber and C-PAM – fines bonds, leading to a weakening of both bonds, which could have a negligible effect on polymer transfer. Polymer cleavage is much more likely to happen during fiber collisions and fiber separation, than during fines or filler detachment from fibers, since the hydrodynamic forces acting on fibers are much larger. For a 10 μm filler or fines particle, the hydrodynamic force exerted on the particle, for a shear rate of 1000 s^{-1}, is less than 1 nN, whereas the force needed to break a covalent bond is in the range of a few nN [28].

The detachment of fines from fibers is likely to happen during papermaking. In our laboratory, few fines were adsorbed on fibers when a TMP suspension with a PEO-cofactor retention aid system was passed through a flow loop with velocities of a few m/s [29]. This implies that under these conditions, much milder than shear in a headbox, little fines deposition takes place, or stated more precisely, the fines detachment rate is much larger than the deposition rate. In papermaking, presumably fines retention takes place after the pulp suspension leaves the headbox via the slice, because in the drainage section the velocity gradients are much reduced as the velocity of the fiber suspension is close to that of the wires.

The finding that no fines deposition occurs in a flow loop (at high speeds) contradicts the finding that fines retention occurs in a dynamic drainage jar [30]. Obviously the hydrodynamic conditions in a flow loop and in a dynamic drainage jar are quite different. Also blocking of the screen by fines might occur. Extensive blocking of screens by fines is observed in experiments where a stirred pulp suspension in a beaker is pumped through a screen, if no precautions are made to prevent it. Conditions in a loop or a jar are different from the hydrodynamic conditions on a paper machine and thus one has to be cautious in extrapolating results of such tests to papermaking conditions.

5 FILLER AND FINES RETENTION DURING DRAINAGE

(a) Capture of single particles in a forming sheet

So far we have been concentrating on the deposition of fillers or fines on fibers (or fiber flocs) freely suspended in the papermaking suspension. When the retention of fillers in the form of individual particles is required, this is the main retention mechanism. But fillers can be captured in the forming sheet as well, either as single particles, which as we will see is difficult, or as aggregates. Fines are larger than fillers and are more readily captured in a forming sheet.

When estimating the rate at which fillers deposit on fibers that are incorporated in the forming sheet, it is useful to consider the sheet as a fibrous porous network. The efficiency with which particles deposit on fibers in the network can be found by considering the interaction of fillers with a single (immobilized) fiber, subject to a uniform flow field. When a suspension of fillers passes through a bed of fibers (or a sheet of paper), the filler concentration decreases continuously, till at the end of the bed ($z = d$), the filler concentration equals [31]:

$$n_c = n_c^o e^{-\gamma_m d} \tag{14}$$

n_c^o being the concentration of fillers at the entrance of the bed. The fiber mat efficiency, γ_m, is proportional to the efficiency, γ_i, of an isolated cylinder, and depends on the bed porosity ε and fiber radius R:

$$\gamma_m = \frac{2(1-\varepsilon)d}{\pi R \varepsilon}\gamma_i \tag{15}$$

γ_i is defined relative to the number of particles crossing a surface $S = 2RL$ (the projected area of a fiber, modeled as a cylinder):

$$\gamma_i = \pi u^{-2/3}\, D^{-1/3}\, A_f^{1/3} / R^{2/3} \tag{16}$$

Here u is the drainage velocity, D the diffusion constant of a filler and A_f a flow parameter, which depends on the porosity and structure of the sheet. Equation (16) is valid for low drainage velocities. For faster drainage rates it needs modifications. Results of a numerical solution of the governing convective diffusion equation are available [31]. By applying this model to filler retention during drainage, it can be concluded that deposition of fillers as single particles during drainage is rather limited, as can be seen in Figure 11. The results are for a machine which runs with a velocity $v = 10$ m/s, a distance between the slice and dryline $s = 10$ m and with an average thickness of wet paper of 0.8 mm. It can be seen from this figure that filler retention during drainage is minimum for a filler size of about 1micron. Smaller fillers have a larger diffusion coefficient which increases the deposition rate. For larger fillers the average gap between a filler and a fiber is smaller, resulting in a shorter diffusion distance, and the deposition rate increases more steeply with particle size (due to impaction). However for all (well-dispersed) fillers the retention efficiency during drainage is very small and only marginally contributes to the overall filler retention.

(b) Filler and fines flocculation

(i) On the paper machine

It follows from the discussion above, that individual fillers are difficult to capture in a forming sheet during drainage, but filler aggregates, fines and fines aggregates can be readily captured. Fines and fillers flocculate readily by polymers or polyelectrolytes. However, when adding polymers to a fiber suspension at high shear, adsorption on fibers is faster than adsorption on fillers.

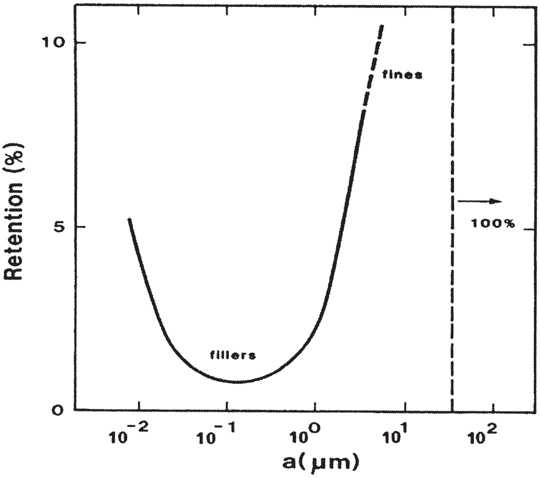

Figure 11 Retention of fillers, of radius a, in a forming sheet, expressed as a percentage of initially free fillers, captured in the sheet. The vertical dashed line indicates that for fillers or fines larger than the smallest pore openings in the sheet, retention becomes 100% (after [32]).

Also filler flocculation is usually too slow on the time scale of papermaking, except when fillers and polymers are added early in the process. Fines flocculation is more important, especially for mechanical grade papers, which contain a large number of fines in the headbox, sometimes exceeding the concentration of long fibers. In such case polymer adsorption on fines is appreciable and fines flocculation is expected to be fast. Such flocculated fines are readily captured in the forming sheet. One can conclude that often filler flocculation in the headbox and slice is negligible, but fines flocculation will occur.

(ii) In the short circulation loop

Non-retained fillers and fines end up in the short circulation loop and are usually returned to the headbox. The residence time in this loop can be several minutes, which provides lots of time for fines and fillers to flocculate. Fillers can have polymers or polyelectrolytes on their surface, due to polymer transfer. Also fines will be partially coated by polymer due to adsorption and transfer. Thus one expects extensive filler and fines flocculation (both homo- and heteroflocculation) in the short circulation loop. When fillers and fines return to the drainage section, these aggregated particles are more likely to be retained in the sheet than the single particles. From this argument it follows that FPR can be very different from SPR (second pass retention).

As examples of how fines flocculate, we consider fines flocculation induced by PEI, C-PAM, or PEO/CF. An example of how PEO/CF flocculates fines is given in Figure 12, together with the break-up of flocs (by increasing the shear) and reflocculation (by the addition of CF/PEO). It can be seen that addition of cofactor (CF) has no effect, whereas subsequent addition of PEO leads to extensive fines flocculation. (PEO/CF ratio: 3/5). Notice that flocculation occurs at an extremely low dosage of PEO, 0.1 mg/g, which corresponds to a surface coverage of about 1–2%. These flocs can be broken up in high shear, indicating that the same is expected on a paper machine. The same conclusion was reached from fines flocculation measurements in a turbulent flow loop [29]. Reflocculation of fines depends strongly on whether the PEO is entangled or disentangled. For entangled PEO the reflocculation is nearly identical to the intial flocculation, but for disentangled PEO the reflocculation is reduced considerably (see Figure 12). When after break-up of flocs at 500rpm, the stirring rate is reduced back to 100 rpm (without any addition of chemicals), no reflocculation occurs at all. Thus surprisingly, the flocculation

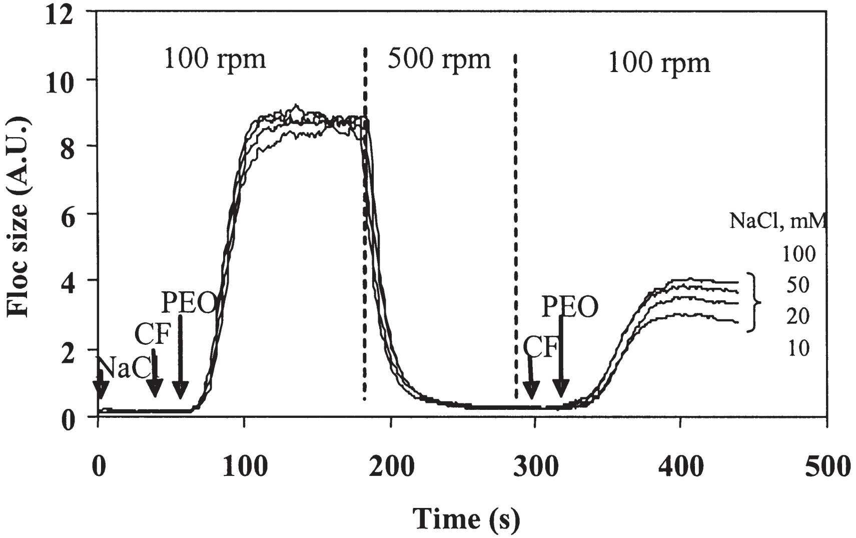

Figure 12 Flocculation, break-up and reflocculation of TMP fines by a cofactor (CF, a carboxylated phenolic resin) and disentangled PEO, in the presence of various NaCl concentrations. [PEO] = 0.1 mg/g fines, [PEO]/[CF] = 3/5. (after [33]).

is not reversible, indicating that the break-up of the flocs leads to changes in the PEO configuration on the surface. One possibility is that the bonds are due to entangled PEO, which disentangles during break-up. When the flocculation is caused by disentangled PEO, the PEO molecules could break in two, or somehow the configuration after break-up is flattened. It can be seen that fines that are broken up are more difficult to flocculate than fresh fines, implying that the FPR will be higher than the SPR. The initial slope in Figure 12 after PEO addition is proportional to the initial flocculation rate, k. Usually this rate is compared to the fast flocculation rate, k_{fast}, occurring when all repulsions between the particles are eliminated. The ratio k_{fast}/k is commonly referred to as the stability ratio W. Thus $1/W = \alpha_{fl}$, the flocculation efficiency.

An example of fines flocculation by cationic polyacrilamide (C-PAM) is shown in Figure 13.

It can be seen that C-PAM flocculated TMP fines, with the fastest rate reached at 10 mg/g. No restabilization occurs above this dosage, likely because van der Waals forces dominate over steric forces (cf. Figure 6). For MCC restabilization occurs, likely because van der Waals forces are weaker (they scale with particle size). Because flocculation is due to macromolecular

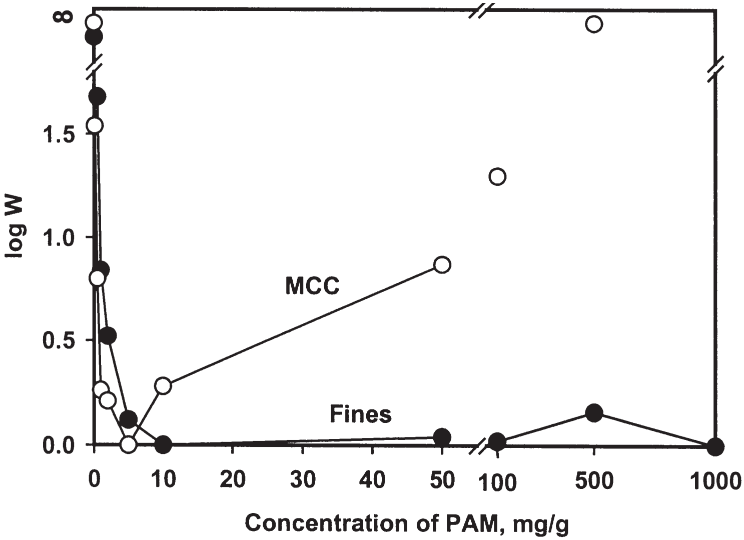

Figure 13 Flocculation of TMP fines, compared to that of MCC (Microcrystlline cellulose) by LCD cationic polyacrylamide. Flocculation of MCC follows classical trend (highest flocculation rate at partial surface coverage), but flocculation of TMP fines is anomalous, since no redispersion at high C-PAM dosages occurs (after [34]).

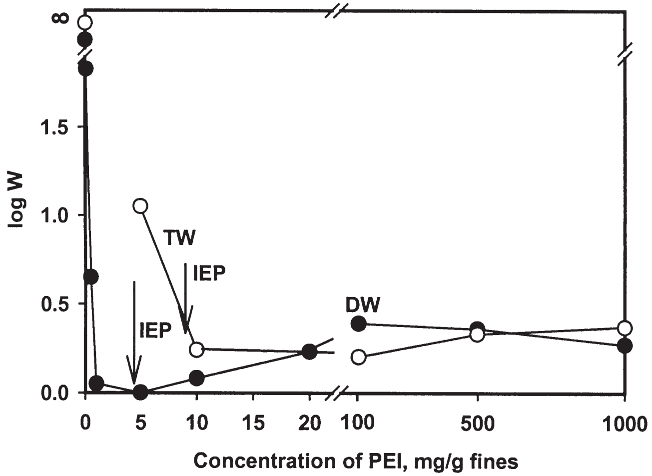

Figure 14 Flocculation of TMP fines by PEI in distilled water (DW) and tap water (TW). In both cases the fastest flocculation rate coincides with the IEP (after [34]).

bridging, the quality of the water has little influence on the flocculation kinetics.

The last example is fines flocculation by PEI. Here the flocculation is due to charge neutralization and the flocculation depends strongly on the quality of the water in which the fines are suspended. Figure 14 shows the flocculation of TMP fines, both in tap water and distilled water by PEI. It can be seen that the fastest flocculation rate is reached at a PEI dosage twice as large in tap water than in distilled water. However, in both cases the fastest rate coincides with the isoelectric point (IEP), indicating that the flocculation is due to the elimination of electrostatic repulsion by PEI adsorption on fines. As for C-PAM, little restabilization occurs for higher than optimal dosages.

(c) Entrapment of aggregates in the forming sheet

It follows from the above discussion that considerable fines and filler flocculation can occur in the short circulation loop, when the particles are destabilized by retention aids. Heteroflocculation between fines and fillers can occur as well [34]. From Figure 11 it can be seen that as soon as the aggregates are larger than the sizes of the pores in the forming sheet (which are in the range 10–20 micron), they will be captured in the sheet. Since little filler flocculation occurs on the time scale of paper formation, most filler aggregates in paper likely result from flocculation in the short circulation loop, followed by entrapment. Again this shows that first pass retention (FPR) of fillers is often very different from second pass retention (SPR). To do any realistic retention modeling on a paper machine, these differences must be considered.

6 IMPLICATIONS FOR ADDITION POINTS OF RETENTION AIDS AND FILLERS

Depending on the type of filler and the properties of the chosen retention aid system, several strategies can be pursued for optimum filler retention. If fillers are to be incorporated as single particles on the surface of fibers, filler flocculation is to be avoided. In such case one can either pretreat the fillers, so that they become very stable, or one can add a retention aid close to the headbox, which as we have seen, favors adsorption on fibers and avoids filler flocculation. The second strategy only works well when the first pass filler retention is very high, otherwise due to polymer transfer from fibers to filler, fillers may become unstable and flocculate in the short white water circulation loop. If a large amount of filler is required (more than a monolayer coverage), one must flocculate the fillers. This can be done by adding both the retention aid and fillers early in the process, allowing sufficient time to form filler flocs. Also one can operate with a low FPR, forming aggragates in the short circulation loop, resulting in a large SPR.

When dual polymeric retention aids are used, it is usually preferred to add the fillers first and the cationic polymer second. This allows the cationic polymer to adhere to both fiber and filler (which even happens when polymer adsorbs first on fiber, due to polymer transfer), thus making all furnish components positive. When next an anionic polymer is added, it can bridge all the positive patches on fibers and fillers, thus creating strong fiber-filler bonds.

When PEO is used, it is good practice to add it as late as possible to the paper machine (just prior to the headbox), since PEO disentangles and flattens with time, making it less effective. The cofactor can be added earlier, the precise location being less critical, since it becomes active only when it encounters PEO.

The optimum location of filler and retention aid addition points depends on the speed of the paper machine. It is possible to estimate the time scales of filler flocculation and filler deposition [1]. These time scales depend on the addition points and on the local shear at and beyond these addition points. More difficult to predict is how retention aids affect fiber flocculation and polymer transfer from fibers to fillers and one must be guided by experiment.

7 FACTORS AFFECTING FINES RETENTION ON A PAPER MACHINE

Laboratory experiments of fines retention can give at best a good indication of the efficiency of retention aids, but paper machines are of such a complexity that choosing the best retention aid and its optimum dosage for a given furnish requires pilot machine and mill trials. In laboratory experiments one can screen potential additives, optimize their use and explore alternative chemistries. One also can perform systematic studies to elucidate the mechanisms by which retention aids function, knowledge that will help considerably in choosing retention aids and optimizing their use. Pilot trials are performed to demonstrate lab results, to prepare for mill trials, to develop new grades or to investigate the effects of process modifications (e.g. progressive system closure) on additives and product quality. Mill trials with retention aids are performed to assess the efficiency of retention aids and the effects machine and process variables have on sheet properties (basis weight, opacity, filler content, formation, strength, sizing, *etc.*). The efficiency of a retention aid depends on its composition (single, dual polymeric, microparticulate, *etc.*), on the location of the addition points, the dosages of the retention aid components, and on the sequence of addition. Machine and process variables of interest are: (i) the furnish (type of pulp, fillers, chemical additives, headbox consistency, *etc.*); (ii) the whitewater (fines and filler content, pH, cationic demand, turbidity, conductivity, *etc.*); and (iii) machine conditions (amperage of refining and wire turning, levels of applied vacuum, location of dryline, press loading, steam requirements in dryer, reel moisture, *etc.*).

A major difference between laboratory (and pilot) experiments and mill trials is the recirculation of whitewater in the short circulation loop. Fines that are not retained and are returned to the papermaking suspension, have different surface properties than virgin fines. Rearrangement of adsorbed polymer can lead to a loss in flocculation ability, since the adsorption of additives on such fines is impaired or does not occur. As a consequence fines that are not retained during the first pass are more difficult to retain in a subsequent pass. We refer to such fines as “poisoned” fines. For instance for a furnish with 30% fines (prior to the headbox) and an average WER of 50%, the fines concentration in the headbox will be 60% if all whitewater is recirculated. However, distinguishing “fresh” fines (that have never passed trough the machine) from “poisoned” fines (that have passed through the machine and returned to the headbox), it could be that the FPR of the fresh fines is e.g. 80%, and the SPR of the poisoned fines only 20%. In this scenario the headbox also contains 60% fines, but the paper will contain 80% fresh fines and 20% poisoned fines, whereas 80% of the fines in the whitewater have gone through the machine more than once. It is clear that in such case one must target the poisoned fines if one wants to improve retention. Alternatively, as we have seen before, fines and fillers may acquire polymer on their surface, but have no time to flocculate prior the passing through the sheet for the first time. Such fines and fillers can flocculate in the short circulation loop. In such case FPR < SPR.

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Transcription of Discussion

FILLER AND FINES RETENTION IN PAPERMAKING

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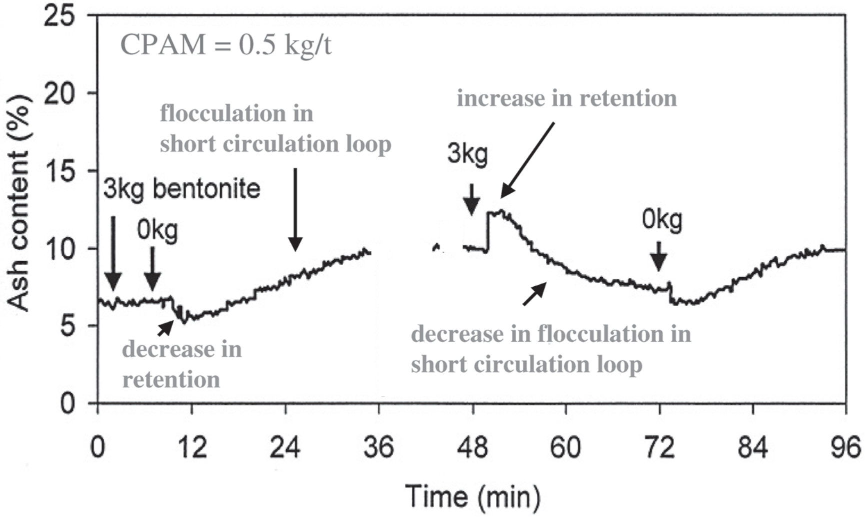
Additional and Corrected Material Supplied by the Author

This slide was presented but not included in the paper:

Retention of calcium carbonate on pilot paper machine



The material is taken from: Byoung-UK Cho, "Dynamics and Control of Retention and Formation on a Paper Machine using a Microparticulate

Retention Aid System", PhD thesis, Sept 2005, Dept. Chem.. Eng. McGill University, Montreal, Canada.

The following is a corrected version of Equation 1:

$$\frac{d\theta}{dt} = k_1(n_o - \theta)(1 - \theta) - k_2\theta$$

DISCUSSION CONTRIBUTIONS

Tom Lindström STFI-Packforsk AB

Thank you for a nice presentation. There is one thing you did not mention and that is the distinguishing characteristics between dual and microparticle retention aids. There is a reversibility (in flocculation) factor which I think is very important and that is specifically relevant when it comes to white water circulation, whether you have a short circulation or not. Generally, you could say that common dual polymers, are irreversible flocculants, in the way that, when you start to stir a fibre suspension you will break the polymer, which is an important factor apart from conformation flattening of the polymer. The distinguishing characteristic of a microparticulate is the reversibility of flocculation and this is presumably because you cannot break the microparticle into pieces as you can with a polymer chain. But now we comes to the really tough thing to understand and that is that, when you have a reversible system and you flocculate it and then it goes into the short circulation, the particles will get more evenly distributed than if you had a common dual polymer system. So it is the opposite of what you forecast in terms of having a fast reaction to begin with or a flocculation in the loop. You can actually have extensive flocculation and still get very good distribution.

Theo van de Ven

I fully agree. You are giving an another example of a difference between first pass retention and second pass retention. They only gave me half an hour, and so I had to skip over some of the details.

Lars Wågberg KTH

I have a minor question. On your Figure 6, you showed the potential energy of interaction between particles. Are you sure that the van der Waals interactions have an extension larger than 200 *nm*?

Theo van de Ven

The Hamaker constant of most fillers is rather large, about $10^{-19}J$, and so it is larger than for most systems which contain organic material like latices or cellulose. The results were calculated from standard van der Waals theory. The van der Waals force also scales with particle size. So for large particles, the energy is much larger. That's why we see this more often for fines than for fillers.

Jean-Claude Roux EFPG-INPG

You mentioned at the beginning of the review paper that some particles may have mechanical entrapment as a mechanism of retention. I was wondering how can this be explained with the Langmuir kinetics model. What is the perturbation induced by mechanical entrapment for explaining retention?

Theo van de Ven

The entrapment cannot be explained by Langmuir kinetics. That only explains how many particles are depositing on the fibres prior to the drainage section. For the entrapment, I do not have a rigorous theory. My theory is simply that particles which are bigger than the holes in the sheet get trapped. So that is simple physics which is not in the Langmuir model at all. But the Langmuir model applies before the fibres have been immobilized in the forming sheet.

Jean-Claude Roux

But have you an idea of the perturbation which is induced by this mechanical effect, that is how the properties of the web are changed by entrapment?

Theo van de Ven

That shows up in reduced drainage rates, for instance, when you block pores in the forming sheet. The change in web properties is thus important for papermaking and depends how you operate a retention aid system. There are retention aids which reduce drainage and those which hardly affect drainage; some people even claim improved drainage. You can adjust the structure of the fibre web that is being made by putting in open aggregates or by blocking pores, which will have different effects on the drainage.

Discussion

Joseph Aspler PAPRICAN

One of the biggest problems in printing occurs when those fillers and fines you retained come off on the printing press, which is a great nuisance for the printer. Do you see any way in which wet end work could help predict and thereby solve the printer's biggest headache?

Theo van de Ven

The obvious answer would be to attach them more strongly to the fibre, so they do not come off. Another way might be to try to avoid them being in the surface layer. Since you are usually interested in scattering it does not really matter where they are. You might also control the distribution of fillers within the sheet which might have some effect on linting as well. But there is no simple answer to this question.