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Interactions between Fibers and Colloidal Particles Subjected to Flow

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ABSTRACT

In papermaking, a fiber suspension, often containing fines (fiber fragments) and fillers (colloidal additives), is subjected to a complex hydrodynamic flow field on a paper machine. The interactions among fibers lead to a dynamic equilibrium between fiber floc formation and break-up. The interactions between fibers and fillers lead to a dynamic equilibrium between particle deposition on fibers and particle detachment. These interactions can be modeled theoretically only in model flows, such as e.g. a simple shear flow. Despite the fact that the actual flow on a paper machine is far more complex, observations follow trends predicted by these models.

INTRODUCTION

In papermaking the flow of pulp fiber suspensions determines to a large extent the properties of the paper made from it. Especially important is fiber flocculation which is the major cause of paper non-uniformity. Equally important are the interactions of colloidal particles (fillers) with fibers, since fillers are often introduced in paper to improve its properties and to reduce costs. The solid content of papermaking suspensions is typically around 1%. A first sight this might seem a rather low concentration and one might consider such suspensions dilute. However, from a hydrodynamic point of view these suspensions are very concentrated indeed. Concentrated suspensions are usually defined as suspensions in which many-body interactions play a major role. Because of the large axis ratio of the fibers (ratio of fiber length to diameter, typically up to about 100), even at 1% consistency, each fiber interacts hydrodynamically with many fibers at any instant. Thus many-body interactions are of crucial importance in papermaking suspensions. Before discussing some of the properties of papermaking suspensions, it is useful to first consider very dilute suspensions in which particle interactions are absent. Similarly it is useful to consider interactions between a single fiber and colloidal particles, before looking at more complex situations.

DILUTE FIBER SUSPENSIONS

When a fiber suspension is sufficiently diluted that interactions are absent, each fiber rotates in such a way that the net torque on the fiber is zero. In a simple shear flow a rigid fiber follows an orbit, closely resembling a Jeffery orbit, given by[1]

$$\frac{d\theta}{dt} = \frac{1}{4} BG \sin 2\theta \sin 2\phi \qquad (1a)$$

$$\frac{d\phi}{dt} = \frac{1}{2} G\left(1 + B\cos 2\phi\right) \qquad (1b)$$

Here θ and ϕ are the polar and azimuthal angles, describing fiber orientation, G is the rate of shear and B is a shape factor, close to one for long slender bodies. As a result such a fiber rotates periodically with a period given by $T \approx 2\pi r_e / G$, r_e being the equivalent axis ratio of the particle. For flexible fibers the period remains periodic when the flexibility is low, but becomes non-periodic for highly flexible or hinged fibers[2]. In flows other than simple shear, the motion is more complicated. In turbulent flow, the rotational motion fluctuates irregularly, and it is customary to describe the flow as having an effective shear rate G_{eff}. From the average energy dissipation per fiber, one can obtain the intrinsic viscosity of a dilute fiber suspension $[\eta]$, defined by $\eta = \eta_o(1+ [\eta]\varphi_F)$ as[3]

$$[\eta] = \frac{r_e^2}{4 \ln r_e} \left\langle \sin^4 \theta \sin^2 2\phi \right\rangle \qquad (2)$$

The term in brackets is an orientational average which depends on the distribution in orbits. For a random distribution in orbits the orientational average equals 4/15. For pulp fibers $[\eta]$ is typically in the range 10^2-10^3, which limits the applicability of Eq.2 to fiber volume fractions φ_F much less than $10^{-3} – 10^{-2}$.

Fiber interactions become significant when the total volume swept out by all fibers exceeds the actual volume fraction Modeling fibers as thin-walled hollow cylinders of radius R, length L, wall thickness d with density ρ_F, can define a critical fiber consistency c_F^* above which interactions play a major role as[4]:

$$c_F^* \cong 12 \frac{Rd}{L^2} \rho_F \qquad (3)$$

Taking as an example R = 15μm, d = 4μm, L = 1mm and $\rho = 1.5 g/cm^3$, leads to $c_F^* \cong 0.1$ g/L or a 0.01% consistency. Papermaking suspensions are a hundred times more concentrated than c_F^*, showing that they must be considered as very concentrated suspensions indeed.

FLOW BEHAVIOR OF PAPERMAKING SUSPENSIONS

The flow of pulp suspensions around 1% consistency, typically encountered in papermaking, is very different from that of dilute systems, because fibers can form flocs by mechanical entanglement. At low flow rates, these flocs fill the whole space and the suspension flows through a tube as a plug flow, the fibers behaving as a single floc. At higher flow rates, shear will break up flocs near the wall, but not in the center of the tube, where the flow remains a plug flow. At very high flow rates the plug flow region disappears and the flow is characterized by a dynamic equilibrium between fiber flocculation and break-up. An interesting way to investigate the role of fiber flocs is studying the flow of pulp fibers in a spouted bed. With this technique a pulp suspension is placed in a conical vessel and flow is applied from the bottom. A photograph of a spouted bed is shown in Fig.1. For certain flow rates, the pulp in the vessel circulates in loops. The pulps moves up in the central region (the spout) and redescends in the outer region of the vessel. When the flow rate is too low, fiber sedimentation prevents spouting, while when the flow is too large, fibers exit the vessel from the top. Besides its use for the study of the flow of pulp suspensions, spouted beds can be used to separate fine materials from fibers (fines, fillers, ink). The fine materials are eluted from the top, whereas the fibers remain in the vessel[5].

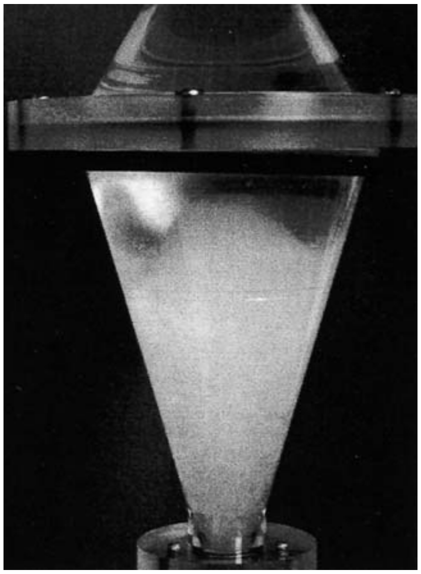

Fig.1 Photograph of spouted bed of pulpfibers[5].

For spouting to work, fibers have to be present in the form of fiber flocs. Suspensions of rigid rod-shaped particles of similar dimensions as fibers and which do not form flocs, do not spout[5], indicating that fiber flocculation is an essential requirement for spouting. The spouted bed technique is thus ideally suited to study the flow properties of fiber flocs.

Spouting occurs above a critical Reynolds number, Re_{crit}, based on the velocity in the inlet tube. The existence of Re_{crit} has been verified by using inlet tubes with various diameters. From measurements of the minimum spouting velocity U_{ms} of beds containing various amounts of pulp it was found that U_{ms} increases linearly with the mass of pulp in the bed. An example of this behavior is shown in Fig. 2.

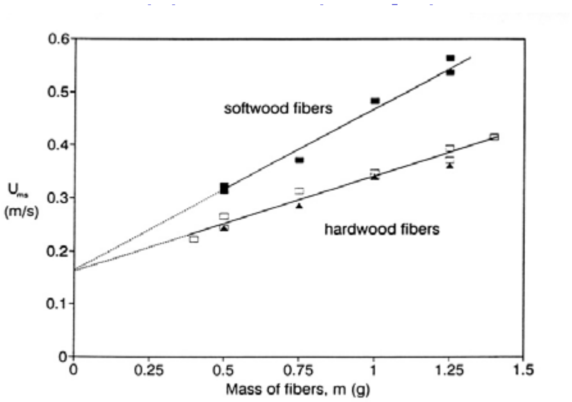

Fig.2 Minimum spouting velocity as a function of the mass m of fibers in a spouted bed[5]. (■ Kraft softwood, ▲ TMP hardwood, □ Kraft hardwood).

The linear relation between the minimum spouting velocity with mass m of the fibers implies that the viscosity of the suspension increases linearly with fiber volume fraction, or, since most of the fibers are incorporated in fiber flocs, with the volume fraction of fiber flocs, φ_{fl}. Hence

$$\eta = \eta_o\left(1+[\eta]\phi_{fl}\right) \tag{4}$$

with the intrinsic viscosity $[\eta]$ close to 2.5, the value for hard spheres. Hence a flocculated fiber suspension can be thought of as consisting of more or less spherical fiber flocs. The difference in slopes in Fig. 2 implies that softwood fibers form larger flocs than hardwood fibers, because the fibers are longer.

It is of interest to note that it is energetically favorable for fibers in a pulp suspension to form flocs. Even at consistencies of up to 0.3%, well above c_F^*, the viscosity of a pulp suspension is still of a similar magnitude as predicted by Eq.4. By forming more or less round flocs, the viscosity continues to increase linearly, instead of the dramatic increase predicted by theory when no flocs form[3]. By forming flocs, the jamming of fibers, each trying to execute its own rotation, is being prevented. The increase in effective volume function (φ_{fl} is about two orders of magnitude larger than φ_F, the volume fraction of the fibers themselves, because of the large amounts of immobilized water flocs contain) is offset by a decrease in intrinsic viscosity (from that given by Eq.2 to $[\eta]\cong 2.5$). The concentration below which fiber flocs do not form can be deduced from Fig.2, which shows that below $m\cong 0.3g$ spouting is absent since fiber flocs can no longer form. This corresponds to a consistency of about 0.1%.

Eq.4 and extensions thereof (effective medium theory, such as the Dougherty-Krieger equation[3]) adequately describe the viscosity of pulp suspensions. Viscosity data on eucalyptus fibers suspended in water show a viscosity of 29 mPas at 1% consistency[6], which corresponds to an effective hard sphere volume fraction of 0.6. This implies that each floc contains 60 weight % of water, a very reasonable value.

FORMATION AND BREAK-UP OF FIBER FLOCS IN FLOW

It is well-known that, depending on volume fraction and fiber axis ratio, two types of floc can be formed in a papermaking suspension: (i) undesirable permanent flocs (also called coherent flocs) and (ii) weak or incoherent flocs which can be broken apart. The permanent flocs form when the suspension exceeds a critical consistency, the value of which depends on the axis ratio of the fiber. Since permanent flocs are detrimental to paper properties, the boundary which separates the coherent from the incoherent flocs, is an upper limit at which conventional papermaking is possible. For long fibers of axis ratios in the range 100-300, the critical consistency is in the range 0.5–1.5%. Papermaking consistencies are in this range and are optimized to stay just below the critical consistency. Besides volume fraction and axis ratio, the critical consistency depends also weakly on the crowding number, a measure of fiber contacts[7].

The formation of coherent flocs can be prevented by choosing the right consistency for a given papermaking furnish. However, incoherent flocs are still being formed and broken up continuously. This floc formation is very different form e.g. the formation of flocs of fillers or other colloidal particles. Fillers flocculate because they are subject to attractive colloidal forces, such as van der Waals, electrostatic and bridging forces. Although these forces are also operating on pulp fibers, the magnitude of the shear forces acting on fibers is orders of magnitudes larger[8] and thus the colloidal forces are negligible compared to the hydrodynamic forces. (The ratio of hydrodynamic to colloidal forces scales with particle size). As a result of the high shear forces operating between fibers, a collision between two fibers never leads to aggregation. The onset of a floc requires the simultaneous interaction of three fibers or more, which aggregate because of mechanical entanglements. After an initial floc has formed, it can grow by collisions with individual fibers which can be incorporated in the floc.

Factors that promote fiber flocculation in the absence of chemical additives are: (i) fiber length, (ii) fiber flexibility; (iii) fiber fibrillation, (iv) fiber surface roughness, (v) shear and (vi) fiber concentration. The first four factors promote better entanglements and thus bigger and stronger flocs, whereas the last two factors increase the kinetics of floc formation and growth.

Shear, which causes fibers to come together to form flocs, can also break up flocs. The rate at which flocs are broken up depends strongly on the type of flow. Model experiments on the break-up of fiber flocs in simple shear and extensional flow show that break-up in extensional flow is nearly ten times more efficient as in simple shear[9]. The reason for this is that a floc in a simple shear flow rotates (according to Eq.1 with $r_e \cong 1$ or $B = 0$.). A particle or floc rotating in such a flow is surrounded by a layer of water, rotating with it. When single fibers leave the floc, they enter this water layer and start to orbit the floc. Hence they are not convected away but stay in the neighborhood of the floc, forming a layer of dispersed fibers around the floc. This layer slows down the break-up of the floc. In contrast, in extensional flow, fibers that leave the floc are immediately convected away and do not interfere with subsequent fiber release.

Besides shear, other factors that promote break-up are opposite to those that promote flocculation: (i) short fibers, (ii) rigid fibers; (iii) smooth fibers and (iv) fibers that are highly “slippery”, i.e. fibers that have a low surface friction. The slipperiness or friction of fibers can be controlled by additives, such as e.g. natural gums. These factors determine the probability that a single fiber will leave a floc.

In the present of flocculating agents (retention aids, drainage aids, formation aids etc.), the strength of a floc depends also on the number of macromolecular bridges between fibers inside a floc. The size and strength of fiber flocs is then determined mainly by two factors: (i) the number of fiber contact points between fibers in a floc and (ii) the bond strength at these contacts. The contact number between fibers is determined by fiber concentration and fiber dimensions. Increasing fiber consistency leads to more fiber-fiber contact points and thus a higher flocculation tendency[7]. Also increasing the fiber length decreases the paper uniformity by increasing the number of fiber contacts and the floc size. The effect of both variables can be expressed in terms of the crowding number, which is defined as the number of fibers in a spherical volume of diameter equal to the mean fiber length[7]:

$$N_{\text{crowd}} = \frac{2}{3}\varphi_F\left(\frac{L}{D}\right)^2 = \frac{\pi}{6}c_F\frac{L^2}{\delta} \tag{5}$$

where φ_F and c_F stand for the volume concentration and mass concentration of fibers, L is the fiber length, D the mean fiber diameter and δ the fiber coarseness.

Fig. 3 clearly shows that an increase in crowding number leads to an increase in the formation index of paper, and thus in an increase in fiber flocculation.

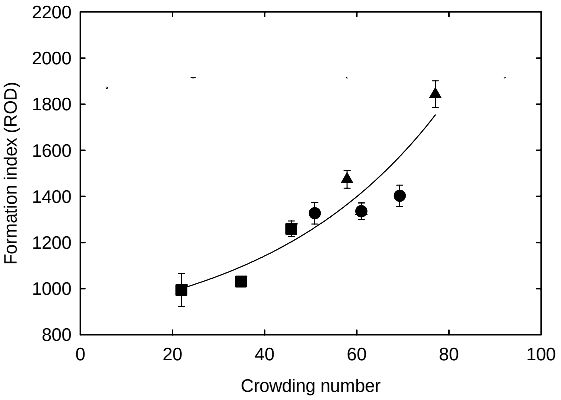

Fig. 3. Effect of the crowding number on formation. Different symbols refer to different ways crowding number was varied, either by varying the mean fiber length or by varying concentration[10]. A higher formation index indicates more fiber flocculation and poorer formation.

For the bond strength at the contact points, we developed a bridging strength model, based on interactions between a single fiber and neighboring fibers in a floc, taking into account the surface coverage of the components of the flocculating systems (retention aids) on the fiber surface. The degree of flocculation is determined by how easily a single fiber can be entrapped inside a floc and how easily a fiber can escape from a floc. Hence, the interactions between a single fiber (*A*) and the neighboring fibers (*B*) in a fiber network are considered.

When a microparticulate retention aid system is used, consisting of microparticles, such as bentonite, and a cationic polymer, such as cationic polyacrylamide (CPAM), fiber surfaces in a floc can be divided into three parts: 1) naked or bare surfaces; 2) polymer covered surfaces (fractional coverage θ); and 3) bentonite covered surfaces on polymer covered surfaces (fractional coverage τ). If we make the following plausible assumptions: 1) Bentonite deposits only on polymer covered sites, not on bare fiber surface (because of electrostatic repulsion between bentonite and fiber); 2) No bond is formed between two fiber surfaces coated by bentonite (because of electrostatic repulsion); 3) No bond is formed between two fiber surfaces coated by CPAM (because of electrosteric repulsion); 4) CPAM and bentonite are distributed evenly over the fiber surface; and 5) The probability of having interactions between two sites is proportional to the area or fraction of fiber surface covered by CPAM, i.e. $\theta(1 - \tau)$, by CPAM and bentonite, i.e. τ, or to the bare area, i. e. $(1 - \theta)$, then under these conditions the bridging strength becomes[10]:

$$\begin{aligned} S_b &= \alpha_{\text{inh}}(1-\theta)^2 + 2\alpha_{\text{pol}}\theta(1-\theta)(1-\tau) \\ &\quad + 2\alpha_{\text{mp}}\theta^2\tau(1-\tau) \end{aligned} \tag{6}$$

Here α_{inh} is the relative bondstrength of the interaction between bare fiber surfaces, responsible for fiber flocculation in the absence of flocculants, α_{pol} is the bond strength of the polymer bridge and α_{mp} that of the microparticle bridge (i.e. a bentonite particle bridging two patches, each on a different fiber, coated by CPAM).

Predictions of this model, together with on-line measurements of paper formation, mainly determined by fiber flocculation, on a pilot paper machine[10], are shown in Fig.4. Taken together with how formation depends on the crowding number (Fig.3), this is good evidence that the strength of flocs, and thus also the floc break-up rate in flow, is mainly governed by the number of contacts in a floc and the strength of these contacts.

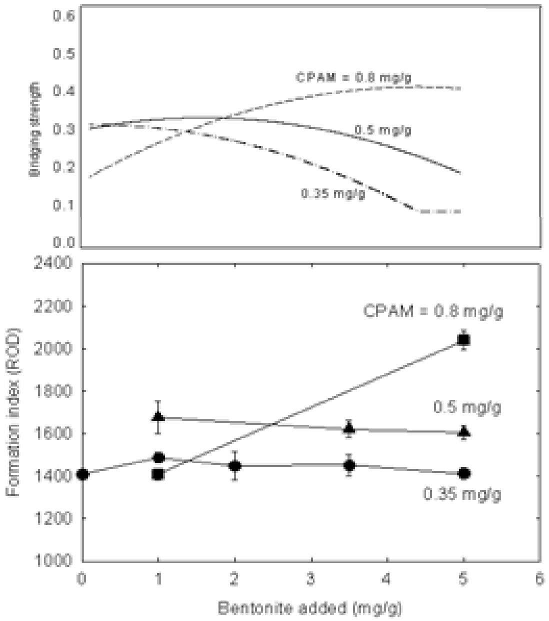

Fig.4. Predictions of the bridging strength of contacts in fiber flocs (top), obtained from Eq. 6, with $\alpha_{inh} = 0.2$, $\alpha_{pol} = 0.5$ and $\alpha_{mp} = 1$, as a function of bentonite dosage for various CPAM dosages (in mg/g of fiber) indicated in the figure[10]. Bottom: Formation index of paper for the same conditions. A large value of the index indicates poor formation and hence more fiber flocculation. Notice similarity in trends.

FIBER-FILLER INTERACTIONS

Fillers rotate in a simple shear flow according to Eqs 1, with the shape factor determined by the shape of the fillers. For round particles, such as some types of calcium carbonate and titanium dioxide, B = 0, whereas for plate-like particles, such as kaolin clay, $B = -1 + 2r_e$, r_e being the axis ratio ($r_e \ll 1$). For more complex flows, we can replace G with G_{eff}. When a filler particle encounters a fiber, it will interact hydrodynamically with the fiber. The relative trajectories of a filler near a fiber have been determined before[11]. Because of the rotation of the fiber, a filler particle can rotate around the fiber many times before it separates and is convected away. When colloidal forces, such as van der Waals or electrostatic forces, or forces induced by adsorbed polymers, are present, the trajectories are modified. When attractive short-range forces are operating, fillers will deposit on the fiber. The kinetics of deposition can be described by Langmuir kinetics[12]:

$$\frac{d\theta}{dt} = k_1\left(n_o - \theta\right)\left(1 - \theta\right) - k_2\theta \qquad (7)$$

Here θ is the fractional coverage of the fiber surface by fillers, t is the time, k_1 the deposition rate constant, k_2 the detachment rate constant and n_o the initial concentration of fillers, non-dimensionalized by the amount required for monolayer coverage. The first term on the rhs of Eq.7 indicates that the deposition of particles is proportional to the particle concentration in solution ($n_o - \theta$) and to the fraction of the surface that is bare ($1 - \theta$). The deposition and detachment rate constants are given by

$$k_1 = \alpha k_{fast}; \qquad k_2 = f\left(G\right)e^{-E/kT} \qquad (8,9)$$

Here k_{fast} is the deposition rate constant when only attractive van der Waals forces are acting between the filler and the fiber, and α is the deposition efficiency, which depends on magnitude of other colloidal forces. Usually α = 0, when the repulsion exceeds a critical value, and α = 1, when below this value. Only in a very narrow rang of conditions is $0 < \alpha < 1$. E is the bond strength between a fiber and a filler, kT the thermal energy and f(G) a function depending on hydrodynamic conditions. A large bond strength E corresponds to a low detachment rate constant.

The fast rate can be expressed as

$$k_{fast} = \beta G_{eff} V_F N_F / \pi \qquad (10)$$

where β is a collision efficiency, which takes into account hydrodynamic and van der Waals interactions. When β = 1, these interactions are neglected and the rate is described by the so-called Smoluchowski-Levich approximation. V_F is the volume of a fiber and N_F the number of fiber per unit volume (i.e. $V_F N_F = \varphi_F$, the fiber volume fraction). The collision efficiency β is independent of fiber length, increases with the size of fillers and decreases with the rate of shear. The effect of particle size is shown in Fig.5, for the deposition of cationic latex particles on pulp fibers. It can be seen that larger particles deposit on fibers faster than small particles. For the same reason aggregates of fillers deposit on fibers faster than single fillers, an effect observed for the deposition of aggregated and well-dispersed clay[14].

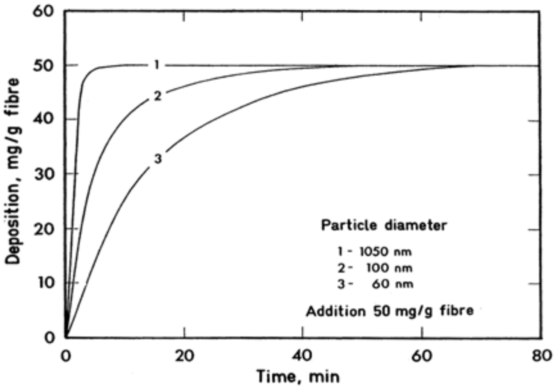

Fig.5. Deposition of cationic latex particles of various diameters on pulp fibers. Latex addition was 50 mg/ g fiber[13].

The advantage of Eqs. 8 and 9 is that the rate constants can be decomposed in hydrodynamic factors (k_{fast} and f(G)) and "chemical" ones (α and E). The hydrodynamic factors depend on the hydrodynamic conditions on a particular paper machine (speed, type etc.), whereas the chemical factors α and E can be studied in the laboratory, without having (too much) to worry about the hydrodynamics.

When retention aids are used to incorporate fillers in paper, they will change the values of α and E. Often $\alpha = 1$, because electrostatic repulsions are screened by the salt present in process waters, especially when deinked pulp is used (containing dissolved calcium carbonate) and for mills with a high degree of water recirculation. In most cases the main role of retention aids is to increase the bond strength, E, between fillers and fibers, or between fillers themselves, when they are incorporated in a sheet as aggregates.

With polymeric retention aids, the fractional coverages, θ_1, on the fiber surface, and θ_2, on the filler surface, are usually less than one. As an extension of the classical theory of polymer bridging, we can then write for the deposition efficiency:

$$\begin{aligned}\alpha = \alpha_1(1-\theta_1)(1-\theta_2) + \alpha_2\theta_1(1-\theta_2) \\ + \alpha_2\theta_2(1-\theta_1) + \alpha_3\theta_1\theta_2\end{aligned} \qquad (11)$$

The four terms on the rhs describe the interaction between bare patches (on fiber and filler), two terms for the interactions between polymer coated patches and bare patches (leading to polymer bridging) and a term for the interaction between two polymer patches. On a paper machine the adsorption of a polymer, added close to the headbox, is usually faster on fibers than on fillers[12]. Hence $\theta_2 \approx 0$ and, because of steric repulsion, $\alpha_3 \approx 0$, and, moreover, since polymer bridging usually involves no repulsion $\alpha_2 = 1$. Then Eq. 11 reduces to

$$\alpha \approx \alpha_1(1-\theta_1) + \theta_1 \qquad (12)$$

with the first term being zero at low salt concentrations and $\alpha_1 = 1$ at high ones.

An interesting case is so-called asymmetric polymer bridging, occurring when the polymer by itself does not adsorb on fibers or fillers. An example of a polymer not adsorbing on fibers is PEO (polyethylene oxide). When used in conjunction with clay, it adsorbs on clay and subsequently can adsorb on fibers (because of the entropy loss occurring upon adsorption on clay). In this case:

$$\alpha = \alpha_1(1-\theta_2) + \theta_2 \qquad (13)$$

This behavior has been observed experimentally[15]. When the polymer by itself does not adsorb on the filler or any other colloidal particle, the deposition efficiency is given by Eq.12. This is observed for CPAM, which does not adsorb on AKD particles (an internal sizing agent), coated by cationic starch. CPAM can however bridge such particles to fibers via asymmetric polymer bridging[16].

FILLER DETACHMENT FROM FIBERS

Eq.7 describes a dynamic equilibrium between filler deposition and detachment in flow. In the presence of retention aids, the detachment rate constant k_2 is reduced. The most common case in papermaking is that polymers adsorb on fibers first and subsequently fillers, with little or no polymer on their surface, deposit on polymer patches on fibers. When a deposited filler detaches itself from the fiber, it often takes some polymer with it. This polymer transfer has two important consequences in paper making:

1) Fillers with transferred polymer that are not captured in the forming sheet usually end up in the short circulation loop, which consists of whitewater returned to the paper machine. In this loop there is sufficient time for them to flocculate. When returned to the paper machine, they are trapped as aggregates in the forming sheet. This flocculation of fillers in the short circulation loop has been observed on a pilot paper machine, as shown in Fig.6, for a microparticulate retention aid system, consisting of CPAM and bentonite.

2) Due to polymer transfer to fillers, the fibers will have less polymer on their surface. This leads to less fiber flocculation and thus to a better paper uniformity. Also this effect has been observed on a pilot paper machine, as shown in Fig.7. When the ash content is increased by increasing the retention aid dosage, rather than by increasing the concentration of fillers in the headbox, more fiber flocculation is observed with ash content[10].

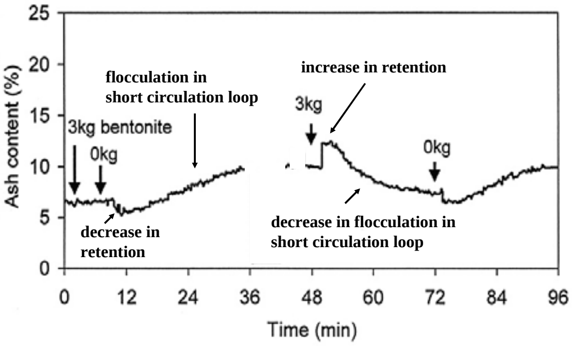

Fig.6. Retention of calcium carbonate fillers, expressed as ash content, on a Fourdrinier pilot machine[17]. CPAM = 0.5 mg/g. Reducing bentonite dosage to zero reduces filler retention initially (as expected), but this decrease is followed by an increase on the time scale of whitewater recirculation, implying flocculation of fillers, followed by entrapment in the sheet on subsequent pass through the machine. This behavior is reversible and reproducible as shown by subsequent step changes in bentonite dosage.

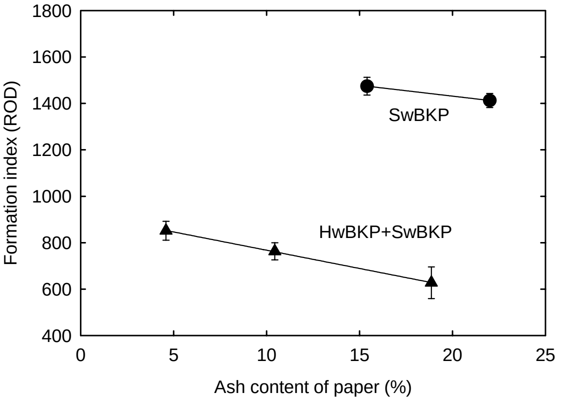

Fig.7. Formation index of paper, inversely related to fiber flocculation, as a function of the concentration of calcium carbonate fillers in paper[9]. Ash content was varied by increasing the concentration of fillers in the headbox of the paper machine, while keeping CPAM and bentonite dosages constant.

CONCLUSIONS

In papermaking fiber flocculation is undesirable as it leads to poor formation. Retention aids usually lead to more fiber flocculation as they reinforce the strength of the contact areas in fiber flocs, thus reducing the floc break-up rate in flow. When fillers are present as well, they deposit on and detach from fibers, and in the processtransfer polymer from fibers to fillers. This transfer increases filler flocculation in the short circulation loop and reduces fiber flocculation on the paper machine.

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