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PHYSIOCOCHEMICAL AND HYDRODYNAMIC ASPECTS OF FINES AND FILLERS RETENTION

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ABSTRACT

From the results of model studies on well-characterized systems, valuable conclusions can be drawn regarding several phenomena occurring in papermaking suspensions relevant to fines and fillers retention. We have shown that long range hydrodynamic interactions are operating between small particles (such as fillers) and spheroids (such as fibers) subto simple shear, preventing small particles iected from approaching large ones to within distances where colloidal forces become important. We can expect similar effects in papermaking suspensions, resulting in very low efficiencies for the deposition of fillers or fines on fibers. The efficiency can be improved by high molecular weight polymers which adsorb on the particles and can reduce the minimum distance of approach between a filler and a fiber. From model experiments on the deposition of TiO, particles on cellophane, it can be concluded that the electrostatic forces also play an important role in fines and fillers retention. Usually no deposition occurs far below a critical deposition concentration (CDC) of electrolyte, slow deposition occurs just before the CDC and fast deposition above the CDC. Charged polymers, such as cationic polyelectrolytes, are most effective in retention because they can reduce the gap between a filler and a fiber during an encounter, and they ensure that electrostatic repulsion is negligible. Besides increasing the efficiency of deposition, retention aids can also increase the bond strength

between a filler and a fiber, thus preventing or minimizing the rupture of fiber-filler bonds.

INTRODUCTION

Papermaking suspensions are complex systems that contain a multitude of particles of various sizes and shapes, such as pulp fibers, fines, fillers, retention aids, etc. When such a suspension is forced through a paper machine under turbulent flow conditions, a variety of phenomena occur, some more de-Particle rotations and interactions sirable than others. lead, among other things, to floc formation and break-up, deposition of fines and fillers on pulp fibers, and flocculation of fillers and fines among themselves. Our knowledge of such interactions is far from complete, mainly due to the fact that particle motions and interactions in turbulent flow are very complicated and, as a result, poorly understood. The aim of this paper is to provide a conceptual framework that allows one, in a qualitative manner, to estimate the importance of several mechanisms operating in papermaking suspensions. То this end we will regard turbulent flow to consist of a distribution of rather simple linear flows. At any given position in the paper machine and at any given time, the flow can be considered laminar in a small region with a length scale much larger than the size of individual colloidal particles or the radius of pulp fibers, but comparable to or smaller than the length of the fibers. Because of turbulence, the type of flow and its intensity will fluctuate at any given position. This simplified view of turbulence allows one to consider the motion and interactions among particles in such idealized flows and to find the overall behavior by averaging over all possible types of flow and intensities. By breaking down turbulence in a number of well-defined flows, rigorous results for particle motions and interactions in such flows can be used in predicting the behavior of complex systems such as papermaking suspensions.

In this paper we will concentrate on the interactions among small particles (fines or fillers) with pulp fibers, in the presence of salts (electrolytes) and polyelectrolytes. Electrolytes are present in mill water due to their natural occurrence in wood, due to various chemical pulp treatments and are added to control pitch and pH (e.g. alum). Polyelectrolytes are often added as retention aids, especially in the production of fine papers. We will first deal with the motion of single particles in papermaking suspensions and subsequently discuss particle interactions, both hydrodynamic and colloidal.

MOTION OF PARTICLES IN PAPERMAKING SUSPENSIONS

Consider a single non-spherical axisymmetric particle (e.g. a pulp fiber or a clay platelet) at the origin of a Cartesian coordinate system and subjected to a general threedimensional linear flow field

$$\underline{\mathbf{v}} = \underline{\mathbf{G}} \cdot \underline{\mathbf{x}} \quad . \tag{1}$$

Here \underline{v} is the velocity of the undisturbed fluid (i.e. in the absence of the particle) at position \underline{x} , and \underline{G} is a tensor whose components describe the magnitude of the velocity gradients in the various directions. In turbulent flow we can describe locally, in the neighborhood of a small particle, the flow by Eq. (1), but with \underline{G} as a complicated fluctuating function of time. In such a flow field the particle will rotate in a complex way.

A simple subclass of the flows represented by Eq. (1) is the general two-dimensional linear flow field

$$\mathbf{v}_{\mathbf{z}} = 0$$
, $\mathbf{v}_{\mathbf{y}} = \gamma \mathbf{G}\mathbf{x}$, $\mathbf{v}_{\mathbf{x}} = \mathbf{G}\mathbf{y}$. (2)

Here G is a parameter describing the intensity of the flow and γ is a parameter denoting the type of flow. In general - 1 < $\gamma < 1$. The flow can vary from pure rotational for $\gamma = -1$ to pure shear (or extensional) for $\gamma = 1$; $\gamma = 0$ corresponds to a simple shear flow of shear rate G. The parameter γ is a measure of the amount of vorticity G(1 - γ) present in the flow (1). When $\gamma = -1$, the vorticity is maximum, for $\gamma = 1$, the vorticity vanishes.

The motion of fibers in simple shear ($\gamma = 0$) is well documented and its importance to papermaking realized (2). In such a flow a rigid fiber rotates according to Jeffery's equations of motion (3):

$$\frac{d\theta}{dt} = \frac{1}{4}BGsin2\thetasin2\phi \qquad (3a)$$

$$\frac{\mathrm{d}\phi}{\mathrm{d}t} = \frac{1}{2}G(1 + \mathrm{B}\cos 2\phi) \quad . \tag{3b}$$

Here (θ, ϕ) are the polar angles describing the orientation of the fiber and B is a shape factor. For spheroidal particles B = $(r^2 - 1)/(r^2 + 1)$, where r is the axis ratio of the spheroid. For other axisymmetric particles we can define an equivalent axis ratio r_e and a corresponding B-value (4). Eqs. (3) describe the change in orientation of the fiber with time. Besides these changes, the fiber also spins about its symmetry axis (except when $\theta = 90^{\circ}$), but this spin does not affect its orientation. Eqs. (3) apply equally to spherical particles (as some "ideal" fillers and fines), with $r_e = 1$ and B = 0.

For flows with $\gamma \neq 0$, the situation is qualitatively similar when γ is smaller than some critical value γ_{crit} , which depends on particle shape (for fibers $\gamma_{crit} = 1/r_e^2$). In such a case the particle rotates continuously. For $\gamma > \gamma_{crit}$ the fiber rotates till it attains a steady orientation. Under turbulent flow conditions, where γ and G are continuously fluctuating in time, such a steady state will never be attained and the fibers will always undergo rotation. In simple shear ($\gamma = 0$), integration of Eq. (3b) shows that a fiber rotates with a constant period, given by

$$T = \frac{2\pi}{G} (r_e + r_e^{-1}) .$$
 (4)

HYDRODYNAMIC PARTICLE INTERACTIONS

Rotating particles have a certain volume of liquid permanently associated with them. For flows considered by Eq. (2), and for particles aligned with the vorticity axis Z, such a volume consists of a region of closed streamlines. Small particles will more or less follow such streamlines while orbiting the reference particle. Trajectories of larger particles are qualitatively similar (5). An example of closed trajectories is shown in Fig. 1 for the case of spherical particles subjected to simple shear $(\gamma = 0)$. Shown are possible trajectories of a particle encountering a reference particle at the center of the coordinate system. Particles having their center in the shaded area are permanently orbiting the central particle. No particles can enter this region;

it is filled only with particles that were there initially (prior to the onset of flow). Particles outside this area are on separating trajectories. For a spherical particle, similar regions of closed trajectories exist in all flows except $\gamma = 1$ (5). For non-spherical axisymmetric particles not aligned with the Z-axis, there also exist regions of permanent orbits (6), provided of course that the particle is rotating, but the orbits are not closed. For non-rotating particles (with y > γ_{crit} and having attained a steady state orientation), no regions of permanent orbits exist. Hence we can conclude that, in general, if particles rotate in a flow, there exists a region of permanent orbits (closed or not closed) associated with them. It follows that particle interactions among rotating and non-rotating particles are very different. Rotating particles can be found in the headbox and non-rotating ones in the forming sheet on a Fourdrinier or twin wire.



 Relative trajectories of small spheres around a large one subjected to a simple shear flow (schematic). Shown are examples of separating (open) trajectories, closed trajectories and the limiting trajectories separating open from closed ones (after ref. (10)). In particle interactions, the relative size is very important. This is reflected in the distance d_{\min} , shown in Fig. 1. This is the minimum distance particles can approach a given particle (excluding the orbiting particles). For equal-sized spheres this distance is 4.2×10^{-5} R, R being the radius of the reference sphere (7). For very small particles of radius a < R, $d_{\min} = 0.16$ R, several orders of magnitude larger than for equal-sized spheres (8). At these large distances, colloidal forces, such as van der Waals and electrostatic double layer forces, are very weak and have a negligible effect on the trajectories. Particles of roughly the same size can approach one another very closely during an encounter and may coagulate when sufficiently strong attractive colloidal forces are operating. Hence selective shear mechanisms are operating that favor the coagulation of similar sized particles (9,10).

Obviously the situation just described is rather unfavorable for papermaking. It is desirable on the one hand to keep similar sized particles, such as fibers, well dispersed, but on the other hand to deposit small particles, such as fillers and fines, onto the fibers. We will discuss what factors allow the deposition of fillers and fines onto fibers and the prevention (or minimization) of fiber flocculation.

EFFICIENCY OF DEPOSITION OF FILLERS OR FINES ON FIBERS

The efficiency, $\beta_{\rm d},$ with which colloidal particles deposit on a fiber subjected to flow can be expressed as

$$\beta_{\rm d} = J/J_{\rm c} , \qquad (5)$$

where J is the actual number of particles (fines or fillers) depositing on a fiber per second, and J_c is the number of collisions per second between colloidal particles and a fiber. We can estimate J_c by extending the theory for interactions among spherical particles in simple shear (11):

$$J_{c} \simeq \frac{4}{3} (1 + q)^{3} n Ga_{eff}^{3}$$
 (6)

Here $q \approx 0$ is the size ratio (fines/fiber), n is the number of colloidal particles per unit volume, G is the shear rate and

 a_{eff} is the effective radius of a fiber which can be approximated as $a_{eff} \simeq \frac{1}{2}(a + b) \simeq \frac{1}{4}L$, a and b being the major and minor semi-axes of the fiber and L the fiber length. Alternatively, the number of collisions can be estimated from turbulent convective diffusion transport theory (<u>12</u>), which leads to estimates of similar magnitude.

The efficiency β_d depends on the ratio of colloidal to hydrodynamic forces and approaches zero when this ratio approaches zero. Since the colloidal forces are approximately proportional to the particle radius and the hydrodynamic forces to the square of the radius, it follows that for large particles β_d is always very small. This is the reason why collisions between two fibers seldom lead to coagulation, or stated differently, no coagulation occurs because the colloidal forces are too weak compared to the hydrodynamic forces. Since the hydrodynamic force is proportional to the flow intensity, it follows that $\boldsymbol{\beta}_d$ decreases with increasing intensity of the flow. On the other hand, the number of collisions, J., increases linearly with increasing flow intensity. The actual number of effective collisions is the product of β_d and J and it can be shown theoretically (13) that this product goes through a maximum for the interactions between small and large particles (such as fillers and fibers). This is shown schematically in Fig. 2 where the fast deposition rate J_{fast} per fiber is plotted versus the intensity of the The fast deposition rate is obtained when no repulsive flow. colloidal forces are acting between particles and fibers and the only colloidal force is an attractive van der Waals force.

When the flow intensity is very small, J_{fast} is determined by diffusion alone, while when the flow intensity approaches infinity, the efficiency approaches zero (for filler-fiber interactions) because small particles go around the fiber at a large distance where the van der Waals forces are negligible. For unequal-sized spheres (14) the maximum is around shear rates G of the order of $10^3 - 10^4$ s⁻¹, depending on the Hamaker constant of the system (which determines the magnitude of the van der Waals dispersion forces). These shear rates are close to those in papermachine headboxes (9) and thus we can expect that under papermaking conditions the number of successful collisions between fillers and fibers is near optimum. This appears fortuitous since headboxes are designed to optimize formation (the dispersion of fibers) and not to optimize the retention of fillers. Since the size of fines is comparable to the radius of a fiber, fines can always approach fibers to within distances where attractive van der Waals forces are important. This leads to a plateau in J_{fast} at high flow intensities (10,15).



 Trends in the fast deposition rate (in the absence of electrostatic repulsion) as a function of the flow intensity of fines and fillers depositing on a fiber (schematic).

The above arguments apply when no electrostatic forces are acting between fibers and fillers. When attractive forces are acting J can be increased, while when repulsive forces are acting J is decreased. When the repulsion is sufficiently strong J = 0, and usually J increases steeply from zero to J_{fast} when the repulsion is reduced to some critical value. When electrostatic forces operate we can define a deposition efficiency, α_d , by

$$\alpha_{\rm d} = J/J_{\rm fast} \quad (7)$$

The deposition efficiency α_d depends on the zeta-potential of the particles and the concentration and valency of electrolyte in the water. For a given fiber-filler system, α_d is zero at low salt concentrations and equal to one at salt concentrations larger than the critical deposition concentration (CDC). In a narrow salt concentration region just before the CDC, slow deposition occurs (0 < α_d < 1). When electrostatic attraction occurs (between oppositely charged particles), α_d > 1 (usually up to 1.5) (16,17).

The deposition efficiency for the deposition of small colloidal particles on spheroidal fibers rotating according to Jeffery's equations (Eqs. 3) can be calculated from the trajectories of small particles near such fibers (18). Such systems can be regarded as model systems for which rigorous results can be obtained. We can expect qualitatively similar results for filler-fiber interactions in more complex flows. In the absence of colloidal forces the trajectories of small particles near rotating fibers are more complex than the equivalent trajectories for spheres shown in Fig. 1. The open (single pass) trajectories are no longer symmetric and instead of closed trajectories we have permanent non-closed trajectories. The surface separating open from closed trajectories for spheres is replaced by a region of transient orbits (where particles approach a reference fiber, rotate around it once or several times and subsequently move away) for fibers. In the presence of colloidal forces, particles can be captured during the first encounter, orbit the fiber several times before being captured or before moving away, and the particle can be captured in the flow field. Despite the fact that the trajectories of small particles around rotating fibers are more complex than the trajectories around spheres, deposition efficiencies (for the deposition of fillers on fibers), calculated from such trajectories, are qualitatively similar to the coagulation of small spheres with big ones (19).

Besides the deposition of fillers or fines on fibers, we must also consider the coagulation of fines and fillers among themselves. The deposition of fillers on fines is similar to the deposition of fillers on fibers. For the coagulation of fines or fillers we can again define two efficiencies by

$$J = \beta_c J_c = \alpha_c J_{fast} , \qquad (8)$$

where for simple shear, J_c is given by Eq. (6) with q = 1 and

 a_{eff} the radius of fillers or fines particles. Again J_{fast} is the fast coagulation rate, due to van der Waals forces only; it is an increasing function of the flow intensity, approaching asymptotically a constant value (similar to the fiberfines interaction, c.f. Fig. 2). Again for electrostatically stabilized systems $0 < \alpha_c < 1$, with $\alpha_c = 1$ when the electrolyte concentration is equal to or larger than the CCC (critical coagulation concentration). Usually the critical coagulation concentration is larger than the critical deposition concentration (CCC > CDC), i.e. there exists an electrolyte concentration region where deposition of single fines and fillers on fibers occurs, while the fillers and fines do not coagulate themselves.

It is important to realize that in papermaking suspensions collisions between fines or fillers and fibers are frequent. E.g. considering a pulp suspension with a 1% volume fraction of fibers of 1 mm length and 20 μ m diameter with a 0.02% volume fraction of filler particles of 0.1 μ m radius (just enough to cover the surface of the fibers with fillers), and being subjected to a shear rate of 10^3 s⁻¹ (typical of a headbox), one can estimate that each fiber (of the 3×10^7 fibers per liter) collides on average five thousand times per second with other fibers, but one billion times per second with fillers, while each filler particle (of the 5×10^{13} fillers per liter) collides with only one other filler particle. If fines are also present, their number of collisions is intermediate between fibers and fillers. Since a typical fiber rotation lasts about 0.3 seconds (cf. Eq. (4)), the fibers are colliding about a thousand times during each rota-These frequent interactions can lead to physical ention. tanglements and floc formation.

The kinetics of deposition can be described approximately by (in the absence of particle detachment) (20)

$$N = N_{\infty} (1 - e^{-t/\tau})$$
(9)

with a characteristic deposition time τ given by

$$\tau = N_{\omega}/J_{\Omega} \qquad (10)$$

Here N is the number of particles deposited on the fiber and N_{∞} the maximum number of deposited particles per fiber; J₀ is

the rate at which particles deposit on a clean fiber (free of particles). In model impinging jet experiments (described below), it was found that, in a stagnation point flow, N_{∞} is only a fraction of a monolayer coverage and its value depended on the interaction between freely moving particles colliding with deposited particles and on surface roughness (21). However in more concentrated dispersions N_{∞} depends on the concentration of colloidal particles (22) and can easily attain a monolayer. It appears that the blocking effects caused by surface collisions are counteracted by multibody interactions in more concentrated systems (23).

Since about a million particles are needed to fully cover one fiber, it follows that in principle it is possible to cover a fiber in a few milliseconds ($\tau \approx 1 \text{ ms}$), provided $\beta_d \approx$ 1. However, values of β_d are usually much lower than one, due to the fact that at $G = 10^3 \text{ s}^{-1}$ the ratio of van der Waals attraction to hydrodynamic forces is much smaller than one. Typically for equal-sized spheres, β_d is of the order 10^{-1} ($\underline{24}$), while for unequal-sized spheres the value of β_d can be several orders of magnitude lower ($\underline{14}$). The reason is again that for unequal-sized particles, small particles cannot approach a large one sufficiently close for colloidal forces to become important.

EFFECTS OF POLYMERS ON THE DEPOSITION EFFICIENCY

The efficiency β_d can be improved appreciably by having high molecular weight polymers adsorbed on the fibers (25). In such a case a particle encountering a fiber can approach closely the tails and loops of the polymer protruding from the fiber surface. This is shown schematically in Fig. 3. For a polymer with a molecular weight of several million, the extension of the molecule can be several hundred nanometers (i.e. it can exceed the diameter of a filler particle).

For simple shear the minimum distance of approach of the center of the particle is typically of the order of 13% of the radius of the fiber, or about 1.5 μ m, corresponding to a gap width of d_{min} \simeq 1.5 μ m - a. This means that a 0.1 μ m particle cannot be captured, not even with a polymer whose size is a fraction of a micron. However the particles can be captured in the region of permanent orbits associated with the rotating fiber and slowly approach the fiber while in orbit around it

(<u>18</u>). Since at a given moment many such fillers are in orbit around the fiber, collisions between orbiting fillers could also decrease d_{min} . Also, in papermaking suspensions, the minimum distance could be less than that in simple shear because of the turbulent nature of the flow and the high frequency of multi-fiber interactions and the polymer could be extended beyond its random coil dimensions. Particles of size 1 µm (such as clays) can be readily captured during a first encounter.





3. Hydrodynamic interaction between a filler and a fiber in the absence of adsorbed polymer (left) and in its presence (right). In the absence of polymer the filler does not approach the fiber sufficiently close for colloidal attractive forces to become important. With polymer the filler can be captured by the loops and tails of the adsorbed polymer.

Obviously the benefit of reducing d_{min} would be the largest if the particles and the fibers are each coated with a high molecular weight polymer and the interaction between the polymers is attractive. In principle this could be achieved by pretreating the fiber by, e.g., a cationic polyelectrolyte and the fillers by an anionic one (or vice versa).

In practice, however, pretreating both fibers and fillers is not done and usually the retention aid is added to the mixture. In such a case the kinetics of polymer adsorption

also plays an important role, since the polymers have only a few seconds to adsorb on the fillers or fibers and capture the fillers. If we take a 10 ppm polymer solution of molecular weight 6×10^6 (enough to cover the fillers and fibers and typical of retention aid addition), and add this to a suspension containing fibers and fillers of concentration 1% and 0.02%, respectively, subjected to $G = 10^3 \text{ s}^{-1}$, we have about 10^{15} polymer molecules of radius 300 nm per liter. According to Ea. (6), a fiber will collide with 2×10^{10} molecules per second, while, assuming a full coverage at 1 mg/m² (26), 6×10^{6} molecules per fiber corresponds to full coverage. It follows that if $\beta_d \simeq 1$, full coverage can be attained in about 0.1 ms. However, even when no energy barrier exists between a polymer molecule and the fiber surface, values of β_A may well be as low as 10^{-3} , in which case full coverage is achieved in 0.1 s. Since there are about 3×10^7 fibers per liter, monolayer coverage consumes 20% of the polymer present. For the adsorption of polymers on the fillers we have about 2 collisions per filler per second due to shear, which is somewhat lower than the rate due to diffusion, about 5 collisions per filler per second. About 10 molecules per filler particle are needed to obtain 1 mg/m^2 coverage. This suggests that the characteristic time for the adsorption of polymer on filler particles is of the order of seconds, in accordance with experimentally observed adsorption times for polymer adsorption under turbulent flow conditions (27). These estimates suggest that it takes more than 10 times as long to fully coat the fillers than the fibers, and most particle interactions are between nearly fully coated fibers and partly coated fillers, despite the fact that the total surface area of fillers exceeds that of the fibers by a factor of three. The above estimates are for polymers that have a high affinity for the fiber and filler surface, such as, e.g., highly charged polyelectrolytes (polyamines, polyethylenimines (PEI), etc.). Polymers of low charge density (as certain polyacrylamides (PAM)) only adsorb in monolayer amounts when the solution contains a large excess of polymers (28). In this case, at low concentrations the polymer adsorption efficiency $\beta_d << 1$ and little polymer adsorbs on the time scale of papermaking, especially on the fillers.

In reality the process of polymer adsorption is more complex than described above. A coverage of 1 mg/m^2 is much more than a single layer of adsorbed polymers in their random coil configuration. Probably the first layer can adsorb rather quickly, but subsequent molecules have to penetrate this layer to get to the surface and their adsorption will be slower. Maybe this seldom happens on the time scale of papermaking. Also, after the polymers are adsorbed they rearrange, typically on the time sale of one second (29). This rearrangement reduces the efficiency with which fillers are captured because the adsorbed layer thickness is reduced during rearrangement. Probably during papermaking, most molecules are still in their original adsorbed configuration.

EFFECTS OF ELECTROSTATIC INTERACTIONS ON THE DEPOSITION EFFI-CIENCY

Both charged and non-ionic polymers will reduce the minimum distance of approach between a filler and a fiber and this increases the number of efficient collisions. But charged polymers have the advantage that for the same molecular weight their extension is larger (due to the repulsion of charged ionic groups), and that they can favorably change the electrostatic interactions between fillers and fibers.

In the foregoing we have defined two deposition efficiencies (β_d and α_d), depending on whether we compare the deposition rate with the actual number of (arbitrarily defined) collisions, or with the number of successful collisions in the absence of electrostatic forces. As such, we can think of β_d as determined mainly by hydrodynamic effects, which are modified by altering the surfaces of the particles by the adsorption of (neutral) polymers. On the other hand, the efficiency α_d describes the deposition rate of electrically charged particles relative to neutral ones, and is determined mainly by electrostatic effects. We have seen that the addition of polymers increases β_d , an effect most pronounced for high molecular weight polymers. Salts (electrolytes) affect α_d , while polyelectrolytes affect both β_d and α_d .

To investigate what factors determine the deposition efficiency α_d , we performed extensive experiments of the deposition of TiO₂ particles on a cellophane surface under welldefined hydrodydnamic conditions (<u>17,21</u>). These experiments were performed with an impinging jet apparatus (<u>30,31</u>) in which the flow near the surface under investigation is a pure stagnation point flow, given by

$$v_r = \alpha r z$$
; $v_z = -\alpha z^2$. (11)

Here v_r and v_z are the components of the fluid velocity in the radial direction r from the stagnation point and the normal direction z to the surface, respectively; α is the strength of the stagnation point flow which can be obtained experimentally from the velocity and dimensions of the jet. The flow field given by Eq. (11) also describes approximately the turbulent flow near a wall, in which case α is a fluctuating function of time (12). The schematics of the impinging jet is shown in Fig. 4. The surface on which the fillers impinge (cellophane or glass) is observed through a microscope and the deposition process is recorded on video for subsequent analysis. The physicochemical conditions near the surface can be controlled by adding various electrolytes and polyelectrolytes to the iet.



4. Schematics of impinging jet apparatus. A colloidal dispersion is pumped continuously around from B to A. Some of the dispersion flows through tube T impinges on collector T and subsequently leaves the cell and enters into B. The speed of the jet can be controlled by valve S. The collector is observed with a microscope M (after ref. (30)).

Fig. 5 shows results of measurements of α_d for the deposition of negatively charged TiO₂ particles (a = 0.22 µm) on a negatively charged glass substrate (similar results were obtained for deposition or cellophane) (21). Also shown are the predictions of α_d obtained by solving the governing transport equation, using the classical theory for colloidal stability (the DLVO-theory) to calculate the magnitude of colloidal forces (van der Waals attraction and electrostatic repulsion).



5. Deposition efficiency for TiO₂ particles depositing on a glass surface as a function of electrolyte concentration. The symbols are for various 1-1 electrolytes. Also included are predictions of the DLVO theory. The arrows indicate the location of the CDC (critical deposition concentration) (after ref. (21)).

It can be seen that a qualitative agreement is found with the theory, namely a slow deposition at low salt concentrations and a fast deposition at high salt concentrations (above the CDC). In these experiments we could not reach the fast deposition rate since the coagulation of fillers started to interfere with deposition close to the CDC. Quantitatively the comparison with theory is not very good since observed CDC's were up to a magnitude larger than predicted by theory and depended on the nature of electrolyte used. These differences can be ascribed to electroviscous forces (32,33), neglected in classical DLVO-theory. It follows from these data that if deposition of single particles is desired, the salt concentration must be carefully monitored as this will only occur when CDC < C < CCC, C being the electrolyte concentration. For monovalent electrolytes the CDC is about 10 mM, but for biand trivalent electrolytes (Mg^{2+} , Ca^{2+} , Al^{3+}), the CDC is about 2^{-6} and 3^{-6} times 10 mM, or about 0.2 and 0.01 mM (Schulze-Hardy rule). This valency effect was observed for the deposition of TiO₂ on cellophane (21). The specific conductance of white water in paper mills is typically of the order of 0.05-0.2 Ω^{-1} m⁻¹, corresponding to salt concentrations of about 10-40 mM of monovalent salts. It appears that usually C > CDC in mills. The value of the CCC (typically 30 mM) is not of much importance for small fillers since, on average, a filler particle undergoes one collision per second with another filler, and on the time scale of papermaking (a few seconds) not much coagulation can take place. The situation is different for fines which are predominately fiber fragments of order 20 um and larger and can make up a significant fraction of the furnish, especially for newsprint. Since they are much larger than fillers, each fines particle will undergo a large number of collisions with other fines (of order 10^6 per second) and thus there is sufficient time for the formation of fines aggregates. Later these aggregates will be trapped in the forming sheet. Since the salt concentration of white water is close to the CCC, retention of fines depends crucially on what and how many ions are present. might be good practice for newspaper mills to monitor and optimize the concentration and type of ions in their furnish. Since newspaper mills often do not add retention aids, little deposition of fines or fibers occurs because of the low value of $\beta_d(\beta_d \neq 0 \text{ as } a \neq \infty)$. Fines are mainly retained by entrapment in the sheet. We showed earlier (34), that the efficiency with which single fines and fillers are captured in the forming sheet is very low and only the capture of fines aggregates or rather large single fines is an efficient mechanism for fines retention. Fillers retention must occur prior to formation and, as discussed above, this is possible due to the increase in $\beta_{\rm d}$ (or $J_{{\rm fast}})$ by retention aids. The retention aids have the additional effect of ensuring that $\alpha_{1} > 1$.

When fillers and fines are both present, fillers can deposit on the (coagulating) fines, which can then be captured by mechanical entrapment. This mechanism is known as "piggy back riding".

The deposition rate depends on how the retention aid is applied. The maximum value of the efficiency β_d is obtained when both fillers and fibers are coated with polymer, thus decreasing the minimum distance of approach. However in such a case the charges of the fibers and fillers will be of the same sign and electrostatic repulsion occurs at salt concentrations C < CDC. Even above the CDC, steric repulsion could occur (35), resulting in $\alpha_d < 1$. On the other hand, very strong bonds are formed between particles coated with cationic polyelectrolytes aggregated at C > CDC (35). To avoid electrostatic repulsion, we can pretreat only the fillers or fibers. From model studies on the deposition of pretreated TiO, particles on bare cellophane or bare TiO_2 particles on pretreated cellophane (17), it follows that the highest deposition rate is observed when the fibers are coated. This strategy also allows a lower dosage of the retention aid. Some studies on pulp suspensions seem to confirm this (36,37), but, as we have seen above, when adding the retention aid to a mixture of fibers and fillers, the fibers are probably coated faster than the fillers and retention will be the same as when fibers are pretreated.

EFFECTS OF BOND STRENGTH

It is not sufficient just to deposit fillers (or small fines) onto the fibers, one must also make sure that they remain on the fibers until the consolidation of the paper sheet. Since the effective shear rate in turbulent flow is a fluctuating function of time, it is possible that a particle can be captured at a low shear rate, but subsequently exposed to a higher shear rate where break-up can occur. Since the hydrodynamic forces exerted on the particles are proportional to Ga^2 , it follows that it is easier to break the bond between fibers and fines than between fibers and fillers. It is even easier to break fiber-fiber bonds.

The break-up is not only determined by the magnitude of the hydrodynamic force, but also by its direction. The force can be attractive when two particles are forced to approach one another, or repulsive when they are forced to separate. Since particles rotate, the force is usually alternating between attractive and repulsive. For equal-sized particles, particles usually separate when the force is repulsive, before the force changes sign, but unequal-sized particles can rotate around each other, being subjected to alternating attractive and repulsive hydrodynamic forces. Thus it is difficult to break up fiber-filler bonds, but easy to break fiber-fines and fiber-fiber bonds (the size of fines is comparable to the diameter of a fiber).

The changes in direction of the hydrodynamic force depend on the vorticity of the flow. When the vorticity is high (such as in rotational flows, $\gamma = -1$), the hydrodynamic force changes periodically in sign, while when the vorticity is low or absent (such as in extensional flow, $\gamma = 1$), the force is attractive when particles approach and repulsive when they separate and no periodic changes occur. This condition is the most favorable for the break-up of flocs (1) and is reflected in modern headbox designs such as Diffusor and Dynoflo headboxes, which consist of a series of converging or diverging steps or channels.

Besides the magnitude and direction of the hydrodydnamic force, the rate at which particles are dislodged from the fibers depends on the bond strength between a particle and a fiber surface. The bond strength depends on the magnitude of the attractive forces between fillers and fibers. These forces can be altered by electrolytes and molecules that can adsorb on the surface of particles and fibers, such as polymers, polylectrolytes, surfactants, etc. In the case of small fillers (e.g. TiO2), the bond strength may be sufficiently strong, even in the absence of any additives. We were unable to detach TiO₂ particles from cellophane surfaces subjected to a wall shear rate of 1000 s^{-1} . TiO₂ particles on rotating fibers will be even more difficult to dislodge. For larger fillers or fines, the bond strength could be too weak to survive break-up. Retention aids that form a macromolecular bridge between the particles and the fibers could increase the bond strength and minimize the break-up of fiber-fines bonds. It has been found that factors such as molecular weight and which surface is coated first with polymer, strongly affect In the presence of polymers, the bond the bond strength. strength is usually a function of time (22).

The rate at which particles are dislodged from fibers also depends on the concentration of fibers and fines. Collisions between freely suspended fines and fines deposited on a fiber might lead to detachment, as suggested by experimental observations of the detachment of latex spheres from glass surfaces induced by surface collisions $(\underline{38})$.

EFFECTS OF SOLUBLE MATERIALS

Papermaking suspensions contain a large concentration of dissolved material, especially in newsprint mills, typically of the order of 1 g/l (i.e. 10% of the solid content). These dissolved materials contain fatty acids, resins, soaps, lignin derivatives, etc. Many of these substances can interfere with fines and fillers retention in several ways. They could adsorb onto retention aids and make them less effective, or they could adsorb on fillers, fines and fibers and either slow down (or prevent) the adsorption of retention aids on fibers, fines and fillers, fines be polymeric in nature and prevent deposition by providing steric or entropic energy barriers between fillers and fibers.

Since little is known about how the dissolved materials interact with the various components in papermaking suspensions, it is difficult to predict how detrimental dissolved material is to retention. The reason why certain retention aids perform well in some mills and not in others could well be related to the quality of their water.

To counteract the detrimental effects of dissolved material, several dual retention aids are available. For example one can add a clay of large surface area to the furnish, hoping that most detrimental compounds will adsorb onto the clay particles which are then subsequently retained by a regular retention aid.

CONCLUDING REMARKS

The foregoing discussion illustrates the importance of hydrodynamic conditions, polymer adsorption and electrostatic interactions on the retention of fillers and fines. Some important conclusions can be summarized as follows:

 In the absence of retention aids, hydrodynamic interactions between fibers and fillers are long range and prevent close approach. At the distance of closest approach, colloidal forces (van der Waals attraction and electrostatic attraction or repulsion) are usually negligible.

- (2) High molecular weight polymers can bridge the gap between fillers and fibers. In their presence fillers can deposit on fibers, provided the electrostatic repulsion is sufficiently reduced (oppositely charged fibers and fillers, or charges of the same sign, but C > CDC). High molecular weight polymers are more effective than low molecular weight ones.
- (3) The efficiency with which fines are captured on fibers is, in the absence of retention aids and above the CDC, larger than the efficiency for fillers (because the minimum distance of approach is smaller). However, the CDC for fines is larger than the CDC for fillers, so repulsion can prevent the capture of fines.
- (4) The capture of single fillers and small fines in the forming sheet is negligible. Only large fines, fines aggregates, fillers deposited on fines or large aggregates of fillers can be incorporated in the forming sheet by the mechanism of mechanical entrapment.
- (5) The kinetics of adsorption of retention aids on fibers, fines and fillers under turbulent flow conditions is important. Rearrangement of polymer configurations after adsorption can reduce the efficiency. Despite the fact that fillers usually have a larger surface area than fibers, the fibers could be coated before the fillers.
- (6) The vorticity of the flow plays an important role in papermaking. Vorticity promotes fiber floc formation and makes floc break-up more difficult. Break-up depends on the amount of vorticity in the flow and the relative size of the suspended particles. For a given flow, fiberfiber aggregates are the easiest to break up, followed by fiber-fines aggregates, while fiber-filler aggregates are very difficult to break up. Vorticity is minimized in modern headbox designs.
- (7) Dissolved materials in white water can interfere with the mechanisms of fines and fillers retention.

Papermaking suspensions subjected to turbulent flow are complex systems. Looking at microrheological and colloidal aspects of such suspensions, as done in this paper, could lead to a better understanding of the processes taking place at the wet end of a paper machine, which in turn might lead to a better control of the papermaking process.

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Transcription of Discussion

PHYSIOCOCHEMICAL AND HYDRODYNAMIC ASPECTS OF FINES AND FILLER RETENTION

Dr. T. G. M. van de Ven

ERRATA: Please note in Volume 1 the title of the paper should start "Physicochemical".

Dr. P.A.C. Gane, ECCI

In your mechanism for the deposition of filler on fibre in the presence of high molecular weight polymers, are you suggesting that it is not necessary to re-define the flow round the site of adsorbed polymer, because if that were the case, the filler particle would once again be held away from the fibre by the hydrodynamic forces.

T.G.M. van de Ven PPRIC

Obviously, you have to re-define the flow because your boundary conditions are different. With absorbed polymer you now have a form of porous material near the surface, and thus there is a flow through this layer because of the porous surface. This means that there are streamlines going through the porous layer, and as a result particles can be captured by the polymer molecule. So the hydrodynamic boundary conditions are changed because of the adsorption of the polymer.

Dr. P.A.C. Gane, ECCI

So there may be some capture as well as just bridging a distance.

Dr. A. Nissan, Westvaco

Does your answer to the question suggest that if we have fibrillated fibres, we would capture and not avoid fillers and fibres, and therefore hydrodynamics may help?

Dr. T.G.M. van de Ven

You are right, it depends on the cross section of the fibril. If this is comparable to the size of the filler, this encourages capture. If the fibril is thicker than the size of the filler, then you will still have a long range hydrodynamic repulsion between the fibril and the filler.

Prof. J. Marton, SUNY

I would like to get further information as to whether the fibres are coated before the filler by polymer as you indicated dealing with polymer particle interaction. We may indeed introduce polymers in the low shear rate section of the paper machine, e.g. in the thick stock, then we have high shear rate in the thin In these cases there should be differences. One finds stock. polymer enrichment on fines and fillers taking as an example cationic starch, that is added just before the head box, i.e. probably in the high shear rate region. Then when the furnish sample is analyzed in terms of starch absorbed on the components by weight, more starch is found on the pulp fines than on fibres. This appears to be related to available surface areas. The question is whether this is only applicable to the equilibrium state?

Dr. T.G.M. van de Ven

The fines are different from fillers because of the different sizes, and so the rates of polymer adsorption on the fines is intermediate between the fillers and the fibres.

Prof. J. Marton

If we analyze the clay filler surface, as an example then there is about 3 times more cationic starch accumulated on this filler compared to fibre, so something is happening in the equilibrium state which you have not mentioned.

Dr. T.G.M. van de Ven

The amount which finally adsorbs on the particle is a completely different problem from that with the initial kinetics. You may get much faster kinetics initially for absorption on one surface, but you may end up with more polymer on another surface, because the final coverage is larger. So the initial kinetics is not determined by the final coverage of polymer on the surface.

Prof. J. Marton

I agree, but I would like to see this investigated in subsequent works, because while the first kinetic phase may influence the processing steps, the second equilibrium phase influences the paper properties.

Dr. T.G.M. van de Ven

I agree with you that if you add your polymers earlier in the process at low shear you may coat your fillers before the fibres having exposed them for a longer time. That is a very different process from adding them just before the headbox. I agree you have to study all these aspects separately.

L. Odberg, STFI

This is more of a comment. We have measured the rate of adsorption of polyamides on fibre in fully turbulent flow at very short times, 0.5 seconds, and we do actually see the fast adsorption that you predict in your equation. After the initial fast absorbtion the rate of absorbtion is much slower.

Dr. K. Ebeling, James River Corporation

Could your initial deposition approach be used to study the retention of fillers and fines during the sheet formation phase, where you have a sheet formed partially, but still have a liquid phase above it containing fines and fillers. As the web gets compacted by hydrodynamic drag, the pore size gets smaller, but the washing action gets higher. Where is the equilibrium?

Dr. T.G.M. van de Ven

Even if the sheet leaves the couch, the porosity is still so large that the average pore size is much larger than the size of a filler particle. In that case, very few filler particles will be captured, but large fine particles can.