Investigations of the flocculation behavior of microparticle retention systems

ERICH GRUBER AND PETER MÜLLER

ABSTRACT: The state of flocculation was characterized by image analysis and by the scattering of laser light in this study on the flocculation behavior of microparticle retention systems in different furnishes. The dosage of cationic polymer was found to influence the floc size strongly, regardless of the kind of microparticle system used. The dosage of the microparticle component has an impact on the floc size only in the case of the cationic polyacrylamide (CPAM)–bentonite system. The floc index, measured by light scattering, is affected in both cases by the dosage of polymer and microparticle component. The floc index correlated well with filler retention during handsheet formation.

Application: Controlling flocculation by adding the components of microparticle retention systems in the right dosage can improve runnability and paper quality.

The decisive step of the papermaking process is the formation of a fiber mat from a suspension consisting of fibers, fillers, and additional ingredients. This process can be controlled by adding paper chemicals sucn as retention and dewatering aids. The basic mechanism of these chemicals is the flocculation of fibers and fillers, which has a strong impact on the runnability of the process and on the quality of the paper produced. Therefore, it is important to characterize and control flocculation.

A few different methods for evaluating flocculation have been developed in the past. Basically, the methods can be divided into two groups according to the measurement principle used, either light scattering or image analysis. Both of these methods were used in this study.

BACKGROUND

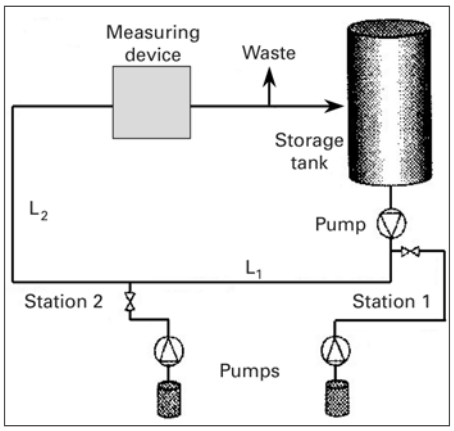
In a simplified view, flocculation can be described as the unevenness of the distribution of fibers in a suspension. Because of the simplicity of this model, many attempts were made to characterize the process by one single parameter, the floc index. The first one to define this index was Wahren, who used the following equation [1]:

$$\textit{floc index} = \sigma\, c_v / C \qquad (1)$$

where

σ = standard deviation of concentration
c_v = local concentration
C = average concentration.

In accordance with this definition, the floc index is a parameter that describes the variation in local concentration and is therefore influenced strongly by the floc density. Many researchers have used this definition or even extended it [2]. Most frequently, the scattering of laser light has been used to obtain information about the variation in local concentration. The "floc index" derived by this approach is just an approximation and is strongly related to the setup of the measuring system.



1. Overview of the basic experimental setup.

The situation is different when the results are calculated via a power spectrum. By this route it is also possible to obtain information on the floc size. The underlying mathematics of this method will not be described here. (For a detailed description of the method, see the work of Norman and Wahren [3], which is the foundation for developments in the measurements of flocculation.)

A more recent development in the field of laser light scattering is a technique called "non-imaging reflectance scanning laser microscopy." As applied to papermaking furnishes, this technique yields measurements that lead to a "mean chord length" [4].

Methods based on image analysis have become more important in characterizing flocculation because the processing speed of personal computers has made it possible to obtain a result within a reasonable timeframe. Another reason for the shift from light scattering to image analysis is the versatility of image analysis.

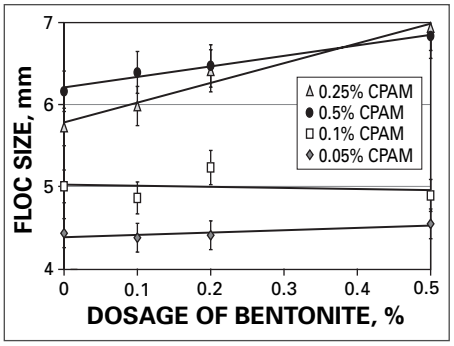
One of the first papers published in the field was from Davydenko and Unger [5]. The transmitted light pictures were taken with a Hi8-Videocamera with a gray scale of 256. The differentiation between floc and background was made by defining a limit in the gray scale for the flocs.

Another method was developed by a group at Åbo Akademi, Finland [6]. In this method, a digital camera takes single pictures in direct light. This method avoids using a limiting value on the gray scale, which is a disadvantage of most of the other image analysis methods.

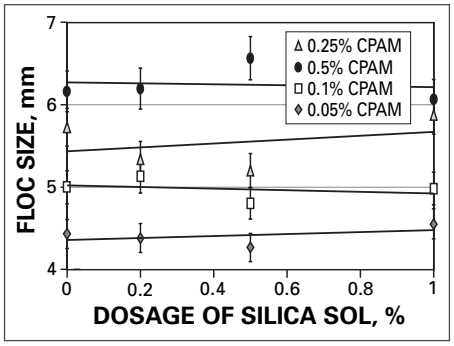
A more recent development is the use of a video camera in transmitted light [7]. Another development based on image analysis was presented by a group of the CTP in Grenoble [8].

METHODS

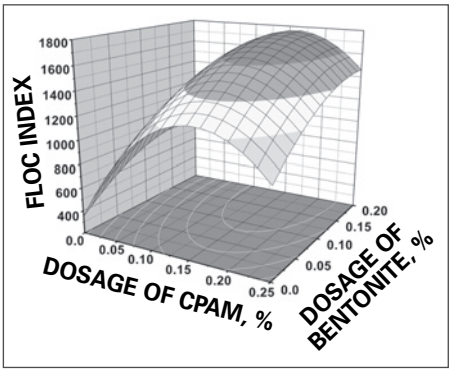
Figure 1 shows the experimental setup, which is similar for both methods and was based on the research of others [9]. The furnish is prepared in a storage tank with a consistency of 0.2%. Before we begin to take measurements, the stock is pumped in the closed circuit to guaran-



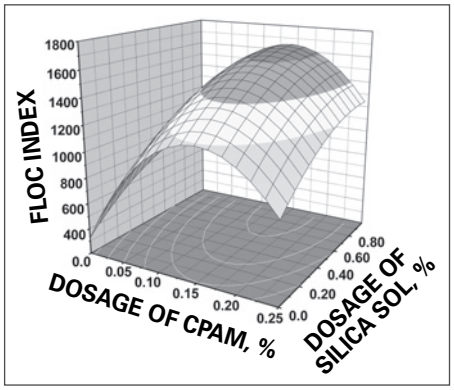
2. Floc size for the system CPAM-bentonite for TMP (tap water, 0.2% consistency, a flow rate of 100 L/min, TMP at 40°SR).



3. Floc size for the system CPAM–modified silica sol for TMP (tap water, 0.2% consistency, a flow rate of 100 L/min, TMP at 40°SR).



4. Floc index for the system CPAM–bentonite for TMP (tap water, 0.2% consistency, a flow rate of 6.8 L/min, TMP at 45°SR).



5. Floc index for the system CPAM–modified silica sol for TMP (tap water, 0.2% consistency, a flow rate of 6.8 L/min, TMP at 45°SR).

tee an even fiber distribution in the furnish. The circuit is open during the trials.

We added the aids at two locations. At the first station, the polymer solution was added, and the microparticle suspension was added at the second station. By varying the tube lengths L_1 and L_2, we controlled the contact times of the additives with the fibers. These experiments are a continuation of earlier work on the interactions of microparticle systems with furnishes [10].

Scattering of laser light

The device we used to measure the flocculation by light scattering is the Monitrol-System from Chemtronics AB, Bohus, Sweden. The measuring unit of this device is based on the work of others [11]. Originally, this device was developed to control retention and consistency online [12]. With some modification of the software, it is also possible to get information about the state of flocculation.

The laser beam transverses the flowing pulp suspension and is scattered by the solids. The intensity of the scattered light is measured under different angles, both for transmitted light and back-scattered light. We can use Eq. 1 to calculate two different floc indices from these data. One index is for the transmitted light, and the second is for the back-scattered light. In this study, we were concerned with the back-scattered light only.

Image analysis

With this experimental setup, it was not possible to vary the times during which the additives were in contact with the fibers. For a given flow velocity of 1 m/s in the measuring unit, the contact times were 4 s between Stations 1 and 2 and another 4 s between Station 2 and the measuring area. The dimensions of this observation area were 120 mm by 80 mm, the depth being 10 mm. These dimensions are sufficiently large to allow the transit of the fiber flocs without major overlapping of the flocs.

The pictures of the flowing furnish were taken with an electronic flash and a black background. Eight to ten digital images comprise one experiment. Each picture is analyzed separately in the machine and cross-machine directions. The final result is then expressed as the average of all spectra.

The power spectrum of transmitted light is calculated in the machine and cross-machine directions by averaging the individual column and row spectra, respectively. Afterwards, the grand average spectrum is transformed to a wavelength spectrum. This wavelength spectrum describes the distribution of the floc length. By solving Eq. 2 in the range of 2–32 mm, we can determine a characteristic wavelength:

$$\int_{2mm}^{\lambda_{char}} E(\lambda)d\lambda = \int_{\lambda_{char}}^{32mm} E(\lambda)d\lambda \qquad (2)$$

This equation is obtained by finding the wavelength λ where the energies to the left and to the right of λ_{char} are equal. The characteristic floc size FS_{char} is considered to be half of the characteristic wavelength. A detailed description of this method can be found elsewhere [6].

MATERIALS

Two different TMP pulps were used. The trials with image analysis were conducted with a bleached TMP from UPM-Kymmene, Rauma, Finland, supplied at a solids content of 30%. Trials using the scattering of laser light as the analysis method were conducted with a thermomechanical pulp from Stora-Enso, Maxau, Germany, supplied at a solids content of about 90%. In all cases, the pulps were diluted with tap water having a conductivity of approximately 500 µS/cm.

The polymer used was a cationic polyacrylamide (Percol 47) produced by Ciba Specialty Chemicals. The doses reported here are on a product basis. The aluminum-modified silica sol (BMA 780) was supplied from Akzo Nobel, while the bentonite (Opazil AO) came from Südchemie. The doses reported here for the microparticles are on an actives basis. The filler was a GCC (Hydrocarb 50 GU) from Omya. The filler was maintained at 35% in all sheet-forming experiments.

RESULTS AND DISCUSSION

Influence of additive dosage on floc size

Results obtained with the image analysis technique show the influence of the dosage of CPAM and microparticle components on the floc size.

As shown in **Fig. 2**, both the dosage of CPAM and that of bentonite influence the floc size. The floc size increases with increasing dosage of CPAM. At low levels of CPAM, the addition of bentonite has no impact on the floc size, but this picture changes as the dosage of CPAM increases. At concentrations of CPAM greater than 0.25%, the floc size increases with an increasing dosage of bentonite.

The flocculation in the CPAM–bentonite system is mainly based on electrostatic interactions. Therefore, a partial reverse of the sign of the charge is needed. With the addition of CPAM, positive domains are generated on the fibers which can interact with the negatively charged bentonite. Flocs can be formed by the interaction of polymers and fibers and also by the interaction of polymers, bentonite, and fiber. Other results showed that the fines are an important partner in forming flocs [9].

When a CPAM–bentonite system is changed to a combination of CPAM and modified silica sol, the behavior changes (**Fig. 3**). The bentonite flocs reach a larger average floc size. This floc size is influenced by the dosage of CPAM but does not depend on the amount of modified silica sol.

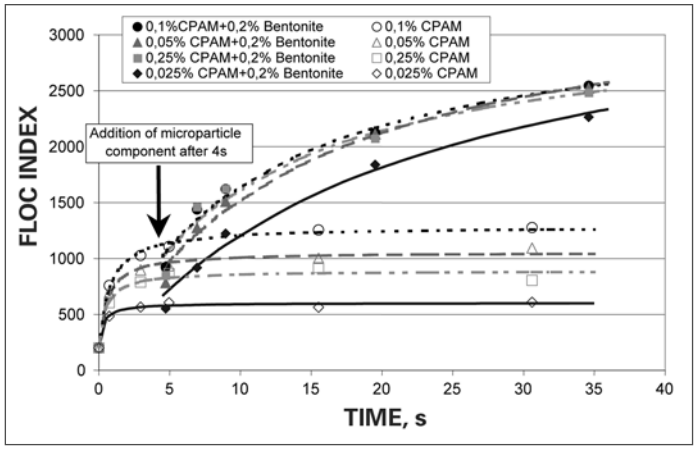
The explanation for this finding is probably quite simple. The average particle size of this modified silica sol is much smaller than that of bentonite. Bentonite has a "platey" structure roughly 300 nm × 100 nm × 5 nm [13], whereas the modified silica sol is a chain with a diameter of about 5 nm and a length of approximately 40 nm. This difference in particle size allows the modified silica sol to penetrate into the flocs, whereas the bentonite particles function as a bridging agent on the surface of the micro flocs. This structure leads to the growth of flocs in the bentonite system.

Influence of dosage of additives on floc index

The results shown were obtained for constant contact times between the additives and the furnish. The floc index was measured by the light scattering method already described.

In the CPAM–bentonite system, the results for the floc index (**Fig. 4**) are similar to those obtained for the floc size. Both floc size and floc index increase with increasing dosage of CPAM and bentonite. In this case, we find that smaller amounts of additives are needed to reach the maximum of the floc index. The reason is that another TMP was used for these experiments, and this TMP was slightly less negatively charged.

Obviously, the results for the floc index of the combination of CPAM and modified silica sol are similar to those for CPAM and bentonite (**Fig. 5**). However, this result differs significantly from the behavior found for the floc size shown in Fig. 3, where the floc size is influenced by the dosage of CPAM but is independent of the dosage of modified silica sol. This finding again may be explained by the differences in particle sizes of bentonite and modified silica sol, respectively. Obviously the smaller particles do not cause an expansion of the flocs. This result, in conjunction with the fact that these systems have proven to perform well in retention measurements, leads to the conclusion that the silica flocs are denser but not larger.



6. Influence of adsorption time of chemical additives on the floc index (tap water, 0.2% consistency, a flow rate of 6.8 L/min, TMP at 45°SR). (Equation 3 was used in data fitting.)

Flocculation kinetics

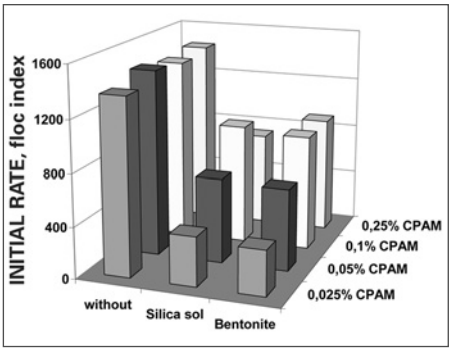
Besides the parameters discussed, finding the correct location for adding the paper additives in the wet-end section is crucial for their performance. Therefore, there is a strong need for a better understanding of the flocculation kinetics. There are only a few studies published on this subject [14–16].

The results for a CPAM–bentonite system are presented in **Fig. 6**. For a better comparison, the results for a one-component system (CPAM) are also included in this figure. Obviously, the adsorption of CPAM onto the fibers is very fast, and the flocs are readily formed in less than 5 s. The differences between plain polymer and microparticle systems are significant even if the exact number may not be meaningful because the flow turbulence in the experiment is not comparable to the turbulence on a paper machine.

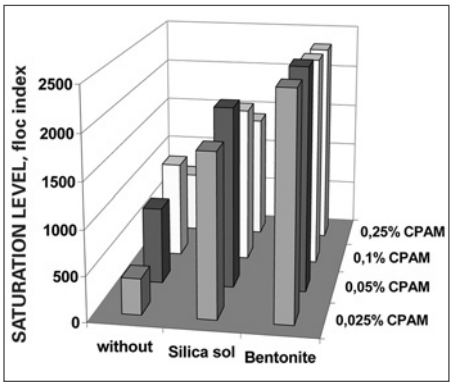
Swerin and Ödberg have shown that the kinetics of adsorption of cationic polymers onto anionic fibers are mainly dominated by the frequency of collisions of the two partners [17]. This parameter is strongly influenced by turbulences in the suspension. It was found that the adsorption is finished in less than 1 s if the shear rate is very high. On the other hand, if the adsorption is diffusion-controlled, which means without any shear at all, it may take some hours until the adsorption process is finished [17].

The flocculation kinetic measurements of microparticle systems were conducted at a constant time of 4 s of polymer adsorption onto the fibers. After this time, we added the microparticle component, and we changed the length of the tube L2 to vary the contact time. The time shown on the abscissa of Fig. 6 is the time after the CPAM was added.

As can be seen in Fig. 6, the flocculation kinetics for the CPAM–bentonite system are different from the kinetics of a one-component system. First, the formation of flocs proceeds more slowly and continues for more than 30 s, while simple polymer flocs are fully formed within 5 s. Second, a microparticle system attains a substantially higher floc index than reached with CPAM alone. The results of the flocculation kinetics for the system of CPAM and modified silica sol are similar to those obtained for the bentonite system.



7. Comparison of initial rates for different retention systems.



8. Comparison of the saturation level for different retention systems.

The experimental data of the kinetic measurements for the different retention systems can be fitted satisfactorily by Eq. 3:

$$y = K_1 \frac{x K_3}{x K_2 + K_3 / K_2} \quad (3)$$

This mathematical description of the data simplifies a comparison of the results obtained for the three systems. The kinetics at the beginning and the final floc index when saturation is reached are of special interest for the flocculation studies.

The velocity in the beginning, which is named "initial rate," is obtained by using the following equation:

$$\textit{initial rate} = K_1 \times K_2 \quad (4)$$

The results obtained by solving this equation are shown in **Fig. 7**.

The most distinct finding is that the initial rate is highest for a one-component system with CPAM. Also, this value does not depend on the dosage of CPAM. This result can be easily understood if we assume that in this case the flocculation is mainly influenced by the adsorption of CPAM onto the fibers. The adsorption of cationic polymers onto anionic fibers always follows a high-affinity-type isotherm. Therefore it is not a surprise to see the initial rate be very high.

The situation is different for the microparticle systems. For these systems, the initial rate of the flocculation is influenced by the dosage of CPAM. This means that the velocity of floc formation increases when the amount of the cationic charges on the surface increases.

The results do not differentiate between two possible mechanisms: (A) Polymer adsorbs on the fiber surface, followed by adsorption of microparticles, which again may serve as anchoring spots for further deposition of polymer and microparticles. (B) Polymer–microparticle flocs form and deposit on the fiber surface.

According to Mechanism A, the first step is very fast. However the second step, the interaction of the microparticles with the fibers, should be slower and should depend on the quantity of cationic charges on the fibers.

For Mechanism B, the first step in the formation of polymer–microparticle flocs should be a fast process, while the adsorption of such flocs may proceed more slowly. While it is not possible from the results to distinguish between these possible mechanisms, the more probable is Mechanism A. In any case, both mechanisms consist of two steps controlled by a slow step.

The saturation level, which is the final value for the floc index after a long time, can also be calculated with the mathematical model. This saturation level is calculated by solving the following equation:

$$\textit{saturation level} = K1 \times (K3/K2) \quad (5)$$

The results obtained solving this equation are presented in **Fig. 8**. The values for the saturation level increase in the order CPAM < CPAM–modified silica sol < CPAM–bentonite.

For this parameter, the effect of the dosage of CPAM is most significant for the one-component system. The saturation level of the microparticle systems is only slightly influenced by this parameter, especially for the bentonite system.

As mentioned, the saturation level is the value of the floc index after a long time. Therefore it is reasonable to assume that the saturation level reflects more or less the situation at equilibrium. Also, the situation at equilibrium is strongly influenced by the charge balance and the sensitivity of a system to changes in charge. The microparticle systems seem less sensitive to changes in the charge balance than a one-component system. When the two microparticle systems are compared, the bentonite system is only slightly influenced by changes in the charge balance. To highlight this point, we turn our attention to the influence of zeta potential on the floc index.

Effect of zeta potential on flocculation

Most commercially available retention systems, except for the PEO–cofactor system, are based on electrostatic interactions. Therefore the charge balance of the furnish influences the performance of these retention systems. For practical reasons, it is also important to know how sensitive the systems are to changes in the charge balance. The measurement of the flocculation kinetic yields some evidence that microparticle systems are less sensitive to changes in charge and that there are differences among the two microparticle systems.

Looking at the influence of zeta potential on the floc index, we can easily check this assumption. Even though the zeta potential is a parameter of some uncertainty, it was chosen to give an idea of the surface charges that are active in the suspension and consequently an idea of the charge balance.

The results in **Fig. 9** were obtained for the same TMP system used in the kinetic measurements. The contact times of the additives with the furnish were held constant.

The experimental data were satisfactorily fit to a second-degree polynomial equation:

$$y = ax^2 + bx + c \quad (6)$$

This equation simplifies the comparison of the results. The parameter *a* describes the shape of the curve. When the value of *a* is great, the curve is more steep. The sign of *a* shows whether the curve opens up or down. The factor *c* is the point of intersection of the curve with the *y* axes at $x = 0$.

The position of the maximum is found by solving Eq. 7:

$$x_{max} = -\frac{b}{2a} \quad (7)$$

The floc index at the peak of the curve is

$$y_{max} = c - \frac{b^2}{4a} \quad (8)$$

As can be concluded from Fig. 9, the maximum of the curves is always close to a zeta potential of zero. The shifts to positive or negative zeta potential are small and show no systematic trend. In contrast, the shape of the curve is characteristic of the different systems.

Figure 10 simplifies the comparison of the systems by displaying the dependence of the parameter *a* from the maximum of the floc index. This figure shows the influence of the charge balance on the performance of the systems.

Obviously, the value of *a* at a given floc index is always, except for one point, more negative for a modified silica sol system than for a bentonite system. This outcome means that the modified silica sol systems are more sensitive to changes of the charge.

A satisfactory explanation for this result could be the ambivalent charge characteristic [13] of bentonite as compared to modified silica sol, which is simply anionic. On the one hand, the positive charge of bentonite assists the flocculation for negative zeta potential, and its negative groups also have bridging capabilities for positive zeta potential.

Correlation of floc index with filler retention

The different flocculation measurements lead to interesting and useful results, but it is also important to evaluate if the flocculation data may be used to get early information concerning paper and runnability properties. The influence of the floc index on filler retention is presented in **Fig. 11**. The results for the filler retention were obtained by ashing laboratory handsheets according to a Zellcheming method [18]. The most interesting aspect of this figure is that the filler retention correlates well with the floc index. This is true for all systems included in this study.

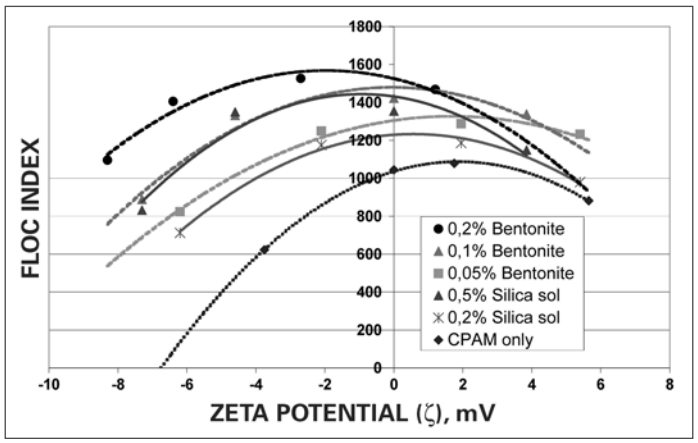
It seems that the measurement of the floc index, which can also be used as an online device, may even be used to predict certain paper properties. Such a measurement may serve as a convenient tool for process control.

CONCLUSION

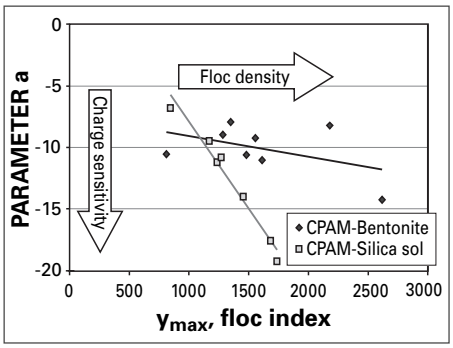
The floc size is strongly affected by CPAM or bentonite but not by modified silica sol. In contrast, the floc index is influenced by CPAM, bentonite, and modified silica sol. This behavior is explained by the formation of denser flocs with the modified silica sol system. The two methods used to obtain the floc size and floc index—image analysis and light scattering—complement one another.

In regard to the kinetics of flocculation, the formation of flocs is slower for microparticle systems than for a CPAM system. Microparticle systems are less sensitive to changes in charge than are one-component systems, with the bentonite system being the least sensitive. This outcome could be proven with zeta potential measurements.

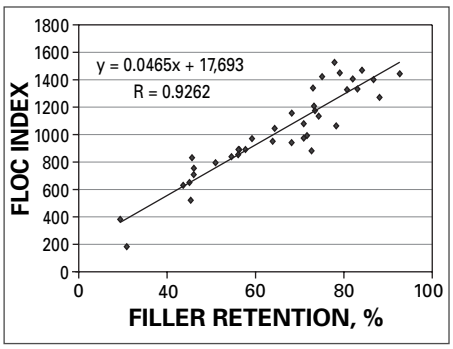
Finally, it was possible to show a good correlation between floc index and filler retention measured with laboratory sheets. **TJ**



9. Influence of zeta potential on floc index (tap water, 0.2% consistency, a flow rate of 6.8 L/min, TMP at 45°SR).



10. Influence of parameter a (charge sensitivity) on parameter c (floc density parameter). Results were obtained by fitting the experimental data with Eq. 6.



11. Correlation of filler retention with the floc index for laboratory handsheets and for different retention systems.

ACKNOWLEDGMENT

This study is funded as part of the research grant AIF-No 11765, sponsored by funds of the German Secretary of Commerce and Technology (Bundesministerium für Wirtschaft und Technologie (BMWi)) via the Arbeitsgemeinschaft Industrieller Forschungsvereinigungen "Otto von Guericke" e.V. (AIF).

LITERATURE CITED

1. Wahren, D., *Svensk Papperstid.* 70(21): 725(1967).
2. Wågberg, L., *Svensk Papperstid.* 88(6): R48(1985).
3. Norman, B., and Wahren, D., *Svensk Papperstid.* 75(20): 807(1972).
4. Gerli, A., Keiser, B.A., and Strand, M., *TAPPI J.* 83(10): 59(2000).
5. Davydenko, E., and Unger, E.-W., *Das Papier* 49(2): 51(1995).
6. Beghello, L., Toivakka, M., Eklund, D., and Lindström, T., *Nordic Pulp Paper Res. J.* 11(4): 249(1996).
7. Wågberg, L., and Nordqvist, T., *Nordic Pulp Paper Res. J.* 14(3):

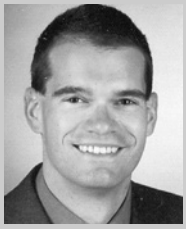
247(1999).
8. Pierre, C., "A new sensor for characterising fiber flocculation in the stock – a tool to control sheet formation," PTS Symposium, Chemische Technologie der Papierherstellung, 2000.
9. Näsman, J., and Eklund, D., "Effect of highly cationic fixing agent and cationic starch on the flocculation and the paper properties of peroxide bleached TMP," *Proceedings of the 1998 EUCEPA Conference*, EUCEPA, p. 355.
10. Müller, P., Gruber, E., and Schempp, W., *Wochenbl. Papier.* 127(7): 460(1999).
11. Wijk, H., "Präsentationsunterlagen zum Monitrol-System," Fa. Chemtronics, Sweden.
12. Frölich, S., and Andersson, K., *Svensk Papperstid.– Nordisk Cellulosa* 98(3): 28(1995).
13. Stockwell, J., "Bentonite in the paper industry," in *Use of Minerals in Papermaking*, Pira Internat. Publ., Leatherhead U.K. 1997, pp. 175-190.
14. Gregory, J., *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 31: 231(1988).
15. Wågberg, L., and Lindström, T., *Nordic Pulp Paper Res. J.* 3(4): 152(1987).
16. Larsson, A., Walldal, C., and Wall, S., *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 159: 65(1999).
17. Swerin, A. and Ödberg, L., "Some aspects of retention aids," in *The Fundamentals of Papermaking Material*, Pira Internat. Publ., Leatherhead U.K.. 1997 pp. 264-350
18. Prüfung von Zellstoff, "Papier und Pappe: Bestimmung des Glührückstandes," Vol. IV, Zellcheming-Merkblatt, IV/40/77, Zellcheming, Darmstadt 1977.

Received: July 10, 2001
Accepted: February 27, 2004

This paper is also published on TAPPI's web site <www.tappi.org> and summarized in the December *Solutions! for People, Processes and Paper* magazine (Vol. 87 No. 12).

Gruber and Müller are with Darmstadt University of Technology, Dept. of Macromolecular Chemistry, Alexanderstr. 10, D-64283 Darmstadt, Germany. Email Gruber at gruber@papier.tu-darmstadt.de.

Gruber



Müller