Water release from fractionated stock suspensions. Part 2. Effects of consistency, flocculants, shear, and order of mixing

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ABSTRACT: The rate of gravity drainage from a papermaking stock suspension is highly dependent on the initial consistency of the stock, and on the presence of cellulosic fines. In this study, we fitted the results of testing to a model based on different linear contributions to drainage resistance from fibers and each type of fines. Deviations from the model at relatively high consistency were tentatively attributed to flocculation phenomena. Substantially higher rates of dewatering were achieved by selectively treating the fines, the fibers, or the combined furnish with cationic polyelectrolytes. Results were consistent with several mechanisms, which might act in parallel during ordinary papermaking. Attachment of cellulosic fines to fiber surfaces can prevent those fines from migrating to choke points within a wet web. Agglomeration of fines to each other can reduce their effective surface area. Flocculation of the fibers can make the fiber mat less uniform, thus providing larger channels for water to flow from the mat.

Application: Cellulosic fines can make papermaking stock drain more slowly, but the effect can be partly overcome by treatment with positively charged polymeric additives. Papermakers can take advantage of such treatments to increase production rates in some cases.

Part 1 of this series [1] demonstrated that the rate of water release from a slurry of fibers can be critically dependent on the type and level of cellulosic fines. The effect of fines was highly nonlinear, with almost no effect on drainage when small amounts of fines were added to fines-free fiber suspensions. Thereafter, resistance to drainage increased out of proportion to the net content of fines. To explain these and other findings, we proposed that unattached fines become stuck at strategic points in a wet mat of fibers, tending to block "choke points" of flow channels in the structure.

Additional experiments were carried out to further evaluate the usefulness of a "choke-point" concept to explain resistance to dewatering. We held the volume of suspension constant in one set of tests, and varied the amounts of filterable solids over a wide range. Thus, the starting consistency was varied, while keeping the relative amounts of fibers and fines constant. As a first step in analyzing the data the content of the freeness test apparatus was considered to have two zones. We regarded the upper zone as a free-flowing suspension, in which fines and fibers were generally unattached to each other. We assumed the lower zone to be a contiguous mat having relatively uniform properties. Resistance to flow through the mat was equated to a sum of linear effects of the fines and fiber amounts that have accumulated in a unit of time.

Further tests were carried out with selective treatments of fines, fibers, or the recombined slurry with a cationic polyelectrolyte. For instance, papermakers frequently apply high-charge-density polyelectrolytes in an effort to increase the rate of dewatering from fiber suspensions [2-6]. Results of such treatments are often explained in terms of charge neutralization [7,8] or the creation of charge patches on the solid surfaces [9,10]. Both of these mechanistic models predict increasing agglomeration among the objects in the suspension. It is logical to expect that results will be different, depending on whether the treatment is applied to the fines component, the fiber component, or to the combined mixture of fibers and fines in suspension.

We used a very-high-mass cationic acrylamide copolymer (cPAM) to "bridge" the suspended materials together into different kinds of flocs, depending on the mixture to which the polymer was added. The idea was to (a) agglomerate the fines together, thus reducing their effective surface area, (b) agglomerate the fibers together, thus increasing flocculation and providing larger channels for fines to pass through the wet fiber mat, or (c) bind fines to fibers, thus preventing the fines from moving to other locations in the wet mat during the process of dewatering.

Some preliminary experiments similar to those described were carried out in an earlier study [11]. We wanted to carry out the tests in a more rigorous manner and determine whether the effects of the treatment would be affected by application of hydrodynamic shear. The polymeric bridges formed by interactions of cationic acrylamide copolymers, though they tend to be rather strong, also tend to be somewhat brittle. Such bridges are known to break down irreversibly if the hydrodynamic shear is large enough to separate the attached objects from each other [12-14]. Different models of how fines contribute to drainage resistance tend to predict different effects resulting from the application of shear.

EXPERIMENTAL

Materials

The cellulosic materials were the same as those described in Part 1 [1]. The "fibers" were obtained by standard disintegration of xerographic copy sheets, using a Bauer-McNett device with a 100-mesh screen to selectively remove the fines fraction. Primary fines were obtained from bleached hardwood kraft pulp, using the "passed" fraction through a 100-mesh screen and concentrating the fines by gravity settling. The secondary fines were obtained by extensive (45 min) refining of hardwood pulp on a laboratory hollander beater, followed by Bauer-McNett classification with a 200-mesh screen. The "P200" fraction was again concentrated by gravity setting over night.

Chemicals were reagent grade, except for the following: poly-diallyldimethylammonium chloride (poly-DADMAC) solution was catalogue no. 409030 from Aldrich, having a nominal molecular mass of 400,000 to 500,000 g/mole. Cationic acrylamide copolymer (cPAM) was a dry-bead product (Percol® 175) from Ciba Specialty Chemicals.

Methods

Modified Schopper-Riegler tests were carried out in the same manner as in Part 1 [1]. An optional high level of hydrodynamic shear was applied to selected slurry samples for 30 s, following various chemical treatments (or blank condition) by means of a Waring blender.

Streaming potential titration analysis was carried out with a streaming potential jar, as described elsewhere [15]. To detect the streaming potential of only the outer surface of the fibers, these tests were carried out at a very low electrical conductivity of approximately 60 µS/cm [16,17]. Turbidity tests were performed with a DRT-15CE turbidimeter from HF Scientific, Ft. Meyers, Florida.

RESULTS AND DISCUSSION

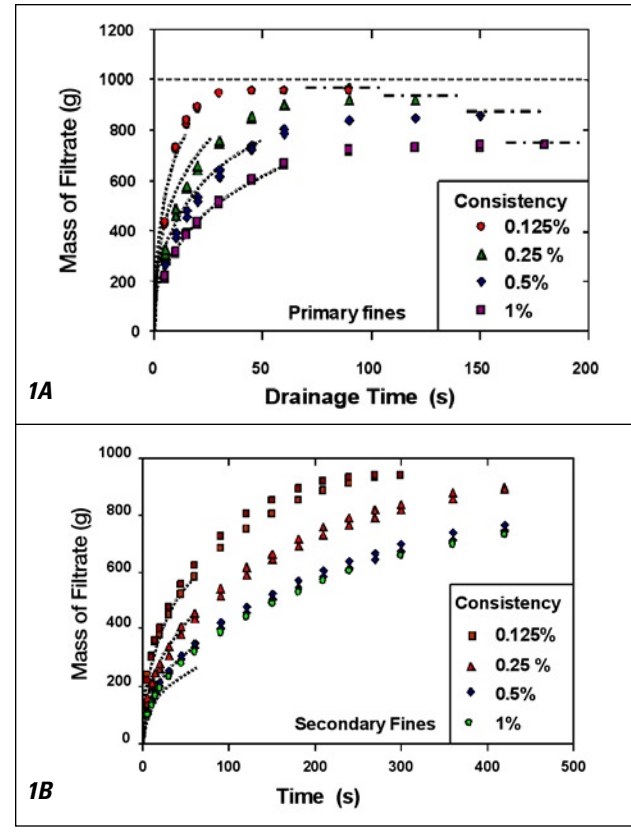
Effects of slurry solids

Figure 1 shows how the initial stock consistency affected the mass of filtrate as a function of time for suspensions comprising 30% of primary (left-hand frame) or secondary fines (right-hand frame). Parallel tests were carried out with fines-free fiber suspensions. Visual inspection suggested that resistance to flow increased with increasing initial consistency and that secondary fines had a greater relative effect than did primary fines.

In our first attempt to fit the data, we used a simple application of the Kozeny-Carman equation [18], which relates flow resistance to sizes and surface areas of objects in a uniform bed. Based on this approach, we would expect the resistance to dewatering to be as follows:

$$dQ / dt = (1/K)\ (1 - C)^3\ S^{-2}\ C^{-2}\ \mu^{-1}$$

where Q is a volumetric flow of liquid, t is time, C is the volume fraction of the solid phase, S is the hydrodynamic surface area, and µ is the dynamic viscosity of the fluid phase. A preliminary attempt to fit the data in Fig. 1 by using these assumptions was unsuccessful. Even when accounting for changes in hydrostatic head during a gravity dewatering test, we could not account for the observed strong decelerations of flow rates as a function of time. Thus, a model based on uniform consistency during dewatering does not appear to be useful in evaluating the present data.



1. Filtrate mass versus time in the presence of 30% of primary fines (1A, top) and secondary fines (1B, bottom) in cellulosic fiber suspensions prepared at different overall consistencies (see insets).

We had much greater success in fitting the data by modeling the process as "simple filtration" [19], and assuming the contents above the forming screen consist of two zones. The upper zone was assumed always to have the same consistency as the initial suspension. The lower zone, representing a contiguous mat of fibers, was assumed to have a much higher, but relatively constant consistency. The thickness of the latter zone was assumed to increase in thickness and in resistance to further flow, in proportion to the amount of filtrate that had passed through it. We also assumed that the flow rate was influenced in a linear way by the applied hydrostatic head of suspension above the level of the screen. These assumptions were evaluated based on the following equation:

$$Q_t = k_1 \int (1000\ \text{mL} - Q_{t-1}) / (k_2 + k_3\ C\ Q_{t-1}\ t)\ dt$$

where k_1 is a coefficient, 1000 mL is the initial volume of sample, Q_{t-1} is the net volume of filtrate collected at

time = *t*-1, k_2 is a coefficient representing the resistance to flow through the bare screen, k_3 represents the resistance to flow past a unit mass of cellulosic material, and *C* is the mass of solids per unit volume.

As shown by the dotted lines through the origins in both frames of Fig. 1, the fit of the equation based on a simple filtration model to the data worked moderately well under the following assumptions: k1 = 0.2; k_2 = 2; k_3 (primary fines) = 30; and k_3 (secondary fines) = 330. An especially notable deviation at the highest consistency in the case of secondary fines was tentatively attributed to increasing importance of fiber flocculation with increasing consistency. Flocculation can be expected to increase the rate of dewatering by gravity [2], which helps to account for the poor fit of data corresponding to a consistency of 1%.

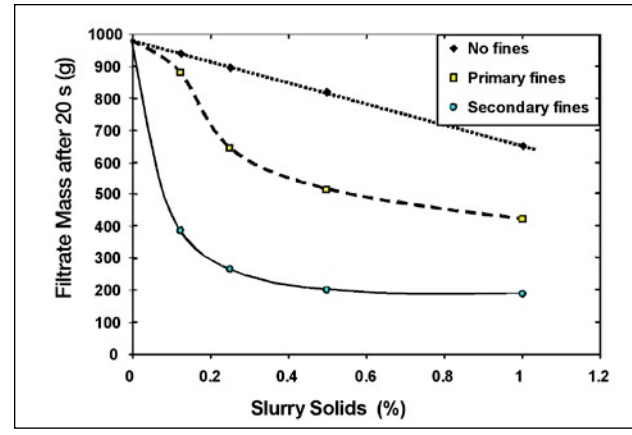
The straight line segments at the top right of Fig. 1A are based on an assumption that the amount of water retained in a fiber mat after gravity dewatering will be directly proportional to the amount of solids present. As shown, this assumption generally yielded a good fit with the data, with the final solids after about 200 s of dewatering set equal to 4.2%. We could not obtain such a fit of the data in the case of secondary fines (Fig. 1B), probably because the filtrate mass values were still changing significantly, even 400 s after the initiation of drainage.

Figure 2 summarizes results for systems containing either 30% of primary fines, 30% of secondary fines, or no fines. The vertical axis, the filtrate mass collected after 20 s of dewatering, can be taken as a measure of the ease of water release. Primary fines greatly increased resistance to dewatering, especially when the slurry solids were 0.25% or higher. But the effect of secondary fines was much greater. In the absence of fines, the results were almost exactly linear with respect to the initial solids level, as would be expected based on the "simple filtration" model described above. Although we would expect all of the trends to pass through a common point of approximately 1000 mL at a consistency of zero, both of the fines-containing systems showed strong deviations from what would be expected for simple filtration.

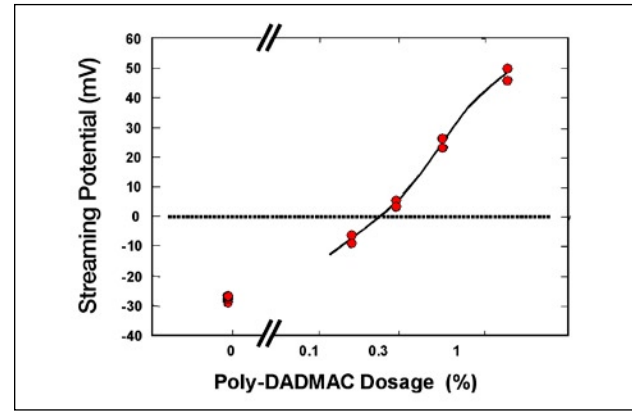
Effects of high-charge cationic polymer

We explored possible explanations for the effects of fines on dewatering by carrying out tests with cationic polyelectrolytes. The choke-point hypothesis [6,11] provides one way to account for the observed nonlinearity in the data in Figs. 1 and 2. Two kinds of cationic polyelectrolytes were added in different ways in an attempt to (a) agglomerate fine particles together, thus reducing their effective surface area; (b) flocculate fibers together, thus making the mat less uniform and less effective as a filtering medium; or (c) attach cellulosic fines to fibers, thus preventing the possibility that fines could migrate to choke points in the wet web structure.

The first series of polymeric treatments involved poly-DADMAC, a high-charge-density, linear cationic polymer with a nominal molecular mass of 400,000 to 500,000 Daltons. The strategy when using this polymer was to selectively reverse the charge



2. Effect of overall slurry solids on the mass of filtrate collected after 20 s of gravity dewatering from 0.5% cellulosic suspensions containing no fines (filled diamonds), 30% primary fines (squares), or 30% secondary fines (circles).



3. Streaming potential titration to determine a suitable addition level of poly-DADMAC to induce electrostatic attractions among fines, fibers, or combinations.

of some of the cellulosic surfaces to positive, while leaving other surfaces in their original, negatively charged condition. Poly-DADMAC of relatively high mass was selected for these experiments to slow the rate of its diffusion below the outer surfaces of the fibers [20-22] and to achieve patch-like coverage of surfaces [9,10,23]. Previous studies have shown that patches of positively charged polymer surrounded by negatively charged cellulosic surfaces can achieve coagulation effects that are more intense than those achieved through neutralization of charge repulsion effects between the surfaces [24].

Streaming potential analysis was carried out to determine a suitable dosage of poly-DADMAC to achieve the effects just mentioned. As shown in **Fig. 3**, approximately 0.24% poly-DADMAC solids on cellulose was sufficient to neutralize the external surface charges of the solids in a suspension of whole pulp, including fines and fibers. In all of the experiments we used 0.6% poly-DADMAC, based on total cellulosic solids, even when selectively treating just the fines or just the fibers. We expected the treated fraction to become strongly positive in charge, leading to very strong fines-to-fiber coagulation upon mixing of the two fractions [24]. Previous work indi-

Item treated with poly-DADMAC	Filtrate mass after 20 s of dewatering (g)		Filtrate turbidity (NTU)	
	Mean	Avg. Dev.*	Mean	Avg. Dev.*
No treatment	804	17	3.8	0.31
To fibers	806	12	2.2	0.13
To fines	844	13	1.4	0.28
To mixture	832	4	1.8	0.17

* Note: The dosage of poly-DADMAC (high mass) was selected so that is was twice the amount needed to neutralize the mixed furnish; the same total amount was used in all tests, except for "no treatment." Each test was carried out twice. *Avg. Dev. = Average deviation from the mean of replicate measurements.

I. Effects of poly-DADMAC treatment and order of mixing on gravity dewatering and filtrate turbidity in the presence of 30% primary fines.

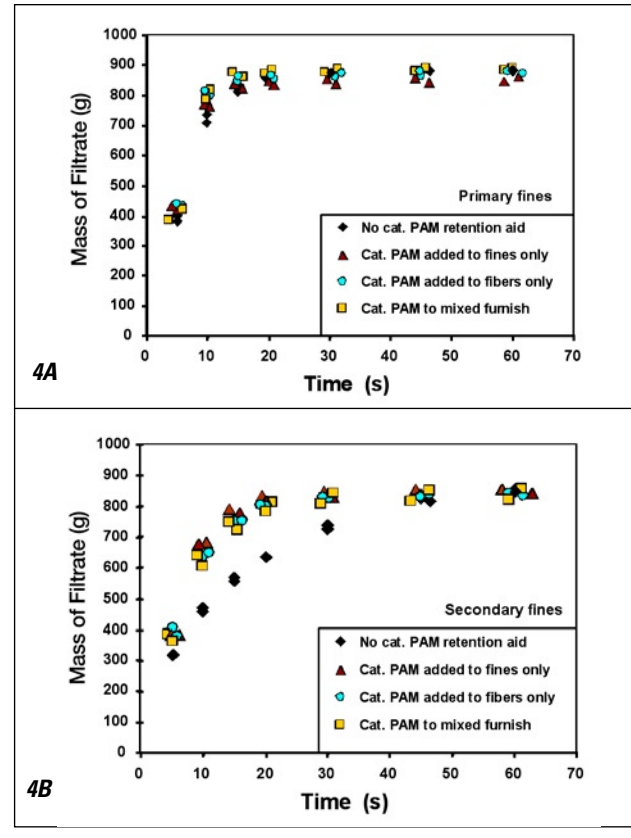
cated that essentially all of the added polymer would adsorb onto fiber surfaces, even when the addition level is more than twice what is required to achieve a neutral surface charge [25]. A higher relative treatment level of the fines (30% of the final mixture) relative to fibers (70% of the final mixture) can be justified based on a substantially higher surface area per unit mass in the case of fines [26].

As shown in **Table I**, selective treatment of the fines fraction with poly-DADMAC yielded a significant increase in the mass of filtrate collected during the first 20 s of dewatering. Increased drainage also resulted when poly-DADMAC was added to the mixed furnish. All of the treatment schemes involving poly-DADMAC yielded significant decreases in the turbidity of the filtrate collected in the course of drainage tests. Based on these results, we concluded that retention of fines in the fiber mat was substantially increased by all three of the treatment options considered. The largest decreases in turbidity were associated with selective treatment of the fines fraction.

Cationic retention aid treatment of furnish components

We were able to achieve the same general effects by use of very-high-mass cationic acrylamide copolymer treatments, i.e., by using a cationic retention aid, but without having to be concerned with surface charges. Past work has shown that such polymers can create relatively strong, but brittle and irreversible attachments between solid surfaces in a suspension to which they are first added [27-29]. We used 0.1% cPAM, based on the total mass of cellulosic materials (except that none was added in the case of the control experiments), and 30% fines, based on the mass of filterable solids.

Figure 4 (A and B) shows the effects resulting from such treatments. To clearly show the different symbols, some of them were moved slightly to the left or right of the exact time of observation (5, 10, 15, 20, 30, 45, and 60 s). As shown in Fig. 4A, the retention aid addition had only a subtle effect in the case of primary fines. Only at an elapsed time of 10 s after the



4. Effect of cationic acrylamide copolymer (cPAM) retention aid addition on the gravity dewatering of furnish containing primary (4A, upper) and secondary fines (4B, lower), depending on whether the flocculant was omitted (filled diamonds), added to the fines fraction only (triangles), to the fiber only (circles), or to the combined furnish (squares).

initiation of dewatering was the filtrate mass corresponding to the untreated suspension noticeably lower than what was observed in the cases involving treatment by the cPAM. It did not appear to matter whether the retention aid was added only to the fiber, only to the fines, or to the combined furnish.

Figure 4B shows a substantial increase in drainage rates resulting from cationic retention aid treatment in all cases. These results suggest that the retention aid was somehow able to overcome or remove one or more mechanisms that are responsible for resistance to dewatering. The results for the systems treated with cationic retention aid became almost as high as those shown in Fig. 4A, even though secondary fines clearly had the potential to retard dewatering to a much greater extent in comparison with primary fines.

To better differentiate the effects of the different ways of adding the cationic retention aid, **Table II** compares the masses of filtrate collected after 20 s of drainage, as well as the filtrate turbidities. In the case of primary fines, treatment with cationic retention aid had a significant effect only in the case of primary fines, and in that case the drainage rate actually was reduced. As shown by the second numerical column, retention efficiency of the fines was very high in all cases in which the polymer was used. The last two columns of Table

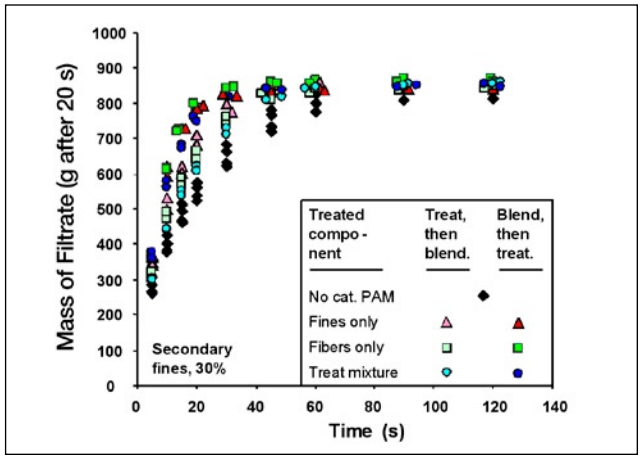
Cationic polyacrylamide treatment	30% Primary fines		30% Secondary fines	
	Filtrate mass after 20 s of dewatering (g)	Filtrate turbidity (NTU)	Filtrate mass after 20 s of dewatering (g)	Filtrate turbidity (NTU)
No treatment	862	2.9	632	3.8
To fibers	860	0.10	802	0.62
To fines	837	0.55	822	0.45
To mixture	878	1.2	804	0.49
Average deviation*	5.4	0.084	4.8	0.038

* Note: These averages were obtained by taking the average deviation for each condition of treatment, then averaging all four such results together.

II. Effects of cationic acrylamide copolymer treatment and order of mixing on gravity dewatering and filtrate turbidity.

II show related results in the case of secondary fines. In contrast to the case of primary fines, all of the treatments with cPAM yielded very substantial increases in dewatering rates. The highest dewatering rates were achieved by selective treatment of the fines fraction. Turbidities again were very low in all of the treated systems. These results suggest that the retention aid substantially increased the amount of fines present in the fiber mats, thus increasing the overall surface area of solids present and increasing the resistance to dewatering. Such an effect would not be expected during commercial papermaking, since unretained fines become recirculated and ultimately most of the fines are retained.

As suggested by Fig. 4 and some of the tabulated data, unattached fines will tend to be drawn through channels of flow as they drain through a wet web of paper, and they will tend to become trapped at "choke points" in the structure. In principle, addition of a cationic retention aid to mixed furnish would be expected to defeat this type of mechanism by attaching the fines to the surfaces of fibers. Another kind of mechanism that finds some support in Fig. 4 is the idea that the high specific surface area of fiber fines can be reduced by forming them into agglomerates. Some evidence supporting this concept was shown in a preliminary study [11], in which sedimentation velocity tests were used to estimate the hydrodynamic specific surface areas of individually suspended versus agglomerated fines. In the case of secondary fines, flocculation by cPAM reduced the hydrodynamic specific surface area by about 64%.



5. Effect of cPAM treatment, order of addition, and strong hydrodynamic shear on the dewatering of cellulosic suspensions containing 30% secondary fines.

Combinations of flocculant and hydrodynamic shear

Tests with the cationic retention aid were repeated with the application of intense hydrodynamic shear, either shortly before or shortly after each treatment with cationic retention aid. Only systems containing 30% of secondary fines were considered. The idea was to find out to what extent the effects shown in Fig. 4B could be reversed by irreversible breakage of polymeric bridges between solid surfaces.

Figure 5 shows close agreement with the trends shown in Fig. 4B in cases where the high-shear "blending" treatment preceded treatment with the cationic retention aid. The preliminary shearing, by itself, had no significant effect. Thus, all of the darker-colored symbols, with the exception of the blank (black diamonds) tended to be clustered together toward the top, indicating substantially higher drainage in comparison with the blank.

In Fig. 5, experiments in which intense shear was applied *after* treatment with cationic retention aid are represented by the lighter-colored symbols. Especially within the period of about 5 s to 30 s after the initiation of dewatering, these data points show distinctly slower dewatering in comparison to application of shear *before* retention aid treatment. The fact that the light triangle symbols were generally at the top of this intermediate group of data points is tentatively attributed to a greater difficulty in separation of fine particles from each other, in comparison to separating larger particles [30,31]. To fully understand the implications of these findings, probably it will be necessary to carry out further work to reveal the extent to which different types of solids become separated from each other following different chemical treatments and different levels of hydrodynamic shear.

CONCLUSIONS

The results of this study led to the following insights:

1. A simple filtration model, based on the assumption of a uniform slurry composition and uniform properties of a gradually thickening mat, was only partly successful in accounting for the effect of initial consistency on the results of gravity dewatering tests in the presence of 30% primary or secondary fines. Deviations from the model, especially in the case of secondary fines at the highest consistency tested (1%), were tentatively attributed to increased mechanical flocculation.

2. In the case of secondary fines, treatments involving cationic polymers were able to significantly increased dewatering rates, compared to untreated systems. Such increases were observed whether the retention aid was added just to the fines, just to the fibers, or to a mixture. These results help support the validity of mechanisms based on (a) agglomeration of fines so that they have less effective surface area, (b) flocculation of fibers so that the fiber mat is less uniform, with relatively open areas for water to flow around flocs, and (c) attaching fines to fibers so that they are not able to migrate to other positions in a wet web where they would tend to block drainage channels. These mechanisms were further supported by the results of tests in which suspensions of fines, fibers, or combinations were sheared just before or just after treatment with a cationic retention aid.

In the case of primary fines, the cationic polymers were not effective for promoting dewatering, and sometimes had the opposite effect. These results suggest that many such fines can pass through a wet web without becoming trapped or retained. Addition of a retention aid polymer under such a situation, during lab testing, can increase the amount of fines in the retained mat, thus increasing the net surface area and resistance to dewatering. **TJ**

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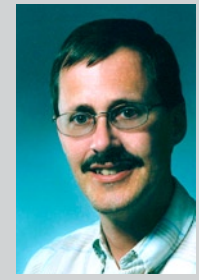

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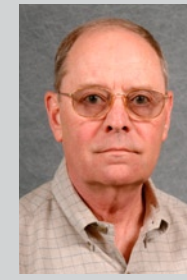

Heitmann

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