Effect of Idealized Flow Conditions on Retention Aid Performance. 1. Cationic Acrylamide Copolymer

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The performance of a cationic acrylamide copolymer retention aid was evaluated with respect to five contrasting flow conditions applied either before or during the formation of a fibre mat. Different levels of pre-shearing of a simulated fine-paper headbox stock were applied after chemical addition, but before constant-rate dewatering. Dewatering conditions included simple filtration, flow pulsations of known amplitudes and frequencies of normal to the forming screen, and continuous stirring during dewatering either with an impeller or at a uniform time-averaged shear rate. Under all conditions of flow the retention aid reduced the turbidity of the filtrate, consistent with improved retention of fine materials. However, the effectiveness of the polymer was irreversibly decreased by high shear before dewatering. The irreversible loss was observed even when the slurry subsequently was subjected to vigorous flow pulsations during dewatering. Results were consistent with a polymer-bridging mode of retention aid action.

Keywords
Cationic acrylamide, copolymer, papermaking, forming, hydrodynamic shear, retention, retention aids

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A recent review of chemical usage identified "retention aids" as the most important class of process additive, accounting for about 46% of the total worldwide cost of papermaking chemicals [1]. Factors responsible for the increasing importance of retention aids include increased filler levels, faster paper machines, and lighter basis weights in various paper grade categories.

Though many studies have evaluated the efficiency of different retention aid chemical programs, questions remain concerning the effects of different kinds of flows to which the furnish is exposed. For example, the fibre furnish experiences intense hydrodynamic shear in hydrocyclone cleaner systems and pressure screens [2]. Studies have shown that the intensity of shear is sufficient to dislodge particles of filler from fibre surfaces to which they were attached, though the likelihood of detachment also depends on the type and dosage of retention aid that may be used in a given case [3-4]. Many retention aid systems are at least partly reversible [5-7], so that detached fillers or fibre fines might become reattached to fibres. This possibility that raises doubt as to whether earlier application of hydrodynamic shear plays a significant role. Thus it is important to consider the relative effects of hydrodynamic shear both before and during dewatering.

Some of the most successful approaches used to elucidate the molecular mechanisms of retention aid polymers have relied on bench-scale simulations of the paper machine process. Such tests were the subject of a recent review article [8]. Laboratory tests may be designed to isolate different parameters of interest. For example, the Dynamic Drainage/Retention Jar test of Britt [9] makes it possible to evaluate consequences of so-called "colloidal retention," *i.e.* the degree of attachment of fine particles to fibres too large to pass through a standard screen, in the absence of formation of a fibre mat. The same apparatus was used to demonstrate the reversibility of various retention chemical treatments [6]. In other words, although strong agitation of a fibre suspension almost always lowers the efficiency with which fine particles adhere to those fibres, certain chemical treatments favour reestablishment of some or all of the lost fibre-to-fine-particle contacts [5-7, 10, 11].

Acrylamide copolymers, especially those having molecular masses in the range of 4 to 20 million Daltons, are among the most widely used chemicals to promote retention of fibre fines, fillers, and other critical ingredients of different paper grades, such as hydrophobic sizing agents [12-15]. Recent work by Nanko and Pan [16] showed that at least some of these very large polymers, when fully extended, can be almost 2 μm in length, which is about 1000 times longer than typical monomeric molecules and ions. It has been commonly accepted that the very large size of retention aid molecules, even if they are in a coiled conformation due to the presence of salt ions [17,18], makes possible a process that has been called "bridging" [19]. The word implies that a single molecule first adsorbs onto one solid surface, and then, instants later, another part of the long-chain molecule adsorbs onto a second surface, resulting in a somewhat shear-resistant molecular bridge. Since these retention aid polymers have dimensions much larger than the range of electrical double-layer repulsion between like-charged surfaces [19,20], it makes sense that they are able to flocculate colloidal suspensions even under conditions where the surfaces remain electrically charged, usually with an excess of negatively charged ionic groups [15, 21, 22].

Another part of the definition of bridging flocculation is that breakage of contacts ought to be at least partly irreversible. Certain systems flocculated by very-high-mass linear cationic polymers, and then redispersed by intense hydrodynamic shear, cannot reflocculate to the same extent when low-shear conditions are re-established [5-7, 11, 15]. In a few cases such redispersal of flocculated suspensions has been found to result in substantial reduction in average molecular mass of the flocculant, consistent with a tearing action that leaves fragments of polyelectrolyte on each of the separated surfaces [23-25].

Not all studies dealing with flocculation by high-mass cationic acrylamide copolymers are in agreement with the bridging mechanism. For example, a high degree of reversibility was observed in a study of latex flocculation [26]. In such cases it might be more appropriate to use the term “charged patch.” The latter term makes sense when describing effects of moderately high-mass polyelectrolytes, especially those that are somewhat branched in structure or, if substantially linear, having molecular mass no larger than about 2 million Daltons [15, 19]. In such cases it is reasonable to expect the flocculant to adsorb quickly and tightly to the first surface that it encounters, reversing the local sign of charge. The charged patch, formed in such a manner, would attract uncovered surfaces of adjacent solids in the suspension [15, 19].

Mechanistic questions arise due to the fact that most popular cationic retention aid products have relatively low charge densities, usually in the range of 1 to 10% based on monomeric groups [27]. By contrast, the early work of Gregory [19], which helped to define the term "polymer bridging" involved a cationic polyelectrolyte in which essentially every monomeric group bore a cationic charge, and the molecular masses were lower, compared to most modern retention aid polymers used in paper manufacture. The rate of flocculation was maximized at approximately 50% coverage of the surfaces by polyelectrolyte [19], an observation that suggests a patch model. Lower charge density is believed to favour a more extended adsorbed conformation of polyelectrolytes onto surfaces of opposite charge [28], which is a reason to think that the bridging model may be more appropriate in the case of the treatment conditions considered in the present study.

Though the cited Britt Jar test [9] has been effective for isolating effects attributable to fibre-to-fine-particle contacts, it has long been recognized that other experimental methods are needed to study effects related to entrapment of fine particles in the fibre mat during the formation of paper [8, 29]. Substantial work has been carried out to help understand the effects of pulsations of pressure or flow acting normal to the plane of the forming fabric [30-36]. Such work has aided in an understanding of the effects of hydrofoils [37], dewatering blades [38, 39], and vacuum boxes [40] that aid the process of dewatering on a paper machine. Recently there has been important work carried out concerning the effects of hydrodynamic shear parallel to the plane of the forming fabric [41, 42]; such studies are important for trying to characterize effects associated with jet impingement on the forming fabric, including jet-to-wire speed differences [43, 44].

Although the cited bench-scale studies have clarified many aspects of retention aid function, there still has been a need for a more quantitative approach to studying different hydrodynamic effects, such as those associated with the approach flow (including pressure screens and hydraulic headboxes), jet-to-wire speed differences, and pulsations normal to the plane of the wet web of paper. A new apparatus has been designed to address such concerns. Briefly stated, the "Positive Pulse Jar" (PPJ) is based on a concept pioneered many years ago by Persson and Osterberg [31]. As in the cited study, average flows normal to the plane of the forming screen are controlled by positive displacement of an incompressible aqueous solution. The solution occupies all of the volume below the screen. Unlike the earlier study, pulsations of controllable amplitude and frequency are created by use of a bellows pump with a variable stroke length. Simultaneously, a gear pump withdraws a constant volumetric flow of filtrate, ensuring that a "dry line" condition is reached approximately 20 seconds after the start of the dewatering process. Another innovative feature of the PPJ design is the optional use of a special rotor to apply a uniform time-averaged hydrodynamic shear stress to the fibre slurry either before or during the dewatering process. The design of the PPJ rotor draws upon the principles of a cone-and-plate viscometer, as in the work of by Arslan *et al.* [41]

and Paradis *et al.* [42], and also on the principles of transitional couette flow, as used in earlier mechanistic studies by Visser [45-47] and Hubbe [3, 48].

EXPERIMENTAL SYSTEM

Materials

The fibrous suspension used in the experiments to be described was comprised of approximately 45% southern U.S. bleached hardwood kraft fibres, 25% fibre fines from the same source, and 30% scalenohedral precipitated calcium carbonate filler (Albacar® 5970 from Specialty Minerals, Inc.) by mass. The fibres and fines were obtained by first refining dry-lap market pulp to 400 ml Canadian Standard Freeness (TAPPI Method T227) with a laboratory Hollander beater (Valley Iron Works, Appleton, WI). Fibres and fines were separated with a Bauer-McNett fractionating device, as described in TAPPI Method T233, using only the final stage, which was fitted with a 200-mesh screen. At the end of the fractionation procedure the number average of fines in the fibre fraction had decreased from an initial 57% to 25%, based on tests with a Fiber Quality Analyser (Model LDA96 from Optest Equipment). The equipment was set up to recognize fines as any particles appearing to be smaller than 0.2 mm. As shown in Figure 1, the initial refining reduced the freeness of the pulp as expected [49], but essentially all of the freeness was recovered in the long fibres after three stages of fractionation. Two stages were used in the present work.

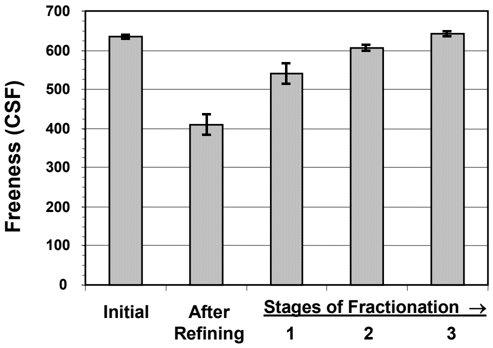

Fig. 1. Effects of sequential refining and three stages of fractionation (to remove fines) on the Canadian Standard Freeness of bleached hardwood kraft pulp

Fines that passed through the screen were collected in large drums, where they were concentrated by overnight settling and removal of the supernatent water. To represent a typical enrichment of fine materials in a paper machine thin-stock cycle [50], the ratio between fines and fibres in the final mixture was adjusted to be approximately three times larger than in the refined hardwood pulp. The final consistency of the stock, consisting of fibres, fines, and filler, was adjusted to 0.5%. The electrical conductivity of the furnish was adjusted to 1000 µS/cm, using sodium sulfate. The pH was approximately 9.3.

The cationic acrylamide copolymer used in the experiments was Percol® 455 from Ciba Specialty Chemicals. This product has a very high molecular mass (in the range of 4-10 million Daltons) and a charge density of 3% based on monomer units. When this polymer was used, the addition level was 0.1%, dry-mass basis.

Apparatus and Procedures

Figure 2 shows a schematic diagram of the apparatus. The upper part of the apparatus is based on components of the Mark IV Dynamic Paper Chemistry Jar from Paper Technology Laboratory, Inc., in Larchmont, NY. The jar itself has an inner diameter of 10.1 cm (nominally four inches), a screen base with rigid support, and three baffles along the side walls, each extending approximately one-quarter inch into the centre. The jar is supplied with an adjustable speed-controlled drive and impeller stirrer (three-blade, maximum radius 1.9 cm), which was positioned 1 cm away from the screen when used.

The gear pump shown in the lower right of the figure was used to create a steady flow of filtrate, causing 500 ml of dilute fibre slurry in the jar to be completely drained in 18 to 23 seconds, at which point air was drawn through the damp pad of fibres. This point was called “the dry line,” using a term borrowed from Fourdrinier papermaking practices. During a typical experiment the vacuum reading of the gauge shown in Figure 2 rose gradually from the beginning of the dewatering process, up to the dry line, and then dropped abruptly to a relatively constant final value. The gear pump was continued ten seconds after the appearance of the dry line in each case before measuring the final vacuum reading, a measure of the air-permeability of the damp paper.

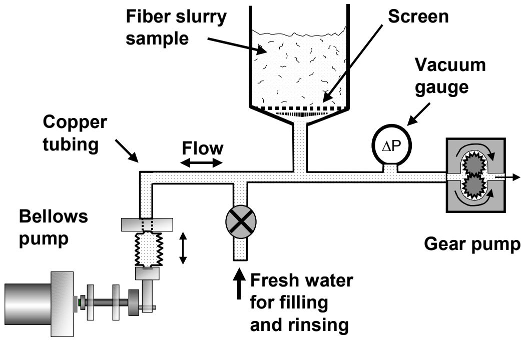

Fig. 2. Positive Pulse Jar (PPJ) apparatus for evaluation of fine-particle retention effects under different flow conditions during dewatering

The bellows pump depicted in Figure 2 was used to create a sinusoidal fluctuating component of flow velocity, which was optionally used together with the gear pump during many experiments. The pump hardware was adapted from an Iwaki-Walchem Model SP80-30, using the middle-sized (size No. 2, nominally 1.5 inch) bellows supplied with the device. To achieve the desired range of frequencies, and also to deal with the flow resistance caused by pads of fibres, the original small motor was replaced with a variable speed drive, Model 850, from Arrow Engineering Co., Hillside, NJ. The stroke length was adjusted to various fractions of its maximum value, including 1, 0.5, 0.25, and 0.125. At full stroke the maximum displaced volume resulted in 0.9 mm of liquid movement normal to the plane of the forming screen. The pumping action was always started simultaneously with the gear pump and stopped at the appearance of the dry line.

To represent hydrodynamic effects occurring above the plane of the forming fabric during dewatering, two kinds of stirring conditions were considered. Motivations for studying effects of flow velocity relative to the forming fabric include reported effects of jet-to-wire speed differences at the moment of jet impingement [43, 44]. Flow components parallel to the forming fabric also arise due to vortices emerging from the slice [51], activity generated by hydrofoils [37], and by application of a shake during operation of slow-moving Fourdrinier paper machines [37, 52]. Figure 3 shows the devices used in the present study to study the effects of such flow components. One of them was a three-bladed impeller. Though an impeller does not impart uniform hydrodynamic shear to the fluid sample at any one moment [53, 54], such devices clearly are very efficient mixers, ensuring that most of the sample volume will pass close to the points of maximum shear within a reasonable period of agitation [55].

Figure 3 shows the so-called PPJ rotor, which is shaped in such a way as to provide approximately uniform time-averaged shear stress throughout the sample of fibre suspension. The average shear stress can be estimated based on considerations of cone-and-plate viscosity testing [41], and partially developed turbulent flow between axial cylinders, the inner of which is rotating [45-48]. In the experiments to be described the PPJ rotor was used as one option for agitating the suspension during the process of dewatering. At the 500 r/min stirring speed used in the present work, the average shear stress was at least 5 Pa throughout 96% of the sample volume, based on the equation of Van Lookeren Campagne, as reported by Visser [56]. The actual shear stress is expected to differ from this estimate due to the reported effects of suspended fibres on the rheological characteristics of fluids [57, 58].

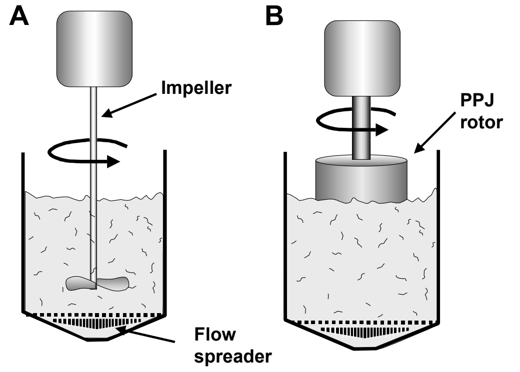

Fig. 3. Two options for applying shear to a fibrous suspension before or during dewatering, A: Conventional impeller stirrer, B: PPJ rotor for uniform average shear

In addition to the flow conditions described above, furnish samples also were exposed for 30 seconds to any one of three pre-shearing conditions before the start of each dewatering experiment. A "low" condition of shear was provided by 30 seconds of agitation of 500 ml of 0.5% consistency stock with a 38mm-radius impeller running at 500 r/min. A "medium" condition was similar, but with a rotational speed of 1000 r/min. "High" pre-shearing involved the lowest setting of blender model 1154 from Dynamics Corporation of America.

Turbidity measurements were obtained with a DRT-15CD instrument from HF Scientific, Inc.

Fines determinations, using the Fiber Quality Analyser mentioned earlier, were carried out by resuspending some of the mat material, optionally including parts of the mat that were split in the plane of the sheet.

The filler content was determined by ashing samples of oven-dried fibre mats. The procedure of TAPPI Method 211 om-93 was modified by extending the time of 525 ^{o}C heating over night. The longer heating time was justified by the need to ensure full ashing, and the absence of black specks, in the relatively thick samples, compared to typical paper sheets. It is worth noting that the ash numbers, obtained in this way, are expected to be lower than in the procedure recommended by Kocman and Bruno, due to partial calcination of the calcium carbonate to calcium oxide [59]. Calibration tests indicated a 4% loss in mass of calcium carbonate subjected to the conditions of the present study.

RESULTS AND DISCUSSION

Baseline tests in the absence of retention aid

Figure 4 shows results of tests in which the default fibre furnish (see Experimental) was subjected to different hydrodynamic shear conditions during dewatering. The histogram bars represent the average values obtained from sets of experiments with three different conditions of pre-agitation of the furnish, giving a total of 9 replications of each condition. “Simple filtration” means that the furnish was unstirred during the dewatering cycle and only the gear pump was used to drain the filtrate at a steady rate. The next three histogram bars correspond to similar experiments in which the bellows pump was run to provide flow pulsations normal to the plane of the sheet. In each of the three cases represented in Figure 4 the maximum upwards velocity was 0.22 cm/s and the maximum downwards velocity was 0.88 cm/s due to the combined actions of the gear pump and the bellows pump. The bar labelled “PPJ rotor” represents a rotational speed of 500 r/min, using the PPJ rotor. The final histogram bar corresponds to 500 r/min rotation of the impeller stirrer during dewatering. The bellows pump was not used during experiments involving either the PPJ rotor or the impeller.

As can be seen by comparing the first four histogram bars in Figure 4, flow pulsations during dewatering increased the turbidity of the filtrate. Turbidity provides an approximate measure of the quantity of fine suspended matter in the filtrate. The observed effect in the case of pulsating flow is consistent with an expected “washing” action of such flows, causing fibre fines to be dislodged from the places in which they were caught in the fibre mat [35, 36, 60]. Previous studies have shown a complex relationship between such washing action and the frequency, amplitude, and basis weight [36]. Here, turbidity increased with bellows stoke amplitude, indicating that the magnitude of the displaced pulsed volume and not the frequency of pulses dominated the effect of pulsations on retention.

The highest turbidity values, as shown in Figure 4, were obtained when using the PPJ rotor under the conditions specified earlier. This effect is consistent with interference with fibre mat formation during the dewatering cycle. In this way the present results for the PPJ rotor are somewhat analogous to those obtained in the procedure developed by Britt [9] in which a fibre mat is essentially prevented during the part of the experiment when filtrate is being collected. The fact that the turbidity was much higher, compared to the previously described cases of pulsating flow, implies that the pulsations detached only a fraction of the total fine materials that were retained in the simple filtration procedure. Results corresponding to impeller stirring were very similar to the case of simple filtration, despite the fact that the rate of rotation was the same as for the PPJ rotor. Previously it was found that it was necessary to increase the speed of impeller stirring to 1500 r/min to achieve the same filtrate turbidity results as the PPJ rotor at 500 r/min [61].

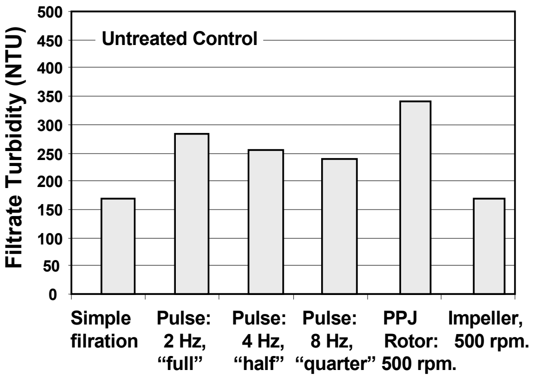

Fig. 4. Turbidity of filtrate resulting from dewatering of untreated suspensions (see experimental) in the presence of different flow conditions. The results shown are averages of three pre-shearing conditions.

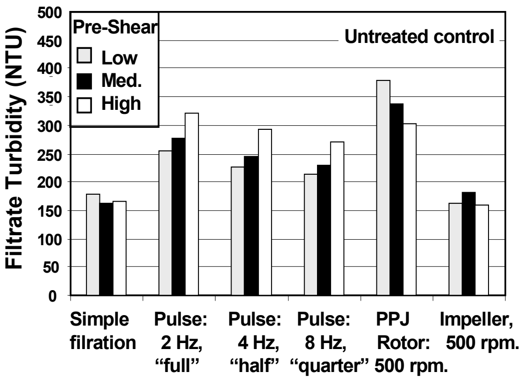

Fig. 5. Effects of different intensities of hydrodynamic shear *before* dewatering on the turbidity of filtrate resulting from dewatering

Effects of pre-shearing intensity are shown in Figure 5. It is notable that filtrate turbidity increased with increasing pre-shearing only in cases involving the bellows pump. Though the cause of this phenomenon has not been evaluated in detail, many of the fibre fines that are dislodged by intense pre-shearing are likely to be caught again by filtration in a fibre mat during simple filtration. By contrast, such unattached fines would be expected to be vulnerable to being washed from a fibre mat, or from a wet web of paper, due to the action of pulsating flows during sheet formation.

Effects of retention aid treatment

Figure 6 compares filtrate turbidity values obtained under different flow conditions with and without treatment of the furnish with the cationic acrylamide copolymer. The data corresponding to the untreated fibre slurry samples are the same as those shown in Figure 4. Data corresponding to cationic acrylamide copolymer were taken from experiments in which a “low” level of hydrodynamic shear was applied after the chemical addition. As shown, retention aid markedly decreased filtrate turbidity in each case. The strong effect of the acrylamide copolymer on fine-particle retention is consistent with the results of previous studies [9, 15].

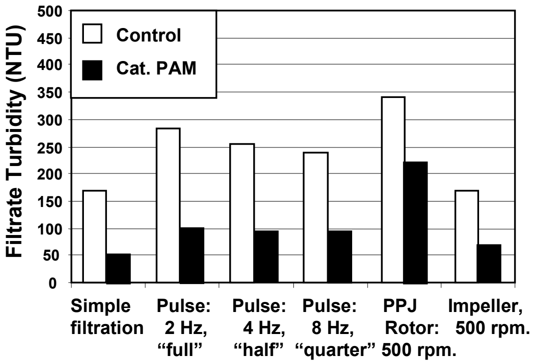

Fig. 6. Effect of cationic acrylamide copolymer on turbidity of filtrate after dewatering in the presence of different flow conditions

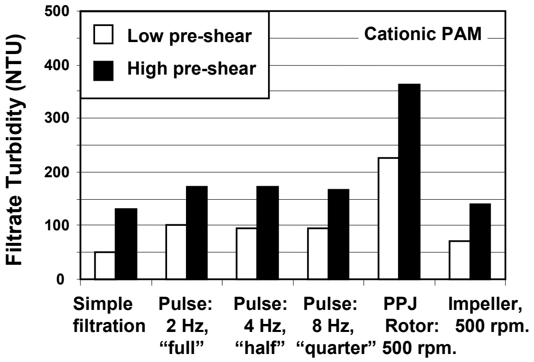

Fig. 7. Effect of hydrodynamic shear, after treatment of the furnish with cationic acrylamide copolymer, but before dewatering under different flow conditions

Figure 7 shows data from the same experiments as in Figure 6, except that the “high” and “low” conditions of pre-shearing are compared. Application of high shear resulted in higher filtrate turbidity in every case, despite large differences in subsequent conditions of forming the fibre mat. The fact that these later conditions of flow did not completely obscure the effects of pre-shearing can be taken as evidence of an irreversible nature of the molecular mechanism [6, 7, 23-25]. In other words, the results are consistent with a mechanism in which polymer bridges, once broken by intense stirring, are not capable of re-forming to establish fines-to-fibre attachments having as high strength as the original attachments. This is the first time that such a phenomenon has been shown to remain significant after application of highly contrasting conditions of sheet formation.

Further results corresponding to the same chemical treatments are shown in Figure 8, comparing the effects of different flow conditions on the level of fibre fines retained. Total retention here means the fraction of solid materials, including fibres, fines, and filler, that was retained on the forming screen, based on gravimetric analysis. The retention aid consistently increased retention efficiency, compared to the untreated controls.

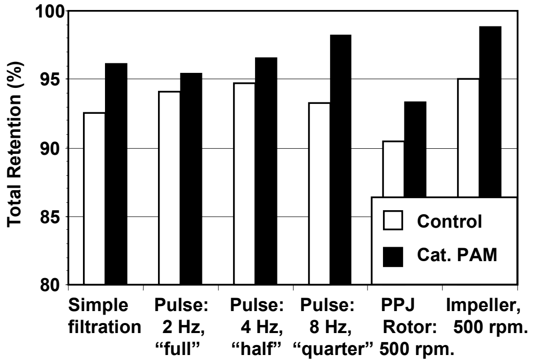

Fig. 8. Effect of cationic acrylamide copolymer on retention of solids in the fibre mat during dewatering in the presence of different flow regimes

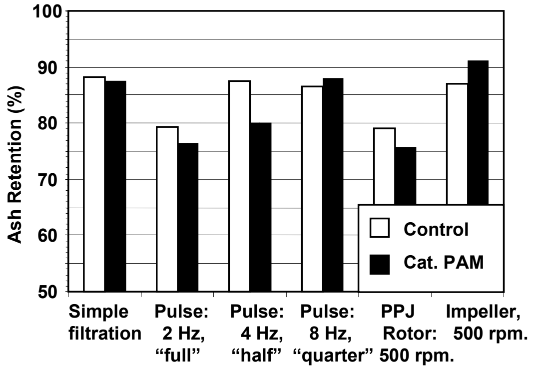

Fig. 9. Effect of cationic acrylamide copolymer on filler retention (by ash analysis) during dewatering in the presence of different flow regimes

Figure 9 shows little apparent effect of the retention aid on the ash content of fibre pads formed during the same set of experiments with different flow regimes. The fact that these results do not show the same retention increases as were apparent from turbidity measurements (Figure 6) suggests that further work needs to be done related to separate quantification of fibre fines retention and filler retention under the influence of different conditions of forming and retention aid treatment. Results of such experiments will be reported later.

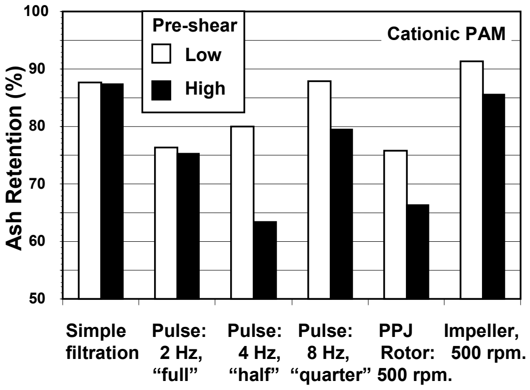

Fig. 10. Effects of different intensities of hydrodynamic shear *before* dewatering on the ash retention during dewatering in the presence of different flow regimes

Figure 10 shows effects of pre-shearing of the polymer-treated furnish on ash contents of the resulting fibre mats. It is notable that more intense shearing appeared to decrease the amount of retained filler in at least four of the cases considered. In general, the ash retention either decreased or was unchanged. These trends, if confirmed by further work, tend to support for the finding that pre-shearing caused some irreversible detachment of fine particles from fibres treated with cationic acrylamide copolymer, and such particles did not later become reattached as strongly as after first addition of the retention aid. A mechanism that could account for this is irreversible breakdown of polymer bridges, caused by the intense shear.

It is worth stressing, based on the results shown in Figure 7, that even the “high” level of hydrodynamic shear treatment, after addition of the cationic acrylamide copolymer, but before dewatering, did not fully reverse the effects of the retention aid. A possible explanation is that polymer-induced attachments between filler particles and cellulosic surfaces are very difficult to break, due to the small size of the filler particles [62-64]. Nevertheless, in the present experiments it is to be expected that a high proportion of the filler particles will be associated with the fibre fines, and that retention of such fines will be lowered by either agitation of the furnish (by impeller or PPJ rotor) of by pulsating flows during dewatering. Such issues are being addressed by further studies involving separate analysis of fibre-fines and filler retention.

CONCLUSIONS

1. Fine-particle retention was affected by flow conditions before and during formation of fibre mats.
2. Treatment of the furnish with cationic acrylamide copolymer retention aid (cPAM) increased retention efficiency under all of the forming conditions considered. However, the rank order of fine particle retention for the different forming conditions remained the same as in the absence of chemical treatment. This result underscores the importance of both chemical and mechanical factors in fine-particle retention.
3. Increased intensity of shearing of furnish samples after treatment with cPAM decreased retention efficiency in all cases, regardless of the subsequent conditions of forming the fibre mat. These results are consistent with an at least partly irreversible breakdown of polymeric bridges by the applied hydrodynamic shear. Since some of

the detached particles are expected to be filler particles, and these are too small to be filtered out efficiently by the fibre mat, it is reasonable to expect more of these particles eventually to pass into the filtrate.

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