Mechanistic aspects of nanocellulose–cationic starch–colloidal silica systems for papermaking

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ABSTRACT: Optimization of a chemical additive program for a paper machine can require attention to both colloidal charges and kinetic effects. This work considered an additive program with two negatively charged substances (nanofibrillated cellulose [NFC] and colloidal silica) and two positively charged items (cationic starch and cationic acrylamide copolymer retention aid). Results were shown to depend on charge interactions; however, that clearly was not the whole story. Some findings related to cationic demand, dewatering, fine-particle retention, and flocculation among fibers were best explained in terms of at least partly irreversible complexation interactions between the charged entities. Adjustments in ratios between oppositely charged additives, their sequences of addition, and effects of hydrodynamic shear levels all affected the results. In general, the most promising results were obtained at a cationic starch level of 0.25% to 0.5% based on sheet solids in systems where the cationic starch was used as a pretreatment for NFC.

Application: Process optimization of chemical additives systems in paper mills are often evolutionary in nature, based on observations during papermaking. This article highlights aspects that merit inclusion in laboratory tests and commercial paper machine trials when the goal is to achieve strength benefits by the addition of NFC at the wet end.

Results recently reported by Garland et al. and Leib et al. showed significant promising improvements in paper strength, while at the same time maintaining dewatering rates, when treating papermaking furnish with combinations of nanofibrillated cellulose (NFC), cationic starch, colloidal silica, and a cationic retention aid (cPAM) [1,2]. Notably, the results showed strong dependencies on the amounts added, as well as their order of addition. The present article will attempt to interpret such effects in the light of further experimental findings, with a focus on likely mechanisms.

The present work fits within a broader context of efforts to increase the bonding strength within paper products. Papermakers are able to achieve a wide range of strength properties by selecting high-quality wood material, carrying out appropriate pulping operations, optimizing conditions of mechanical refining, and using conventional dry-strength additives [3]. The NFC and related highly-fibrillated cellulose products offer a potential way to go beyond what can be achieved by such means [4,5,6]. Such options might be considered, for instance, when a papermaking operation utilizes recovered fibers that already may have been subjected to heavy refining and still are deficient with respect to interfiber bonding ability.

Though there have been reports pertaining to the potential benefits of adding NFC to paper furnish as a means of achieving higher strength, there has been a need for more research considering the interactive effects of other papermaking process additives relative to the performance of the NFC. For example, NFC particles are very small, and without the use of some kind of retention aid system, the NFC may tend to accumulate in the white water rather than being efficiently retained in the paper sheet [7]. Fine material within papermaking furnish that is unattached to fibers can be expected to plug up drainage channels within the wet web of paper, thereby negatively affecting the dewatering process [8]. In addition, there was a need to follow up on some previously reported findings showing a highly synergistic relationship between cationic starch and NFC in increasing strength properties of the resulting paper [9].

As background, it is known that the retention of fine particles during papermaking can be achieved with addition of different chemical additives [7,10,11]. For example, one option is to treat the furnish solids by adsorption of a highly cationic polymer and then following up with an anionic flocculant, i.e., a very high mass copolymer of acrylamide and acrylic acid [12,13]. In such cases, the high-charge cationic additive creates anchoring sites that can be used by the anionic additive. Another kind of dual system was employed in the present work, involving combinations of a cationic copolymer of acrylamide (cPAM) and very small negatively charged particles, colloidal silica. Studies involving such additive systems, when suitably optimized, can strongly accelerate the release of water during paper

formation [14]. Such additives programs were selected for the present work because NFC often slows the dewatering of papermaking furnish [6].

As a starting point for understanding the various dosage dependencies and apparent optimal treatment combinations reported in the previous articles in this series [1,2], it is reasonable to assume that the interactions among NFC, cationic starch, colloidal silica, cPAM, and fiber surfaces may be dominated by ionic charges. In other words, the effects on fine-particle retention, dewatering, and even the development of increased paper strength can depend on charge-induced adsorption of polyelectrolytes [15], as well as the formation of polyelectrolyte complexes [16,17]. It will be further assumed that the measured zeta potential of the system can be used to predict the degree to which charged substances adsorb onto fiber surfaces [18].

The fact that both fine-particle retention and dewatering rates can depend on a balancing of ionic charges has been shown in earlier studies. For example, Strazdins found that the efficiency of fine-particle retention was highest when the zeta potential of the system was near zero [19]. Studies have shown that the fastest rates of water release from papermaking fibers suspensions are when the amounts of different chemical additives had been adjusted to achieve a zeta potential near to zero [20,21]. Of particular relevance here, studies involving the use of colloidal silica in combination with cationic particles in papermaking systems have also found that near-neutral zeta potential corresponded to the highest dewatering rates [22].

Not all evidence, however, supports the expectations previously outlined here. In particular, it has been reported that the bridging mechanism of fine-particle retention, brought about by the action of a cationic retention aid (e.g., cPAM), can show maximum effects when zeta potential is not near zero [23]. The likely explanation for some such results is that retention aid polymers are so large (e.g., 5 to 20 million g/mol) that their effects can be dominated by hydrodynamic and physical aspects rather than charge. Various mechanistic questions, as outlined here, were considered in the present work.

EXPERIMENTAL
Chemicals and materials

The chemicals and materials employed in this work were all the same as those specified in a previous article [1]. Briefly stated, the main fiber furnish was prepared by repulping of a 100% recycled copy paper product, trademarked Boise ASPEN 100 Multi-use Recycled Copy Paper from Packaging Corporation of America, Boise Paper Division. The NFC consisted of the spray-dried, freeze-dried, and TEMPO-oxidized products supplied by the University of Maine (Orono, ME, USA). In addition, a less highly refined product, microfibrillated cellulose (MFC), was included in some of the work. This was obtained from Stora Enso Oyj (Helsinki). The cationic starch was Chargemaster L340

from Grain Processing Corp. (GPC; Muscatine, IA, USA). The colloidal silica type used in most of the work was Fennosil 2180, a product of Kemira Oyj (Helsinki). The cationic retention aid was Accurac® 90, a very-high-mass cationic copolymer of acrylamide (American Cyanamid). Dilution and other preparation steps were the same as reported earlier [1].

Procedures

The basic procedures used for the reported work were the same as reported earlier [1]. As in the cited work, reported results were selected from a larger set of completed tests. Criteria for selection included the following: a) the quality of the work, as indicated by the statistical agreement of replicate runs; (b) showing effects that would be interesting to readers of the journal; and (c) showing results that were generally representative of the findings as a whole.

Tests involving NFC were carried out at a 5% level, based on furnish solids. Due to the high amount of refining energy required to produce NFC, papermakers may be motivated to minimize the amount of NFC, perhaps opting for relatively low addition levels such as 1% or 2%. The relatively high level of 5% was selected for the current series of work with the goal of achieving statistically significant effects.

RESULTS
Fiber suspension characteristics

Table I presents cationic demand results for two types of experiments. The term "direct titration" means that the listed substance was added to deionized water, followed by a titration with the standard cationic polymer, poly(diallyldimethylammonium chloride) or the standard anionic polymer, the potassium salt of poly(vinyl chloride). The term "titration of filtrate" means that the substance being evaluated was added to the default papermaking furnish, then filtered through a 200-mesh screen, and the filtrate was titrated. In each case, there were four replicate tests.

Results of the direct titrations showed some distinct differences within each class of additive. For example, the TEMPO-oxidized nanofibrillated cellulose (TONFC) had a cationic charge demand that was almost 100-fold greater than that of the freeze-dried version (FDNFC). This is consistent with the relatively low content of carboxyl groups that would be present on ordinary bleached softwood kraft pulp of the type used to prepare FDNFC [24,25]. By contrast, TEMPO-oxidation, depending on the details of treatment, can provide as much as one negatively charged carboxylate group per exposed anhydroglucose unit of the cellulose [26]. The highest charge density colloidal silica happened to be the high-structure type. The term "structure" is used here in a qualitative sense, indicating the degree of gel structure, in which primary particles of colloidal silica are joined together as chains [22].

Additive	Direct Titration, µeq/L		Titration of Filtrate, µeq/L	
	Mean	95% C.I.	Mean	95% C.I.
Default furnish	-	-	54.6	29.1
FDNFC	9.8	7.6	18.8	6.5
TONFC	828	83.7	524	114
MFC	6.0	4.7	18.5	5.6
SiO$_2$ low structure	608	23.5	353	27.5
SiO$_2$ medium structure	717	12.4	396	35.1
SiO$_2$ high structure	1238	8.5	553	65.6

C.I. = confidence interval; FDNFC = freeze-dried nanofibrillated cellulose; TONFC = TEMPO-oxidized nanofibrillated cellulose; MFC = microfibrillated cellulose; SiO$_2$ = silicon dioxide.

I. Comparing results of direct cationic demand titrations (in deionized water) with titrations of filtrate when the same amount of each substance was added to the default furnish.

Two notable observations were made when comparing the results for filtrate titrations with the direct titrations. First, there was a relatively small but significant contribution to cationic demand coming from the default furnish. This is especially evident when comparing the results for FDNFC and MFC in the two titration modes. In both of these cases, the filtrate had a higher cationic demand compared to the highly fibrillated cellulose by itself in deionized water. The negative charge of typical papermaking furnish can be attributed to such components as hemicellulose present in the fibers. In addition, anionic polyacrylates are widely used as dispersants for mineral additives [27,28]. Because the fibers employed in this study were from 100% recycled copy paper, such anionic substances may have come from a variety of paper grades. By contrast, when the substance being added had a relatively high cationic demand by itself (direct titration), then the corresponding cationic demand for the filtrate was much lower. Such results suggest that some of the TONFC or colloidal silica was being retained on the fibers. Thus, less of it was present in the filtrate that was titrated.

Figure 1 shows results of follow-up tests in which colloidal silica was added to the default fiber suspension that had been optionally treated with cationic retention aid (cPAM). Each mixture contained 10 mL of default furnish (0.5% consistency), 1 mL of NFC (1% solids), and 1 mL of cationic starch (Chargemaster 340). The colloidal silica was Fennosil 2180, and the addition levels shown are based on the total solids. Charge titrations were carried out with filtrates obtained by passing the furnish through a screen. Though there was some scatter in the data, the addition of silicon dioxide (SiO$_2$; high-structured) to untreated furnish generally resulted in a linear increase in cationic demand. This is consistent with the negative character of colloidal silica, as was shown in Table I. Two effects were evident in

the systems where cPAM had been added to the system before the SiO$_2$. First, consistent with the cationic charge of cPAM, the cationic demand values were generally lower than in the absence of cPAM. In addition, there was a minimum in cationic demand when the SiO$_2$ addition was in the range of 0.1% to 0.3%. These results are tentatively attributed to a maximizing of retention efficiency at a favorable ratio of cationic starch to SiO$_2$ [22]. Retention of colloidal material, including nanocellulose, colloidal silica, or cationic starch, onto fiber surfaces can be expected to decrease the amount remaining in suspension. Such retained material, depending on its net charge, can be expected to affect results of cationic demand titrations of the filtrate. It is not known why, in the absence of colloidal silica, the
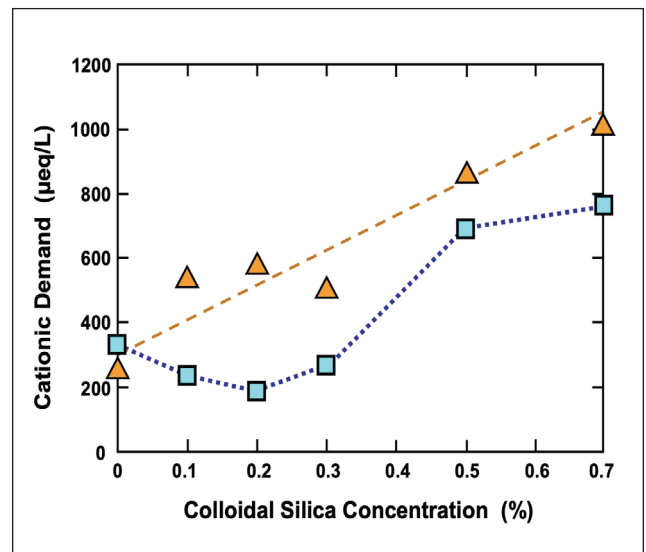
1. Effect of increasing colloidal silica addition on the cationic demand of the default furnish that was either untreated (triangles) or treated with cationic retention aid (squares).
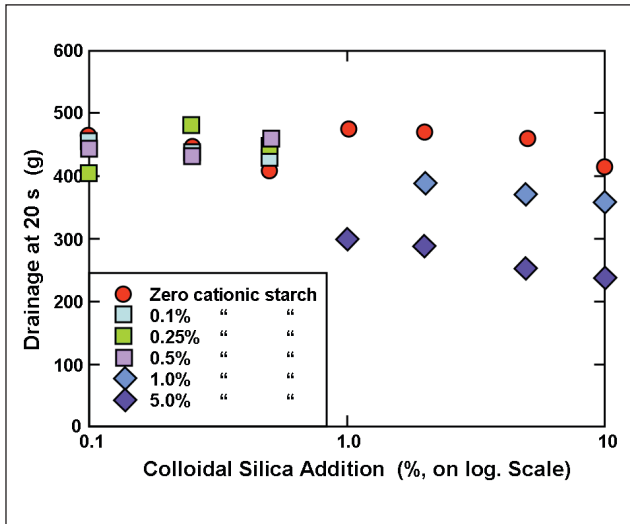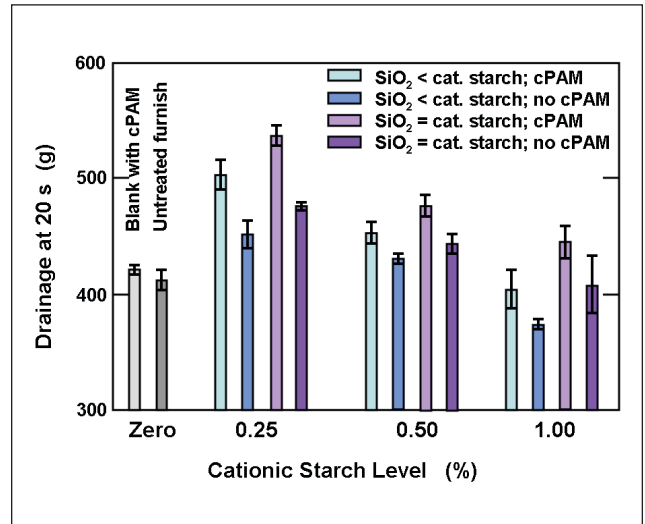
2. Effect of colloidal silica addition level on the drainage amount (evaluated at 20 s) of default furnish pretreated with different levels of cationic starch. Note the logarithmic horizontal axis.

3. Dewatering results obtained for systems in which freeze-dried nanofibrillated cellulose (FDNFC) was pretreated with cationic starch, then colloidal silica (SiO_2) at the indicated levels, and then added to the default furnish, with optional addition of cPAM retention aid, as noted in the legend.

mean value of cationic demand was higher in the case where cPAM had been added, though the apparent difference was not statistically significant.

Dewatering tests

Some uncertainty has remained, following the publication of results by Rice et al., about the most suitable level of cationic starch [9]. In the cited work, high levels of stiffness and tensile strength were achieved at high reported levels of cationic starch. To follow up, **Fig. 2** shows results of modified Schopper-Riegler dewatering tests that were carried out over a very wide range of addition of both cationic starch and colloidal silica. Consistent with common papermaking practices, the most favorable results were achieved with a modest addition level of cationic starch (0.25% on dry fibers) and a modest dosage of colloidal silica (0.2% on dry fibers). By contrast, relatively high levels of the cationic starch (represented by diamond symbols) yielded substantially slower drainage. Notably, even with addition of correspondingly high levels of colloidal silica, the dewatering rate remained well below what had been achieved with lower amounts of cationic starch. This could be related to plugging of drainage channels by agglomerated colloidal materials, which hinders the flow of water though the fiber mat. It can be concluded from this finding that an excess of complexed cationic starch and colloidal silica does not necessarily contribute to faster drainage; rather, it is necessary to employ dosage levels that are optimized for each type of furnish.

Figure 3 considers drainage results for a series of systems in which FDNFC was treated with cationic starch at the levels shown, followed by colloidal silica, mixing with the default furnish, and then optional treatment with cPAM retention aid as the final additive. Drainage was monitored by recording the mass of filtrate collected 20 s after open-

ing the sealing cone of the BTG DFR-05 device (BTG Instruments; Éclépens, Switzerland). When the retention aid (cPAM) was added to the furnish containing NFC that had been pretreated with cationic starch and silica, a significant enhancement in drainage was obtained. As shown in Fig. 3, addition of cPAM into a system containing silica and cationic starch at the same concentration (0.25%) led to a 30% increase in drainage when compared to a control without silica or cationic starch. Significant drainage enhancements were also obtained under conditions where the cPAM was present in combination with cationic starch. A possible hypothesis to explain these results could be due to the different conformations that might be adopted by the retention aid, cPAM, in contact with the fibers. Coiling and entanglement of the cPAM on fiber's surface might tune the interaction of positively charged silica particles with fiber surface, leading to a reduction in pore clogging and therefore enhancing dewatering. However, there is an issue of concern. Sometimes an increased level of flocculation of fibers can be a cause of more rapid initial dewatering [29], as represented by the 20 s filtrate amounts shown in the figure. This issue will be considered later when discussing some results of flocculation tests.

Figure 3 also provides some insight regarding optimization of addition levels. Note that the 0.25% level of cationic starch addition provided the highest drainage mass amounts. In addition, the 1:1 mass ratio of cationic starch and colloidal silica provided significantly higher dewatering than when the colloidal silica was at half of that level for specific cases. These results are consistent with the idea that a system involving colloidal silica that has well-balanced charges is likely to provide higher dewatering rates [22,30]. However, as was noted earlier, decreased opera-
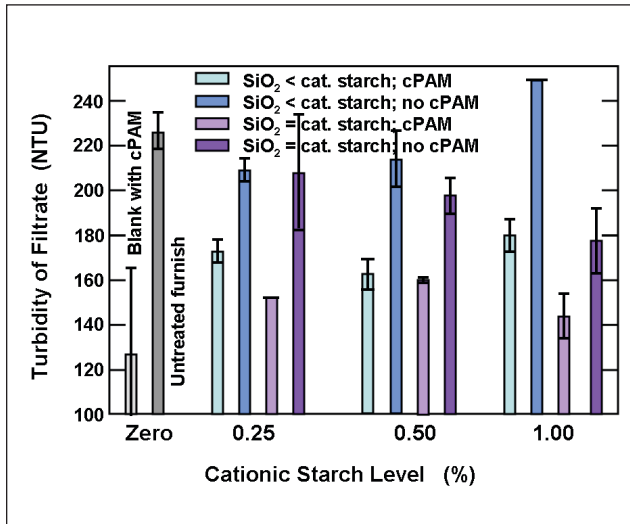
4. Retention test (Britt jar) results obtained for systems in which FDNFC was pretreated with cationic starch, then colloidal silica (SiO₂) at the indicated levels, and then added to the default furnish, with optional addition of cPAM retention aid, as noted in the legend.
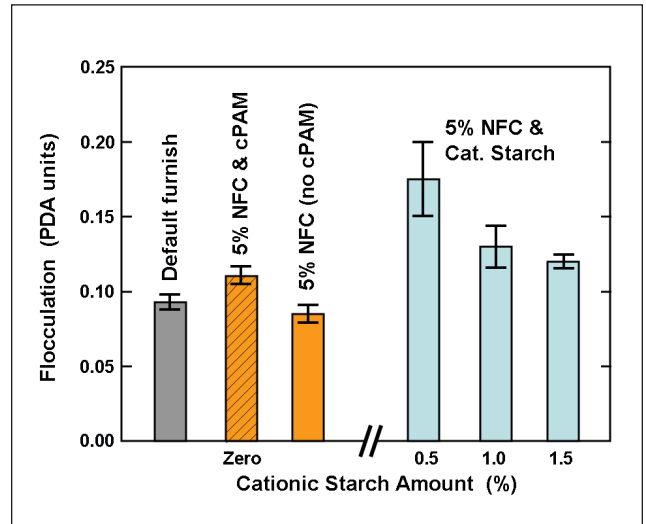

5. Flocculation tests comparing an untreated default furnish with other systems to which 5% FDNFC (either treated or untreated) had been added.

tional performance can be expected when there is an excess of cationic starch or colloidal material beyond what can be well accommodated by the solid surfaces that are present.

Retention tests

The order of preparation and mixing of ingredients shown in **Fig. 4** is essentially the same as that shown in Fig. 3. Treatment of the paper furnish with the retention aid cPAM as the final additive led to a significant reduction in turbidity of the system when compared to the system based on just addition of pretreated NFC to the default furnish. As before, the level of NFC was 5% on furnish solids, and it was treated at the indicated levels of cationic starch and colloidal silica before being added to the default furnish. This highlights the effect of the cPAM on fines retention. The same level of retention obtained with the cPAM alone was not achieved for the systems containing silica and cationic starch. Interestingly, in all cases the retention was enhanced at equal concentrations of cationic starch and silica in the presence of cPAM. Without addition of cPAM, the retention efficiency was poor. These results provide further insights into the mechanism of enhanced drainage generated by the combined action of NFC, cationic starch, colloidal silica, and addition of a retention aids. A substantial enhancement in dewatering is obtained when fine particles are efficiently retained in the paper furnish.

Flocculation tests

In an ideal world, papermakers would prefer to achieve high levels of first-pass retention and rapid dewatering while still enjoying a very high uniformity of the paper. In other words, the presence of fiber flocs is undesirable. As

indicated in **Fig. 5**, addition of NFC to the default furnish in the absence of cationic starch did not by itself lead to any significant change in the level of flocculation. The second histogram bar shows that cationic retention aid addition (shown for the system with 5% NFC) yielded a small increase in flocculation. This is consistent with the expected bridging type of flocculation caused by the cPAM [31,32].

The final set of three histogram bars (light blue color) in Fig. 5 correspond to systems in which the NFC had been pretreated with cationic starch at the indicated levels. No cPAM was used in these specific tests. Thereafter, the mixture was added to the default furnish. It is notable here that the level of flocculation reached a maximum at the 0.5% level of cationic starch in the system. Whether or not such flocculation will be of concern in a papermaking operation depends greatly on the kind of paper forming equipment. Modern, high-speed paper machines typically have such high levels of hydrodynamic shear that typical fiber flocs become well dispersed [33,34]. However, certain cylinder formers can be very sensitive to even moderate levels of chemical-induced flocculation of fibers.

Handsheet properties

An ideal outcome, from a papermaker's perspective, would be to increase paper strength using relatively low amounts of selective additives. Handsheet data for tests involving TONFC showed the most consistent effects, based on statistical significance, so those results are reported here. Similar trends (not shown) were obtained when using FDNFC. As shown in part A of **Fig. 6**, a mean value of about 2.9 kN/m was achieved at a 5% level of TONFC when the cationic starch treatment was at its lowest level, 0.25% on sheet solids. Note that the TONFC has a much higher negative charge in comparison to the FDNFC shown in other tests [1]. The TONFC content was 5% relative to total
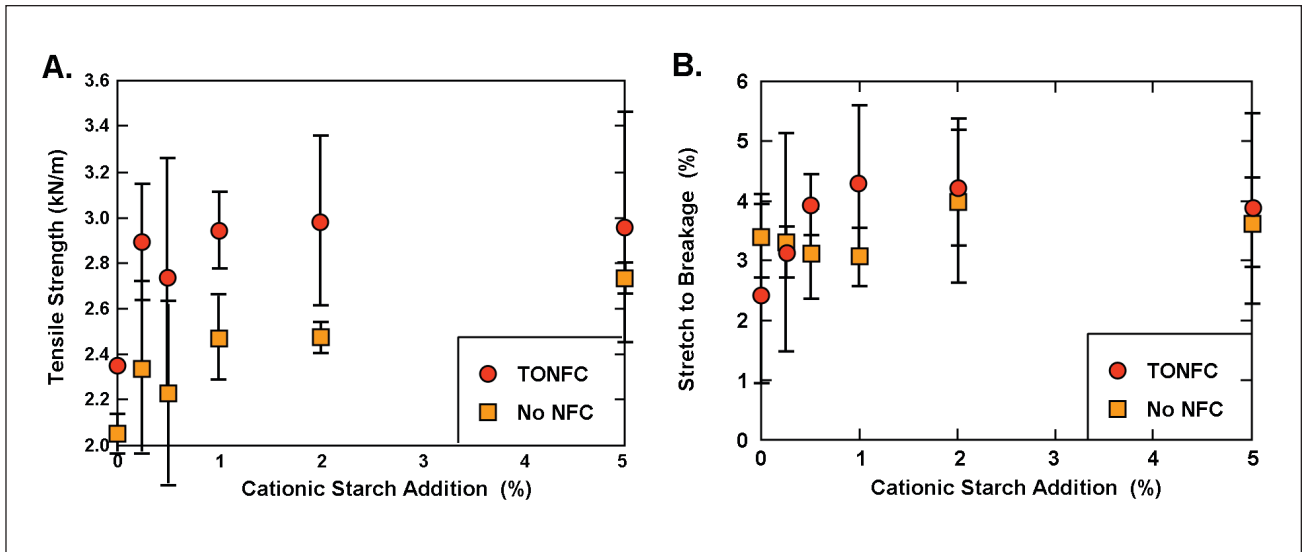
6. Effect of TEMPO-oxidized nanofibrillated cellulose (TONFC) on (A) tensile strength and (B) stretch to breakage of handsheets pretreated with cationic starch at the specified levels.

solids. At higher cationic starch levels, in the presence of TONFC, no further significant gains in strength were realized. One way to interpret these results is to envision the cationic starch acting partly as a retention aid for the TONFC. It is well known that for purposes of first-pass retention, only a small amount of cationic polymer is needed. Interestingly, however, the plotted squares in part A of the figure show a progressive increase in tensile strength with increasing cationic starch. In fact, the tensile strength with only 5% cationic starch addition (no TONFC) showed a significant increase relative to the strength at lower starch levels. These findings highlight the synergistic action between the two kinds of bonding agents.

When materials such as plastics are reinforced by the addition of solid particles, which sometimes include nanocellulose, a common finding is that the plastic materials become more brittle. In other words, the stretch to breakage tends to decrease with increasing addition of the reinforcing particles to a continuous plastic phase [35]. Results in part B of Fig. 6 are related to this issue in the case of TONFC, in combination with starch, being used as a paper strengthening agent. A general trend shown by the mean values is that stretch to breakage, upon addition of TONFC at the 5% level to the paper, gave stretch-to-breakage values that were generally as high or higher than those in the absence of TONFC but at the same levels of cationic starch. However, considering the 95% confidence intervals shown, it is clear that none of the plotted points were statistically different from each other. Thus, it can be concluded that the incorporation of TONFC in the paper did not contribute to any loss of elongation ability.

Figure 7 shows some selected data from tests that were similar to those just discussed, but colloidal silica was the final additive. The colloidal silica was added in two different modes, generally corresponding to the two options described by Leib et al. [2]. A stem-and-whisker plot was used in this case to highlight the fact that the median values did not necessarily correspond to the mid-point of the range of data. The default furnish (with no NFC or other additives) achieved an average tensile index of about 445 kN/m. Addition of 5% FDNFC that had been pretreated with cationic starch (at the 0.5% level, based on final sheet solids), increased the mean value to almost 500 kN/m. Interestingly, however, further addition of colloidal silica (at the 0.25% level) after the cationic starch, but before addition of the FDNFC to the default furnish, caused a significant decrease in tensile index. An even larger decrease in tensile index was observed when the colloidal silica was added to the system after the treated FDNFC had
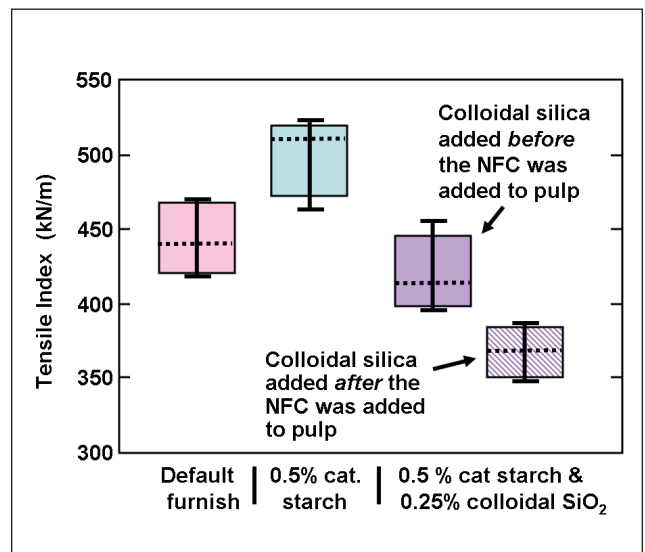
7. Effect of FDNFC, cationic starch, colloidal silica, and order of addition on the tensile strength of handsheets.

been added to the default furnish. These results are consistent with the flocculation test results shown in Fig. 5. It is well known that laboratory tests are prone to overflocculation of fibers, leading to poor paper uniformity in some cases [29,36]. Though such issues are often overcome by the higher hydrodynamic shear levels often present during full-scale papermaking, it is ultimately necessary to carry out on-machine trials of additive systems that show promise during laboratory work.

DISCUSSION

The research examples described in this paper highlight two critical issues. As emphasized in the research by Garland et al. [1], the first area of concern is the balancing of ionic charges. The nanocellulose materials, as well as the fiber furnish employed in this work, clearly had net-negative surface charges in aqueous suspension. The cationic starch and retention aid (cPAM) had positive ionic charge. Accordingly, the addition of colloidal silica, which has a strong negative charge, can be envisioned as a way to balance the charges. One might envision the negatively charged colloidal silica particles diffusing to within the loops of charged cationic starch molecules. Such a neutralization interaction would be expected to cause a crimping of the polymer chains, resulting in a dewatering action. One can think of a papermaking system as being like an immense titration experiment involving the formation of polyelectrolyte complexes [37]. The titration analogy is consistent with various studies that have shown the most favorable results, in terms of such issues as retention, drainage, and paper strength, when the positive and negative charge contributions to the system have been approximately balanced [20,22,30]. A recent review article highlighted studies showing how polyelectrolyte complexes can be used as the basis for preparing effective barrier coatings for packaging applications [17]. Those systems likewise tend to be optimized when the positive and negative additives are in a suitable balance.

However, the examples provided in this article, as well as in the preceding article by Leib et al. [2], make it clear that the balancing of ionic charges is not the whole story. The charge interactions by themselves do not explain the prominent role played by orders of addition. It is proposed here that kinetic issues are responsible for the observed effects of orders of addition. Certain interactions between polyelectrolytes, surfaces, and colloidal matter have irreversible character. Due to the multiple interactions between opposite charges on opposing polymers or colloidal particles, the charged entities can become stuck in positions that depend on their initial conformations when they first came into contact, i.e., trapped non-equilibrium states [38]. Once polyelectrolyte bridges connecting solids together in a papermaking system become broken, the attachments cannot become reattached with equal strength after the high levels of hydrodynamic shear abate [39].

The interplay between charge interaction issues and kinetically-dominated issues can be seen in several of the examples featured in this article. For instance, the results in Table I showed strong differences in charge titration results, depending on whether the tests were done directly or by titration of filtrate, after the same mixtures had been added to the default furnish. Because the default furnish would have always contributed the same cationic demand, regardless of what had been added to it, one might have expected that the results of the two different methods compared in Table I to differ by a fixed amount, but they did not. Likewise, in Fig. 1, one would have expected that the addition of a fixed amount of cPAM would have had a fixed effect on the cationic demand. These two examples suggest that trapped non-equilibrium interactions were sufficiently important to overcome the tendency of many polyelectrolyte mixtures to interact in a 1:1 stoichiometric relationship [37].

The deterioration of dewatering results at high levels of cationic starch, as shown in Fig. 2, represents a way in which physical-type issues can overpower the expected effects of charge interactions. Many studies have shown that systems comprising cationic polyelectrolytes and colloidal silica tend to give the highest dewatering when sufficient colloidal silica has been added to neutralize the charges [22]. However, Fig. 2 shows that dewatering actually slowed down even more with increasing addition of colloidal silica when the cationic starch level was 1% or higher. These results suggest a mechanism in which the polyelectrolyte complexes formed between the cationic starch and colloidal silica can block the drainage channels within the wet web of paper. Results in Fig. 3 and Fig. 4 add further support for such an interpretation. Further testing would be needed to confirm the suggested mechanism.

Results shown in Fig. 5 and Fig. 6 suggest that a third aspect needs to be emphasized, in addition to charge balancing and kinetics. That is the critical importance of hydrodynamic shear. Figure 5 shows increased flocculation, especially at the 0.5% level of cationic starch addition, but there was only a low level of hydrodynamic shear involved with those experiments. The relatively large sizes of the 95% confidence limits for the mean values in Fig. 6 might be interpreted as evidence of nonuniform formation in the handsheets, possibly attributable to a relatively low level of hydrodynamic shear under the standard conditions of handsheet formation. As was shown by Roberts et al. [36], application of a sufficiently high amount of hydrodynamic shear can completely change the results of adding cationic starch to papermaking furnish. At low shear, their laboratory tests yielded large decreases in the strength of the resulting paper sheets. The effects were attributed to excessive flocculation of fibers, leading to poor uniformity of the paper. However, at high shear, the cationic starch provided a strong increase in paper strength. Because such results can be dramatic, one needs to be careful to avoid an excessive number of trials of different additive strate-

gies at the production scale level of papermaking. Instead, it is advantageous to carry out preliminary tests in the laboratory. Such laboratory experiments need to be carefully designed, using sufficiently vigorous agitation to mimic what would be experienced on the paper machine. Because of the importance of these issues, relative to the additive systems described in this article, follow-up experiments are being planned.

CONCLUSIONS

Laboratory tests were carried out to probe some mechanistic issues related to papermaking wet-end systems employing combinations of NFC, cationic starch, colloidal silica, and cationic polyacrylamide-type retention aid when added to a furnish comprised of 100% recycled copy paper. Though the results showed the importance of the net ionic charge, as evidenced by effects of changing dosages of charged additives, some other observed effects appeared to be controlled by kinetics. The interactions among the studied additives appeared to be somewhat irreversible in character, such that their order of addition to the system affected papermaking operations (retention, drainage, and flocculation), as well as paper properties. Though the present work did not specifically focus on hydrodynamic shear, some of the results highlighted the importance of agitation conditions. Results showed that favorable retention, drainage, moderate fiber flocculation, and paper strength can be achieved with NFC that has been treated with an optimized level of cationic starch and with judicious usage of colloidal silica as a drainage-promoting additive. **TJ**

LITERATURE CITED

1. Garland, L.J., Leib, B.D., Barrios, N.A., et al., *TAPPI J.* 21(10): 563(2022). *https://doi.org/10.32964/TJ21.10.563*.

2. Leib, B.D., Garland, L.J., Barrios, N.A., et al., *TAPPI J.* 21(10): 572(2022). *https://doi.org/10.32964/TJ21.10.572*.

3. Lu, C., Rosencrance, S., Swales, D., et al., in *Make Paper Products Stand Out* (M.A. Hubbe and S. Rosencrance, Eds.), TAPPI Press, Peachtree Corners, GA, USA, pp. 155-196.

4. Lavoine, N., Desloges, I., Dufresne, A., and Bras, J., *Carbohydr. Polym.* 90: 735(2012). *https://doi.org/10.1016/j.carbpol.2012.05.026*.

5. Yi, T., Zhao, H.Y., Mo, Q., et al., *Materials* 13(22): 5062(2020). *https://doi.org/10.3390/ma13225062*.

6. Salas, C., Hubbe, M., and Rojas, O.J., "Nanocellulose applications in papermaking," in *Production of Materials from Sustainable Biomass Resources* (Z. Fang, R.L. Smith, Jr., and X.-F. Tian, Eds.), Biofuels and Biorefineries Ser. 9, Springer, New York, 2019, pp. 61-96. *https://doi.org/10.1007/978-981-13-3768-0_3.*

7. Brodin, F.W., Gergersen, O.W., and Syverud, K., *Nord. Pulp Pap. Res. J.* 29(1): 156(2014). *https://doi.org/10.3183/npprj-2014-29-01-p156-166*.

8. Hubbe, M.A., Sjöstrand, B., Nilsson, L., et al., *BioResources* 15(4): 9672(2020). *https://doi.org/10.15376/biores.15.4.Hubbe*.

9. Rice, M.C., Pal, L., Gonzalez, R., et al., *TAPPI J.* 17(7): 395(2018). *https://doi.org/10.32964/TJ17.07.395*.

10. Hubbe, M.A., Nanko, H., and McNeal, M.R., *BioResources* 4(2): 850(2009). *https://doi.org/10.15376/biores.4.2.850-906*.

11. Balea, A., Fuente, E., Monte, M.C., et al., *Molecules* 25(3): 526(2020). *https://doi.org/10.3390/molecules25030526*.

12. Britt, K.W., *Tappi* 56(10): 46(1973).

13. Wågberg, L. and Lindström, T., *Nord. Pulp Pap. Res. J.* 2(2): 49(1987). *https://doi.org/10.3183/npprj-1987-02-02-p049-055*.

14. Andersson, K. and Lindgren, E., *Nord. Pulp Pap. Res. J.* 11(1): 15(1996). *https://doi.org/10.3183/npprj-1996-11-01-p015-021*.

15. Wagberg, L., *Nord. Pulp Pap. Res. J.* 15(5): 586(2000). *https://doi.org/10.3183/npprj-2000-15-05-p586-597*.

16. Heermann, M.L., Welter, S.R., and Hubbe, M.A., *TAPPI J.* 5(6): 9(2006).

17. Hubbe, M.A., *BioResources* 16(2): 4544(2021). *https://doi.org/10.15376/biores.16.2.Hubbe*.

18. Hubbe, M.A., Rojas, O.J., Lucia, L.A., et al., *Cellulose* 14(6): 655(2007). *https://doi.org/10.1007/s10570-006-9098-4*.

19. Strazdins, E., "Application of electrokinetics in optimization of wet-end chemistry," in *Wet-Strength Resins and the Application* (L.L. Chan, Ed.), TAPPI Press, Atlanta, 1994, pp. 63-83.

20. Horn, D. and Melzer, J., *Papier* 29(12): 534(1975).

21. Bhardwaj, N.K., Kumar, S., and Bajpai, P.K., *Colloids Surf., A* 260(1-3): 245(2005). *https://doi.org/10.1016/j.colsurfa.2005.03.011*.

22. Hubbe, M.A., "Microparticle programs for drainage and retention," in *Nano- Microparticle Technology* (J. Rodriguez, Ed.), TAPPI Press, Atlanta, 2005, Chap. 1.

23. Horn, D. and Linhart, F., "Retention aids," in *Paper Chemistry* (J.C. Roberts, Ed.), Blackie, Glasgow, UK, 1991, Chap. 4, pp. 44-62. *https://doi.org/10.1007/978-94-011-6474-0_4*.

24. Herrington, T.M. and Petzold, J.C., *Colloids Surf.* 64(2): 109(1992). *https://doi.org/10.1016/0166-6622(92)80089-K*.

25. Hubbe, M.A., Sundberg, A., Mocchiutti, P., et al., *BioResources* 7(4): 6109(2012). *https://doi.org/10.15376/biores.7.4.6109-6193*.

26. Isogai, A., Saito, T., and Fukuzumi, H., *Nanoscale* 3(1): 71(2011). *https://doi.org/10.1039/C0NR00583E*.

27. Moody, G., *Miner. Eng.* 5(3-5): 479(1992). *https://doi.org/10.1016/0892-6875(92)90227-Z*.

28. Gliese, T., *Wochenbl. Papierfabr.* 134(22): 1314(2006).

29. Britt, K.W. and Unbehend, J.E., *Tappi J.* 68(4): 104(1985).

30. Strazdins, E., *Tappi* 60(7): 113(1977).

31. La Mer, V.K. and Healy, T.W., *Rev. Pure Appl. Chem.* 13: 112(1963).

32. Lindström, T., "Some fundamental aspects on paper forming," in *Fundamentals of Papermaking, Trans. of the IXth Fund. Res. Symp. Cambridge 1989* (C.F. Baker and V. Punton, Eds.), FRC, Manchester, 1988, pp. 311-412.

33. Tam Doo, P.A., Kerekes, R.J., and Pelton, R.H., *J. Pulp Pap. Sci.* 10(7): J80(1984).

34. Hubbe, M.A., *BioResources* 2(2): 296(2007). *https://doi.org/10.15376/biores.2.1.1-2*.

35. Ezenkwa, O.E., Hassan, A., and Samsudin, S.A., *Rev. Chem. Eng.* 37(8): 907(2021). *https://doi.org/10.1515/revce-2019-0027*.

36. Roberts, J.C., Au, C.O., and Lough, C., *Tappi J.* 69(10): 88(1986).

37. Lalwani, S.M., Eneh, C.I., and Lutkenhaus, J.L., *Phys. Chem. Chem. Phys.* 22(42): 24157(2020). *https://doi.org/10.1039/D0CP03696J*.

38. Claesson, P.M., Poptoshev, E., Blomberg, E., et al., *Adv. Colloid Interface Sci.* 114: 173(2005). *https://doi.org/10.1016/j.cis.2004.09.008*.

39. Hedborg, F. and Lindström, T., *Nord. Pulp Pap. Res. J.* 11(4): 254(1996). *https://doi.org/10.3183/npprj-1996-11-04-p254-259*.

ABOUT THE AUTHORS

A mechanistic understanding sometimes can lead to improvements in procedures, as well as future opportunities to improve papermaking efficiency and product attributes. This research paper helps to interpret results of fresh lab tests, in addition to results presented in two other papers in this set of three that were previously published in *TAPPI Journal* [1,2]. The authors were motivated to carry out this work as a follow-up to earlier promising research results, with the help of some newly acquired equipment for automated evaluation of dewatering rates. This article focuses on the mechanisms involved.

A wide variety of test results needed to be studied and compared in order to find explanations that were consistent with all of the observations, as well as past research. It was surprising to discover how laboratory-based findings are often more interesting than one could have imagined at the start of a project. Of particular interest was to find that by carefully balancing the ratio between charged additives, it may be feasible to employ rather high levels of cat-

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ionic starch in combination with nanocellulose and colloidal silica.

For mills, wet-end addition of nanocellulose will always involve potential problems associated with retention of the nanomaterials and slow drainage. Both of these problems can be overcome. The authors expect that researchers and papermakers will continue with testing of nanocellulose, in combination with various chemical additives, to find best fits for the technology.

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