

Effects of water hardness (CaCl_2 addition) on performance of papermaking additives for fine-particle retention, dewatering, and flocculation

SKY F. JOHNSON, NATHAN J. GILLESPIE, DANIEL ZHANG, KIMBERLY D. GOODWIN, CORI G. SUTTON, AND MARTIN A. HUBBE

ABSTRACT: Water hardness, which can be defined as the concentration of calcium and magnesium ions, is known to vary greatly depending on geographical locations. Laboratory tests were carried out to evaluate effects of large differences in water hardness on the performance of certain wet-end additives to the paper machine process. Tests were carried out at hardness levels of 25, 125, and 225 ppm (as calcium carbonate equivalents).

Increased water hardness was found to have a generally negative effect on the performance of a cationic acrylamide-type retention aid, although the extent of performance loss depended on experimental details. Likewise, rates of dewatering in systems containing cationic retention aid were adversely affected by increasing hardness, though the effects were not statistically significant in all cases considered. The tendency of bridge-forming flocculants (cationic retention aid or sequential addition of a cationic additive and then anionic retention aid) fell slightly with increasing water hardness.

Application: A practical take-away message, based on laboratory testing, is that cationic acrylamide-type retention aid is quite tolerant of different water hardness conditions. Such products can promote both retention and drainage in paper machine systems even when operating under very low or very high water hardness conditions, as are often found at mill sites in different regions.

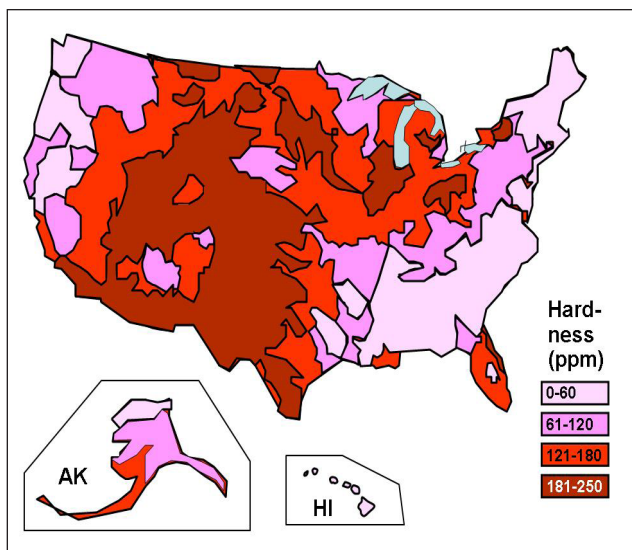
Water hardness can be defined as the net concentration in water of dissolved calcium and magnesium ions [1]. Taking advantage of the fact that calcium carbonate (CaCO_3) has a molecular weight of 100 g/mole, hardness is most often quantified in ppm units of CaCO_3 equivalents.

The hardness of the process water in a paper mill depends strongly on its geographical location. As shown in **Fig. 1**, different regions of the United States have hardness values ranging from about 25 ppm in Raleigh, NC, USA, to about 200 ppm in Chicago, IL, USA [2]. The differences can be mainly attributed to the differences in the bedrock underlying different parts of the United States. A relationship between the bedrock composition and that of the adjacent soil has been reported [3]. High levels of hardness are often associated with CaCO_3 as a main component of the soil and of the bedrock [4]. By contrast, relatively low levels of hardness are commonly found in regions where the soil and bedrock are rich in granite or clay. Some paper mills obtain water from more than one source, such as a well and an adjacent river. In such cases, the river may have a lower level of hardness, especially when the ions have become diluted by recent rains [5].

The importance of water hardness is perhaps best

known in terms of its effect on the use of soaps and detergents, as in bathing and laundering [6]. Traditional soaps, which are based on the sodium or potassium carboxylate forms of fatty acids, are especially vulnerable to the effects of high hardness levels [7]. Divalent metals associate with the negatively charged carboxylate groups and tend to precipitate the soap from solution as a scum [8,9]. Such precipitation also can take place in paper machine systems, especially when some of the fatty acid or resin acid soaps from a pulping process fail to be washed from the pulp fibers before they are sent to the paper machine system. To some extent, such effects can be mitigated by adding chelating agents, which have the job of complexing such divalent ions [9]. Alternatively, as in the case of modern laundry detergents, non-ionic surfactants can be used instead of traditional soap molecules [10].

Papermakers can also consider options to remove hardness ions. For instance, operators of kraft pulp mills routinely remove water hardness ions by nanofiltration, a process that requires the use of membranes and high pressures [11,12]. Another practice is to apply water softening treatment to incoming fresh water [13]; however, the high expense of such treatments discourages their widespread usage for paper machine applications.



1. Map of water hardness in the United States based on U.S. Geological Survey, 1975 [2], redrawn by authors using a new color scheme.

It is also possible that water hardness may have beneficial effects on the performance of papermaking additives. For example, improved retention and “exhaustion” of certain direct dyes onto fiber surfaces may result when hardness levels are increased [14]. Another example of a positive effect involves an interaction between hardness ions and anionic acrylamide-based retention aid polymers, when the latter is being added to papermaking furnish shortly before the headbox [15]. In that case, it appears that the divalent ions lead to transient association among the macromolecules [16], giving an effect that is analogous to increasing the molecular weight. An increased concentration of Ca^{+2} ions in solution can render the surfaces of CaCO_3 filler particles less negative or more positive in zeta potential [17,18], which sometimes might be regarded as a benefit.

On the negative side, there are numerous reported examples of adverse effects of hardness ions in papermaking systems. For example, rosin sizing generally becomes less efficient with increasing water hardness [19]. The effect has been attributed to the divalent metal ions competing with the intended “setting” of the rosin soap molecules by interaction with aluminum sulfate (papermaker’s alum) species [20]. As noted by Pruszyński et al. [21], hardness ions are suspiciously present in a wide range of deposits that have been scraped from papermaking equipment. These include scales, such as calcium oxalate and calcium silicate, as well as scum (from the precipitation of soaps). Hardness ions are also expected to decrease the swelling tendency for cellulosic fibers in water [22], which may decrease their conformability and ability to form strong inter-fiber bonds.

From the studies cited previously, few experiments have been carried out in which known amounts of hardness ions were added to papermaking fiber suspensions, and the effects were reported regarding only a limited number of

chemical additives [15,23]. In many reported studies focused on the effects of ion concentrations on papermaking, it is difficult to distinguish effects due to hardness differences because of the involvement of confounding variables such as pH and monovalent salt ion concentrations. For instance, studies cited by Goodwin et al. [24] considered different levels of ions resulting from increased recirculation of water within paper machine systems. In such cases, it is not possible to separate the effects of water hardness changes from the effects related to increases in monovalent ions and in levels of dissolved polymeric and colloidal materials. Accordingly, the present work compared effects on fine-particle retention, dewatering rates, and flocculation at three different hardness levels in a bleached kraft furnish. The lowest level, about 25 ppm as CaCO_3 , can be regarded as the lowest value likely to be encountered in a paper mill not employing water softening technology. The next level, about 125 ppm CaCO_3 , is an intermediate value. The highest hardness, about 225 ppm, is near to the highest hardness to be expected based on Fig. 1. The water hardness values used in this work were selected to represent the full range of likely intake values, based on natural fresh water available in different locations in the United States. Additives such as calcium carbonate will also contribute to a mill’s water hardness. Another known limitation of the present study is that it does not consider the likely buildup of various organic substances as a result of recirculation and reuse of process water in a paper mill.

EXPERIMENTAL

Fiber sources and pulp preparation

The experimental materials were similar to those described in previous research [24], with some exceptions. As in the cited work, tests were carried out with a 75:25 mixture of hardwood and softwood bleached kraft pulps, which had been co-refined in a laboratory Hollander beater to a Canadian Standard Freeness (CSF) of 450 mL.

Table I describes the three sub-batches prepared in the present work to evaluate the effects of different water hardness conditions. In each case, sufficient sodium sulfate was added to a suspension of the refined pulp dispersed in tap water to reach an electrical conductivity of 1000 $\mu\text{S}/\text{cm}$ at a consistency of 0.5%. Since the tap water in Raleigh, NC,

Pulp Batch	II	IV	V
Hardness (ppm CaCO_3)	25	125	225
Conductivity ($\mu\text{S}/\text{cm}$)	1000	2650	4330
pH	7.5	7.6	7.5

I. Pulp batches for evaluation of retention, dewatering, and flocculation performance of additives at different levels of salinity (CaCO_3 : calcium carbonate).

ADDITIVES

has a known water hardness of about 25 ppm, that value was taken as the nominal hardness of pulp batch II, to which no calcium chloride (CaCl_2) was added. By contrast, calculated amounts of CaCl_2 were added to pulp batches IV and V to reach the higher levels of water hardness and electrical conductivity (at room temperature) shown in Table I.

Chemical preparation

The retention aid polymers were dry-bead acrylamide products that were prepared by immediate dilution to 0.1% solids in briskly stirred distilled water using a magnetic stirrer for at least 1 h. The cationic retention aid was American Cyanamid Corp.'s (Wayne, NJ, USA) Accurac 90 (10% cationic, very high molecular mass). The anionic retention aid was Floerger (Andrézieux-Bouthéon, France) AN 910 BPM (10% anionic, very high molecular mass).

Other additives were prepared at a solids level of 1% before addition to the pulp. The polyvinylamine (PVAm) was Hercobond 6350 from Solenis (Wilmington, DE, USA). The colloidal silica was Fennosil 2180 from Kemira (Helsinki). Default nanofibrillated cellulose and TEMPO-oxidized nanofibrillated cellulose (TONFC), both in freeze-dried form, were the standard products provided by the University of Maine (Orono, ME, USA).

Two kinds of minerals were used in certain tests, generally at a 5% content based on fiber solids. Clay was a conventional coating grade. Calcium carbonate was Albacar precipitated calcium carbonate from Specialty Minerals (Minerals Technologies, NY). These dry mineral products were prepared for testing by dilution to 1% solids in deionized water, followed by swirling for 60 s in an ultrasonic bath.

Many of the results reported in this work include “control” sets, meaning that no additional chemical additives had been added to the furnish (other than mineral particles in some cases). The control sets may be different in the various figures shown because of variation in pulp batches, researchers, and the day of the experiment.

Retention tests

Retention efficiency was determined by means of a Britt dynamic drainage/retention jar using a 200-mesh screen. The first step of each individual test was to take 500 mL of freshly stirred suspension from one of the sub-batches of refined pulp. Additives, as specified with the results to be shown later, were added to each 500-mL specimen with constant stirring at 650 rpm and 10 s between successive additives when there was more than one additive.

Turbidity tests were carried out starting at about 10 s after addition of the final additive to the suspension. Two different procedures were used depending on whether or not a mineral filler was being used. In tests not involving clay or CaCO_3 , an initial 10 mL specimen of filtrate was collected from below the pinch-clamp of the Britt jar and immediately returned to the suspension. A second specimen was used for measurement of the turbidity. By gently overturning the vial, two

measurements were obtained for each filled vial. The process was repeated five times to obtain 10 readings for each individual test. When clay or CaCO_3 had been added to the pulp, a similar procedure was carried out, but after returning the first filtrate specimen to the suspension, the second filtrate specimen was diluted 10-fold, and all tests were subsequently based on that diluted sub-batch. Final results (in nephelometric turbidity units, NTU) were multiplied by a factor of 10 when using the procedure with dilutions.

Dewatering tests

The dewatering tests were carried out with a modified Schopper-Reigler device, as described in more detail earlier [24].

Flocculation tests

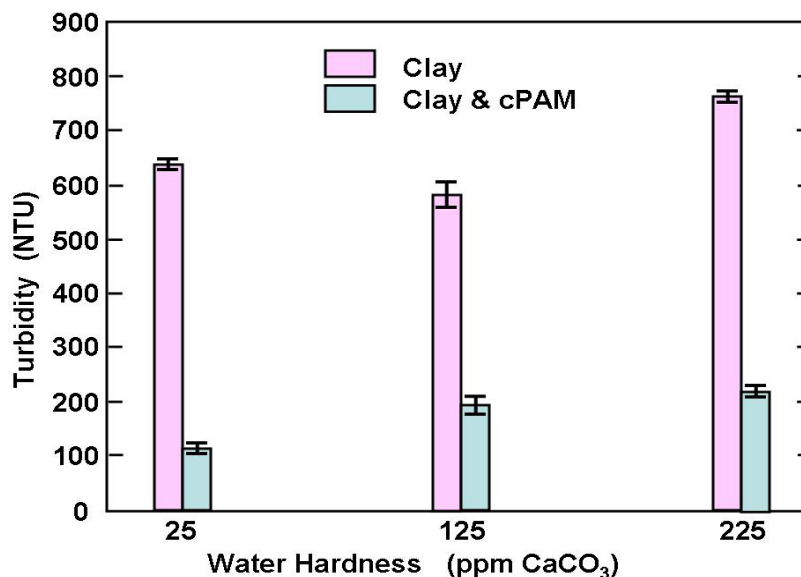
Effects of flocculant addition on the extent of fiber flocculation were evaluated by means of a photometric dispersion analyser (PDA) from Rank Brothers (Newberry, UK) [24].

RESULTS AND DISCUSSION

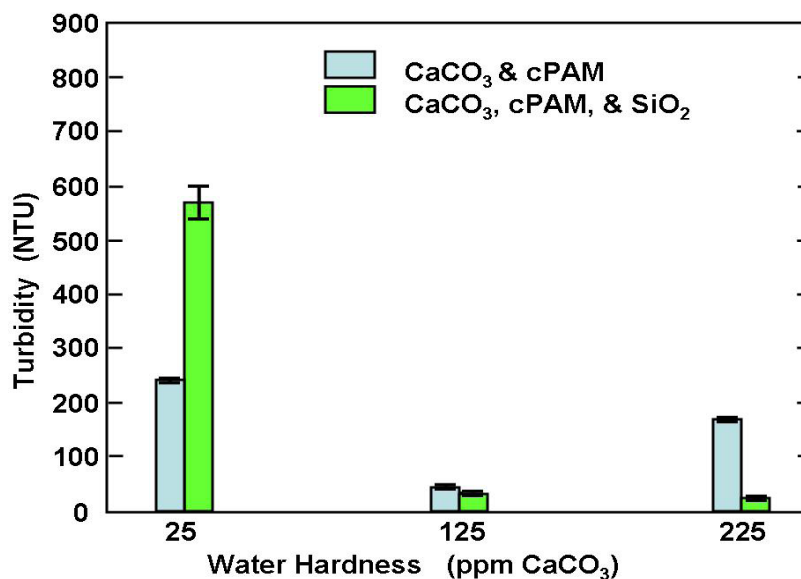
Retention

At 25 ppm CaCO_3 hardness, the cationic polyacrylamide (cPAM)-treated furnish with 5% clay showed a substantially lower turbidity compared to the untreated clay furnish (**Fig. 2**). This cPAM-driven turbidity reduction persisted across all hardness levels (25, 125, and 225 ppm). This means that the cationic retention aid was effective, though its effectiveness decreased to a measurable extent with increasing hardness. The untreated clay furnish exhibited a U-shaped turbidity trend (lowest at 125 ppm, highest at 225 ppm), while the cPAM-treated furnish showed monotonic increases in turbidity with hardness (lowest at 25 ppm). For the cPAM-treated clay furnish, turbidity differences between 125 ppm and 225 ppm were not statistically significant.

Figure 3 shows related results, but this time considering systems in which calcium carbonate had been added to the default furnish at the 5% level. The treatment conditions compared were cPAM at 0.1% level (solids basis) and the same level of cPAM followed by colloidal silica (SiO_2 , 0.15% solids basis). As shown, an intermediate level of water hardness strongly benefited both additive systems, with respect to fine-particle retention, compared to the hardness provided by the tap water alone. The combined treatment with cPAM and colloidal silica continued to provide superior retention performance at the highest level of hardness, whereas the treatment with cPAM alone became less effective. These results are consistent with the idea that the charge densities of the cPAM (positive) and the SiO_2 (negative) were sufficiently strong that the interactions between the two remained strong, even in the presence of high hardness. By contrast, calcium ions can be expected to compete with cPAM for adsorption sites, especially at the highest hardness level, thereby hurting the performance of the



2. Effect of water hardness on the turbidity of Britt Jar filtrate with 5% by mass of clay on the default furnish, or the same treated with cationic PAM (cPAM) retention aid at the 0.1% level by mass (CaCO_3 : calcium carbonate).

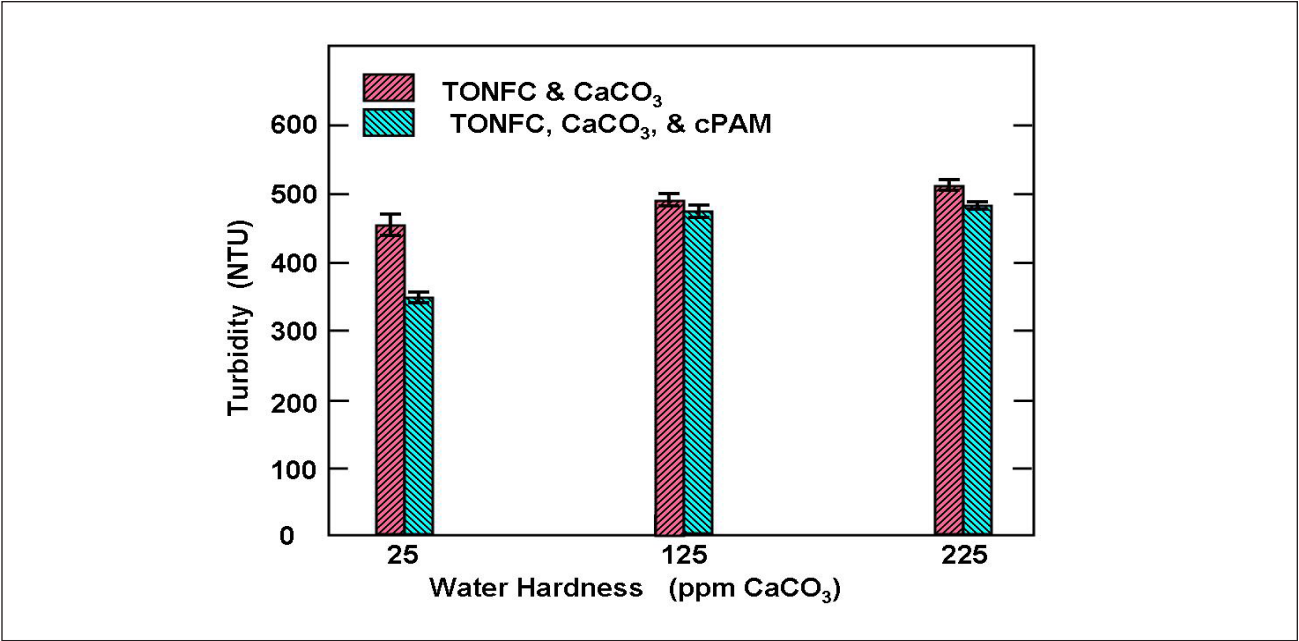


3. Effect of water hardness on the turbidity of Britt Jar filtrate with 5% by mass of CaCO_3 , comparing treatments with just cPAM retention aid at the 0.1 level by mass and the same cPAM dosage followed by colloidal silica (SiO_2) at a 0.15% dosage.

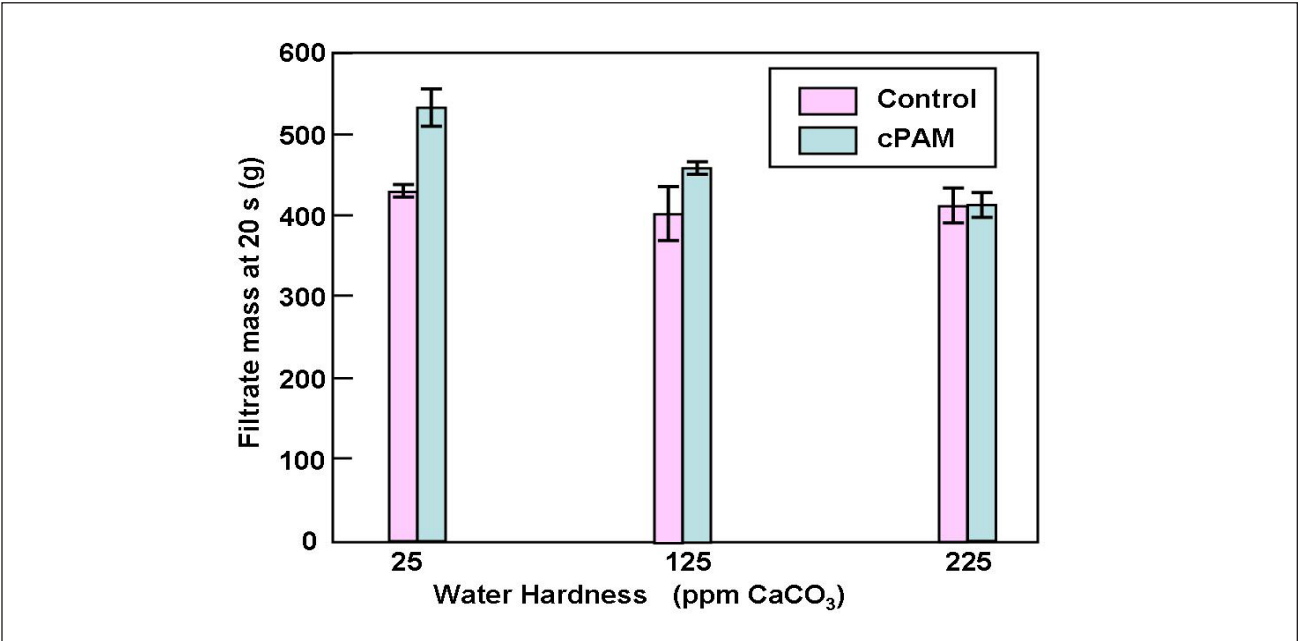
cPAM treatment by itself. Further testing would be needed in order to demonstrate the viability of these concepts.

The presence of TONFC, which has a high negative charge, appeared to have an adverse effect on retention of CaCO_3 , especially at the intermediate and highest levels of water hardness. This is evident when comparing the results in **Fig. 4** to the previous two figures. Note that at the lowest water hardness level, the turbidity decreased by only about 25% upon addition of cPAM, whereas in Fig. 2

(with clay) the corresponding change was about 88%. It is speculated that the negative charge of the TONFC had shifted the charge balance of the furnish to such an extent that the positive charge provided by the cPAM was insufficient to provide the expected increases in retention. In particular, at the middle and high levels of water hardness, though the cPAM achieved statistically significant decreases in turbidity, the effects were not large enough to be useful. Similarly, TONFC/ CaCO_3 furnishes with and without



4. Effect of water hardness on the turbidity of Britt Jar filtrate with 5% by mass of CaCO₃, plus 5% of TEMPO-oxidized nanofibrillated cellulose (TONFC) on the default furnish, or the same treated with cPAM retention aid at the 0.1% level by mass.



5. Effect of water hardness on the amount of filtrate collected within 20 s with the default furnish or following treatment with cPAM retention aid at the 0.1% level by mass.

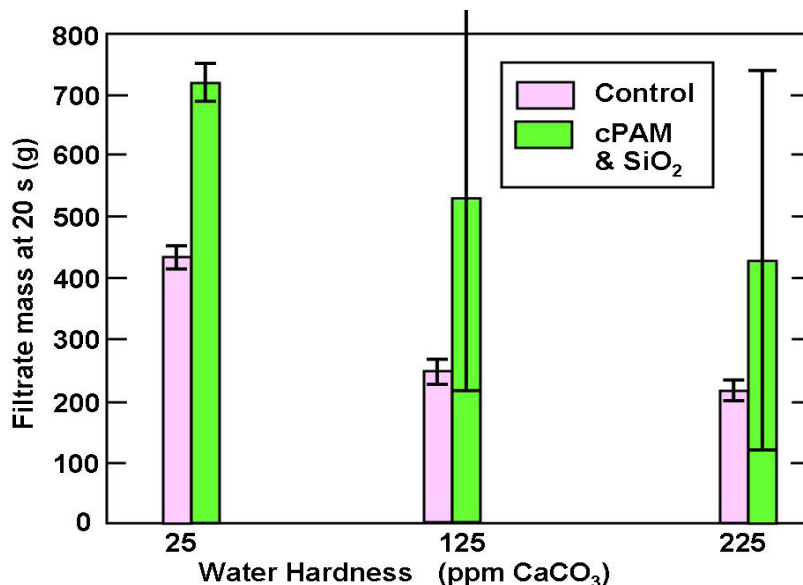
cPAM showed overlapping error bars with similar mean turbidity at 125 ppm.

A possible explanation for the lack of effectiveness of the cPAM retention aid in the presence of TONFC and water hardness is that hardness ions had undergone an ion exchange process with the highly anionic surfaces of the nanocellulose. By replacing counter-ions such as sodium at the oxidized surfaces, the charge balance of the system would have been changed. It is speculated that the shift in

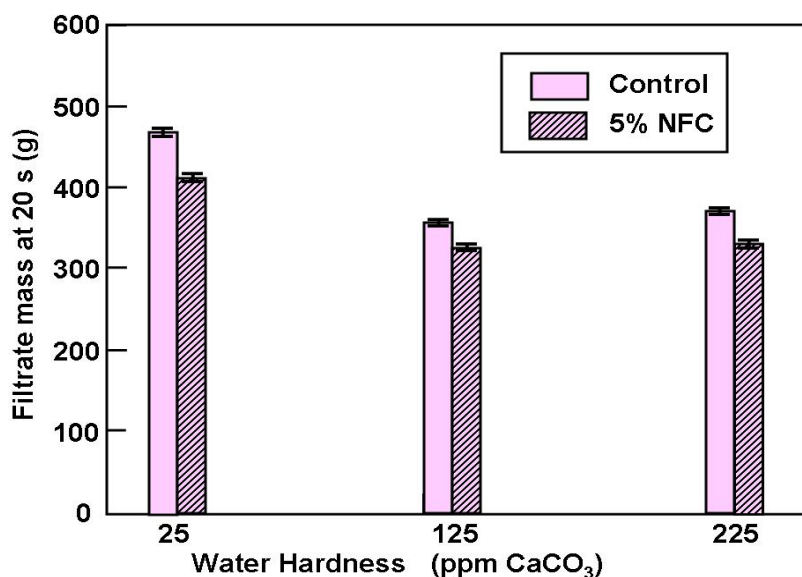
charge balance of the system was enough so that the cPAM no longer was effective in helping to retain the calcium carbonate particles onto the fiber surface.

Dewatering rate

In soft water (25 ppm CaCO₃ hardness), treatment of the default furnish with the cPAM retention aid significantly increased the rate of drainage. The filtrate mass (20 s) of the cPAM-treated systems declined with increasing hard-



6. Effect of water hardness on the amount of filtrate collected within 20 s with the default furnish or following treatment with sequential cPAM retention aid at the 0.1% level by mass and then SiO₂ at the 0.15% level.



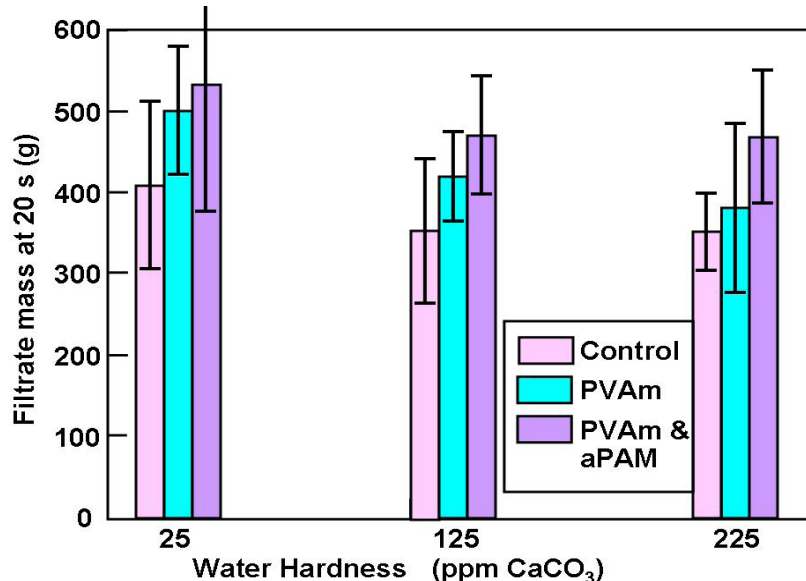
7. Effect of water hardness on the amount of filtrate collected within 20 s with the default furnish or following addition of default TONFC at the 5% level.

ness. At 225 ppm, the default and cPAM-treated furnishes performed comparably. However, while the default furnish maintained nearly the same filtrate mass across hardness levels, the cPAM-treated furnish exhibited statistically distinct behavior at each hardness (Fig. 5).

The results just described are consistent with competition between the calcium ions and cPAM for adsorption sites at the surfaces of CaCO₃ particles and fibers. To be effective, there needs to be strong adsorption of the cat-

ionic polymer segments onto the kraft fibers, which are well known to have a relatively low but negative surface charge [24].

The furnish treated with cPAM (0.1 %) followed by colloidal silica (0.15%) showed elevated variability with large error bars, obscuring statistical significance across hardness levels (Fig. 6). However, mean filtrate mass decreased with increased hardness. The cause of the high variability of tests involving cPAM and colloidal silica at the middle



8. Effect of water hardness on the amount of filtrate collected within 20 s with the default furnish or following treatment either with polyvinylamine (PVAm) at the 0.2% level or the same followed by anionic polyacrylamide (aPAM) retention aid at the 0.1% level.

and high water hardness levels was traced to partial plugging of the forming screen. This implies that papermakers may have to devote more attention to wire-cleaning spray treatments when using certain combinations of drainage-promoting additives in the presence of hard water. Follow-up work, with scrupulous cleaning of the screen, will be needed in order to determine whether the drainage-promoting effect of the cPAM and colloidal silica is adversely affected by water hardness.

The 5% TONFC furnish replicated prior trends: no significant difference between 125 ppm and 225 ppm, but a marked filtrate mass reduction from 25 ppm to 125 ppm (**Fig. 7**). The decrease in filtrate mass in the presence of nanocellulose is expected from previous work [24-27]. However, the fact that the two higher levels of water hardness, even in the absence of NFC, significantly decreased the drainage rate is new information. The results are consistent with a mechanism of increased blockage of drainage channels in the wet web, either by fiber fines or by a combination of fiber fines and NFC particles.

Furnishes treated with either PVAm alone or PVAm followed by anionic polyacrylamide (aPAM) showed no statistical differences from the default furnish at any hardness, nor across hardness levels (**Fig. 8**). It is worth noting that there was a general decrease in drainage with increased water hardness across all of the sets of data. This trend is consistent with what had been shown in the previous figure.

Flocculation

Flocculation output for the default furnish was affected only to a modest extent by water hardness (**Fig. 9**). The

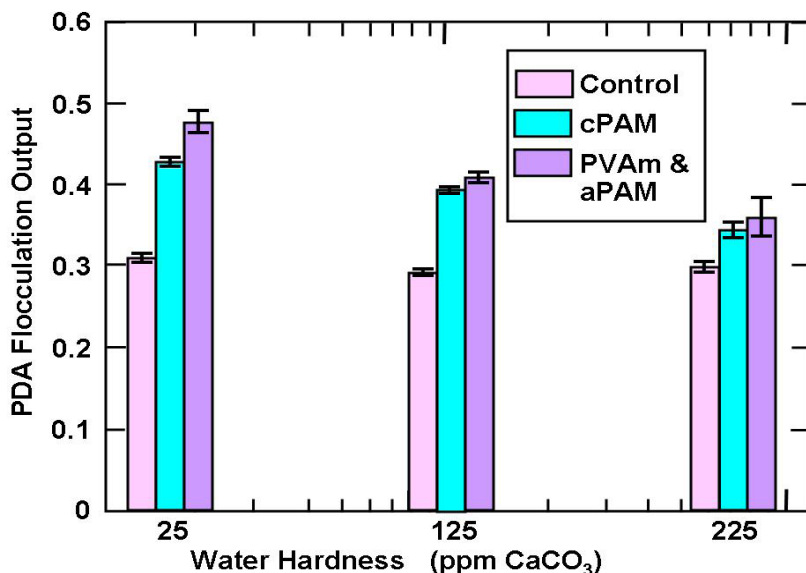
furnishes treated with cPAM and PVAm/aPAM showed increased flocculation, especially at the lowest hardness. The differences relative to the control (“default”) furnish became less important with increasing hardness. In general, each of the sets of additives showed declining flocculation output with increasing hardness.

One of the most statistically significant effects shown in **Fig. 9** was the effect of going from 25 to 125 ppm of hardness in a system with successive treatment by the cationic PVAm agent and then the anionic retention aid. Such systems have been shown to impart significant levels of flocculation at relatively high pH and low levels of water hardness [28]. The results, once again, can be tentatively attributed to a competition between the hardness ions and the polyamine for adsorption sites on the fibers.

All additive-modified furnishes exhibited some level of hardness-dependent behavior, while the default furnish remained more stable across most tested conditions.

CONCLUSIONS

Water hardness values were systematically varied in the course of laboratory tests related to papermaking chemistry with a bleached kraft pulp furnish. Results were generally consistent with what can be expected based on a tendency for divalent metal ions to associate with the carboxylate groups on either the fibers themselves or on certain papermaking additives. Thus, the performance of cationic acrylamide-type retention aid, which has the same ionic charge as the metal cations, was not affected to an important extent by differences in water hardness. Neither was polyvinylamine, which can be classed as a high charge cationic additive. By contrast, high levels of hardness ions appeared



9. Effect of water hardness on the extent of fiber flocculation, as assessed by the photometric dispersion analyzer (PDA) device, when comparing the default furnish, and optional treatments either with cPAM at the 0.1% level or a sequence of PVAm at the 0.2% level followed by aPAM at the 0.1% level.

to interfere with the performance of anionic colloidal silica when it was being used in sequence with cationic polyamine for enhancement of drainage. The results of this work are in agreement with a general observation that paper mills making a wide variety of grades are being successfully run in locations where the prevailing water hardness can span a huge range, from about 25 ppm to about 250 ppm. **TJ**

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ABOUT THE AUTHORS

We studied this topic because it is known that levels of water hardness have huge variations when comparing different mill sites. Hardness ions are known to form transient complexes with fiber surfaces, and there have been very few published studies dealing with this issue.

The most difficult aspects of this study were the logistical challenges in varying the hardness in a systematic way, while keeping other variables and methods precisely according to a research plan. We ultimately found that the performances of cationic additives, such as cationic retention aid, were hardly affected by drastic changes in water hardness.

Through this study, mills relying upon the use of negatively charged (anionic) additives can better understand why such additives perform differently in mills with different water sources.

The research team was not able to obtain reproducible results related to rosin sizing or alkaline sizing with changes in water hardness, and as a next step, such work still needs to be done.

Johnson, Gillespie, Zhang, Goodwin, and Sutton are undergraduate students in the Paper Science and Engineering program of the Department of Forest



Johnson



Gillespie



Zhang



Goodwin



Sutton



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