Effect of conductivity on paper and board machine performance— a review and new experiences

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ABSTRACT: The current trend to further reuse water within paper mills has resulted in more accumulated salts, as reflected by increased conductivity values. Although conductivity measurement is widely used in paper mills, its fundamental principles and interpretation are not often fully understood. This keeps papermakers from reaching the full benefits of using conductivity measurements to help manage the wet end chemistry of paper or board machines. High and variable conductivity affects the intrinsic properties of pulps, the performance of chemical additives, and the interaction between them. This paper reviews principles of conductivity; its measurement; its effect on important aspects of papermaking operations, such as retention, drainage, sizing, strength development and deposit control; and the fundamentals behind the effects of conductivity on the papermaking process. Specific mill examples are also provided. Potential solutions for operating a mill under high and variable conductivity conditions are discussed.

Application: Understanding the principles of conductivity measurement and its limitations can help mills interpret the effect of high ion concentration on the papermaking processes. It will also help papermakers gain insight into issues associated with increased and changing conductivity for troubleshooting.

Originally, the papermaking process relied solely on the physical process to filter fiber slurries, fines, and mineral additives, forming a paper sheet. Today, the papermaking process increasingly relies on the application of chemical additives to enhance the performance of the paper machine and final paper products. Higher machine speeds, stronger shear in the forming section, more restriction on fresh water consumption, and significantly more closure of machine water systems lead to higher concentrations of dissolved and colloidal substances and bring the system closer to the point of potential destabilization.

These increasingly difficult machine conditions coincide with technological and market trends that require finely tuned operating conditions, frequent grade changes, and stringent quality expectations. Alkaline conversion introduced chemically reactive fillers (calcium carbonates) and hydrolysable sizing molecules, such as alkyl ketene dimer (AKD), low melting point alkylene ketene dimer (AIKD), and alkenyl succinic anhydride (ASA). Use of those additives requires better control over such conditions as pH, temperature, hardness, alkalinity, cationic demand, and conductivity than was required in the past. New, advanced, high performance and multicomponent retention programs and sophisticated strength programs require strict control over paper machine conditions to avoid variability in their performance, assuring machine efficiency and product quality.

Many studies have been published recently to describe the effects of various factors on the performance of retention and drainage programs. Factors that affect the performance of these drainage and retention programs have been well reviewed by several authors [1-5]. Those findings and others justify the need for reviewing the effects of important wet end chemistry components and their effects on machine operations. This paper focuses on the effects of ionic contamination, collectively represented by measurement of conductivity. Brown and Hart [6] recently reviewed the relevance of conductivity in the pulping process. This paper will focus entirely on the wet end of the paper machine. Because many of the consequences of increased or variable ionic strength are general in nature, they apply to paper, board, and tissue applications, although the relevance of individual effects might differ from grade to grade. In addition to the general effect of conductivity, we will briefly review the specific effects of calcium ions (Ca^{+2}) and magnesium ions (Mg^{+2}) associated with hardness.

This paper is a literature review that includes several of the authors' real-world experiences intermixed. Although the effects of conductivity, at a general concept level, are well understood by skilled and experienced wet end chemists, the authors realize that reviewing this topic to provide fundamental principles and bring practical examples with potential solutions could help papermakers better understand the relevance of conductivity and consider it as a very important wet end chemistry parameter. This becomes increasingly important now, as many mills plan to reduce fresh water consumption, either voluntarily or otherwise.

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DISCUSSION

Conductivity fundamentals

In general, detrimental substances that accumulate in the papermaking systems are either inorganic or organic. This review considers the effect of inorganic dissolved solids, in general terms of conductivity, and the specific effect of Ca^{+2} and Mg^{+2} ions that contribute to water hardness.

When an electrical potential is applied to a pair of electrodes immersed in an aqueous solution containing ions, positive ions (cations) migrate toward the cathode, and negative ions (anions) migrate toward the anode. The conductivity (ability to conduct an electrical current) of the solution is a function of the rate of charge movement in the potential field. The conductivity value can be affected by the migration speed of individual ions, the charges and concentrations of the ions, and interactions among individual ions.

Conductivity can be expressed as the reciprocal of the resistivity normalized to a 1 cm cube of a liquid at a specified temperature, which is reported in micro-Siemens per centimenter (μS/cm). The term specific conductance is used in this paper when measurements are made at or corrected to the standard temperature of 25°C. In simple terms, conductivity is a function of ionic concentration and specific conductance. Without getting into details, the ability of ions to impart conductivity depends on their charge and mobility. Thus, not all ions contribute to conductivity to the same degree, as illustrated in **Table I** [7].

Although hydrogen (H+) and hydroxide (HO-), originating from water, have the highest specific conductance, they have only a small contribution to the total conductivity of a solution unless the solution is at an extremely high or low pH value. At near neutral pH conditions, the concentrations of H+ and HO- are low, resulting in only a small effect on total conductivity. In typical papermaking conditions, most conductivity and its variations come from contributions of other ions.

Conductivity increases with temperature at a rate of 2% to 3% per degree Celsius above 0°C. This is because of the effect of temperature on liquid viscosity and density. The viscosity of water decreases by about 2% per 1°C when heated, resulting in reduced resistance to flow, thus increasing conductivity. Both direction and magnitude of the temperature effect on viscosity closely match its effect on conductivity. Conductivity correlates with the concentration of ions and its change with temperature should lead to a decrease of concentration from temperature expansion of water by 0.025% per 1°C. Because the change in conductivity caused by temperature is not related to a change in the ionic strength of solution, it is not expected to correlate with paper machine performance. Because not all conductivity meters have temperature compensation, it is recommended to collect temperature data together with conductivity to check the effect of temperature on conductivity trends.

Effect of mill closure

Paper mill water closure results in the accumulation of soluble materials that have a pronounced effect on paper machine operations and product quality. This buildup of ionic material is an unavoidable consequence of water closure and dictates how far mill water circuits can be closed. On the research level, the effect of ionic strength to the system is well understood. In practical application, ionic concentrations will continue to increase with reduced use of fresh water in paper and board production. Understanding, preferably in quantitative terms, the nature of this effect and the way to mitigate it might, therefore, open the way to further the progress of water closure projects in a mill. The degree of accumulation of any substance in the paper machine system depends on the nature of the contaminant, its influx level to the system, and the degree of system closure. Equation 1 represents the degree of concentration or enrichment factor (ER) of any substance that fully follows the water phase (shows no affinity to the fiber):

$$ER = \frac{1}{1-r} \tag{1}$$

where r is the recycle ratio, or the amount of white water recycled divided by the total amount of water to the headbox [8]. This equation can be used to predict the steady state concentration of the simple electrolyte, provided it has no or very low affinity for the sheet of paper [9]. This equation was also used to predict the degree of closure when final concentration of the accumulated tracer (lithium [Li+]), added at a known concentration of tracer, was measured [10]. Equation 1 applies well to ions that contribute to conductivity. At the recycle ratio r = 0.9, the enrichment factor ER = 10 can be calculated for ions that are not removed with the sheet of paper. There is always some degree of removal of ionic species with the water entering the press section (if pressate is not reclaimed). Nevertheless, any source of salts undergoes significant enrichment with increasing recycle ratio. A lot of attention needs to be devoted to understanding sources of conductivity and their reduction.

Equation 1 does not account for the adsorption of dissolved solids onto the fibers. Xu [11] modified Eq. 1 to account for the adsorption of dissolved solids to the formed web

Ion	Specific Conductance, $\Omega^{-1}cm_2mol^{-1}$	Ion	Specific Conductance, $\Omega^{-1}cm_2mol^{-1}$
H+	349.8	1/2 Ca+2	59.50
HO-	197.8	1/2 Sr+2	59.46
Na+	50.11	1/2 SO4-2	80.0
K+	73.52	Cl-	76.35
1/2 Mg+2	53.06	HCO3-	44.5

I. Specific conductance of selected ions.

of paper (Eq. 2):

$$C_{r,eq} = \frac{(\frac{Y}{M})(1-r)}{\left[\frac{1}{1-K}\right]-r} \qquad (2)$$

where:

    $C_{r,eq}$ = equilibrium concentration
    Y = sum of the concentration of species of interest in different water flows on machine at equilibrium
    r = recycle ratio
    K = percentage of species of interest removed by adsorption
    M = total amount of water coming from outside sources

This model, validated by the authors through experimental evaluation of the buildup rates for sodium (Na^+) and Ca^{+2}, allowed prediction of the final concentration and time required to reach equilibrium for species with some adsorption ability to the fiber. Because of higher adsorption of Ca^{+2} to the fiber, its final concentration was lower and time to reach equilibrium shorter.

Mittal and coauthors [12] discussed buildup of dissolved solids related to mill water closure contributing to conductivity in a paper board mill. This work focused on critical substances such as chlorine (Cl^-), sulfate (SO_4^{-2}), Ca^{+2}, Mg^{+2}, silica (SiO_2), and Na^+.

Sources of conductivity

Papermaking raw material and additives can introduce ions to the process. Wood contains different ions, such as Ca^{+2}, Mg^{+2}, and barium (Ba^{+2}), depending on its growing environment. If wood is chemically pulped and bleached, pulping and bleaching chemicals will be a great source of ions. The amount of ion carryover is determined by the efficiency of the various washing processes. Brightness development of mechanical pulps is the biggest contributor to conductivity in grades such as newsprint, improved newsprint, mechanical pulp-based coated grades, and supercalendered grades. The application of brightening chemistries, typically hydrosulfite (Y), peroxide (P), or combined PY bleaching, often results in high levels of ionic contamination. The contamination level is proportional to the brightness target and depends on the available thickening stages acting as water blocks between bleaching stages and the paper machine. Additionally, reaching desired brightness levels often requires change of dosages of brightening chemicals, leading to significant variation in water chemistry, including but not limited to conductivity. The effect of water blocks such as twin-wire presses on system contamination and wet-end stability is well documented [13].

For paper mills using virgin pulps, one of the main sources of conductivity at the wet end is the pulp. Mills using unbleached pulps (brown mills) will experience conductivity swings that directly correspond to upsets in the brownstock washers. These mills typically receive some amount of inorganic sodium compounds (typically reported as equivalent sodium sulfate [Na_2SO_4]), which remain in the pulp after washing. Several organic sodium salts might also be present from dissolved lignin and carbohydrate fragments remaining in the washed pulp. As upsets occur in the brownstock washing, the concentration of these materials changes, resulting in conductivity spikes on the paper machine. Work has been performed to correlate dissolved sodium concentration in stock to conductivity measurements [14]. University investigators [15] reported a linear correlation between the measured conductivity and the inorganic levels found in black liquor filtrates of a brownstock washing system. Sodium, the most prevalent inorganic component of black liquor, usually represents all the inorganics. This implies that conductivity can be correlated to sodium content.

Conductivity affecting paper machines making bleached grades comes from the pulp leaving the last stage of bleaching. Often, there is a need to adjust pH of the stock leaving the bleach plant going to the paper machines. These adjustments are performed with either sulfuric acid or caustic soda. Both materials will increase wet-end conductivity. As with brown pulps, upsets in the last stage of bleach plant washing will also increase the amount of material being sent forward to the paper machines, thus increasing the amount of chemical required to adjust pH of the stock. Therefore, upsets in the last stage of bleach plant washing might impart a double effect on conductivity variability.

For recycled fiber, the amount of ionic material it contains is mainly determined by previous manufacture and consumer history, on which a mill generally has less control. One good practical control method is to sample and sort recycled material. This will not reduce the total amount of ion, but can decrease the variation of conductivity from time to time to minimize its effect on the papermaking process. Broke (internal recycled fiber) should be more manageable by a mill. Most wet-end and dry-end additives, such as surface treatment or coating, are returned to the wet end through repulped broke. If a mill is expected to use a fair amount of broke, materials used at the wet end and dry end should be carefully chosen, considering the ion accumulation effect through broke system.

Incoming fresh water contains ionic material, especially Ca^{+2}, if the water is hard. Acid and caustic soda for pH adjustment will add additional ions. Most papermaking additives are designed in a salt form for good water solubility. Rosin soap and surfactant of dispersed rosin size, AKD, and ASA give Na^+ or K^+. Aluminum species (alum or poly-aluminum-chloride [PAC]) introduce Al^{+3}. Most cationic polymer additives (strength agent, retention aid, drainage aid) are salts of polymeric acid and release ions after dissolving. Dye is usually a salt of organic acids as well, which contributes ions after disassociating in water. If coated broke is used, coating material might become an ion source. For example, acidic process water can dissolve calcium carbonate ($CaCO_3$) pigment to generate Ca^{+2}. Some additional contribution to the ionic strength of the system can come from starch, biocides, dyes, and optical brightening agents.

PAPERMAKING

Effect of conductivity on papermaking process

Conductivity affects wet-end operations through general charge interactions and leads to changes in the conformation of charged additives (polymers, starches), fiber surface properties, and colloidal stability. Additionally, accumulation of specific ions contributing to conductivity often leads to issues such as scale formation, deposits, and strength and sizing losses. These specific ionic interactions are primarily associated with the ions related to hardness (Mg^{+2} and Ca^{+2}) and to Ba^{+2}, which often results in scale formation. For the Al^{+3} ion, because of its weak base character, its effect is from various hydrolysis products formed in all pH ranges of practical papermaking.

Conductivity or, in wider terms, ionic content of water can affect the papermaking process in several ways:

- Colloidal stability
- Fiber properties
- Performance of chemical additives
- Direct interactions between ions leading to scale formation

Colloidal stability is particularly important for paper machine wet-end operations. Electrical double-layer repulsive forces are fundamental in providing stability of colloidally dispersed matter. Increased ionic strength, or in practical terms, increased conductivity, compresses double layer thickness. This reduces repulsive forces between colloidal particles and leads to colloidal destabilization.

High conductivity and large variations of conductivity significantly affect the stability of wood pitch particles and make pitch control more difficult. This is especially important for pulps exposed to high pH in pulping or bleaching processes that are stripped of steric protection of sugars and rely solely on electrostatic stabilization. When troubleshooting pitch or stickies deposition problems, mills should consider conductivity shock, along with the traditionally culpable check points,

such as temperature shock, pH shock, and shear.

Increased water closure, more aggressive bleaching processes, higher deinked pulp content, and higher shear at forming sections on new and modern paper machines result in increased levels of contamination at the wet end of a paper machine. Several studies have discussed the degree of the expected buildup of detrimental substances resulting from an increased degree of closure [16-21]. Several papers also reported on the effect of conductivity on formation of tacky sickies deposits on machines using recycled furnish [22-24].

Reduction of repulsive forces from high conductivity is not limited to colloidal material. **Figure 1** shows the effect of salt concentration (conductivity) on swelling of unbleached kraft pulp fiber, illustrated by water retention value changes with different salt concentration [25]. Higher conductivity (salt concentration) reduced repulsion between charges on the fiber and decreased its swelling, resulting in lower water retention value. Changes in water retention value also affected the water removal in the press section (Fig. 1, right side).

Dobbins [26] reported results from a pilot machine study of an effect of increased mill water closure on machine operation and paper quality. Furnish for the study contained a high content of groundwood pulp (75%). Varying degrees of machine closure were simulated by adding certain amounts of calcium chloride ($CaCl_2$), Na_2SO_4, sodium chloride (NaCl), potassium chloride (KCl), and magnesium sulfate ($MgSO_4$) to the white water system. Even at the highest degree of ionic contamination of 20,000 ppm of salts, which exceeded the electrolyte level of a mill recirculating 100% of its water, paper still could be produced. However, cationic retention aids were found to have limited effectiveness. Some strength losses were observed and associated with the sheet ash increase from incorporation of the salts after water was evaporated.

Davison [27] studied an effect of pH, ionic strength, calcium ion, and aluminum ion impurities on the retention of fines and fillers using a mixture of hardwood and softwood
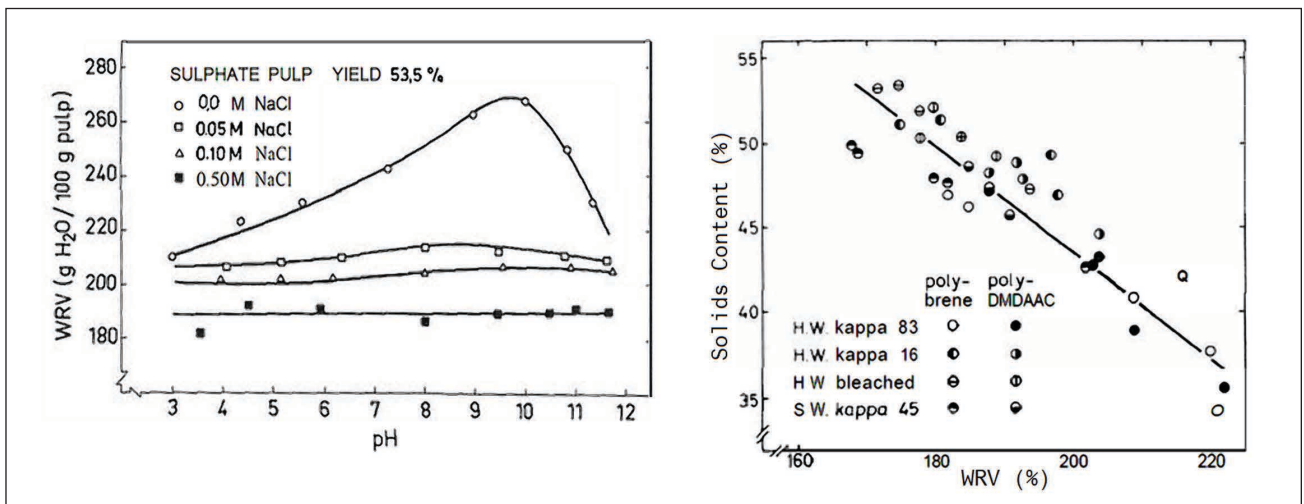
1. Effect of pH and conductivity on water retention value (left) and solids content after presses (right) (reproduced with the permission of Nordic Pulp and Paper Research Journal).

kraft pulps blended in a 3:1 ratio. Anionic and cationic retention polymers were negatively affected by increased concentration of either Na_2SO_4 or NaCl. Conductivity of the system was adjusted between 200 $\mu S/cm$ and 3000 $\mu S/cm$. An average drop of observed retention level between 5% and 18% was observed, at the same polymer dosage, for various retention polymers.

Lindstrom [28] studied the adsorption of cationic polyacrylamide polymers onto the surface of bleached softwood kraft pulp at different levels of simple electrolytes (NaCl, $CaCl_2$, and Na_2SO_4). Assuming the important role of fiber adsorption for the performance of polymeric retention additives, this paper provided fundamental answers about their performance under a high degree of ionic contamination. An increase in adsorption observed at the lower range of salt concentration was explained in terms of increased hydrodynamic size of polymer at more extended conformation. A further increase of salts concentration led to a decrease of adsorption and was attributed to ionic double layer compaction to reduce attractive forces between the polymer and fiber.

Buontempo [29] used a Britt jar technique to study the effect of ionic species on the performance of cationic flocculants with different charge densities. At a low starch dosage, all studied flocculants retained a high level of performance when conductivity was changed between 45 and 3000 $\mu S/cm$. For furnishes containing starch, all studied flocculants showed a marked decrease in performance when conductivity was increased. The authors concluded that the structure-performance relationship was not clear, and an empirical approach of screening a wide range of retention polymers and selecting the best program for given conditions was necessary in the process to select a retention program.

Because of the non-ionic character of the polyethylene oxide (PEO) molecule, PEO retention programs generally showed higher resistance to elevated conductivity and cationic demand that accompany increased water closure at a mill. A significant number of publications on water closure and contamination studied PEO – cofactor dual retention programs [3,4,30-33]. PEO-based programs typically showed strong performance of flocculation that might lead to sheet formation problems. Additionally, shear and chemical sensitivity (oxidizing agents, surfactants) contributed to the fact that PEO-based programs were not widely used.

Hulkko [23], Allen [3], Laivins [4,25], Polverari [24,26], and Trigylidas [25] reported negative effects of conductivity and cationic demand on retention programs using cationic polymers. In contrast, Miyanishi [34] reported that increasing levels of conductivity in wood-containing grades had little effect on the performance of cationic polymers (single, dual, and microparticle programs).

In principle, resistance of non-ionic polymers to increased levels of ionic contamination could be expected. However, the gap between non-ionic and cationic additives in the performance might be smaller than suggested in recent papers.

This, plus the complexity of performance requirements (combination of retention, drainage, formation, and printability), made cationic polymers a viable option, even in highly closed mill systems. With increased use of recycled fibers and higher levels of fillers in newsprint production, cationic flocculants remained a major component of the retention program for this grade.

Brown and Hart [6] recently reviewed the principles of application of conductivity measurement in monitoring and inferring black liquor losses from brown stock washing. The paper provided fundamental information on conductivity measurement and its interpretation to pulp mill application.

To quantify the effect of increased ionic loading in the system, Pruszynski [5,35] studied the sensitivity of various types of retention programs in thermomechanical pulp furnish with varying levels of several different contaminants and two pH levels (pH 5 and pH 7). Free drainage measurement was selected as a response. Simplicity of this measurement allowed performing large numbers of experiments to provide statistically significant results. The contaminant data generated for Na_2SO_4 and NaCl were of special interest because observed performance could be attributed solely to the conformational changes of retention polymer (little surface modification) because of the low affinity of sodium ion to the fiber. Reduction of the radius of gyration, or in simple terms, folding of the polymer chain because of reduced repulsive forces between charges segments on the polymer backbone, led to less effective bridging capabilities at higher conductivity levels. The authors presented results in terms of the percentage loss of drainage benefited from the retention program in the clean system as a function of ionic contamination (Eq. 3):

$$\Delta_{var}(\%) = \left[(V_{ct} - V_{00}) \Big/ (V_{ot} - V_{00}) \right] \times 100 = {\Delta V_{ct}} \Big/ {\Delta V_{ot}} \times 100 \quad (3)$$

where:

V_{00} - drainage for clean sample without retention program
V_{0t} - drainage for clean sample treated with studied dosage of retention program
V_{ct} - drainage of sample with selected concentration of added contaminant and treated with studied dosage of retention program

Figure 2 shows the relationship between the dosages of model salts in parts per million (ppm) and conductivity. Conductivities of samples were adjusted with NaCl at 460–25000 $\mu S/cm$ and Na_2SO_4 at 460–15000 $\mu S/cm$, when the concentration of ions reached 10000 ppm.

These conditions exceed the level of ionic contamination typically found in most papermaking systems. **Figure 3** (based on the extensive experience of the authors) shows typical conductivity levels for major types of paper machines.

Figure 4 presents an observed relationship between performance of a typical dual polymer retention program, based on the coagulant and cationic flocculant, with various levels
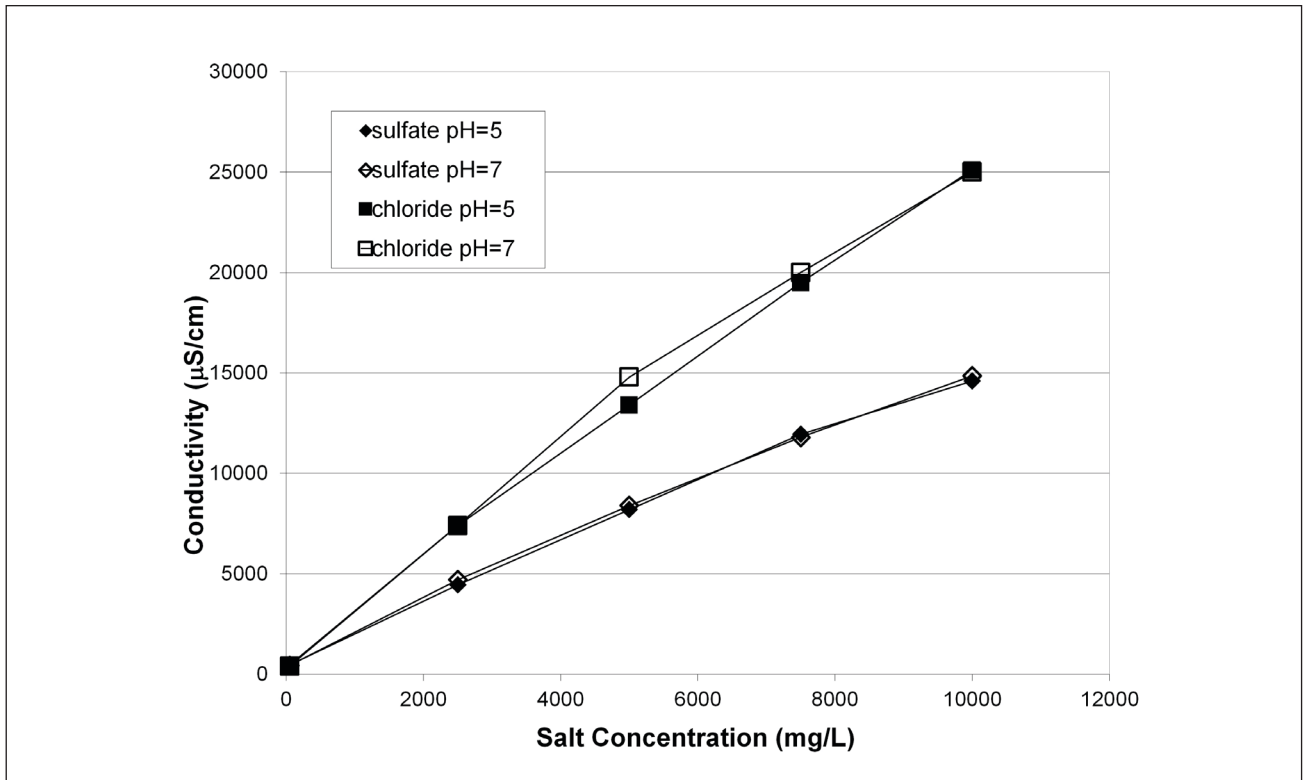
2. Concentration of ionic contaminants and measured conductivity in pH 5 and pH 7.
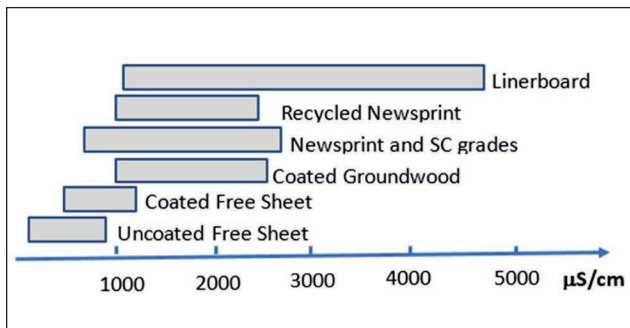
3. Typical estimated conductivity levels for major grades of paper and board.

of ionic impurities at pH 7. Looking at the dotted lines representing experiments with NaCl and Na_2SO_4, the gradual loss of drainage gain from polymer application in a clean system (100%) could be observed.

Similar trends could be observed for a single polymer program and for a dual polymer program with both high and low charge density cationic flocculants at pH 5 and pH 7.

Although the range of conductivities covered by these experiments extended beyond the typical value at a paper mill, loss of drainage and retention because of increased conductivity was significant. These data were consistent with the earlier work of Lindstrom [21], who studied the effect of sulfate and chlorides on adsorption of cationic polyacrylamides. The observed loss of drainage could be a combination of changes to polymer adsorption and its conformation.

When bentonite was added before low charge density cationic flocculant, a significantly different response of drainage to conductivity was observed [36]. In this case, an initial increase in drainage was observed, followed by its reduction at the higher salt concentrations. This observation confirmed a proposed earlier mechanism [37-39] that involved interaction between flocculant and bentonite platelets to stiffen the network and prevent conformational changes impairing bridging capabilities. Changing the order of addition by adding cationic flocculant first significantly reduced resistance to conductivity increases. This suggested that interaction between flocculant and bentonite needed to occur before flocculant adsorbed onto the fiber.

Based on results shown in Fig. 4, silicates are detrimental to single cationic flocculant and dual polymer programs. This effect is based mainly on their ability to act like ionic trash and to form complexes with cationic polymers rendering them inactive [40-42].

Gratton and coauthors [43] studied the effect of conductivity on retention and sizing. Several types of retention programs were evaluated in the laboratory. Observations from the laboratory were fully confirmed on a fine paper machine and indicated reduction of retention level, driven by lower filler retention (**Fig. 5**). At least in this paper machine system, a significant drop in retention was observed at conductivity changes of 2000–3000 $\mu S/cm$.

Reduced retention at the higher conductivity level was well illustrated by higher flow of cationic flocculant required to
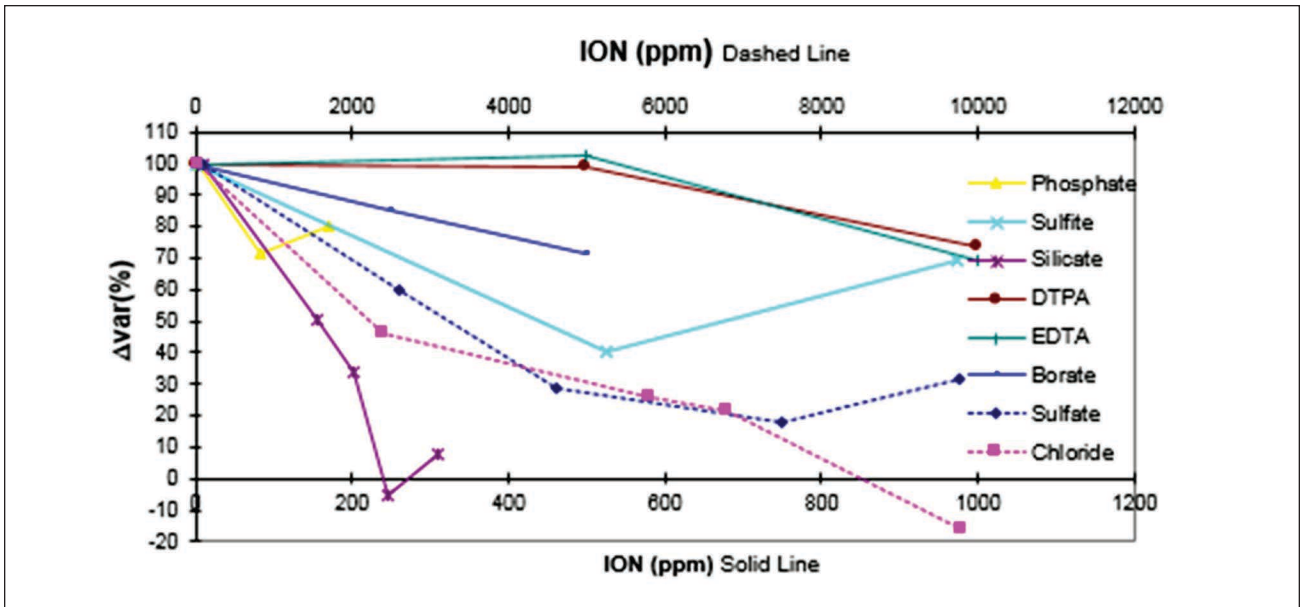
4. Effect of ionic contamination on the drainage loss (%) for the dual polymer program, based on coagulant and cationic flocculant measured in pH 7.
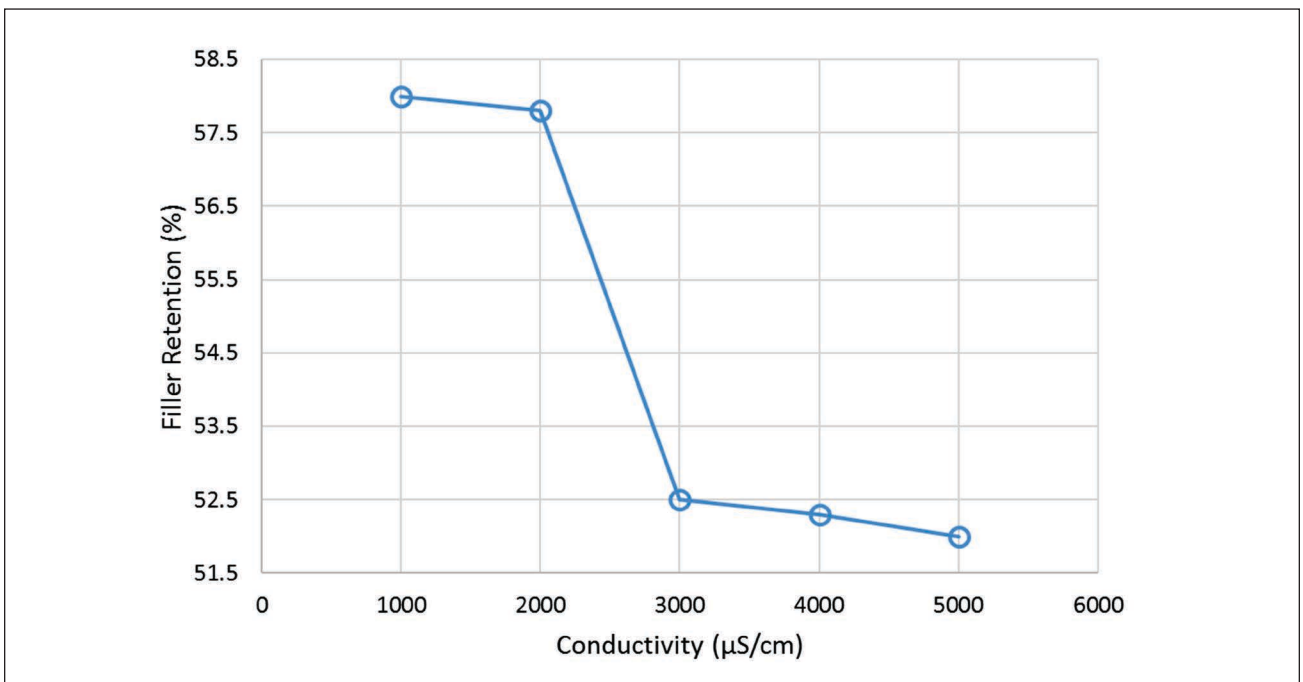
*5. First pass filler retention as a function of conductivity.*

maintain targeted white water consistency in the closed loop retention control application on the paper machine (**Fig. 6**).

The authors observed a negative effect of conductivity on AKD sizing [43]. **Figure 7** illustrates an increase of AKD dosage required to meet sizing specification with increasing conductivity levels.

Similar results were observed in a study of the effect of conductivity on the performance of cationic starches (**Fig. 8**). In this work, cationic starches were used for ASA

emulsification and sizing response was a measure of starch performance as emulsifier [44].

A negative effect of conductivity on various cationic starches was observed in terms of impaired sizing performance. Conductivity was varied in a wide range up to 5000 μS/cm. It was found that high levels of conductivity negatively affect the performance of cationic starches in terms of filler retention and internal sizing. All types of cationic starches, regardless of biological source, were affected. Starches with a high
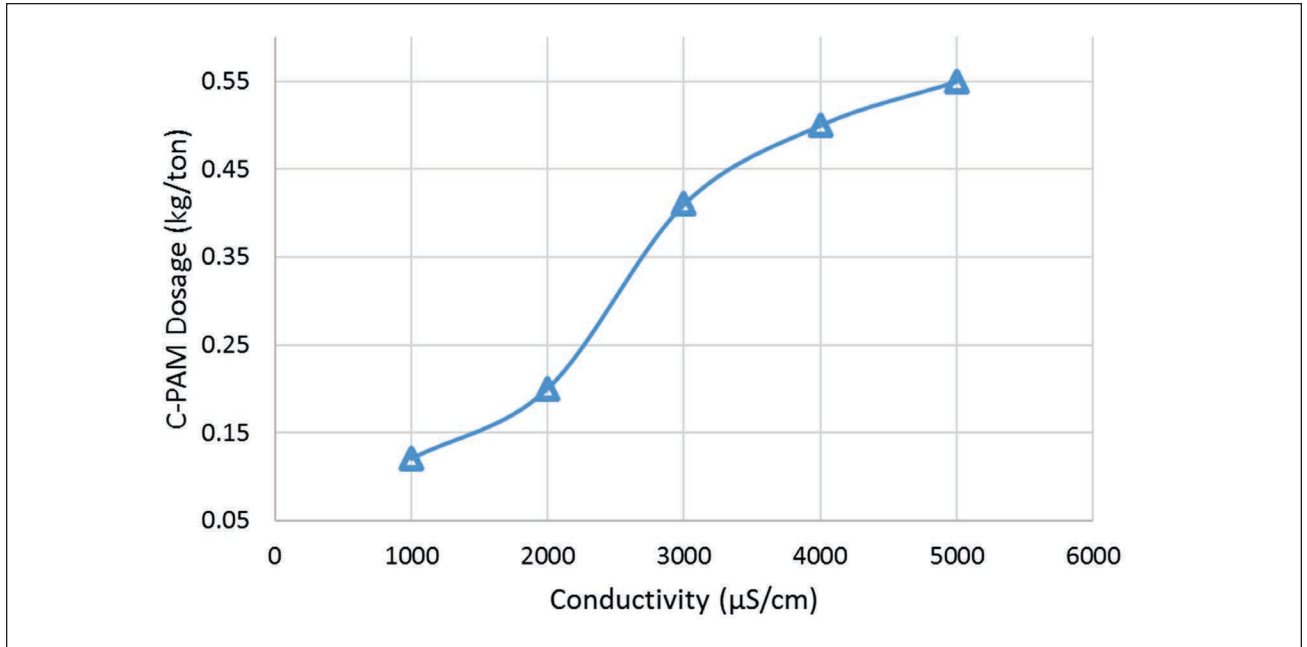
6. Effect of conductivity on the dosage of cationic polyacrylamide (C-PAM) required to reach target white water consistency.
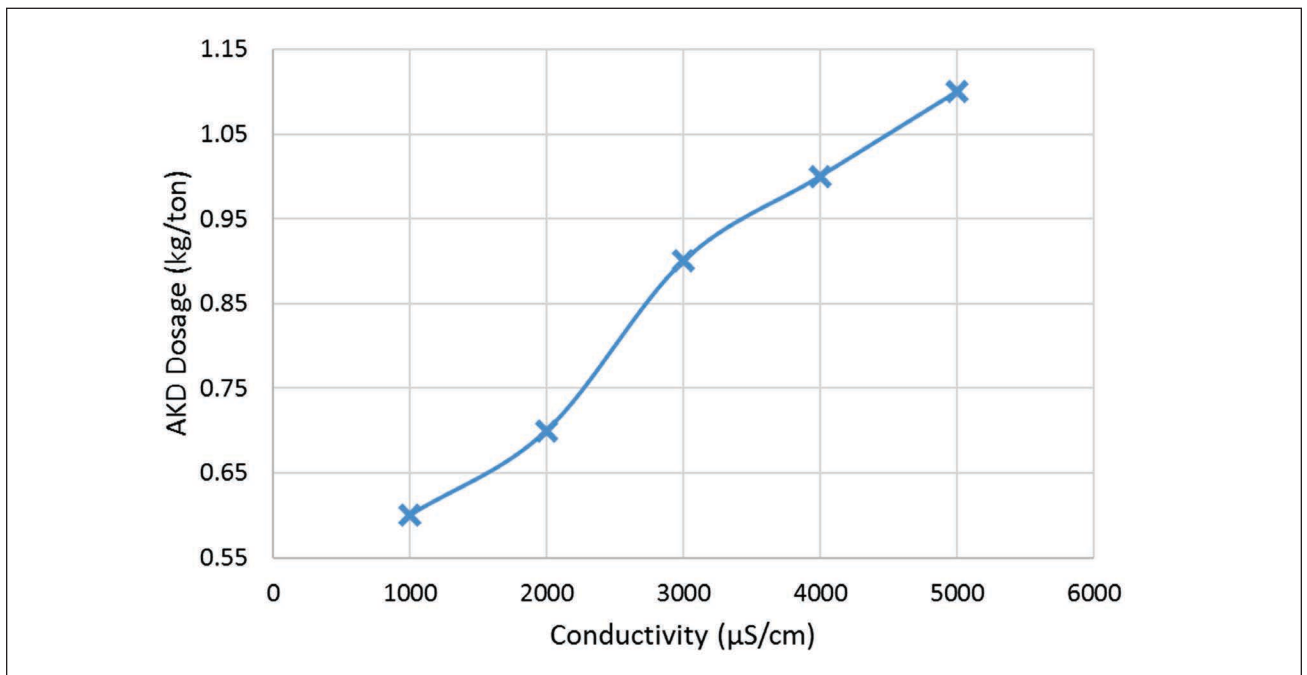

7. Effect of conductivity on dosage of alkyl ketene dimer (AKD).

degree of substitution (0.073) showed the best resistance to increased conductivity.

Zakrajsek [45] studied the effect of the level of dissolved and colloidal substances on paper sizing with a rosin/alum system. The effect of mill closure, conductivity, fresh water usage, and sulfate concentration were reported. Sizing response was expressed using $Cobb_{60}$ (g/m^2) value. The negative effect of a reduction in fresh water usage was studied in the range from 35 m^3/ton to 3 m^3/ton and was found to increase sharply when the fresh water usage was reduced to below 10 m^3/ton. Excellent relationships were observed between $Cobb_{60}$ value and conductivity, concentration of sulfate ion, and accumulation of unretained rosin sizing in the process water. In terms of conductivity, a change of 750–1050 μS/cm resulted in a 28.3–49.6 g/m^2 change of $Cobb_{60}$.

Conductivity affects water removal on the paper machine in various ways. By affecting the ability of retention aid to flocculate, conductivity reduces chemically induced free drainage
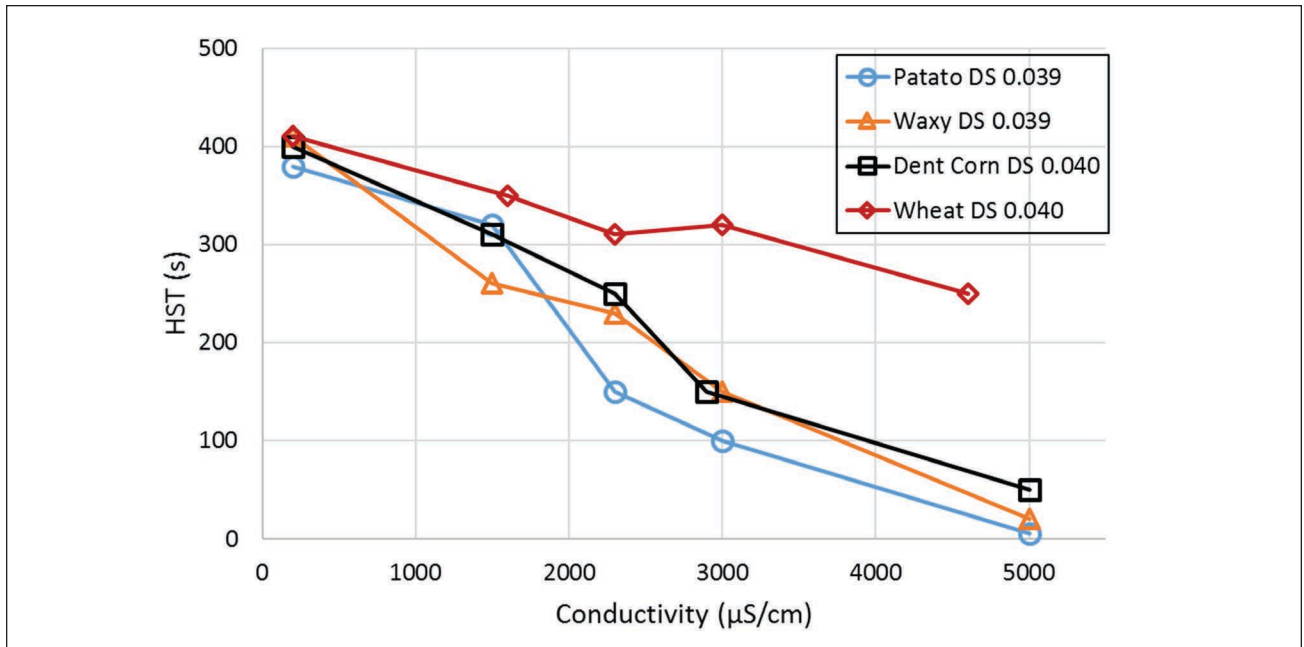
8. Effect of conductivity on performance of alkenyl succinic anhydride (ASA) emulsified with different starches.

or chemically induced freeness of the stock. On the other hand, high conductivity reduces fiber swelling, as measured by water retention value, and this becomes relevant when water closely bound to the fiber is removed in the press section. Thus, when conductivity increases, mills might see slower drainage early in the forming section, but increased water removal through the presses. Because the amount of water removed in the early forming section, affected by flocculation, is by far greater than in the press section, we might expect that increased conductivity will have an overall negative effect on the combined water removal process.

For machines operating at high conductivity levels, some mechanical or chemical corrective options may be used to reduce the negative effects of high conductivity. For example, molecular weight or charge density of retention aids or starch can be adjusted. In some cases, the configuration of the feed points can be changed. Converting from the typical dual polymer retention program, based on consecutive addition of coagulant and cationic flocculant, to a pre-mix configuration improved retention and drainage at high conductivity conditions. Authors suggest [42-45] that repulsive interaction between cationic charges of coagulant and flocculant, either still in solution or after initial adsorption to the surface, delays conformational changes of polymer to the extent of allowing for more effective flocculation. This increases performance at any level of conductivity, but is especially important at high conductivity levels that drive polymer coiling processes faster. Considering how fast flocculation processes are at high turbulence levels, this delay in polymer coiling does not have to be large to noticeably boost performance. **Figure 9** shows results of the transition from consecutive addition to pre-mix configuration for a high brightness newsprint machine. With

a total dosage of coagulant staying unchanged, the flow to the pre-screen position (1) was gradually reduced, with the balance mixed into the flocculant line (2). The paper machine operated with on-line consistency control, and because of improved performance, the dosage flocculant (3) gradually was reduced.

In addition, this paper machine producing high brightness supercalendered grade paper used a two stage (P-Y) brightening strategy—hydrogen peroxide followed by sodium hydrosulfite. This strategy required pH adjustment after alkaline hydrogen peroxide application, before application of sodium hydrosulfite. If the pH adjustment was not done properly, a significantly higher dosage of sodium hydrosulfite was required to reach the brightness target. The increased dosages drove system conductivity significantly higher than normal. Thus, conductivity variation from 800 $\mu S/cm$ to 4000 $\mu S/cm$ occurred and was observed to affect machine drainage and runnability. Although co-mixing coagulant to cationic flocculant brought an immediate relief to drainage problems, the mill also paid more attention to proper pH control between the two brightening stages.

Practical recommendations

Earlier discussion clearly illustrates that conductivity affects such fundamental aspects of paper machine performance as retention, drainage, and colloidal stability. It is therefore important that monitoring conductivity and developing response strategies should be a part of wet-end management. Understanding sources of conductivity and correcting its variability at the source will lead to improvement in paper machine stability. More closure unavoidably increases conductivity levels, but if the influx of electrolytes can be reduced, the
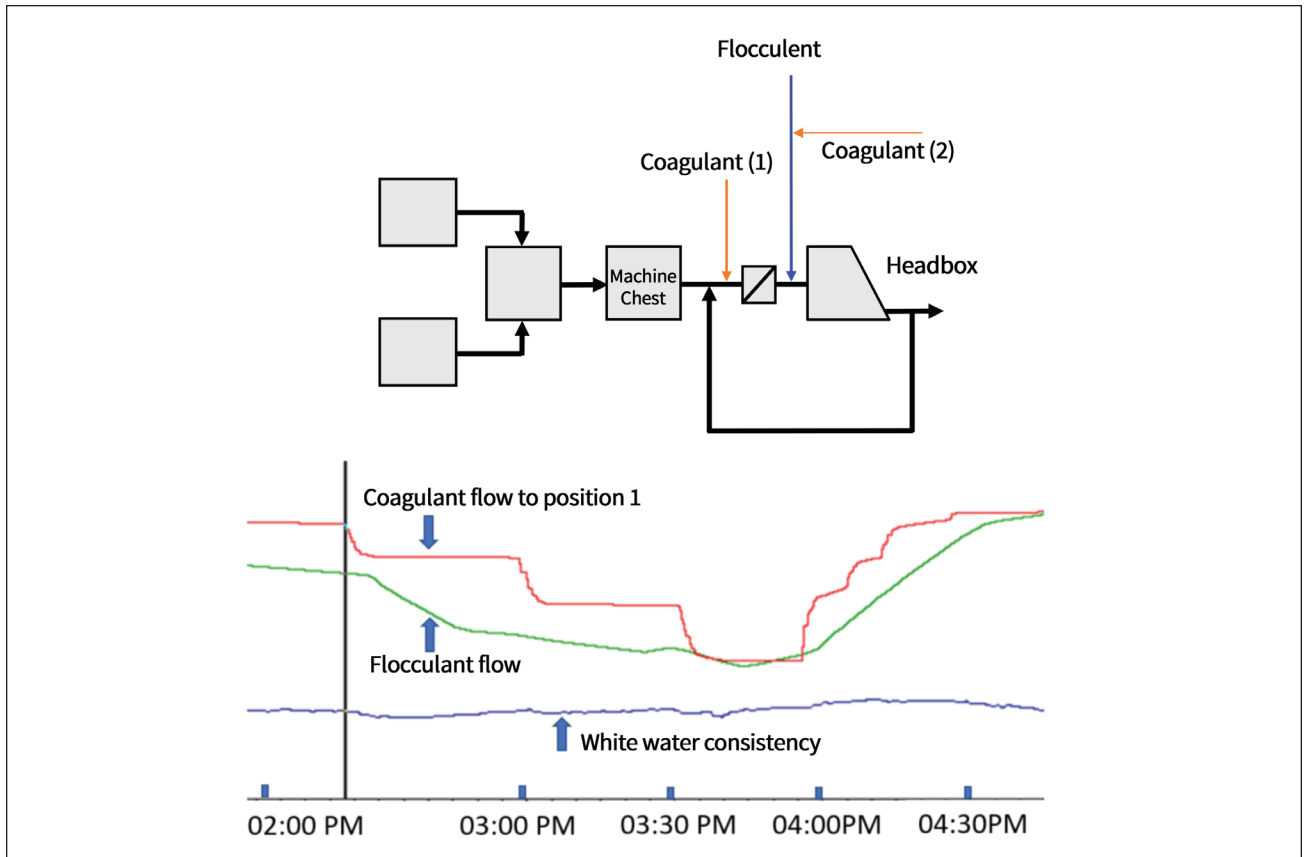
9. Improvement of performance of retention program with the move of coagulant feed point from pre-screen position to pre-mix with cationic flocculant.

conductivity increase at any given degree of closure will be minimized. Because simple ions have little affinity to the fiber, and through recirculation of machine water, conductivity levels tend to reach similar levels across the machine system. In the case of mechanical grades, with their integrated character, increasingly aggressive bleaching strategies, and limited pulp thickening opportunities, optimization of bleaching conditions to ensure the lowest possible usage of bleaching chemicals is the single most effective way to control conductivity levels. Monitoring conductivity on line in the headbox or tray should be a standard element of wet-end chemistry management. Changes in conductivity can provide an early warning of changes in drainage and press solid and draw variation, possibly allowing operators to prevent web breaks. Application of conductivity probes or frequent manual tests back in the system allow the mill to develop an understanding of the sources of conductivity and assist troubleshooting and improvement projects.

A conductivity probe is a simple, yet robust device that makes conductivity a common on-line measurement, even for older machines. If a mill does not have an on-line wet-end monitor or lacks staffing to run routine wet-end tests, conductivity measurement can be a useful tool to diagnose wet-end problems. For example, a containerboard mill running a mixture of unbleached kraft and recycled corrugated containers

had an issue of losing strength and sizing. The mill only had on-line pH, temperature, and conductivity sensors around the machine. After reviewing these data, the mill noticed a strong correlation between increased conductivity of unbleached kraft pulp and quality issues. The increased conductivity indicated possible high pulp mill carryover. Based on this information, the mill checked the brownstock fiber line and found operational issues around the washer. After addressing the issues, conductivity on the paper machine returned to normal levels. The strength and sizing values were brought back to target. From this example, we see that the change of conductivity, rather than its absolute value, was valuable to gain insight into a wet-end issue.

Hardness

Because of their affinity to fiber surfaces and formation of insoluble salts, the hardness ions Ca^{+2} and Mg^{+2}, in addition to contributing to general conductivity levels, can also be responsible for very specific operational problems.

Several anions react with Ca^{+2} or Mg^{+2} to form insoluble calcium or magnesium salts that often trigger deposits or scale on the paper machine. Such precipitation processes take place only if the product of reacting ion concentration exceeds the solubility product (K_{sp}) for a given temperature. Typical examples of such salts are barium sulfate, calcium oxalate, cal-

cium carbonate, and calcium phosphate. These represent the most common scales formed in paper mills. The pH alters the forms of weak acid in solution and affects scale formation potential. For example, formation of calcium carbonate and calcium phosphate scale requires participation of CO_3^{-2} and phosphate (PO_4^{-3}) ions, both present only in the high pH environment. Similarly, calcium oxalate precipitation requires the presence of oxalate anion — $(COO)_2^{-2}$, which is formed in significant amount at greater than pH 3 [46]. Papermakers may reduce the risk for troublesome scale related issues by understanding the ionic composition of water circuits and mineral components from wood sources, optimizing the use of alum, understanding the effect of pH on scale formation, and operating peroxide bleaching in a way to reduce oxalic acid formation.

The ability of calcium and magnesium ions to form insoluble salts with carboxylic acids leads to other operational and quality problems, such as pitch and hydrolyzed ASA deposition, which is further discussed in the following. These problems typically are raised at greater than pH 6, when the carboxylic acid functionality exists in its anionic form.

A product of ASA hydrolysis, dicarboxylic acid, forms tacky and troublesome deposits. Magnesium-related deposits with ASA were particularly difficult. Avoiding ASA hydrolysis through proper emulsification conditions (low pH, low temperature) and carefully controlling hardness are necessary to ensure successful, deposit-free application of ASA. Limiting the time for ASA to circulate in the machine water loop through elevated first pass retention is another strategy to reduce the potential for hydrolysis and consequent deposits. A small amount of added alum, even in alkaline papermaking systems, provides competition for reaction with hardness ions and helps in preventing this deposition.

Calcium and magnesium ions also can form insoluble salts with the acidic components of natural pitch. Pitch deposition problems triggered by this precipitation mechanism are especially troublesome at levels greater than pH 6, at which a significant fraction of the carboxylic groups (-COOH) exist in their anionic form (-COO-). Reducing pH reduces the concentration of carboxylate anion, but in the case of systems using calcium carbonate fillers, hardness levels will increase. Identifying and minimizing sources of hardness should be part of every pitch control strategy. Variation of the calcium cation concentration could be caused by the following factors:

- Natural variation of the hardness level in the incoming fresh water
- Decomposition of calcium carbonate filler, as a function of pH
- Calcium in wood species and other incoming raw material, such as recycled board produced in high hardness systems

Yuan [47] discussed several aspects of hardness interaction with the fiber. The authors described an effect of accumulation of metals ions on the wet end of the paper machine.

Despite the significant affinity of Ca^{+2} ions to the fiber surface, which loaded Ca^{+2} onto the paper product and removed it from the wet end, its concentration in the headbox often reached high levels. As discussed earlier, this is a function of the amount of hardness fed from short loop and system closure. Product (paper or board) manufactured in high hardness systems contains calcium salt after water is evaporated in the dryer section. When those products are recycled and repulped, the carryover calcium salt becomes an additional source of hardness for the upcoming papermaking process. The authors presented the isotherms of Ca^{+2} adsorption on kraft pulp and determined the exothermic and spontaneous character of this process (ΔH^0=-30.9 kJ/mol and $\Delta\Sigma^0$= -14.2J/molK). Thus, Ca^{+2} is easily adsorbed on the surface of the fiber and the bond is strong enough that it is not desorbed easily. Additionally, the amount of Ca^{+2} ion (0.0165-0.0167 mmol/g) was found to be close to half of the amount of carboxyl groups in the pulp used (0.0366 mmol/g), indicating 2:1 stoichiometry, with one Ca^{+2} ion reacting with two carboxylate functions. The negative effect of Ca^{+2} on the performance of cationic polyacrylamides in terms of retention and drainage was also reported and explained in terms of negative effect on available negative adsorption sites on the fiber. The same mechanism was also responsible for impaired strength development with cationic starch and sizing with AKD. The effect of Ca^{+2} on retention and drainage was also significantly higher than Na^+ at the same total conductivity levels. This indicates an additional contribution of fiber surface charge modification (in the case of Ca^{+2}) over general conformational changes related to conductivity.

SUMMARY

This report reviewed the effect of conductivity on the papermaking water system and on various aspects of paper machine operations. Conductivity can affect retention, drainage, press dewatering, sizing, strength, deposit formation, and scale. Based on the range of applications affected, conductivity needs to be closely monitored. Installation of conductivity probes in the tray should be an industry standard. Adding measures of conductivity to the paper machine distributed control system enables mills to build an understanding of how conductivity affects the paper machine performance and develop response strategies. For example, on-line measurement of conductivity might help operators predict changes in drainage, center roll release, pitch and stickies deposits, sizing, and strength. System conductivity profiles throughout the mill would allow engineers to identify major sources of conductivity and its variation. In most cases, conductivity is contributed by the pulp and bleaching chemicals, washing efficiency, and chemical additives for process and performance purposes. Opportunities for improvements in these applications should be reviewed to reduce their contribution to increased conductivity. Questions to consider include the following:

- Can required brightness level be reached with lower bleaching chemical consumption?

PAPERMAKING

- Is my inter-stage bleaching pH control strategy effective in reducing unnecessary pH swings and the need for large pH corrections?
- Is my pH control accurate enough to prevent brightness losses (mechanical pulps) that would lead to excessive dosages of bleaching additives?

These are some of the questions that when addressed reduce conductivity levels and reduce overall cost of mills operations.

Two important factors affect the level of conductivity: 1) the amount of ionic materials added to the system and 2) the amount of fresh water used. Opening the mill system and adding more fresh water, in many cases, is not a best option to reduce conductivity. In fact, with many mills targeting reduced water usage for sustainable growth, the focus must remain on reduction of the amount of ionic materials introduced to the system, application of best practices of counter-current water management, and generation of the waste stream with high levels of dissolved materials and low consistency.

Finally, with increased levels of mill closure, it is valuable to explore possible mechanical and chemical options to reduce negative effects of high conductivity on machine performance and sheet quality. The need to focus research in this area, to include conductivity and other contaminants, will continue. **TJ**

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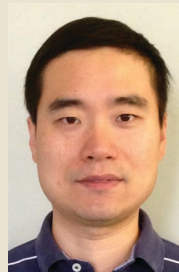47. Yuan, G., Dai, H., Ye, C., et al., *BioResources* 6(3): 2790(2011).

ABOUT THE AUTHORS

We did this review because papermakers might overlook the benefit of conductivity measurement. This study summarizes previous research and shares additional experience. The most difficult part of the research was finding mill examples that fit the theoretical areas we were discussing. Although we have seen them several times, finding well-documented examples was time consuming.

Although conductivity has been used for several years as a control parameter, it is not particularly well understood and not particularly exclusive to the properties it is being used to control. Stabilized conductivity is more manageable than low, yet varying conductivity.

Mills can benefit from this study by better understanding the principles of conductivity measurement and its limitations and make use of the information for better wet-end operation.

Our next step is to attempt to stabilize conductivity and reduce its overall effect on paper machine performance.

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