Water chemistry challenges in pulping and papermaking – fundamentals and practical insights: Part 2: Conductivity, charge, and hardness

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ABSTRACT: Although water is essential to the papermaking process, papermakers often overlook its importance and focus on fibers, fillers, and chemical additives. A better understanding of water properties and chemical interactions associated with water at the wet end leads to a sound foundation for high-quality paper production and smooth operation.

Water is an excellent solvent for ionic substances, both organic and inorganic. These substances contribute to system conductivity, charge, and hardness and significantly impact the papermaking process. Part 1 of this paper, published in *TAPPI J.* 21(6): 313(2022), discussed fundamental water properties, water chemistry, and the impact of pH on pulping and papermaking operations. In this paper, we review definitions, sources, and the typical symptoms of the effect of conductivity, charge, and hardness on the productivity of the papermaking process. Sources of conductivity, charge, and hardness impacting these factors, measurement methods, and available correction strategies for their control are also discussed.

Application: By gaining comprehensive and fundamental understanding on how conductivity, charge, and hardness affects wet end chemistry, mills can be better prepared to address water challenges on a paper machine for more efficient operation.

The papermaking process involves the use of large quantities of water. Water is an essential medium for all relevant chemical and mechanical interactions between pulps, fillers, dissolved and colloidal materials, and chemical additives used to make all paper products. Frequently, water is the single most significant raw material employed in an integrated pulp and paper mill. Typical headbox consistency is between 0.5%–1 % so that more than 99% of the material used by the papermaker to make paper represents water. Unfortunately, it is still common for a papermaker to underestimate the water component's relevance to machine performance and paper quality.

Several current industry trends make a better understanding of water chemistry increasingly crucial for paper production and product quality. The paper industry is making a substantial effort to reduce water usage to minimize cost, energy consumption, and environmental footprint. Water closure and reuse are common approaches to save water, resulting in significant changes in the quality of process water. In most cases, these changes are detrimental to water quality and reduce the margin of safety for process disruption in overall process management.

Changes in pulp quality, virgin and recycled, represent another significant contributor to shifting water quality. Cost considerations, quality requirements, process washing limitations, grade development requiring new pulp sources, and water usage reduction lead to the increasing impact of pulps on overall water quality. Therefore, understanding water chemistry fundamentals, staying prepared to face these trends, and finding practical ways to shelter machine operations from potential problems are more critical now than ever.

Understanding the chemistry of a paper machine's water circuits is crucial to stable operations, high and consistent product quality, controlled cost, and effective utilization of assets. Papermakers must do more to make consistently high-quality products with often declining fiber quality and less freshwater. There is little room for deviation from chemical best practices. The paper machine's chemical environment needs to be optimum and stable. In addition, potential incompatibilities between different chemicals should be well-understood, avoided, or reduced [1].

The papermaker must adequately control the paper machine's wet-end chemistry holistically. These controls must incorporate the intricate relationships between various wet-end parameters. Such decisions are only possible if the fundamentals of chemical factors are understood. Recently, papers dedicated to water basics, pH, and conductivity [2,3] were published that included basic definitions, typical values, impact on machine performance, and avail-

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able control strategies.

Based on the significant interest generated by these papers, the authors decided to publish a review of water properties and related wet-end chemistry. Herein, basic definitions, typical values, relationships between discussed parameters, application of best practices, and control strategies are reviewed. We hope this information helps equip papermakers with the tools to face increasing wet-end chemistry challenges.

DISCUSSION

Detrimental substances

Detrimental substances that accumulate in the paper machine water system can significantly impact machine operations by directly affecting conductivity and charge. These substances can be divided into two groups:

- *Simple salts* are measured by conductivity. Salts have a minimal affinity for the formed web of paper, and their accumulation is closely related to the degree of closure of machine water circuits.
- *Polymeric anionic substances* are responsible for the increased cationic demand of the system and excessive consumption of cationic polymers and other cationic additives.

The impacts of each of these groups are covered in detail below.

Conductivity

Conductivity measures the ionic content of the liquid in terms of its ability to conduct electrical current. Conductivity is defined as the reciprocal of the resistivity, normalized to a 1 cm³ liquid (in most cases water) at a specified temperature and reported in µS/cm. In simple terms, conductivity is a function of ion concentration, type, and temperature (affecting liquid viscosity). Brown and Hart recently discussed conductivity in a detailed review [4]. It is essential to realize that the contribution of various ions to system conductivity varies and is best described by the specific

| Ion	Specific Conductance, $\Omega^{-1}cm^2mol^{-1}$
H_3O^+	349.80
HO^-	197.80
Na^+	50.11
K^+	73.52
½ Mg^{+2}	53.06
½ Ca^{+2}	59.50
Cl^-	76.25
HCO_3^-	44.50

H_3O^+ = hydronium ion; HO^- = hydroxide; Na^+ = sodium ion; K^+ = potassium ion; Mg^{+2} = magnesium ion; Ca^{+2} = calcium ion; Cl^- = chloride ion; HCO_3^- = hydrogen carbonate ion.

I. Specific conductance of typical ions in papermaking.

conductance expressed in $\Omega^{-1}cm^2mol^{-1}$. Simple, mobile ions with high charge density contribute most to the system conductivity (**Table I**).

Systems at neutral pH display the lowest background conductivity. At pH = 7, H_3O^+ and HO^- ion concentrations are low and equal to 10^{-7} mol/L. At pH = 2, the concentration of H_3O^+ equals 10^{-2} mol/L, resulting in a significant increase in conductivity compared to the system at neutral pH. A similar conductivity rise occurs when pH increases above the neutral value. These examples illustrate how the change in pH value affects conductivity even in the absence of other ionic species. The impact of pH on other wet-end chemistry parameters is discussed in Part 1 of this series [2].

Xu, Pruszynski, and Hart [3] discussed the sources of ions contributing to conductivity in detail. These ions enter a paper mill with pulp, water, and papermaking additives. The conductivity between papermill circuits varies widely depending on the paper grade and the degree of mill water closure [5]. **Figure 1** illustrates the typical paper mill conductivity range by paper grade. In the case of linerboard,
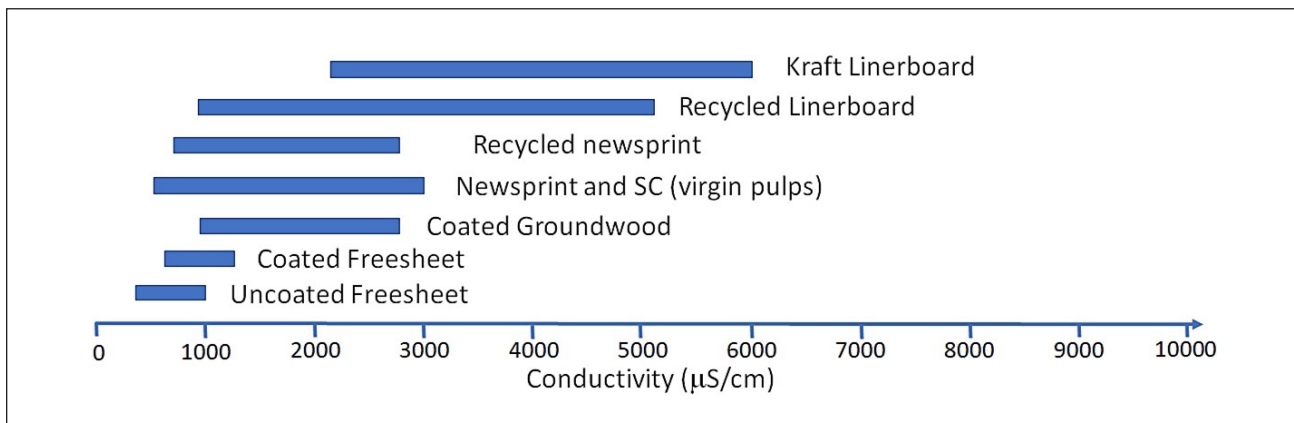
1. Typical conductivity ranges of paper and board mills by grade (SC = supercalendered).
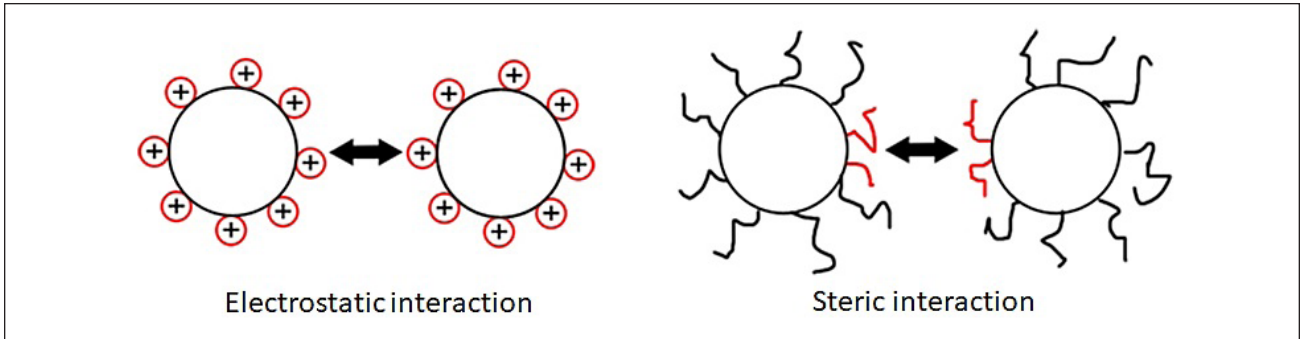
2. Electrostatic and steric stabilization of colloidal systems.
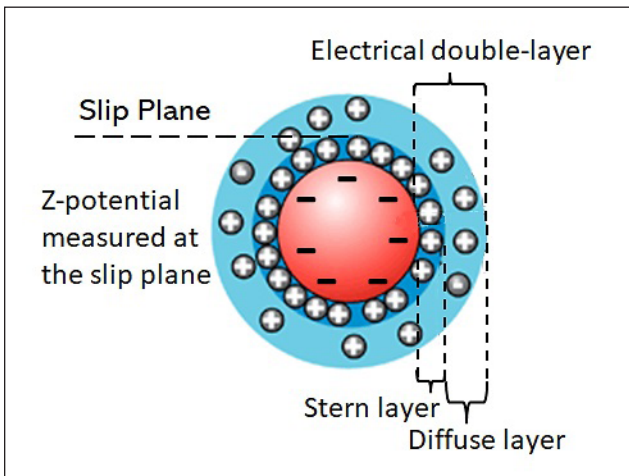
3. Colloidal particle double-layer model: Stern and diffuse layers.

the conductivity is typically higher for kraft linerboard than for recycled linerboard systems.

High conductivity generally negatively impacts a wet-end additive's performance, especially when it reaches an approximate level above 3000 µS/cm [6]. Sudden changes in conductivity may cause issues, even at lower conductivity levels, and compromise the performance of many typical wet-end additives, including but not limited to starch, size, and polymer for strength, drainage, and retention [7,8]. Very high levels of conductivity can even negatively impact fiber-to-fiber bond strength.

Colloidal stability, so crucial in papermaking, results from electrostatic repulsion or steric protection, as depicted in **Fig. 2**. Electrostatic interactions, either attraction between opposite charges or repulsion between the exact charges, play a critical role at the wet end of the paper machine.

How is the colloidal particle formed? A charged solid core attracts oppositely charged ions from the solution in an aqueous environment. The first layer of the oppositely charged ions is strongly attracted to the solid core's surface and forms the so-called Stern layer. The colloidal particle travels with the Stern layer surrounding the particle core. The core of a colloidal particle may be liquid (emulsion) or solid (dispersion). Since the Stern layer does not neutralize all negative surface charges, more oppositely charged ions form a loosely associated diffuse layer, as illustrated in **Fig. 3**. This structure is known as a colloid's electrical double-layer. The boundary between the Stern and diffuse layers represents the so-called slip surface. The charge measured at the slip layer is called zeta potential and defines the electrokinetic properties of the colloid.

Colloidal particles can interact with each other when their double layers overlap. The double-layer thickness expands at low conductivity and shrinks at high conductivity (**Fig. 4**). The ionic strength of the solution describes the concentration of ions (cations and anions), correlates with the conductivity, significantly impacts the double-layer thickness, and influences colloid stability and interactions between ions.
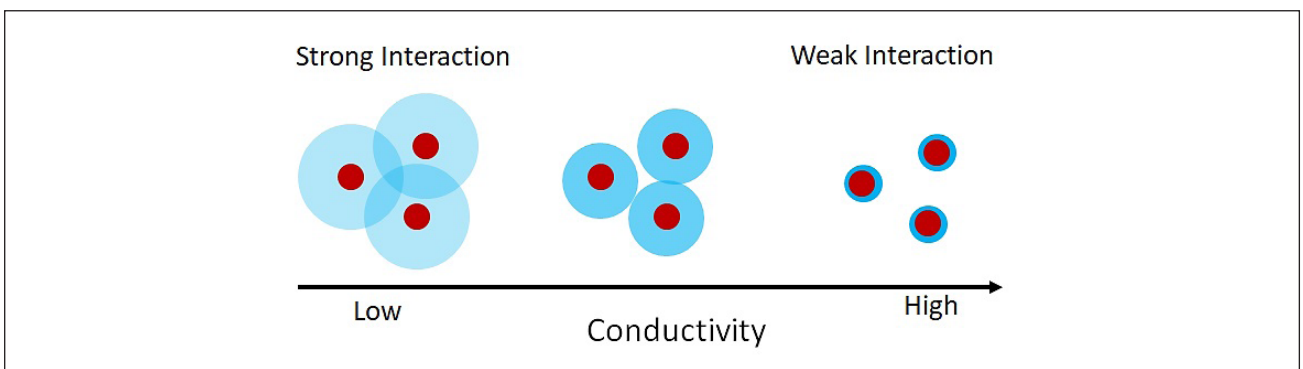
4. Colloidal interaction and double-layer thickness as a function of conductivity.
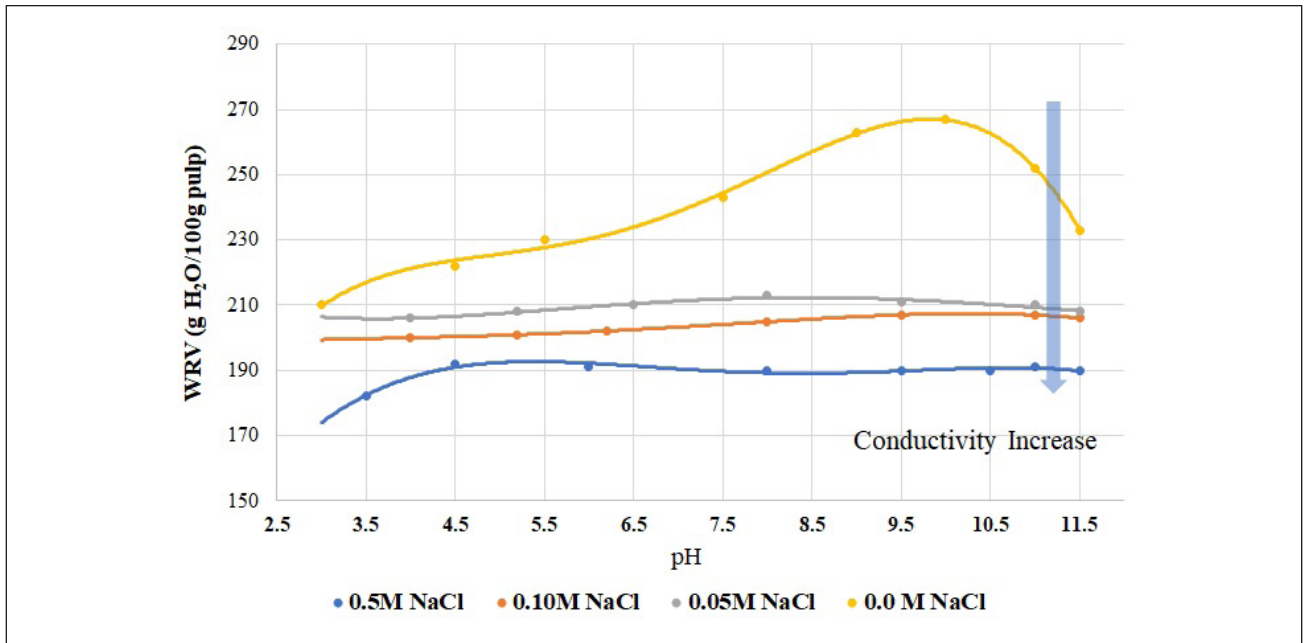
5. Impact of pH on fiber swelling measured by the water retention value (WRV).

Interactions between the ions, attractive or repulsive, depending on the level of the ionic charge and the concentration of ionic species in the water phase, are measured as conductivity. Repulsive forces between anionic colloidal pitch particles are responsible for stable pitch dispersion. Attractive forces between various cationic additives and anionic fibers/fines are responsible for the performance of cationic retention aids, fixatives, sizing agents, and strength additives. Loss of effectiveness of papermaking additives due to increased conductivity can negatively impact colloidal interaction at the wet end. Higher conductivity screens charged particles and reduces their repulsive and attractive forces. High levels or sudden conductivity changes may result in pitch particles' destabilization, deposits, retention and drainage losses, low efficiency of sizing applications, and lower strength.

Figure 5, from work by Lindstrom [9], presents a good illustration of how conductivity impacts charge interactions among cellulose material in a solution. In our earlier discussion, we established the link between pH and charge. Higher pH results in a higher surface charge on the fiber. Stronger repulsive interactions increase fiber swelling as measured by water retention value (WRV), which is represented by the blue line. Higher conductivity reduces the impact of increased pH on fiber swelling. The repulsive interaction between anionic charges is lower at higher conductivity (higher concentration of sodium chloride [NaCl]), and the swelling measured by WRV is less dependent on pH.

Though high conductivity reduces the efficiency of paper additives, running a machine efficiently at high but stable conductivity is still possible. Serious runnability issues arise during sudden swings in conductivity. Therefore, in systems prone to conductivity swings, an appropriate conductivity monitoring strategy must be the first step to understand and potentially address conductivity-related issues.

Papermakers must investigate and understand the source of high conductivity levels and variability in their systems to successfully mitigate their negative impact on operations. Several sources of conductivity and conductivity swings exist in the mill. Questions posed below help to pinpoint the solutions in the specific case:

- Is it possible to better wash pulp to reduce pulping chemical carryover?
- Is it possible to reduce the addition of papermaking additives contributing to conductivity?
- Is it possible to sort recycled pulp bales to reduce conductivity variation?
- Is it possible to minimize bleaching chemicals for mechanical pulp application?

The well-controlled wet-end operation should include conductivity measurement online in the whitewater tray and the stream responsible for its highest level or most variability. Real-time information about the change in conductivity provides the papermaker with early warning about the potential issues listed previously. Building the database of the machine responses to varying conductivity, often associated with grade changes, will allow action steps to minimize their impact on machine performance and product quality. Pruszynski and Jakubowski [8] documented reduced drainage at higher conductivity for several different retention programs.

Figure 6 illustrates the impact of conductivity on the drainage of TMP-based furnish treated with two different retention programs:
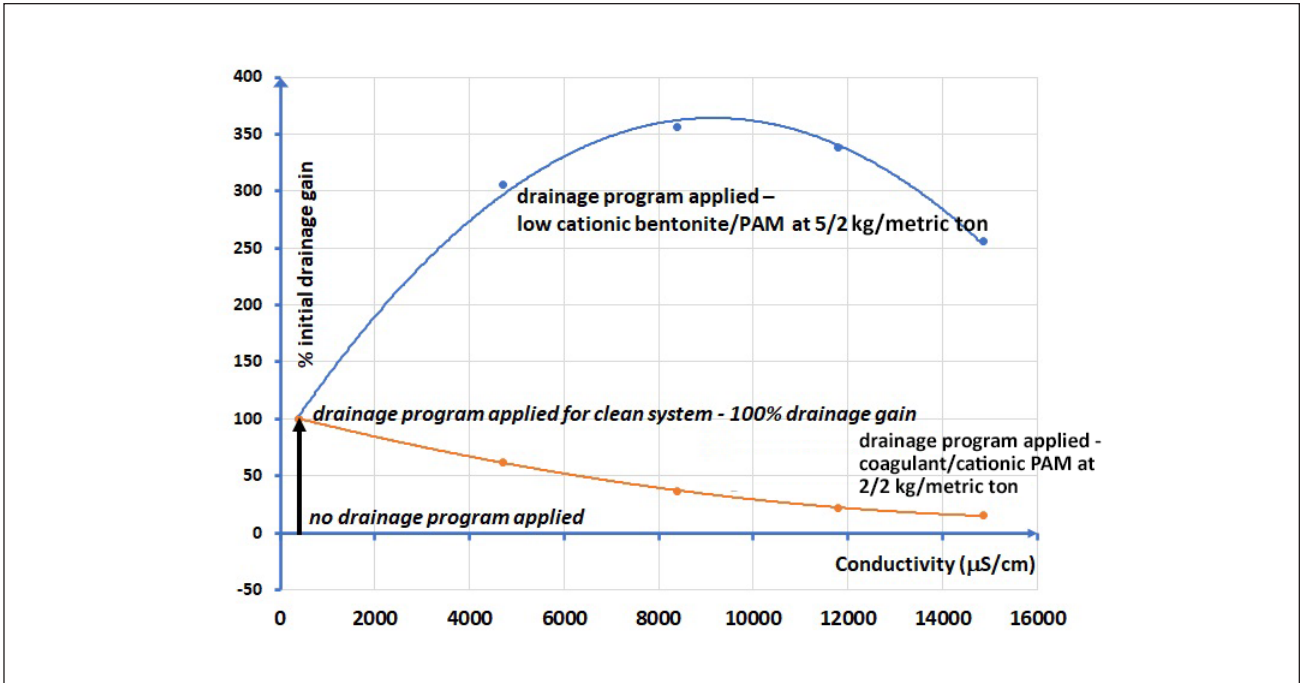
6. Impact of conductivity on performance of retention programs in thermochemical pulp (TMP)-based furnish (PAM = polyacrylamide).
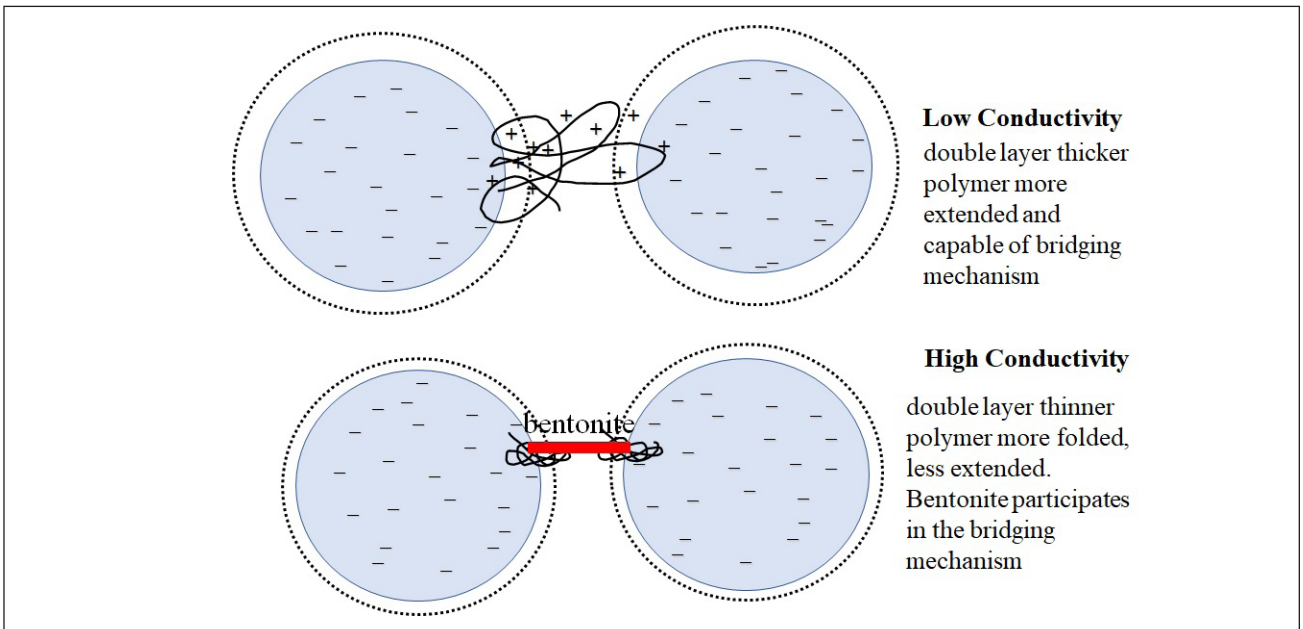

7. Illustration of synergy between bentonite and polyacrylamide flocculant.

- Dual retention polymer program consisting of sequentially added coagulant and cationic polyacrylamide flocculant, both at 2 kg/metric ton dosage (orange line)
- Bentonite followed by the low charge cationic polyacrylamide at 5 kg/metric ton and 2 kg/metric ton, respectively (blue line).

The 100% point on the drainage axis represents the gain in drainage recorded for low conductivity ("clean") samples treated with the selected retention program. In the case of the typical dual polymer program, despite maintaining the same level of treatment, increasing conductivity (NaCl addition) resulted in erosion of the drainage benefit observed for the clean sample. In the case of the combined bentonite (low charge cationic polymer program, blue line), the treated sample's drainage increased further, despite higher conductivity. Based on these observations, Pruszynski [10] proposed
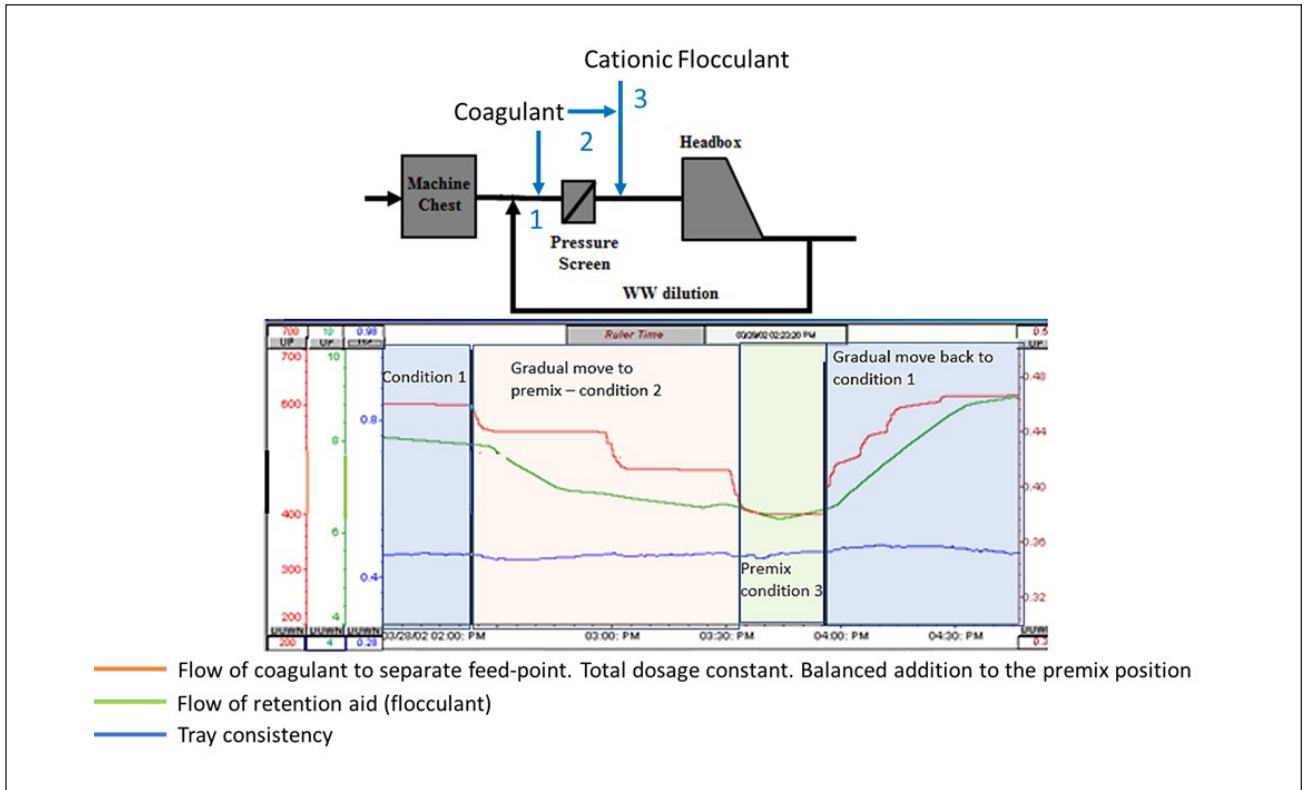
8. Example of premix application of coagulant and cationic flocculant in a high conductivity system (WW = white water).

a mechanism explaining bentonite performance (**Fig. 7**). During the swelling process, bentonite forms thin platelets with the cationic charges on the edges and anionic charges on the faces, which interact with polyacrylamide retention aid. The coiling of the polyacrylamide polymer chain at high conductivity conditions, responsible for loss of performance in the case of the dual polymer program, is prevented by the participation of the rigid bentonite platelets in the bridging flocculation mechanism. This mechanism resembles the formation of the polyelectrolyte complex (PEC) with one inorganic and amphoteric in nature. The recent paper by Khan et al. [11] reported the improved performance of the PEC as a drainage aid at higher conductivity conditions. This observation is consistent with the performance of the bentonite-polyacrylamide program presented in Fig. 6. The reduced repulsion between the retention polymer's charges leads to its flat, collapsed conformation, and lowers its performance in terms of flocculation and drainage. In practice, reduced free drainage on the forming section leads to increased moisture entering the press section, affecting draws, center roll release, steam consumption, or paper/board machine speed. With the on-line conductivity measurement, the papermaker may proactively monitor roll release and draws, change the roll release program's dosage, and reduce break frequency.

It is hard to fully control conductivity sources. Alternatively, papermakers may consider more robust papermaking programs to maintain chemical efficiency. The tradi-

tional cationic wet-end starch performance is known to suffer when conductivity rises [12]. This loss of performance results in lower retention, lower dry strength benefits, sticky deposits, and center roll release issues. A significant amount of research has been done to maintain starch performance against increased conductivity [13]. It has been reported that converting pure cationic charge structure to amphoteric, a combination of a positive and negative charge, helped maintain starch performance in high conductivity wet-ends. Similarly, amphoteric polymeric additives, such as dry strength [14], retention aid [15], and drainage aid [16], also showed their capability to hold performance in more challenging conductivity conditions. The application of bentonite, combined with an anionic or low charge cationic flocculant [10] (Fig. 6, Fig. 7) and an application of polyethylene oxide (PEO)/cofactor systems have also been successfully applied in highly contaminated systems [17].

Besides the alternative molecular structure and charge of additives, papermakers also can change the sequence of additive feeding points to mitigate the negative impact of high conductivity. The typical dual polymer retention program in mechanical grades involves the consecutive addition of coagulant and cationic flocculant, represented by feed points 1 and 3 in **Fig. 8**. The dosage of coagulant to position 1 is represented by trendline 1. During the on-machine trial, the dosage to feed point 1 was gradually reduced by premixing the coagulant with the flocculant (feed
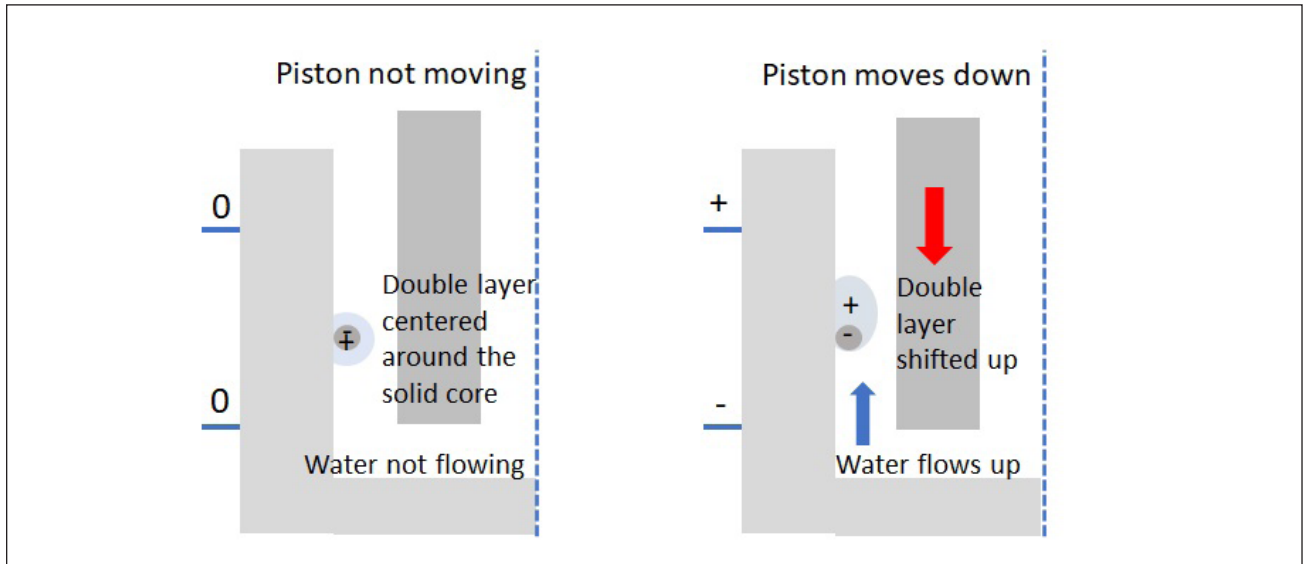
9. Endpoint detection of colloidal titration using streaming current (or streaming potential) piston device.

point 2). The total dosage of the coagulant during this transition remained unchanged. The flocculant dosage was controlled in the closed loop with the whitewater consistency sensor during this experiment. Relocation of the addition point of coagulant into the flocculant line resulted in the reduction of flocculant flow (green trendline) required to maintain the target white water consistency (blue line). Similarly, the premix addition of coagulant and cationic flocculant significantly improved drainage on the newsprint machine in Scandinavia that operated at extremely high conductivity levels due to a very aggressive pulp brightening process [18].

CHARGE

Two types of charge concepts exist in papermaking. Papermakers must distinguish between the two charge concepts: charge demand (for fines and colloids in water), and zeta potential (for colloids and fiber surface). In mill practices, these two charge measurements are not always clearly differentiated. Many mills do not measure the type of charge critical to their operation. For example, in board mills, the surface charge on the fibers should have a high significance. Still, mill personnel typically measure and try to control the cationic demand in a soluble fraction. An attempt has been made to clarify this confusion by discussing the various charge-related measurements.

Charge demand

Charge demand describes the total content of charged substances in the sample, including fibers, fines, and colloidal and dissolved substances (CDS). Academic studies tend to filter fibers out of solution before performing this measurement, while mill operations often test the stock sample as collected. Measurement of the charge demand always involves titration with a standard solution of the oppositely charged additive of known concentration. Hubbe and co-authors reviewed the origin, types, and measurement of the charge demand in papermaking waters and suspensions [19]. Since the anionic charge is dominant in papermaking furnishes, these systems typically display various levels of cationic demand as measured by titration with the standardized solution of the cationic polymer, typically 10^{-3}N poly-DADMAC. The result of these titrations is then reported based on volume (mEq/L or µEq/L) or, after correcting by sample consistency, on the mass of solids (mEq/g or µEq/g).

With the increased use of recycled fibers (both broke and post-consumer recycled paper), which may already contain a fair amount of cationic agents, some mills may reach the cationic charge on the wet end and display anionic demand. An anionic titrant (potassium polyvinyl sulfonate [PVSK]) is used for the titration.

The point on the titration curve where the amount of cationic polymer solution neutralizes the negative charge of the titrated sample (isoelectric point) is known as the titration endpoint. There are several endpoint detection choices, but the piston devices operating on the streaming potential principle are the most popular. Several types of piston streaming current (or streaming potential) devices are used in the industry. The mechanism of their operation is explained in **Fig. 9**.

The measuring principle has been well-reviewed in the literature [20-22] and will be briefly discussed here. The negative core of the colloidal particle attaches to the surface of the device wall. In the absence of movement, the Stern layer of positive counter ions is symmetrically distributed around the attached solid particle. When the device's piston moves down, it generates the up flow of the sample, causing the upward shift of the Stern layer surrounding the immobilized attached particle, generating streaming current
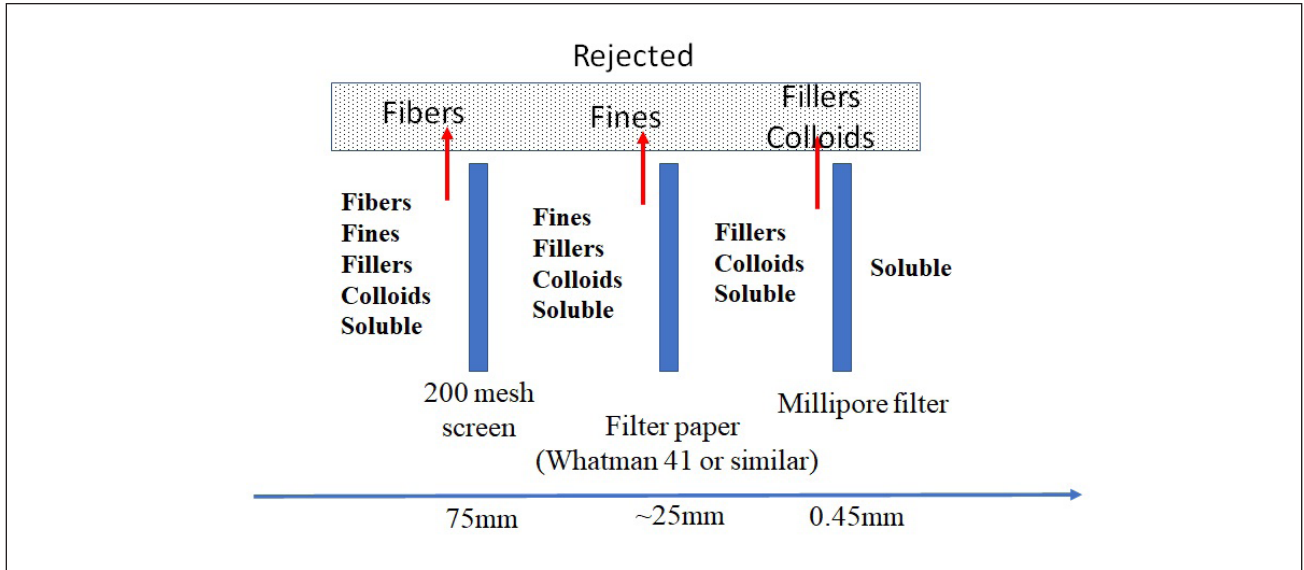
10. An example of the typical fractionation of the original stock sample for cationic demand determination.

measured by the electrodes placed in the chamber. The opposite polarization is generated when the piston moves up. Proper synchronization of the detection of the potential with the movement of the piston allows for continuous, steady measurement of the streaming potential (or current). Adding cationic polymer neutralizes the negative charge in the sample, including particles attached to the cell wall. When all the negative charge in the sample is neutralized, no streaming current is generated; we are at the isoelectric point and have reached the end of the titration.

Authors frequently observe that mills and suppliers assign the negative sign improperly to cationic demand values. It creates confusion in communication between mills, even in the same organizations. Cationic demand represents the demand for cationic polymer required for total charge neutralization; therefore, it is a positive value. For example, if the cationic demand for a headbox sample is 100 µEq/L, we need 100 µEq of cationic charge to completely neutralize 1 L of the headbox sample. In the typical measurement, Eq. 1 is used to determine cationic demand:

$$N_1 V_1 = N_2 V_2 \tag{1}$$

where:

N_1 = charge concentration of the sample, which is unknown
N_2 = charge concentration of the titrant, which is typically 0.001 N (0.001 Eq/L) poly-DADMAC
V_1 = volume of the sample, which is typically 10 mL or 0.01 L
V_2 = volume of the titrant solution added to reach the endpoint

Using typical values for the most common industry equipment and procedure:

$$N_1 = \frac{N_2 \times V_2}{V_1} \tag{2}$$

If the volume of 10^{-3} N poly-DADMAC was V_2 = 5 mL (0.005 L), the typical calculations are:

$$N_1 = \frac{0.001(\frac{Eq}{L}) \times 0.005(L)}{0.01(L)} = 0.0005\left(\frac{Eq}{L}\right) \, or \, 500(\frac{\mu Eq}{L}) \tag{3}$$

In case 10 mL of 10^{-3}N poly-DADMAC was used to reach the titration endpoint for the 10 mL sample, the cationic demand in mEq/L may be calculated by multiplying the volume of titrant in mL by the factor of 100.

The cationic demand measurement provides information about the sample's ability to consume a cationic charge. Proper sample preparation through various screening or centrifuging procedures allows measuring the cationic demand of a specific fraction of the furnish (fibers, fines, colloids, or soluble fraction). Typical sample fractionation techniques recommended for preparing individual sample fractions are listed in **Fig. 10**.

There are no standard procedures for sample fractionation. Some mills centrifuge their sample before measurement of the cationic demand of the soluble/colloidal fraction. Whatever the sample preparation may be, it must be written in the laboratory procedure for the mill and strictly followed by the mill and all suppliers, as it allows for effective and seamless communication of the results. The cationic demand data are extremely valuable in wet-end chem-

istry optimization and troubleshooting efforts and must be recorded and communicated clearly across the mill, the organization, vendors, and consultants. In our travels between many mills, we often found it challenging to gather a clear and consistent picture of charge situations, because the mill did not have a well-documented description of its testing procedures.

In some cases, various suppliers follow different methodologies. The mill is responsible for ensuring consistency in charge measurement between all suppliers. It would be ideal for larger companies to provide such testing consistency on the organizational level, so sharing the data between mills is effective.

Fines and colloids compete for cationic additives with fibers. Measuring each fraction's cationic demand can help to choose addition points or adjust the wet-end condition to improve targeting additives more selectively towards long fibers. Examples of such strategies include anionic trash neutralization attempted before adding starch, cationic strength additives, and cationic sizing dispersions. These additives are better retained within the paper web and more effective if initially attached to the long fiber [23].

The pH significantly impacts the amount of charge developed, both on the surface and in the solution. It is considered best practice to report charge demand value with the pH at which it was measured. Numerous studies made during the neutral pH conversions indicated a 30% increase in cationic demand for the same furnish when pH changed from 5 to 7 [24]. The sensitivity of charge demand measurement using the streaming current detector of the endpoint highly depends on the conductivity of the sample. High conductivity significantly reduces the sensitivity of cationic (anionic) demand measurement. The double layer of ions surrounding the charged core becomes much tighter, making sample polarization less sensitive to the movement of liquid caused by the movement of the piston. Although the volume of titrant required to reach the isoelectric point should not be affected by conductivity, titration curves become flat, making deciding on the endpoint difficult. It isn't easy to run the test directly on a sample with high conductivity. In this case, protocol dictates testing a diluted sample and back-calculating charge demand according to the dilution factor [1].

Pulping and bleaching operations have the most significant impact on the water chemistry of the papermaking furnish [25]. The impact of virgin fiber on water chemistry results mainly from the pulping/bleaching processes (wood species, pulping chemicals, reaction conditions, and washing processes). An example of such a trend may be the increased content of high yield pulps (HYPs), driven by the bulk requirements and economically desired higher pulp yield, increasing anionic detrimental substances and conductivity [26]. Recycled fiber may not cause extremely high levels of anionic substances and conductivity, but it leads to higher day-to-day variation in mill water chemistry. Pulp-

ing, brownstock washing, and bleaching can contribute silicon particles (from defoamers), dissolved organics, and inorganic materials (e.g., sodium, potassium, oxalate, chloride, chlorate, and chlorite ions), which accumulate in paper machine white water. Typical wood-derived components found in the white water of the paper machine using virgin pulps include polygalacturonic acids, a hemicellulose component, and various fragments of lignin, often present in sulfonated or oxidized forms. Extractives and their derivatives, such as abietic acid, a component of resin acids in softwood, and triglyceride fat, are often present in white water as a mixture of fatty acids of various saturation. Mechanical pulps typically contain significant levels of colloidal pitch-type materials and high levels of fines. Mechanical pulps brightened with hydrogen peroxide at high pH have extremely high levels of cationic demand, attributed partly to polygalacturonic acids, the product of alkaline hydrolysis of pectins [27,28]. Recycled fiber pulp brings additional dissolved and colloidal material to the paper machine. Examples of these materials include a nonionic deinking surfactant (hydrophobic alkyl chain with ethylene and propylene-oxide); calcium salts of stearic acid often present as a wetting agent and used in deinking; polyacrylate, used as a dispersant; and various stickies materials, including ethylene-vinyl acetate (EVA), a component of pressure-sensitive additives.

Often, these carryover colloidal and suspended materials originating with the pulp need to be sequestered or coagulated to remove their negative impacts on the papermaking system [29]. Very stringent quality requirements drive the use of sophisticated functional chemicals that require closely controlled conditions to provide expected consistent results and cost, as well as adequate machine efficiency.

Washing capabilities and the amount of freshwater employed vary significantly between various paper and paperboard machine systems, so even for a similar mix of pulps, the chemistry of water circuits may dramatically differ.

Ni et al. [30] compared typical water retention values, specific surface area, and charge density of bleached chemithermomechanical pulp (BCTMP) and bleached hardwood kraft (BHK) pulps (**Table II**). It is crucial to conclude that fines from BCTMP pulps, and any other HYPs, are more hydrophobic, have lower WRV, higher surface area, and higher cationic demand values.

Papermakers looking for increased bulk and using HYP must prepare to overcome lower retention levels, reduced drainage, and higher consumption of various, especially cationic, chemical additives. For board producers, the impact on sizing and edge wicking is the major challenge. Despite these challenges, HYP remains the most feasible way to improve bulk and related sheet strength properties. Pruszynski and Sirois [26] focused on the chemical approaches used to mitigate impacts on the wet-end of paper machines related to increased HYP usage. It is important

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Property	Pulp Type	
	BCTMP	**BHK**
WRV, g/g	1.50	2.05
Specific surface area, m²/g	14.3	5.0
Anionic charge density, meq/g	59.6	8.0
Zeta potential, mV	-54	-56
Soluble cationic demand, meq/L	34.5	3.9

II. Impact of market bleached chemithermomechanical kraft pulp (BCTMP) and bleached hardwood kraft pulp (BHK) on water chemistry (WRV = water retention value).

to note that adding coagulants is often recommended to control cationic demand variation. The addition of coagulants needs to be carefully monitored, as they work through the formation of detrimental PECs with anionic substances that may impair paper machine runnability (drainage, holes, deposits, center roll release).

Application of coagulants for cationic demand control should be performed further back in the system with carefully monitored dosage control, as too aggressive attempts to reduce cationic demand may cause runnability issues. Their effectiveness in reducing cationic demand is limited based on simple stoichiometric calculations. For example, using 1 kg/metric ton (2.2 lb/metric ton) of coagulant with a typical cationic charge density of 2 mEq/g (as product) to treat the stock at 1% consistency, stoichometric calculation predicts reduction of cationic demand by about 20 µEq/L.

Another indication of the degree of contamination of various pulps relevant for wet-end operation and impact on the wastewater plant operation is the chemical oxygen demand (COD) value. The authors made a global review of the old corrugated container (OCC) values for different pulps. Typical COD values may span a wide range, even for seemingly identical pulps. The COD values range between less than 10 kg/metric ton for well-washed kraft pulps, 10–20 kg/metric ton for North American OCC, 40 kg/metric ton for European OCC, 5–30 kg/metric ton for various types of market bleached mechanical pulps (BCTMP, alkaline peroxide mechanical pulp [APMP]), and up to 60 kg/metric ton for poorly washed hydrogen peroxide bleached thermomechanical pulp (TMP).

Hydrogen peroxide bleached mechanical pulps represent a case of extremely high levels of generated cationic demand values. Pruszynski et al. [31] discussed sources and available control strategies for reducing the cationic demand in these systems. Applying coagulants, improved pulp washing (thickening stages as water blocks), the trend from medium to high consistency peroxide brightening, and replacing sodium hydroxide (NaOH) with magnesium hydroxide (Mg(OH)$_2$) as a source of alkalinity can be moderately effective. These approaches may result in a 40%–50% reduction of dissolved contaminants and a similar reduction in conductivity and cationic demand. Some negative consequences of these approaches include the formation of detrimental PECs (coagulants application), process yield losses and energy losses (application of thickening presses with sewering of the pressate stream), lower strength, and lower brightness results (Mg(OH)$_2$ replacement for NaOH). The authors demonstrated the unique effectiveness of the pectinase enzymatic treatment based on examples of laboratory studies and mill applications [31]. Pectinase applications followed excellent work by Thornton et al. [27,28], who identified poly-galacturonic acids, a product of hydrolysis of pectins, as a source of about 50% of the total cationic demand measured in hydrogen peroxide bleached TMP pulps. Enzymatic de-polymerization of these natural polymers leads to their increased solubility in water, resulting in the loss of reactivity towards cationic additives. Once the degree of polymerization (DP) reaches around 6, these short-chain polymers become stable in water and thermodynamically not reactive towards cationic additives, thus not anymore a part of "anionic trash." Pectinase requires pH<5.5 to be fully effective. Based on practical mill applications, Pruszynski demonstrated that if pH and temperature conditions are right, a pectinase dosage between 40–80 g/metric ton reduced cationic demand from approximately 1500 mEq/L to around 700 mEq/L. This change was equivalent to more than 10 kg/metric ton of a typical coagulant (with the cationic charge density of 2 mEq/g) used for charge neutralization. **Figure 11** shows the history of cationic demand changes during the Pectinase trial in a paper mill producing high-brightness mechanical paper based on hydrogen peroxide bleached TMP.

Pruszynski [10] also studied the combined effect of the impact of conductivity and cationic demand. In these experiments, conductivity and cationic demand were controlled by adding sodium sulfate (Na$_2$SO$_4$) and polygalacturonic acid, respectively. An experimental design approach was used to study the mixed effects of both variables. Results indicated that sensitivity in drainage loss to conductivity was higher when the system was already stressed by higher cationic demand.
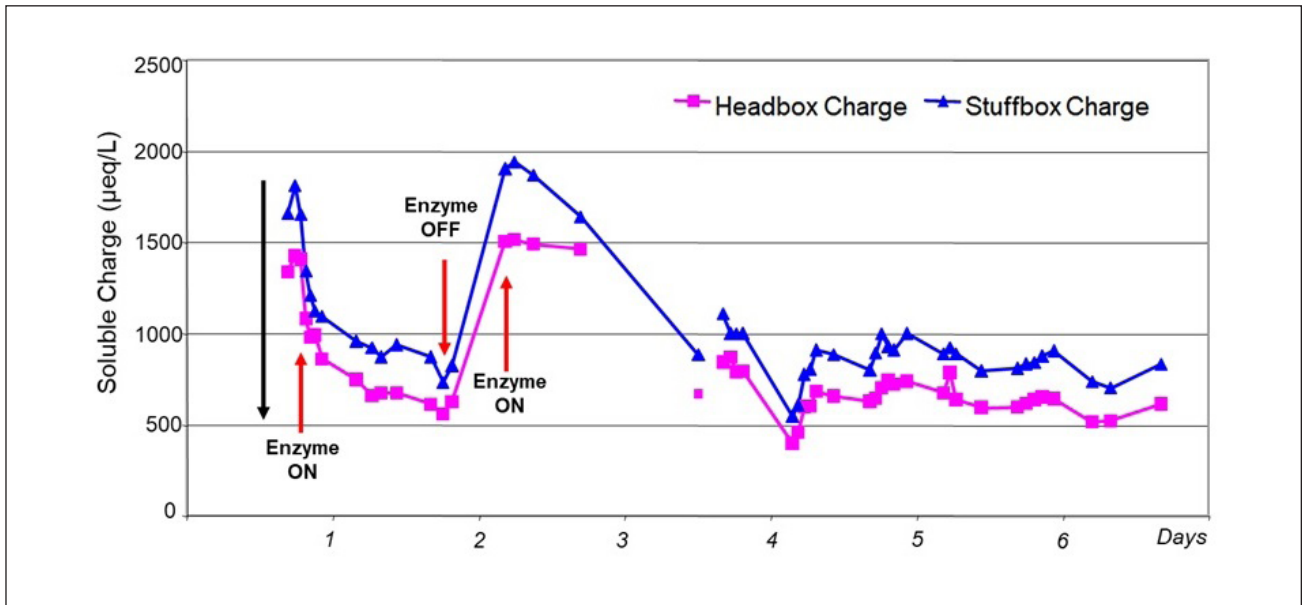
11. Cationic demand changes during the pectinase trial in the hydrogen peroxide-bleached thermomechanical pulp (TMP) mill system. Both headbox and stuffbox cationic demand values were reduced by about 60%. Stopping and restarting the trial confirmed initial observations.

Zeta potential

In this paper, we discussed the basics of the colloidal particle earlier (Fig. 3) when talking about the interactions between charged particles and the impact of conductivity. Zeta potential was defined as a charge on the slip layer of the colloidal particle. It is less than the charge on the surface of the colloidal particle's core, as the Stern layer of the counter ions partially neutralizes it. In practical terms, zeta potential is associated with fiber surface charge. Knowing the fiber's surface charge value can help papermakers understand the interaction between fibers and cationic additives. One of the electrokinetic techniques can be used to determine zeta potential. Initially, the methods based on electrophoresis were used, where the particle's velocity moving towards the oppositely charged electrode was proportional to zeta potential. Various instruments, from simple optical to Doppler effect-based units, were used to measure the speed of particles. Recently, pad forming units are most often used that measure streaming potential across the pad when liquid flows through it. Temperature and conductivity affect the direct measurement of speed or streaming potential and are used to calculate the zeta potential value. Unfortunately, there is no reliable online zeta potential measuring equipment available at this time. Some piston devices are used to measure streaming current, rarely continuously, and their response must be corrected for conductivity changes.

The term "zeta potential" is also used in the case of some papermaking additives, such as fillers (small particles) and emulsions (colloids). An electrophoretic mobility device or light scattering device can measure the zeta potential of this material. The potential streaming device, measuring zeta potential on fiber, is not applicable for these materials. The small objects' surface charge status (typically in the micrometer or sub-micrometer size range) is critical for their stability. It is crucial when applying for retention, strength, and sizing programs.

It is essential to measure zeta potential when dealing with systems close to the isoelectric point that could be over-cationized. For example, some recycled board applications require the addition of several cationic additives to reach required properties such as strength and sizing. Proper management of the zeta potential on the fiber to ensure the best possible adsorption of these additives is essential. In such cases, zeta potential measurement is more critical than titration for cationic demand.

The fundamental differences between the cationic demand and zeta potential measurements are presented in **Table III**.

HARDNESS

The Ca^{+2} and Mg^{+2} ions, in addition to their contribution to overall system conductivity, also impact papermaking systems in more specific ways. Calcium and magnesium salts are less soluble than sodium and potassium salts. This observation applies to salts with both organic and inorganic acids. There are several potential sources of calcium ions in paper/board applications. Hardness developed from exposure of calcium carbonate ($CaCO_3$) filler to lower pH remains the one that papermakers can control (discussed in the section on pH in Part 1 of this work [2]). The hardness coming with the water source and recycled material is more difficult to overcome. It is worth mentioning that paper or board products made in a high-hardness environment retain all

Charge Type / Item	Zeta Potential	Charge Demand
Description	Charge at the slip plane of the colloidal system Charge on the surface of the solids (fiber, fines, fillers)	Amount of charge required to neutralize the charge of the sample. In papermaking, the sample is typically anionic, so we generally deal with cationic demand.
Units	mV	meq/L meq/g (corrected by consistency)

Measurement	Electrokinetic measurement:
	  • Electrophoresis of streaming current (potential)
	  • Measuring streaming current across the pad formed
	
	The actual electrokinetic measurement is corrected for conductivity to determine the zeta potential value.
		Titration with a standardized solution of cationic polymer. Typically, a 1×10^{-3} N solution of poly-DADMAC is used for cationic demand (the sample is anionic).
		
		The end point of titration:
		  • Piston devices using streaming current
		  • Colorimetric using o-Toluidine Blue
		
		Procedures:
		  • Direct titration
		  • Back titration – known excess of 1×10^{-3}N poly-DADMAC added. Sample back titrated to neutral with anionic polymer 1×10^{-3} PVSK.

Sample Preparation	• As is for pulp samples	• As is (typically for tray samples) • Filtered: - 200 mesh screen (remove fibers) - Whatman filter paper (remove fines) - Millipore 45 mm (to remove colloids)
Relevance	Essential to understanding the adsorption process of cationic additives – cationic starch, ASA, AKD, and cationic strength additives. Need to be measured in the grades where the above products are used. More negative zeta-potential cationic additives may be adsorbed.	The measure of the potential for detrimental impact on the cationic additives – retention, drainage, strength, sizing, and others. The higher the value of cationic demand, the higher is the danger of unproductive consumption of cationic additives.

DADMAC = diallyldimethylammonium chloride; PVSK = potassium polyvinyl sulfonate; ASA = alkenyl succinic anhydride; AKD = alkyl ketene dimer.

III. Summary of charge types in papermaking systems.

hardness present in the water after the press section (typically about 50% solids) when the remaining water is evaporated. Bringing this hardness back to highly closed papermaking systems will significantly increase the steady-state hardness levels. Problems related to increased hardness levels include scale formation, pitch, and stickies deposits.

Scale formation

Calcium phosphate, calcium carbonate, calcium silicate, and calcium oxalate are the most common scale issues in a papermaking system. For a scale to form, both components of the scale salt material need to be present, and the solubility product of the scale material (K_{sp}) must be exceeded (carbonate 10^{-9}, oxalate 10^{-9}, and phosphate 10^{-34}).

The system's pH significantly impacts scale formation, as it impacts the form of the acid that contributes to scaling. The need for PO_4^{-3} and CO_3^{-2} ions for phosphate and carbonate scale formation requires high pH. In the case of di-basic oxalate acid with pKa values of 1.27 and 4.27 [32] at pH=5, there is enough oxalate ion ($C_2O_4^{-2}$) to generate scale, even at moderate hardness levels. The presence of other system components (ions, organic materials) can strongly impact scale formation.

Pitch and stickies deposits

As discussed earlier in this paper, calcium ions form insoluble salts with carboxylic acid groups in the system. Pohle [33] compiled the solubility data for calcium salts of

Calcium Soap Of:	Solubility (mg/100 cm³) at 50°C
Longleaf pine rosin	63
Slash pine rosin	47
Abietic acid	39
Dehydroabietic acid	20
Palmitic acid	7
Stearic acid	3
Oleic acid	32
Commercial stabilized rosin	30

IV. Water solubility of selected calcium soaps of fatty/resin acids at 50°C.

fatty acids and resin acids at 50°C, a typical whitewater temperature. Some examples of the fatty/resin acids relevant to paper production are listed in **Table IV**.

Data in Table IV confirm the extremely low solubility of calcium soaps of the typical saturated fatty acids (palmitic and stearic acids). Change in the conformation of the fatty acid chain due to the introduction of the unsaturated bond lowers its hydrophobicity and increases the solubility, as seen in the case of oleic acid.

Fatty and resin acids are responsible for the surface anionic charge of a colloidal particle. These acids have pKa of around 4.8–5.0 and undergo dissociation even in a mildly acidic environment. Their solubility in water depends on pH. Resin and fatty acids are distributed between two primary forms: dissolved in water (mainly resin acids), and elements stabilizing the outside layer of typical colloidal pitch particles. The interaction of calcium (magnesium) ions leads to the precipitation of the dissolved fraction of these acids.

Additionally, interaction with the fraction incorporated with the colloidal particle reduces the electrostatic stabilization of organic colloids and triggers their agglomeration and deposition. This reaction occurs on the colloidal particle's surface and in solution with the soluble resin and fatty acids.

It is worth mentioning that the mechanism of deposition described earlier is also responsible for deposits when rosin and alkenyl succinic anhydride (ASA) sizing are applied. The ASA calcium salt deposition is a significant issue for alkaline fine papermaking with calcium carbonate fillers. Hydrolysis of the anhydride group of ASA leads to forming a carboxylic group that can react with calcium ions. Controlling the hydrolysis of ASA and the hardness level of the system is essential to the successful application of ASA in such grades of paper.

Impact of hardness on the surface properties of the fiber

Calcium ion is also reactive towards carboxylic groups on the fibers/fines surface. The surface carboxylic (-COOH) groups dissociate at lower pH values than soluble carboxylic acids [2] and are responsible for the crucial anionic surface charge of the fibers. The reaction of calcium ions reduces anionic surface charge measured as fiber zeta potential. Yuan et al. [34] discussed the adsorption of Ca^{+2} ions on the surface of fibers and its impact on the performance of retention, strength, and sizing applications. The charge screening effect of calcium ions affects the adsorption and performance of cationic starch, cationic strength additives, and sizing. Handsheets prepared from pulps pretreated with calcium chloride ($CaCl_2$) solution compared with those pretreated with deionized water and NaCl solution showed:

- 20% lower tensile index values
- 10%–15% higher Cobb values when sized with alkyl ketene dimer (AKD)

Yuan [34] illustrated the potential impact of Ca^{+2} ions on deposit formation by measuring the increase of turbidity of solutions of sodium rosinate, sodium oxalate, and sodium stearate.

Calcium ions are an essential factor contributing to problems related to closing whitewater systems. Every source of additional Ca^{+2} ions will contribute to the system's accumulation and must be addressed. At 95% closure, approximately a 20 times accumulation factor applies, and a source of 5 ppm Ca^{+2} will result in a steady-state level of about 100 ppm. Using calcium carbonate fillers, fresh or from recycled raw material, pH management must be fine-tuned to maintain a hardness level at the acceptable level.

Hardness problems in recycled grades

One of the biggest challenges in the recycled board grades is excessive hardness levels affecting the performance of the anaerobic reactors in the effluent treatment plants. High levels of COD in the raw material, originating primarily from the corrugation medium treated with high levels of native starches, result in reductive environments forming ideal conditions for anaerobic bacteria growth. These anaerobic bacteria produce low molecular weight, volatile fatty acids (VFA) as respiration products. This VFA formation results in significant odor problems in the final board grades produced. In addition to the odor issue, VFA formation drives the pH down and decomposes calcium carbonate fillers in the recycled raw materials, leading to high hardness levels. Hardness levels of 1200 ppm or higher have been recorded in the recycled board industry, depending on the level of mill closure. Deposits, scale, decreased performance of cationic additives, and reduced board strength are significant consequences of increased hardness levels. High hardness is also a substantial concern for wastewater treatment, leading to severe scaling and loss of

efficiency in anaerobic reactors. It is generally accepted that a calcium level of 400–600 ppm offers acceptable runnability in paper and board production.

A combination of physicochemical, engineering, and biological controls should be taken to prevent anaerobic conditions and to control hardness at an acceptable level. Physicochemical actions to avoid anaerobic conditions include: lower temperatures, higher pH, and higher oxidation-reduction potential (ORP). Engineering and system control actions may include lowering system volume, increasing system flows, and improving agitation and stock aeration [35]. To prevent anaerobic bacteria activity, microbiological control should focus primarily on using oxidants (stabilized chlorine such as mono-chloramine or ClO_2), but it may need to include some non-oxidizing biocides. Increasing the system's alkalinity provides buffering and prevents pH drop with VFA formation. The goal of increased alkalinity could be achieved by adding sodium bicarbonate or chlorine dioxide (CO_2)/NaOH, known as an ADALKA technology [36].

SUMMARY

Water quality parameters such as conductivity, surface charge, charge demand, and hardness significantly influence paper productivity and product quality. This paper reviewed the basic principles of these parameters, their typical ranges, related problems, and available remedies. With several decades of combined industry experience, the authors focused on practical aspects of wet-end chemistry management. Several trends in the industry, such as increasingly closed white water circuits and lower quality of recycled raw materials, make understanding the wet-end chemistry impact more critical.

The impact of conductivity on colloidal interactions and double-layer thickness, which affect the zeta potential, have been discussed, referring to the real-mill experience. Excessive conductivity and hardness lead to poor strength development, reduced fiber bonding, reduced wet-end additive performance, and potential quality issues in a mill.

The impact of the charge, both dissolved and surface charge measured as zeta potential, on additive performance and demand has been shown to impact the adsorption of cationic additives, confirmation of water-soluble polymers, and lead to stress on retention programs and strength. Awareness of soluble charge sources and benchmarking their value and trends allow mills to control their levels and design proper addition sequences of additives. The goal here is to best utilize the anionic charge on the surface for the adsorption of cationic additives and to minimize the detrimental impact of soluble anionic substances rendering cationic additives inactive.

In recycled board applications, anaerobic conditions lead to volatile fatty acids (VFA) generation. In the presence of calcium carbonate fillers, VFA generate high hardness levels. In these cases, high levels of hardness coincide with odor issues. Therefore, monitoring and controlling conductivity and hardness water quality parameters should be considered the best practice for quality paper machine operation.

The authors hope that despite most of these topics covered earlier in the listed references, compiling them in this two-part series, with the simplified theoretical background and mill examples, will be of value to process engineers in the paper and board mills. **TJ**

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ABOUT THE AUTHORS

Water chemistry is a fundamental topic for wet-end additives and operation. Many new engineers do not fully understand these fundamentals, so we are attempting to provide good literature reviews to assist them as they start their new careers. This review highlighted current industry trends (more recycled content, more closed water systems, and higher percentage of young employees). A previous work, *TAPPI J.* 21(6): 313(2022), focused on water chemistry fundamentals and pH. The current article covers conductivity, charge, and hardness.

Water chemistry has broad impacts on wet-end additives and operation. The authors of this review come from both the chemical supplier side and the papermaker side to provide a comprehensive view and knowledge.

In compiling this review, we saw that basic/fundamental factors have broader impact and are therefore more important. It is always interesting to review how much a small pH change in the papermaking pH range can alter chemical performance.

This research offers mills a comprehensive view
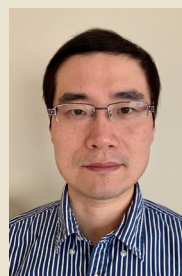
Pruszynski   *Xu*   *Hart*

on how water affects wet-end additives and how to make the best use of them. The work highlights the need for good understanding of wet-end chemistry and can be a good training material for new employees.

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