

# *Water chemistry challenges in pulping and papermaking – fundamentals and practical insights: Part 1: Water chemistry fundamentals and pH*

PRZEMYSŁAW PRUSZYŃSKI, LEBO XU, AND PETER W. HART

**ABSTRACT:** Water is an essential component of the papermaking process. Nevertheless, papermakers often overlook its importance compared to fibers 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. Not all fresh water and process water is the same. Fresh water varies from mill to mill, primarily due to the location and availability of water sources. Some industrial trends, such as enhancing water conservation and production yield, gradually shift process water quality over time.

The current work serves as a primer on water and water chemistry fundamentals to help the papermaker prepare for the future challenges of increased contamination of process water associated with reduced fresh water usage. This paper focuses on basic water chemistry definitions and discusses the impact of pH on wet-end operation. It is clear that pH is a fundamental factor that directly affects the process and impacts other factors relevant to the papermaking process. It is crucial to understand what pH represents, how it is measured, how to select the proper pH and carefully control it, and how to closely maintain the process at target setpoints. Understanding the sensitivity of operation to pH change will lead to an appropriate focus on these issues. In addition to basic theory, we also review onsite experience and practical mill cases. It is imperative to stress that, although critical, pH is not the only chemical parameter impacting papermaking operations. Other factors, such as ionic concentration measured by conductivity, surface, soluble charge, and hardness, are critical and will be discussed in Part II of this series. As pH is a primary and independent factor that impacts various forms of charge and conductivity, the authors decided to start the current series of papers by discussing pH.

**Application:** By gaining comprehensive and fundamental understanding on how pH affects wet end chemistry, mills can be better prepared to address water challenges and obtain more efficient operation.

The paper industry is experiencing a rapid loss of experienced technical and operations personnel. Well-seasoned papermakers and engineers are retiring and taking decades of experience away from the mills. Younger engineers, scientists, and operators are being rapidly promoted into positions of authority without their predecessors' years of operational experience. Even though the new generation of papermakers is well-educated in engineering and scientific fundamentals, it is beneficial for them to understand how crucial water chemistry and pH control are for papermaking.

The impact of water on the papermaking process depends on multiple water quality parameters, such as conductivity, surface, soluble charge, suspended and dissolved solids, acidity/alkalinity, oxidation reduction potential (ORP), hardness, and pH. The current series attempts to provide a primer where important water/wet-end chemistry concepts that occasionally fool even experienced people are collected and explained. The present work focuses on the importance of water chemistry and pH. The reason pH is so important is that it impacts the performance of the

entire sheet forming and additive processes. Poor machine performance may result if pH and its impacts are not well controlled and understood. Additional water properties and their impact on papermaking and wet end chemistry will be reviewed in the second paper in this series.

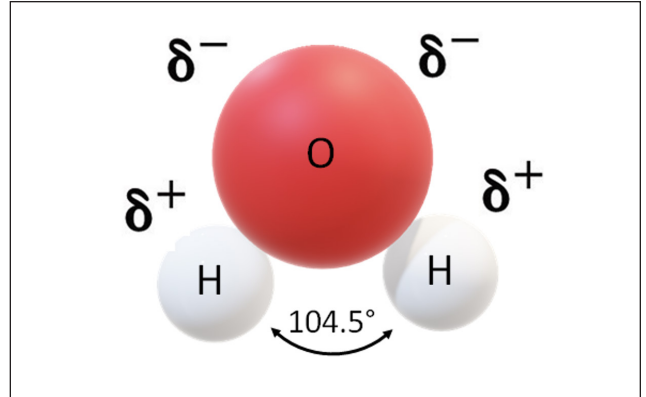
In the last 30 years, the industry has experienced a wave of significant changes in the pH of operations. Many papermaking processes have moved from acid grades utilizing large quantities of alum, rosin sizing, and kaolin clays to alkaline woodfree calcium carbonate-filled grades of paper and neutral pH applications specific to mechanical pulps. These pH conversions illustrate the importance of pH, as they required a significant effort to develop chemical technologies that operate at higher pH values.

For both virgin and recycled mills, changes in pulp quality represent another significant contributor to shifting water quality. Cost considerations, quality requirements, process washing limitations, grade development requiring new pulp sources, and water use reduction have increased pulp's impact on the overall process water quality.

Water is an essential component of the papermaking

# PAPERMAKING

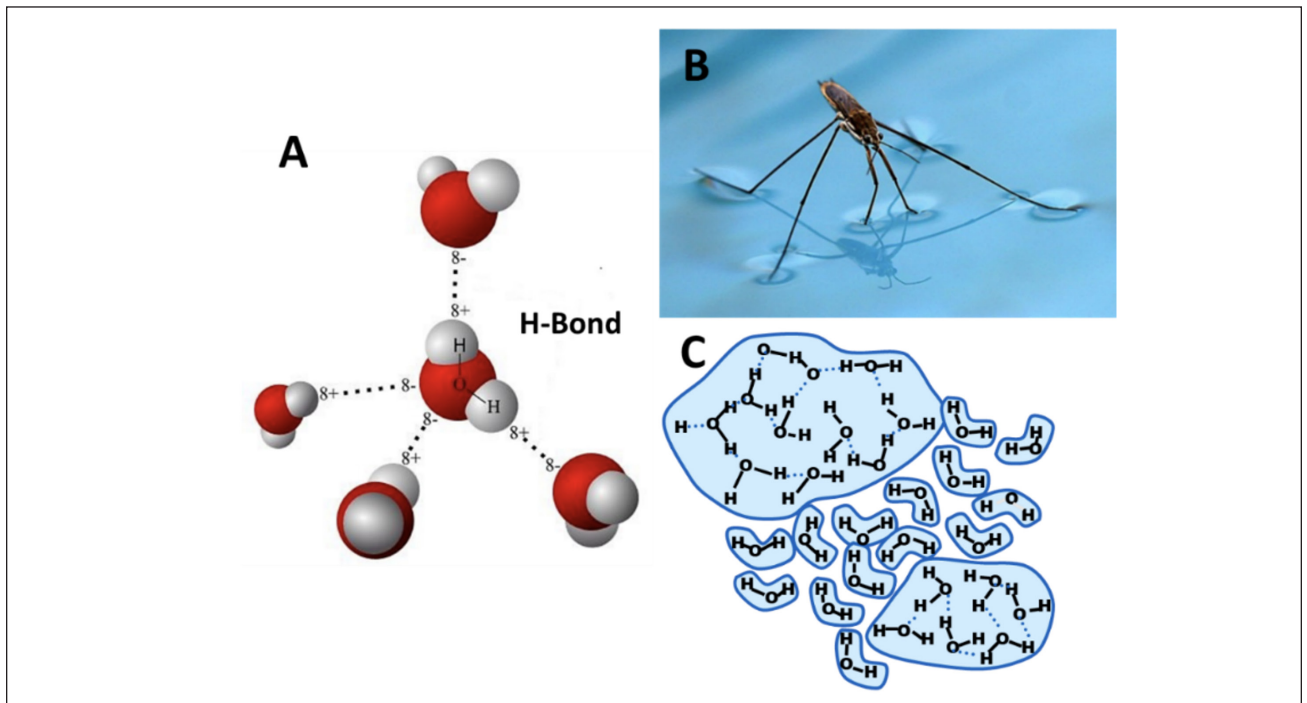
process, although it is not a part of the final product. It serves as a medium for the dilution and transportation of papermaking solids to allow the formation of a uniform sheet of paper/paperboard. Water facilitates many processes involving fiber development and delivery of chemical additives and serves as a medium for several chemical and mechanical interactions associated with papermaking. After the diluted papermaking slurry is prepared and delivered to the headbox (typical consistency 0.5%~1%), the essence of making paper becomes water removal. This removal process starts as physical filtration on the forming section of paper machine and continues in the press and dryer sections. In the papermaking process, water is primarily recirculated and, with every pass, becomes contaminated with soluble and colloidal materials that negatively impact the papermaking process. Part of the process water needs to be replaced with fresh water. More fresh water addition means more sewerage water must be treated in the effluent treatment plant. A significant part of fresh water addition is the energy required to maintain the required process water temperature. Therefore, reducing the amount of fresh water used per ton of the product, besides reducing an environmental footprint, reduces the cost of fresh water and its treatment, reduces the cost of effluent treatment, and saves a significant amount of energy. Current industrial trends have forced papermakers to attempt to do more to make consistently high-quality products with often declining fiber quality and less fresh water. There is little room for deviation from chemical best practices if quality and productivity are attainable goals. The paper machine's chemical environment needs to be optimum and stable. In addition, potential



1. Structure of water molecule.

incompatibilities between different chemicals should be well understood and avoided or reduced [1].

The papermaker must adequately select and control the paper machine's wet-end chemistry. These decisions must include the intricate relationships between various wet end parameters. Such decisions are only possible if the fundamentals of wet-end chemistry are understood. Recently, a paper was published dedicated solely to conductivity [2], including basic definitions, typical values, impact on machine performance, and available control strategies. Based on this paper's significant interest level, the authors decided that a review of fundamental water properties and related wet end chemistry would be of value to the industry. Herein, basic definitions, typical values, relationships between discussed parameters, best practices, and control strategies associated with water fundamentals are reviewed.



2. Hydrogen bond between water molecules (A), high water surface tension (B), and water molecular organization (C).

### WATER CHEMISTRY BASICS

Water is a ubiquitous compound around us. It is abundant, covering about 71% of our planet's surface area. It is critical for life, occupying about half the volume inside biological cells, and crucial for most industrial processes, including pulping and papermaking. Though people use water every day, few realize it exhibits several unique properties. Water (H<sub>2</sub>O) has a molecular weight (MW) of 18 g/mole. It has stronger intermolecular interactions than other substances made of molecules with equivalent sizes, molecular weight, and geometry. For example, hydrogen sulfide (H<sub>2</sub>S) (molecular weight of 34 g/mole) or carbon dioxide (CO<sub>2</sub>) (molecular weight of 44 g/mole) are gases under room conditions due to their lower cohesive force.

An example of water's unique "packing" property is its unusual volumetric anomaly, with the density of water's solid form (ice) being lower than its liquid form (water). This anomaly explains why ice forms on top of rivers and lakes rather than sinking to the bottom and results from the liquid phase being more organized than the solid form of water. The strong organization of water molecules in their liquid form has relatively high surface tension, melting point, boiling point, and heat capacity. As a result, ice floats on the water surface and melts under pressure, making skating possible.

It is beneficial to review water's molecular structure to understand water properties better. There has been a continuous effort, even recently, to explore water molecular coordination and arrangements [3-5]. A water molecule consists of two hydrogen atoms and one oxygen atom. These three atoms are connected in sequence as H-O-H, with a bond angle of 104.5° (Fig. 1). Since oxygen is strongly electronegative, it attracts electrons, shared with hydrogen atoms, to form bonds. As a result, the oxygen side (of a water molecule) bears a partial negative charge, and the hydrogen side carries a partial positive charge. This molecular polarity makes water an excellent polar solvent to disperse cellulosic material and papermaking additives, such as cellulose derivatives, starch, polymer compounds, and inorganic salts.

The hydrogen bond, a term often used when explaining interactions in the papermaking process, is another feature that makes water unique. The oxygen atom in one water molecule has excellent, unhindered access to a hydrogen atom in other nearby water molecules. The simple molecular structure makes it possible to develop a relatively strong interaction, defined as a hydrogen bond (Fig. 2A). The hydrogen bond is responsible for water's organization and unique properties, including high boiling point, high specific density, and high surface tension (Fig. 2B). The hydrogen bond organizes water molecules, packing more molecules in a defined volume (Fig. 2C), making liquid water density higher than ice.

#### pH – proton (hydrogen ion) concentration

Pure water dissociates into a proton (H<sup>+</sup>) and hydroxyl anion (HO<sup>-</sup>). This dissociation takes place in the presence

of and is driven by the contribution of other water molecules, best represented by Eq. 1:



In pure water, the concentrations of both ions are identical and equal to 10<sup>-7</sup> mol/L. The product of both concentrations is, therefore, constant and equal to:

$$[\text{H}_3\text{O}^+][\text{HO}^-] = 10^{-14} \quad (2)$$

Since the concentration of both water ions is constant, once we know the concentration of one of these ions, we can easily find the other ion's concentration. Equation 3 defines pH value:

$$\text{pH} = -\log[\text{H}_3\text{O}^+] \quad (3)$$

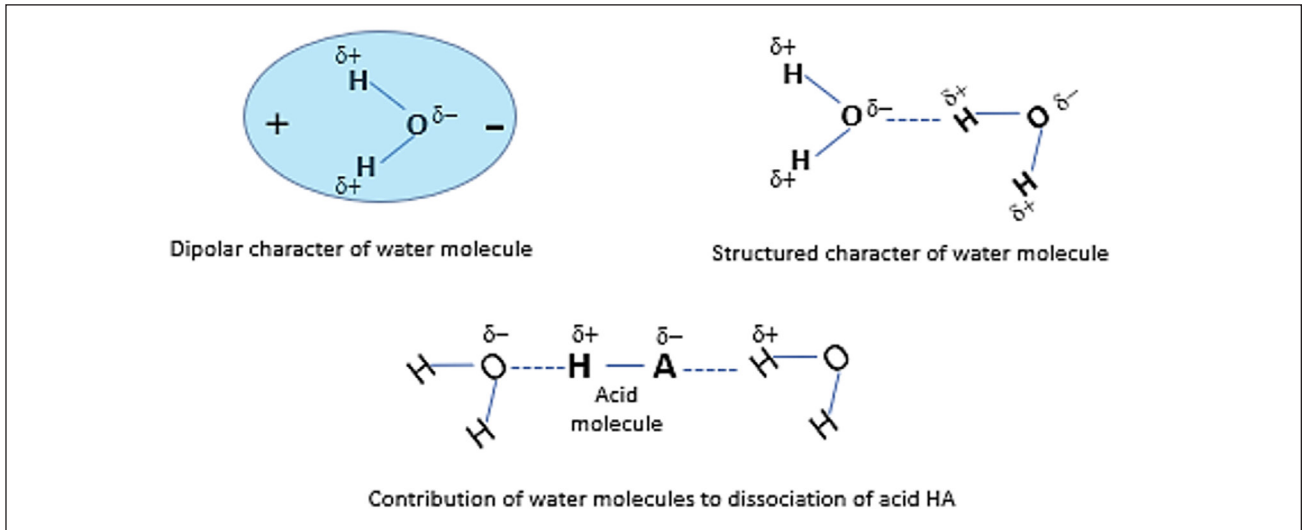
#### Acids and bases

Acids are substances that, in water, provide additional H<sub>3</sub>O<sup>+</sup> ions. Acids have the H atom attached to oxygen or another highly electronegative atom. This electronegative character of the atom (A) directly linked to a hydrogen atom makes the bond A-H highly polarized, with electrons shifted towards the A and away from H atoms. This polarization of the H-A bond is responsible for interactions with water dipoles, referred to as hydration (Fig. 3).

If the energy released from interaction with water dipoles, called hydration, exceeds the energy of the A-H bond, the complete dissociation of this bond occurs, leading to hydrated ions A<sup>-</sup> and H<sub>3</sub>O<sup>+</sup>. This process is called dissociation. Since H<sup>+</sup> interacts with a water molecule to form H<sub>3</sub>O<sup>+</sup>, the formula (H<sup>+</sup>-H<sub>2</sub>O) reflects water's role in this process.

There are two major classes of acids:

- **Strong acids:** All molecules of strong acids undergo complete dissociation into H<sub>3</sub>O<sup>+</sup> and A<sup>-</sup> when placed in water. There is no undissociated form of strong acid left in the solution. Therefore, there is no equilibrium between dissociated and undissociated states of the acids. The concentration of H<sub>3</sub>O<sup>+</sup> equals the initial concentration of the acid if the acid has one H atom capable of dissociation. Therefore, if we prepare a 1x10<sup>-3</sup> M solution of strong, monoprotic acid (e.g., hydrochloric acid [HCl]), the concentration of the H<sub>3</sub>O<sup>+</sup> ion will also be 1x10<sup>-3</sup> M. The pH of this solution would be equal to 3.
- **Weak acids:** All acids that do not wholly dissociate when dissolved in water are weak acids. For weak acids, there are both forms, dissociated and undissociated, existing in equilibrium. The concentration of H<sub>3</sub>O<sup>+</sup> is smaller than the concentration of the acid. To calculate the concentration of H<sub>3</sub>O<sup>+</sup> ion, we need to know the dissociation constant of the weak acid, K<sub>a</sub>:



### 3. Dipolar character of water, water structure, and interaction with polar and ionic species leading to dissociation.

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \quad (4)$$

where:  $[H_3O^+]$ ,  $[HA]$ , and  $[A^-]$  are equilibrium concentrations of hydronium ion, dissociated, and undissociated acid, respectively. A specific  $K_a$  value for each weak acid is often presented as a  $pK_a$  (Eq. 5). This equation is a measure of the strength of the weak acid:

$$pK_a = -\log K_a \quad (5)$$

Equation 4 and  $K_a$  value do not apply to strong acids since they fully dissociate, and no undissociated form is available in the equilibrium.

The most common weak acid group in papermaking is the carboxylic group (-COOH), with the approximate  $pK_a = 4.8$ . It is worth stating that the  $pK_a$  value for the same acid function may differ based on neighboring groups in the molecule. In general, electron-withdrawing groups increase the acid strength (lower  $pK_a$  value), and electron-donating groups lower the strength of the acid (higher  $pK_a$  value).

#### Practical aspects of pH control

Based on Eq. 1:

$$[H_3O^+] = K_a \frac{[HA]}{[A^-]} \quad (6)$$

$$-\log[H_3O^+] = -\log K_a - \log \frac{[HA]}{[A^-]} \quad (7)$$

$$pH = pK_a - \log \frac{[HA]}{[A^-]} \quad (8)$$

Equation 8 is known as the Henderson-Hasselbach equation. It allows for a fundamental understanding of how advanced the dissociation is at a given pH for any weak acid if we know its  $pK_a$  value. Since dissociation of weak acids is also a source of charge in papermaking systems, this

equation provides information about the system's charge development. It is interesting to conclude that for the situation where  $[HA] = [A^-]$ , midpoint for the dissociation process, Eq. 5 becomes:

$$pH = pK_a \quad (9)$$

Based on Eq. 9, we can draw some conclusions:

- For any weak acid, the  $pH = pK_a$  value represents a situation where the concentration of acid form (HA) and its anionic form (A) are equal (half-point of the ionization).

- When  $pH = pK_a - 1$ :  $\frac{[HA]}{[A^-]} = 10$  (10)

- lowering  $pH$  by one from the  $pK_a$  value increases the concentration of acid (no charge) by ten-fold.

- When  $pH = pK_a + 1$ :  $\frac{[HA]}{[A^-]} = 0.1$  (11)

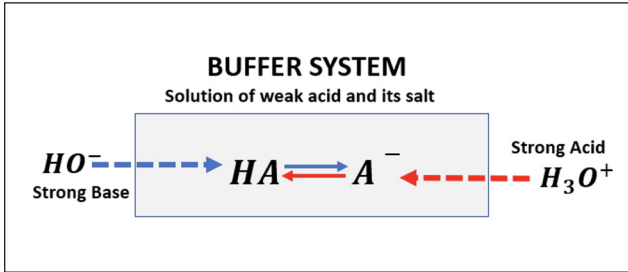
- increasing  $pH$  by one from the  $pK_a$  value increases the concentration of dissociated form (anionic charge) by ten-fold.

Based on Eq. 10 and Eq. 11, we can conclude that the change between 10% and 90% ionization of weak acid occurs in the range of two pH units,  $pH = pK_a \pm 1$ . The complete ionization process (1%~99%) occurs in the range:

$$pK_a - 2 \leq pH \leq pK_a + 2 \quad (12)$$

with the steepest change of ionization located close to  $pH = pK_a$ .

Since the  $H^+$  concentration has a logarithmic relationship with pH units, a slight shift in pH value represents a significant change in  $H^+$  concentration (1 pH unit change = 10 times  $[H^+]$  concentration change). Additionally, changing pH in a different pH scale range requires different amounts of acid or base. Reducing pH requires ten times more base



**4. The model explanation of the buffer system.**

with every pH unit going down. For example, correcting pH from 3 to 2 requires 10,000 times more strong acid than the pH change between 7 to 6. These facts stress the importance of tight pH control for smooth machine operation and the performance of chemical additives. The best practice in pH control on many large, fast paper machines is to operate with variations within  $\pm 0.1$  units range from the target pH.

Besides total acid usage, it is also essential to properly design the dosing method of pH control acid or base to maintain a desired control of pH. For example, using diluted acid is better than adding concentrated acid. Split, multipoint dosing is better than one-point massive dosing. Higher acid flow velocity than stock flow velocity and good mixing is also essential. Designing a good control loop requires a well-operating pH sensor and the use of the proper algorithm that correlates the required dosage of acid or base with the observed pH of the treated stream. Sulfuric acid, phosphoric acid, sulfamic acid, and  $CO_2$  are most commonly used to reduce the pH. Caustic soda, sodium bicarbonate, and sodium carbonate are most often used when correction to higher pH is desired. The application of  $CO_2$  has recently become increasingly more important, primarily in thick stock applications, because it allows pH reduction in the systems using calcium carbonate fillers, with minimum hardness development [6]. This technology,

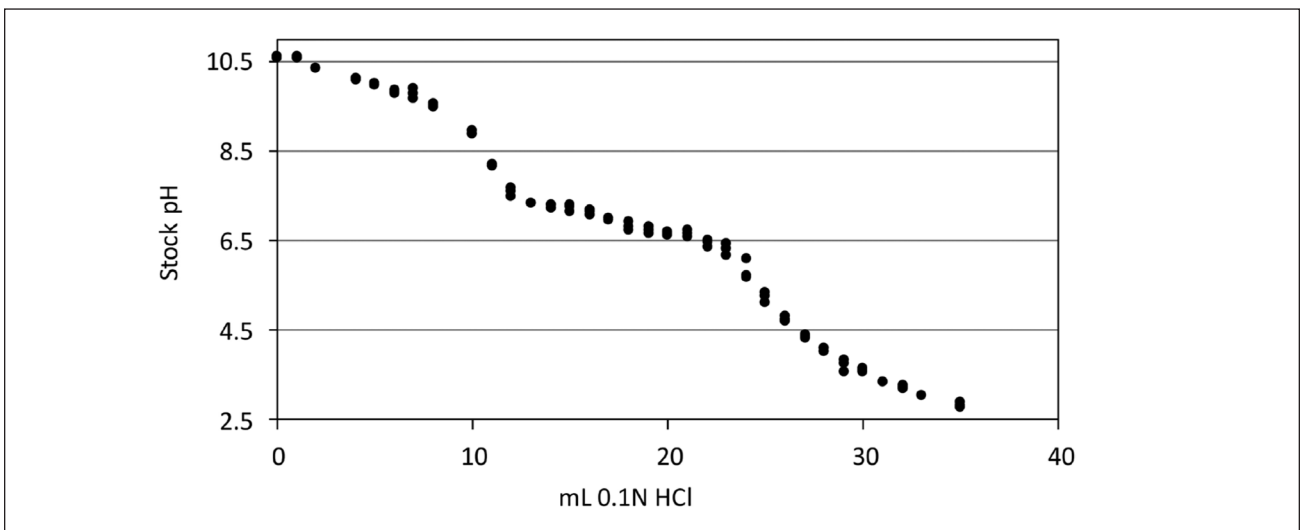
known as ADALKA, allows a mill to effectively reduce the pH of alkaline stock to about 7.2–7.4 and is very important for grades operating with mechanical pulps that experience significant brightness losses at higher pH.

**Buffering**

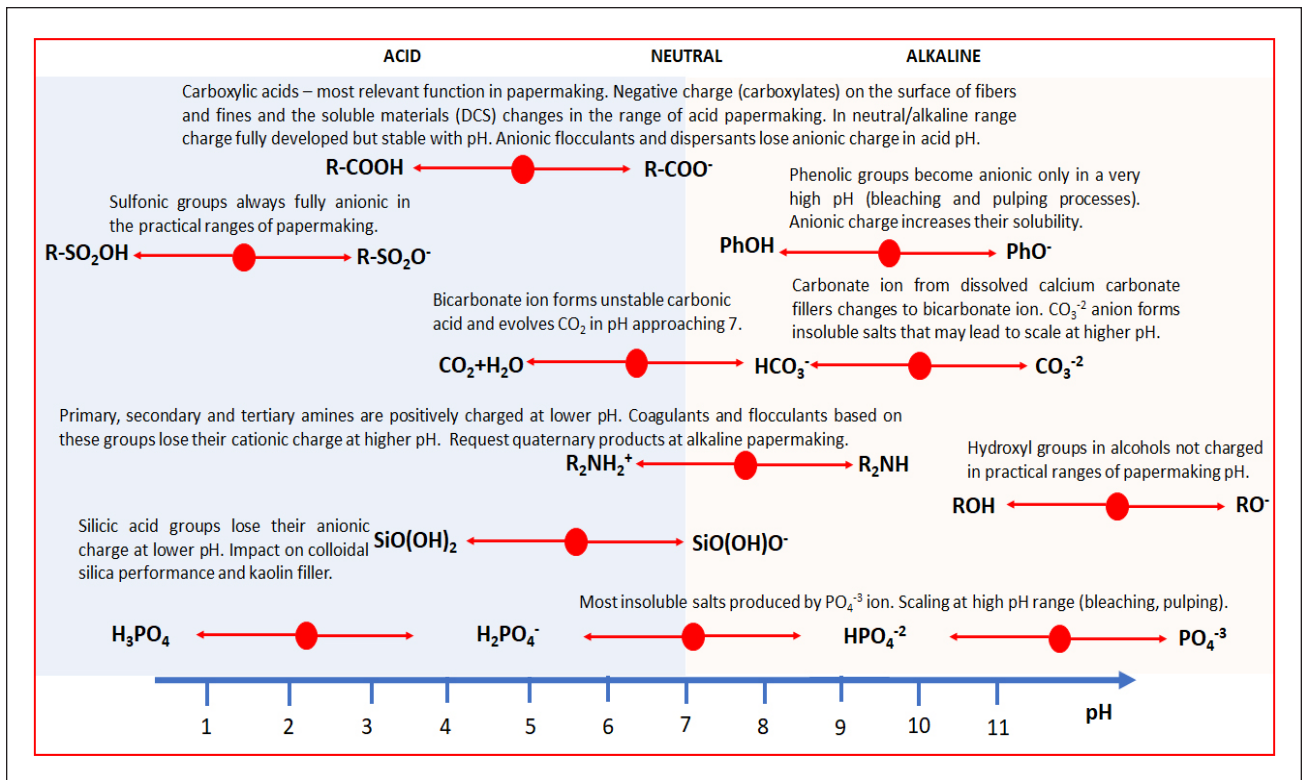
Equation 8 explains buffering—a fundamental property of solutions containing a weak acid and its conjugate anion. Buffering reflects resistance to pH change on the addition of strong acid or strong base. The addition of strong acid, or strong base, to the solution containing buffer components resists a sharp shift in pH until either the weak acid or its anion ceases to exist. Adding strong acid or strong base does not directly increase or decrease the concentration of  $H_3O^+$  ion but changes HA and  $A^-$  ratio in the equilibrium (Eq. 8). This effect reduces the total impact of adding a strong acid or strong base on pH. **Figure 4** illustrates the mechanism of pH buffering of weak acid/anion solutions. Hydronium ions (red arrow) from added strong acid do not impact pH directly. Instead, they react with a weak acid's anion ( $A^-$ ) and increase HA concentration. Similarly, hydroxyl anion ( $OH^-$ ) from an added strong base does not impact pH directly but reacts with the weak acid (HA), increasing the anionic  $A^-$  form concentration.

The buffer performs best in the range of pH close to the  $pK_a$  value of the weak acid. Therefore, for carboxylic acid ( $COOH$ ) with  $pK_a \sim 4.8$  (in acetic acid  $pK_a = 4.75$  at  $25^\circ C$ ,  $pK_a = 4.78$  at  $50^\circ C$ ) [7], pH between 3.8–5.8 represents the best performance range.

Various forms of calcium carbonate, precipitated calcium carbonate (PCC) or ground calcium carbonate (GCC), fresh or introduced with recycled fiber, present an essential buffering system. The bicarbonate ion ( $HCO_3^-$ ) can consume added acid, prevent pH drop, and form unstable carbonic acid, decomposing to  $H_2O$  and  $CO_2$ . Since  $CO_2$  evolves from the system, this buffer is irreversible.



**5. The pH Curve for 1 gram of unbleached pine fiber (kappa number 25) diluted to 0.5% consistency and titrated in the presence of fiber with 0.1N HCl. Data from [8].**



**6. Most relevant weak acid systems and pH ranges of their dissociation reaction.**

It is essential to know that the pulp fiber itself impacts buffering. Due to acidic groups with different acidity ( $pK_a$  values), pulps may buffer an impact of added strong acid or base around the pH close to the  $pK_a$  value. What groups are present on the pulp depends on the pulping technology, lignin content, wood species, etc. Being aware of the pulp buffering ranges and capacity may be very helpful in designing the pH control loop in the mill. **Figure 5** shows the titration curve of the pulp suspension, revealing the presence of two buffering groups as the semi-plateau regions in the plot of stock pH as a function of the amount of 0.1N HCl added [8].

### Practical implications

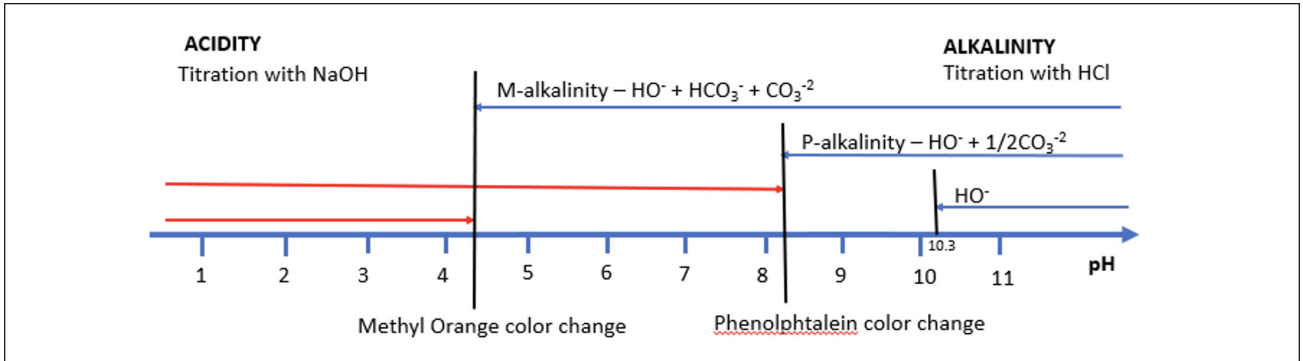
It is significant for paper machines operating in the acid pH range that most of the conversion between charged and uncharged forms of the carboxylic acid functions occurs in the pH range of their operation. This pH sensitivity dictates special requirements for pH control to prevent sudden system charge changes.

**Figure 6** presents the position of  $pK_a$  values and pH ranges for 10% and 90% dissociation for most of the weak acids relevant to papermaking. We also included general comments reflecting on the practical impact of a given acid group's dissociation on the papermaking process. It is essential to mention that the  $pK_a$  of any acidic group may change significantly based on its chemical environment. Functional groups that donate electrons (-OH, -NH<sub>2</sub>, -OCH<sub>3</sub>)

make acid weaker, increasing its  $pK_a$  value. On the other hand, groups that are capable of withdrawing electrons (-NO<sub>2</sub>, -CN, C=O) from acidic bonds undergoing dissociation make acids stronger, decreasing their  $pK_a$  value. Using potentiometric titration, Laine [9] measured the  $pK_a$  values on the surface of kraft fiber. These  $pK_a$  values varied between  $pK_a = 3.4$  for uronic acid in hemicellulose to  $pK_a = 5.5$  for acid groups in lignin. These values may be different for the soluble acidic species. For our discussion, the authors selected  $pK_a = 5$  for carboxylic acids in the soluble form.

Controlling pH in a papermaking system is the most fundamental process control activity. It is essential for retention, drainage, deposit control, scale prevention, sizing, and strength development; wet-end chemistry truly starts with a proper pH control strategy. Controlling pH requires knowledge of the pH change observed with the addition of a strong acid or strong base. **Figure 7** illustrates that pH drop due to strong acid addition is minimized in the presence of substances that consume hydronium ions. How any given system responds to acid addition cannot be predicted based solely on pH but must be checked experimentally by titration with a standardized HCl solution to determine the system's *alkalinity*.

Similarly, weak acid presence reduces the impact of a strong base on pH and represents system *acidity*. The pH value does not predict how a system responds to pH correction, due to a lack of a direct relationship between weak acid or base concentrations and pH. Alkalinity and acidity



7. Concepts of acidity and alkalinity of the system.

must be measured empirically by titration with strong acid or strong base. Figure 7 illustrates the concepts and measurement of the acidity and alkalinity of the system.

**CHARGE DEVELOPMENT IN THE PAPERMAKING PROCESS**

Carboxylic acid groups (-COOH), with the  $pK_a$  of about 5, are the most significant source of anionic charges. As discussed earlier (Eq. 8), the steepest part of the dissociation curve coincides with the pH equal to the  $pK_a$  value. Equation 8 explains why acid papermaking, with a pH close to 5, represents a unique sensitivity of charge development due to pH variability, making the need for proper pH control of critical importance. **Figure 8** illustrates anionic charge development for carboxylic (-COOH) and sulfonic (-SO<sub>2</sub>OH) groups. Neighboring acid functionalities impact their dissociation, and the actual curves may be slightly flatter. The higher the pH, the more anionic a papermaking system can be.

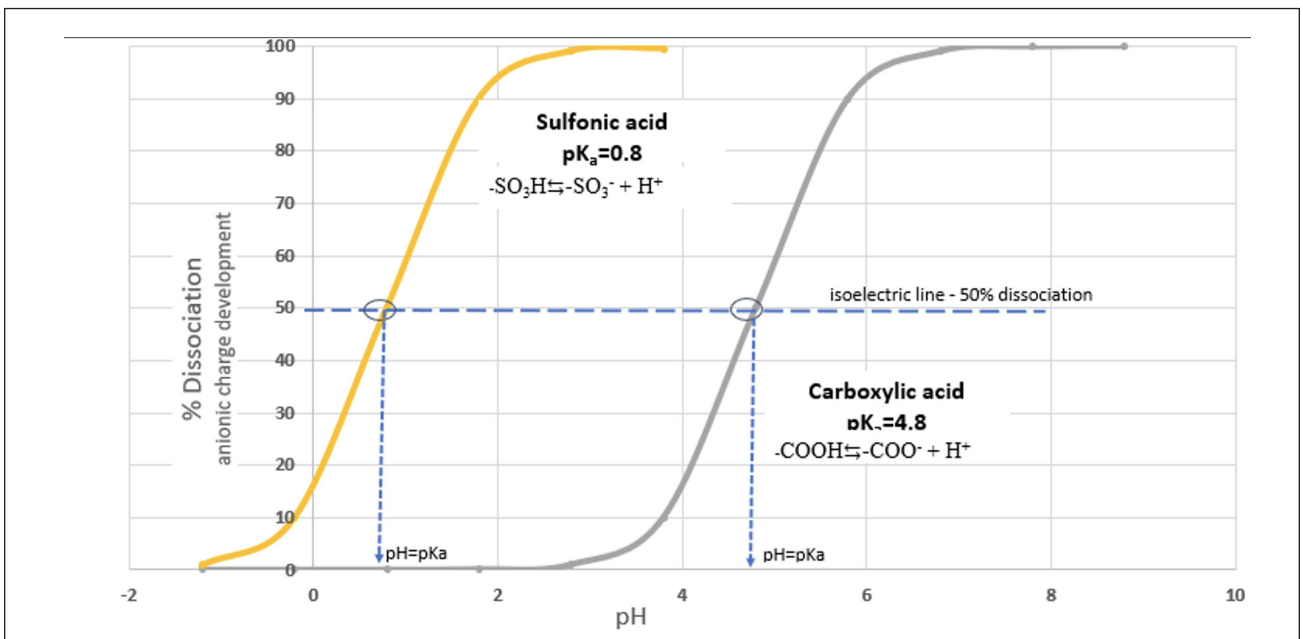
The sulfonic, hydroxyl, and phenolic groups do not

significantly affect charge or charge variability in papermaking systems. The sulfonic group is much more acidic ( $pK_a < 1$ ) and will practically always fully dissociate in the range of papermaking pH. Therefore, it fully contributes to the overall negative charge at any pH but not to charge variability. Hydroxyl group (OH) ( $pK_a > 14$ ) and phenolic ( $pK_a \sim 10$ ) groups are much weaker acids, and their dissociation takes place at very high pH values that are not practical for papermaking, except for some pulping processes.

**Practical considerations**

The follow is a list of some practical considerations related to charge development:

- pH is an essential factor affecting stability for grades operating in an acid pH range.
- Neutral (pH = 6.8–7.4) and alkaline (pH = 7.5–8.2) papermaking systems are always more anionic but far less sensitive to the pH-induced variability of charge than grades operating in an acid pH range.



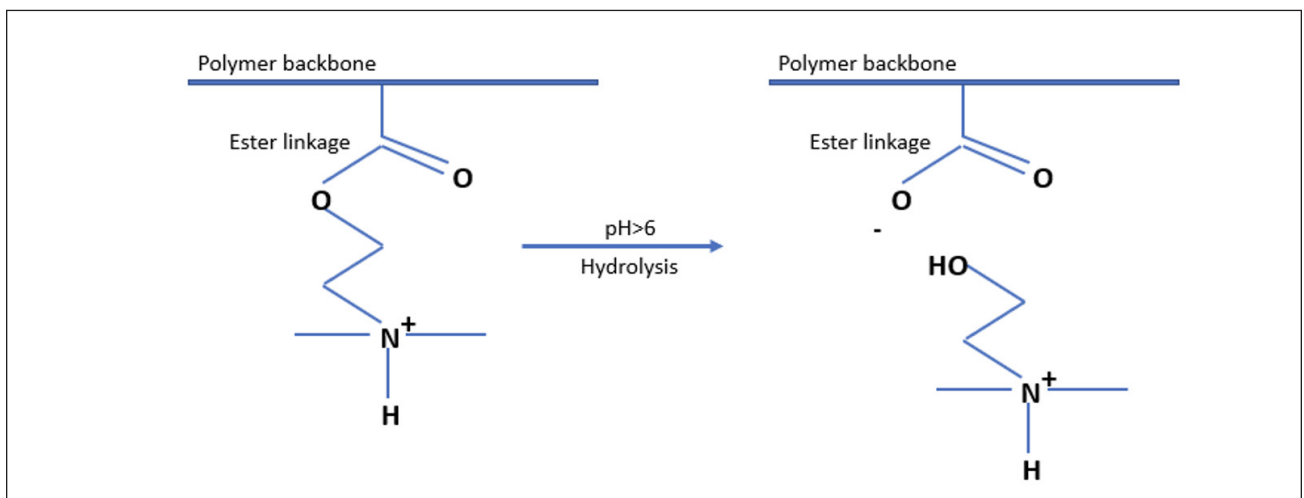
8. Theoretical dissociation curves for single carboxylic acid ( $pK_a=5$ ) and sulfonic acid ( $pK_a=1$ ) groups.

# PAPERMAKING

- The solubility of organic materials increases with elevated pH. Charged species are more soluble in water. Thus, exposing the fiber (especially high yield mechanical fiber) to higher pH increases soluble organic materials concentration. These materials are known collectively as dissolved and colloidal substances (DCS) and present challenges to cationic papermaking additives, including cationic starches.
- The level and variability of detrimental anionic substances (DCS) affect the performance and stability of retention and drainage polymers.
- The level and variability of surface charge of papermaking elements leads to variation in adsorption of additives, fiber swelling, strength, and water retention values. The impact of pH on the fiber swelling, strength, and drainage can be significantly reduced at higher conductivity levels. Higher pH increases the internal negative charge of the fiber and increases its swelling and water retention value (WRV).
- Fiber swelling associated with higher pH stock around pH 8 to 9.5 is also beneficial for fiber strength development during the refining process. Refining at lower pH results in excessive fiber shortening, while operating at a higher pH level increases refining energy demand to obtain a target freeness or strength property.
- Changes in the amount of the anionic charge alter the stability of colloidal dispersions of pitch and stickies material. Changes in this repulsive stabilizing force explain the well-known pH shock trigger to massive pitch or sticky deposits. Understanding that a lower pH reduces the anionic charge and that the gradient of charge loss is the highest around  $pH = pK_a$  of the carboxylic group, one could define downward pH change, reaching pH <5 as the worst type of “pH shock.” Although very important, pH shock is not the

only trigger of deposit formation. Other chemical and mechanical factors such as hardness, conductivity, and shear contribute to this problem, which we will discuss in our later paper from this series. However, it is essential that papermakers closely analyze pH range and pH variation in the case of deposit problems. It is crucial to avoid the local pH variation around addition points of acidic materials as a potential source of initial colloidal destabilization.

- Anionic additives, including anionic retention polymers and dispersants, experience a loss of anionic charge at a lower pH. In the products with anionic charge derived from carboxylic acid groups, this anionic charge loss will be significant at pH <5, leading to performance deterioration. This loss of performance determines pH limits for applying anionic polymers. Anionic polymers are an excellent choice for neutral or alkaline operations, where their full anionic charge is displayed. It is important to remember that charge on the polymeric chain of flocculants (cationic or anionic) and its impact on adsorption are primarily responsible for maintaining their extended conformation in solution and improved bridging capabilities. Loss of this charge or lowering the repulsive interaction between the same charges results in coiling of flocculant molecules, decreasing their effective length and reducing their bridging capabilities.
- Most cationic additives get a positive charge from various amine functionalities and may be pH-dependent. For primary, secondary, and tertiary amines, the cationic charge from the related ammonium salt comes from the amine protonated form (Eq. 13):



**9. Hydrolysis of the ester bond in cationic flocculant leads to charge loss as a cationic charge of the substituent is replaced by an anionic charge. This reaction occurs faster at higher pH and a higher temperature—lower pH for storing flocculant solution.**



This equilibrium and charge development (Eq. 13) depends on the amine's strength as a base as described by the  $pK_a$  of the ammonium salt ( $pK_a_{RNH_3^+}$ ). Typical values for aliphatic amines that resemble molecules used to produce the cationic flocculants (dimethylamino-ethyl acrylate) have  $pK_a \sim 10$ . In the practical range of papermaking, the charge on these amines is relatively resistant to higher pH levels. However, an ester bond's hydrolysis connecting amine function to the polymer chain undergoes hydrolysis with apparent charge loss [10] (Fig. 9):

Other typical coagulants based on ethylene imine chemistry,  $pK_a = 8.04$  [7], are more sensitive to deprotonation and charge loss. One may see the difference in fixation performance at pH 6.5 and higher. In one interesting case of a newsprint machine operating with a blend of TMP and recycled fiber, loss of charge of coagulant related to the conversion from acid to neutral pH led to significant loss of paper machine efficiency from increased calender stack deposition [11-12].

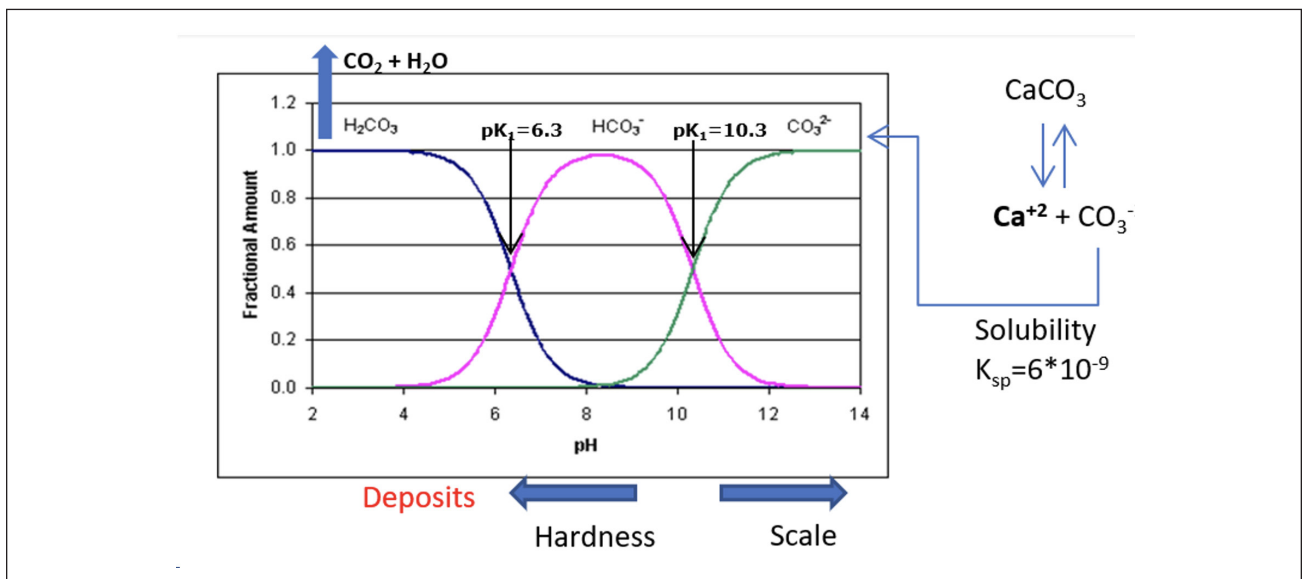
Cationic additives with the quaternized amine functionality ( $R_4N^+$ ) carry a cationic charge independent of protonation, as they do not undergo acid-base equilibrium. Therefore, the charge density of quaternary ammonium salts practically does not depend on pH. The authors strongly recommend, especially for alkaline operations (pH = 8 and higher), quaternized amines as cationic additives (fixatives, starches) for the best performance level and stability.

**IMPACT OF pH ON SOLUBILITY OF CaCO<sub>3</sub> REACTIVE FILLERS**

Another aspect of pH control involves the impact on the systems using various forms of calcium carbonate (CaCO<sub>3</sub>) fillers. Calcium carbonate, although generally insoluble,

shows slight solubility in water, as illustrated by its low solubility product,  $K_{sp, CaCO_3} = 6 \times 10^{-9}$ , leading to the formation of  $Ca^{+2}$  and  $CO_3^{-2}$  (carbonate) ions. Carbonate ion undergoes a series of pH-dependent equilibriums (Fig. 10), leading to unstable carbonic acid ( $H_2CO_3$ ) and  $CO_2$  gas evolution.

The evolution of  $CO_2$  makes this process irreversible and results in the accumulation of  $Ca^{+2}$  ions. Increasing pH will not correct the resulting increase in water hardness, and the papermaker should pay careful attention to avoiding lower pH areas, either system-wide or locally. This process includes selecting the proper pH of operation, well-designed feed points of acidic additives, and control over microbiological issues that could lead to local pH drops. Good broke management in  $CaCO_3$ -containing papers and excellent microbiological treatment of broke has proven beneficial in several mill applications. The authors strongly recommend adding the routine of frequent and regular hardness measurement of the broke stream containing calcium carbonate filler to detect local pockets of microbiological activity in the tower. Papermakers must pay special attention when controlling pH using acids or adding acidic additives to avoid localized pH drops. The best practices are diluting the acid and selecting the feed point where  $CaCO_3$  filler consistency is low. The concern for excessive hardness development also led to  $CO_2$ -based pH control technology [6]. This technology is an excellent way of reducing pH to  $pH \sim 7.4$  without significant hardness development. If  $pH < 7.4$  is targeted, it becomes increasingly difficult (cost-wise) to reach the target pH due to carbonic acid's weak character. A pH control with  $CO_2$  is used in the thick stock area of the pulping and paper machine systems. Its value is evident in the presence of calcium carbonate fillers.



10. The pH equilibria of carbonate ion. Solubility of  $CaCO_3$  fillers supplies carbonate ion ( $CO_3^{-2}$ ). As we lower pH value, carbonate ion exists in equilibrium with bicarbonate ion ( $HCO_3^-$ ) and hypothetical carbonic acid ( $H_2CO_3$ ) that decomposes to  $CO_2$  and water. Since  $CO_2$  leaves the system, it leads to the gradual dissolution of  $CaCO_3$  and the buildup of hardness in the system.

# PAPERMAKING

The addition of strong mineral acid could lead to filler yield losses with corresponding hardness increase development, potentially leading to deposits and scaling.

## IMPACT OF pH ON SOLUBILITY OF FATTY AND RESIN ACIDS

Fatty and resin acid constituents are a part of natural extractives. These materials are typically a part of the outer layer of colloidal pitch particles, remaining in direct contact with the water phase and stabilizing the particles against agglomeration. This process occurs at a much lower pH level for resin acids than for fatty acids. At higher pH, the increasing anionic charge on the carboxylic groups of these acids increases their solubility. At pH = 7, close to 50%–80% of the resin acids dissociate [13]. The need for additional energy to free the hydrophobic chain of fatty acids from the hydrophobic interior of pitch particles significantly increases the colloidal  $pK_a$  value for fatty acids [12]. The presence of resin acids and fatty acids in the soluble form creates an opportunity to precipitate their salts with  $\text{Ca}^{+2}$  and  $\text{Mg}^{+2}$  as an alternative mechanism for pitch deposition.

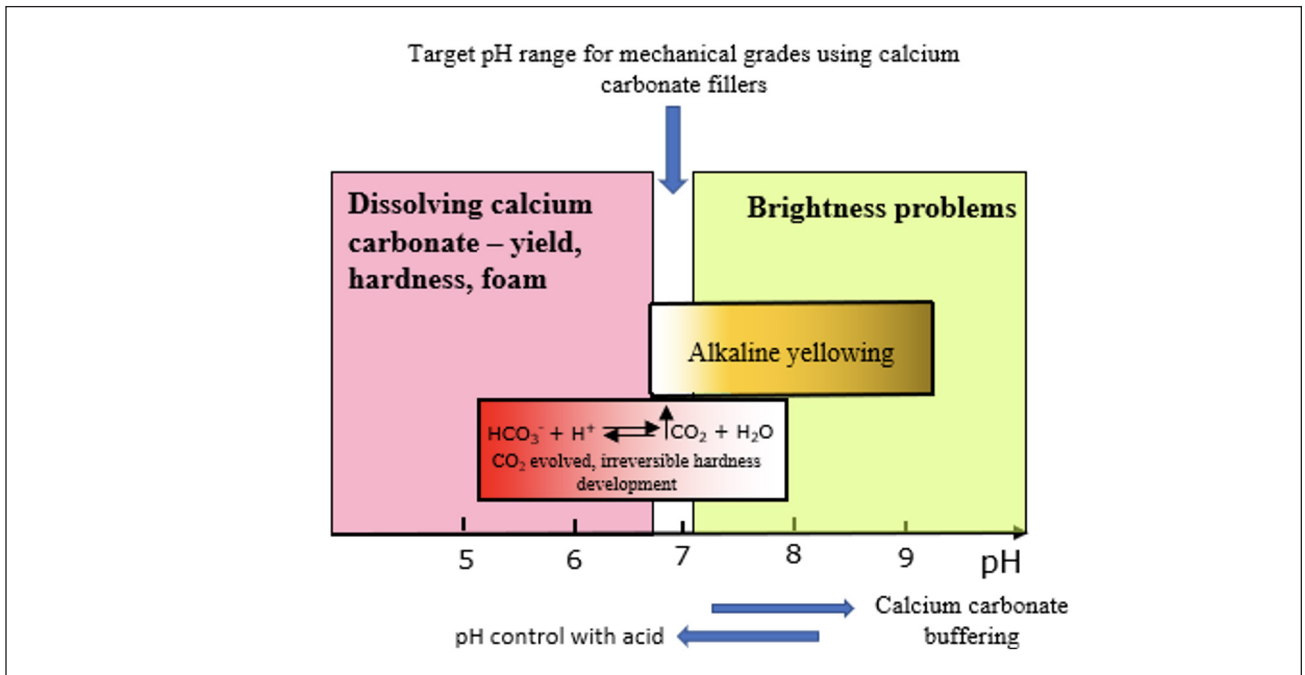
## IMPACT OF pH ON BRIGHTNESS CONTROL

Mechanical pulps undergo the well-known alkaline yellowing process at higher pH levels. Alkaline yellowing is related to chemical changes in the structure of lignin. Therefore, it is a problem almost exclusively associated with high-yield, wood-containing pulps like thermomechanical (TMP), stone groundwood (SGW), and pressurized groundwood (PGW), as well as recycled newsprint to a lesser extent. Although the degree of alkaline darkening also de-

pends on the wood species, it is a universal problem for all mechanical grades.

The trend toward higher pH, driven by the desire to utilize calcium carbonate fillers, increases the potential for brightness loss of mechanical pulps. It was estimated that the change from acid to neutral pH operation results in losing about two brightness points [14]. The increased sheet strength at higher pH compensates for this initial brightness loss by applying higher brightness  $\text{CaCO}_3$  fillers (PCC or GCC) and a high filler content target. Accommodating calcium carbonate fillers in the furnish requires a minimum pH of 6.8–7.2. A special acid-resistant PCC grade was developed for mechanical grades, offering lower hardness generated at neutral pH but not widening the application range significantly. Any higher pH level may result in unnecessary brightness losses that will require increased dosages of bleaching chemicals.

**Figure 11** summarizes the pH sensitivity for mechanical grades using virgin fiber and calcium carbonate fillers. The sensitivity of the brightness of mechanical pulps to pH differs between wood species and brightening technologies. Allison and Graham discuss the alkaline darkening phenomenon and its mechanisms for Radiata pine-based pulps [15]. Even one point of brightness loss for high brightness mechanical pulps translates to significantly increased bleaching costs (up to \$10/ton) and consequent excessive contamination of the wet end. With this in mind, it is crucial to understand that mechanical pulp-containing grades, especially virgin pulps, require operating at the narrow band of pH to control calcium carbonate dissolution (pH >6.8) and reduce the impact on brightness (pH <7.2).



**11. The pH range for mechanical grades with calcium carbonate fillers. Natural buffering by bicarbonate ion needs to be controlled by accurate acid addition to prevent pulp yellowing without triggering excessive hardness development.**

It is worth mentioning that brightness sensitivity is lower for recycled mechanical furnish, allowing operation up to  $\text{pH} = 7.8$ .

### IMPACT OF pH ON HYDROLYSIS REACTIONS IN PAPERMAKING

Organic compounds containing carbonyl functions ( $\text{C}=\text{O}$ ), such as esters, amides, acetals, and ketenes, undergo a reaction with water (hydrolysis) that is most effectively catalyzed with bases, particularly by  $\text{HO}^-$  ion. This family of reactions is called base-catalyzed hydrolysis. The concentration of  $\text{HO}^-$  ion increases with pH, making hydrolysis reaction faster at higher pH. An example of the relevant papermaker reaction is alkenyl succinic anhydride (ASA) hydrolysis, which leads to the loss of sizing response and formation of the dicarboxylic acid and deposits [16]. The formation of the dicarboxylic acid is a competing reaction to actual sizing development through a reaction with the fiber. Hydrolysis of ASA is an unproductive pathway, leading to losses of efficiency, generation of a de-sizing dicarboxylic acid, and increasing potential for deposition of its calcium salts. This hydrolysis reaction generally defines the upper pH range for uncoated freesheet grades since brightness concerns, typical for mechanical grades, do not apply to bleached chemical pulps. Exceeding a pH of 8.0–8.2 for these grades coincides with reduced sizing effectiveness and deposit formation. As discussed earlier, the formation of deposits in these cases would increase with some local pH drops (e.g., from microbiologically driven pH drops in broke towers), resulting in a higher hardness level. Running ASA sizing at higher pH without deposits may be possible at low hardness levels, but lowering pH to the best practices range will slow ASA hydrolysis down and increase its efficiency. Other alkaline hydrolysis reactions relevant to papermaking include alkyl ketene dimer (AKD) sizing application, generation of pectic acids contributing to soluble anionic trash, and free fatty and resin acids from their esters.

### CONCLUSIONS

Water is an essential element in the papermaking process. Due to its molecular structure and polarity, water offers unique solvent properties. It makes water an ideal medium to disperse cellulose fiber and promote hydrogen bond development. Water is also an excellent solvent for various organic and inorganic materials. Water dissociates, forming hydrated proton ( $\text{H}_3\text{O}^+$ ) and hydroxyl anion ( $\text{HO}^-$ ). Concentrations of both these ions are interrelated and typically expressed by pH value. Process pH is the most crucial water chemistry parameter affecting the properties of cellulose fiber and additives, both process and functional. The pH indirectly affects charge properties in terms of surface charge and charge demand. The pH conditions also affect retention, drainage, strength, water absorption, deposits, sheet defects, and scale. Finding proper pH to satisfy the

often-conflicting needs of the previously-listed applications is the most complex chemistry decision facing papermakers. It seemed essential to these authors to assist papermakers by collecting the basics of acid-base interactions, basic definitions, and intricate ways pH influences their operations. A sound understanding of these basic principles will build more attention to selecting the optimal and stable pH value for their process.

Not all papermaking systems are equally sensitive to pH levels and their variability. Based on the discussion in this paper, one can quickly identify papermaking systems where pH control is of essential importance to machine performance and product quality. As a minimum, papermakers need to measure pH in the headbox or tray water. We recommend that pH measurements be performed continuously online and correlated with relevant paper machine performance data and product quality. Over time, the analysis of generated data will provide information on the sensitivity of the given papermaking system to pH and the optimum pH range. Determination of the sources of pH variation and an effort to eliminate them should then take a preference over the aggressive pH control approach. An online, automatic pH control loop should be developed to provide the final pH level control and stability control. The importance of this approach may vary between grades. Papermakers could miss potential gains from addressing pH issues without initial pH monitoring and correlation efforts.

### SUGGESTED READING

As we prepare this paper, TAPPI Press is completing the first printing of a new textbook, *Process Chemicals for Papermaking*, edited by Martin A. Hubbe and Scott Rosencrance. Chapter 2 by Temple Ballard, John Williamson, and William Tuck covers “Influent water: Starting with the right water.” Other relevant chapters include Chapter 3, “Charge control agents, acids, and bases: Aiming for balanced conditions” by Martin A. Hubbe and Chapter 7, “Wastewater treatment: Making sure it ends well” by Angeles Blanco, Ana Balea, Borja Ojembarrena, Daphne Hermosilla, Antonia Gasco, and Carlos Negro. **TJ**

### LITERATURE CITED

1. Pruszyński, P. and Gratton, R., “Wet-end chemical applications: Paper machine chemical environment and interactions between chemical additives,” in *Advances in Papermaking Wet End Chemistry Application Technology* (M. Hubbe and S. Rosencrance, Eds.), TAPPI Press, Peachtree Corners, GA, USA, 2018.
2. Xu, L., Pruszyński, P., and Hart, P., *TAPPI J.* 16(10): 567(2017). <https://doi.org/10.32964/TJ16.10.567>.
3. Luzar, A. and Chandler, D., *Nature* 379: 55(1996). <https://doi.org/10.1038/379055a0>.
4. Dill, K.A., Truskett, T.M., Vlachy, V., et al., *Annu. Rev. Biophys. Biomol. Struct.* 34: 173(2005). <https://doi.org/10.1146/annurev.biophys.34.040204.144517>.

# PAPERMAKING

5. Brini, E., Fennell, C.J., Fernandez-Serra, M., et al., *Chem. Rev.* 117: 12385(2017). <https://doi.org/10.1021/acs.chemrev.7b00259>.
6. Jansson, A-C., "Carbon dioxide based applications for optimization of calcium carbonate containing papermaking processes," *PAPTAC Annu. Meet., 95th*, PAPTAC, Brossard, QC, Canada, 2009, p. 429.
7. Dean, J.A., *Lange's Handbook of Chemistry*, 14th edn., McGraw-Hill, New York, 1992.
8. Hart, P.W and Rudie, A.W., *The Bleaching of Pulp*, 5th edn., TAPPI Press, Atlanta, 2012, p. 156.
9. Lovgren, L.J., Stenius, P., and Sjoberg, S., *Colloids Surf., A* 88(2-3): 277(1994). [https://doi.org/10.1016/0927-7757\(94\)02834-6](https://doi.org/10.1016/0927-7757(94)02834-6).
10. Ekberg, R. and Wagberg, L., *J. Appl. Polym. Sci.* 38(2): 297(1989). <https://doi.org/10.1002/app.1989.070380211>.
11. Dechandt, A., Watkins, T., and Pruszynski, P., *Appita J.* 57(1): 13(2004).
12. Richardson, D., Waller, N., Parsons, T., et al., "Optimization of neutral papermaking wet end chemistry for pitch-free newsprint manufacture," *Appita Annu. Conf. Proc., 57th*, APPITA, Macleod, Vic, Australia, 2003, p. 219.
13. McLean, D., Vercoe, D., Stack, K., et al., *Appita J.* 58(5): 362(2005).
14. Evans, B. and Slozer, M., "Neutral groundwood papers: Practical and chemical aspects," *Int. Pap. Coat. Chem. Symp., 5th*, PAPTAC, Brossard, QC, Canada, 2003.
15. Allison, R. and Graham, K., *J. Pulp Pap. Sci.* 16(1): 28(1990).
16. Farley, C.A. and Wasser, R., in *The Sizing of Paper* (W.F. Reynolds, Ed.), TAPPI Press, Atlanta, 1989, p. 54.

## ABOUT THIS PAPER

### Cite this article as:

Pruszynski, P., Xu, L., and Hart, P.W., *TAPPI J.* 21(6): 313(2022). <https://doi.org/10.32964/TJ21.6.313>

**DOI:** <https://doi.org/10.32964/TJ21.6.313>

**ISSN:** 0734-1415

**Publisher:** TAPPI Press

**Copyright:** ©TAPPI Press 2022

[About this journal](#)

## 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 a useful review 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). An earlier work focused on conductivity, and future work will address other fundamental areas.

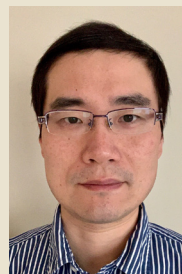
As water chemistry has a broad impact on wet-end additives and operation, the author team was comprised of members from both the chemical supplier side and papermaker side to provide a comprehensive view and knowledge in this review.

Through this study, we gained a greater appreciation for the importance of basic/fundamental factors with broad impacts. It is always interesting to revisit how much a small pH change in the papermaking pH range can alter chemical performance.

With this review, mills gain a comprehensive view of how water affects wet-end additives and how to make optimal use of them. The work highlights the



**Pruszynski**



**Xu**



**Hart**

need for good pH control. It also can function as a good training resource for new employees.

Our next step is to put the knowledge in this review paper to work and to develop the next paper in our wet-end chemistry series.

---

*Pruszynski is technical director and owner at Pruszynski Paper Chemistry Consulting LLC, Naperville, IL, USA. Xu is senior research scientist/engineer and Hart is director, Fiber Science and Innovation, at WestRock in Richmond, VA, USA. Email Xu at [lebo.xu@westrock.com](mailto:lebo.xu@westrock.com).*