Wet end chemistry ch 1

WPS, CBNU
1.1 wet end chemistry and paper properties

A. Categories of paper properties influenced by wet end chemistry

- Structural properties (Basis weight, caliper formation, directionality, two-sideness, porosity, roughness, dimensional stability)
- Appearance properties (color, brightness, opacity, gloss)
1.1 wet end chemistry and paper properties

- A. Categories of paper properties influenced by wet end chemistry
  - Barrier and resistance properties (sizing)
  - Permanence properties (durability, color reversion, chemical stability)
1.1 wet end chemistry and paper properties

• B. Structural properties

  - Basis weight: control by paper machine’s stock metering system.

  - Formation: a function of 3 dimensional distribution of materials throughout the sheet

  - Two sideness: occurs primarily when web drainage from one side only during sheet formation
1.1 wet end chemistry and paper properties 4

• C. Mechanical properties

- Mechanical properties: functions of bond strength, fiber strength and sheet formation.
- Fiber–fiber hydrogen bond: enhanced by dry strength agents
- Filler and sizing agents: interfere with fiber–fiber bonding and reduce paper strength
D. Appearance properties

- Dyes and minerals: a principal means of influencing the appearance of paper.
- Color, opacity and brightness
- Scatter light more effectively than fibers
- Selectively absorb specific visible light wavelengths
- For high opacity and brightness: necessary to retain high levels of mineral fillers in the formed web
1.1 wet end chemistry and paper properties 6

• E. Barrier and resistance properties
  – Wood fiber: poor resistance to water penetration
  – Internal or external sizing: water–resistance properties by sizing treatment
  – give hydrophobic properties to wood fiber
  – Machine cleanliness and runnability problems
1.1 wet end chemistry and paper properties 7

- F. Permance
  - Interest primarily to librarians and archivists.
  - Acid paper: alum
  - Neutral paper: synthetic polymer
1.2 Wet end chemistry and machine runability

- Drainage
- Deposits and scale
- Foam and entrained air
1.3 Current trends

• Acid paper to neutral paper

• Uses in recycled fibers

• Increased chemical additives use in grade other than fine papers
Wet end chemistry ch 2

WPS, CBNU
The geometry of water molecules

• Bond angle: 105

• Polarity of molecules – can be determined as dipole moment

  – Examples
    • Sodium chloride: 9.0
    • Water: 1.85
    • Methanol: 1.70
    • Carbon tetrachloride: 0
Figure 2-1. The geometry of the liquid water molecule, $H_2O$. Each hydrogen atom is bonded to the oxygen atom. The O-H bond length is 0.096 nm and the H-O-H bond angle is 105°.
Figure 2-2. Strong hydrogen bonding between Clusters
The hydrogen bonding ability of water molecules

- Polarity of the water molecule $\rightarrow$ leads to their association through hydrogen bonding interactions
- Many of unique properties of water come from hydrogen bonding ability
  - Ex: specific heat, freezing point, boiling point, Latent Heat of evaporation (in Table 2.2), surface tension
Chemical equilibria in a water environment

- Chemical equilibrium in a water environment
- A: a dynamic equilibrium
- B: definition of pH
Acidity

**Acidity Example**

\[ H_2O \rightleftharpoons H^+ + OH^- \]

**Alum Ionization**

\[ Al_2(SO_4)_3 \rightleftharpoons 2Al^{3+} + SO_4^{2-} \]

**Alum Hydrolysis**

\[ Al^{3+} + OH^- \rightleftharpoons Al(OH)^{2+} \]
\[ Al(OH)^{2+} + OH^- \rightleftharpoons Al(OH)_2^{+1} \]
\[ Al(OH)_2^{+1} + OH^- \rightleftharpoons Al(OH)_3 \]

\[ [Al^{3+}][OH^-] = 9 \times 10^{-33} \]
Alkalinity Example

\[ \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^- \]

**CaCO}_3\text{ Ionization**}

\[
\text{CaCO}_3 \rightleftharpoons \text{Ca}^{+2} + \text{CO}_3^{-2}
\]

\[
[\text{Ca}^{+2}][\text{CO}_3^{-2}] = 9 \times 10^{-9}
\]

**Reaction Between Carbonate Ion and Hydrogen Ion**

\[
\text{CO}_3^{-2} + \text{H}^+ \rightleftharpoons \text{HCO}_3^{-1}
\]

\[
\text{HCO}_3^{-2} + \text{H}^+ \rightleftharpoons \text{H}_2\text{CO}_3^{-2}
\]

\[
\text{H}_2\text{CO}_3^{-2} \rightleftharpoons \text{H}_2\text{O} + \text{CO}_2 \quad \text{(gas)}
\]
Effect of pH on Carboxyl Groups

\[ \text{RCOOH} \rightleftharpoons \text{H}^+ + \text{COO}^- \]

\[ \frac{[\text{H}^+][\text{RCOO}^-]}{[\text{RCOOH}]} = 2 \times 10^{-5} \]

Low pH

\[ \text{RCOOH} \rightleftharpoons \text{H}^+ + \text{RCOO}^- \]

High pH

\[ \text{RCOOH} \rightleftharpoons \text{H}^+ + \text{RCOO}^- \]
<table>
<thead>
<tr>
<th>Concentration, Wt. %</th>
<th>Specific conductance, mS/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>1.7</td>
</tr>
<tr>
<td>0.50</td>
<td>8.2</td>
</tr>
<tr>
<td>1.00</td>
<td>16.0</td>
</tr>
<tr>
<td>2.00</td>
<td>30.2</td>
</tr>
<tr>
<td>4.00</td>
<td>57.3</td>
</tr>
<tr>
<td>8.00</td>
<td>105</td>
</tr>
<tr>
<td>16.0</td>
<td>179</td>
</tr>
</tbody>
</table>
Hardness refers to a special subset of dissolved ions and their effects. The traditional definition of hardness referred to “the soap-consuming capacity of water.” More recently, hardness has been defined as the “concentration of calcium and magnesium cations in water, independent of the anions present, expressed as ppm CaCO$_3$.”

Hardness is often determined by titration with disodium ethylenediamine tetraacetate (EDTA) plus Calgamite indicator. The endpoint is a red-to-blue transition.
Summary of this chapter

Water is a critical ingredient in papermaking. It is the suspending medium from which paper is formed and it is the medium within which all of the furnish components are dissolved or dispersed prior to sheet formation. It promotes the formation of fiber-fiber bonding. The wet end chemist must be very familiar with the classical water chemistry concepts of pH, acidity, alkalinity, solubility, conductance, and hardness and understand how they affect the performance of papermaking materials.
Wet end chemistry ch 3

WPS, CBNU
Papermaking fibers
a. fiber morphology

• Softwood: fiber length (3–7mm), fiber width (20–50μm), cell wall thickness (3-7 μm), tracheid

• Hardwood: shorter fiber (1–2 mm), fiber width (10–40μm), nonfibrous element (vessel element, ray cells, parenchyma cell)

• Fiber ultrastructure: lumen, S3, S2, S1 layer, Primary layer, middle lamella
  – S2 layer : main part of fiber
Papermaking fiber
b. fiber chemistry

• Chemical composition (Table 3.1)
  – Cellulose, glucomannan, xylan, lignin, extractives

• Cellulose: main structural components of wood fiber

• Hemicelluloses: glucomannan and xylan

• Lignin: residual lignin in pulp, MP, CP

• Location of components within fiber wall: S2

• Extractives
<table>
<thead>
<tr>
<th>Main Components</th>
<th>Spruce</th>
<th>Pine</th>
<th>Birch</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose</td>
<td>41</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>Glucomannan</td>
<td>18</td>
<td>17</td>
<td>3</td>
</tr>
<tr>
<td>Xylan</td>
<td>8</td>
<td>7</td>
<td>30</td>
</tr>
<tr>
<td>Other carbohydrates</td>
<td>4</td>
<td>5</td>
<td>4</td>
</tr>
<tr>
<td>Total Carbohydrates</td>
<td>69</td>
<td>67</td>
<td>74</td>
</tr>
<tr>
<td>Lignin</td>
<td>27</td>
<td>27</td>
<td>20</td>
</tr>
<tr>
<td>Extractive Substances</td>
<td>2</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>
Figure 3-5. Distribution of chemical components across the fiber wall
<table>
<thead>
<tr>
<th>Component</th>
<th>Pine</th>
<th>Birch</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose</td>
<td>35</td>
<td>34</td>
</tr>
<tr>
<td>Glucomannan</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>Xylan</td>
<td>5</td>
<td>16</td>
</tr>
<tr>
<td>Other carbohydrates</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Total Carbohydrates</td>
<td>44</td>
<td>51</td>
</tr>
<tr>
<td>Lignin</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>Extractive Substances</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Total</td>
<td>47</td>
<td>53</td>
</tr>
</tbody>
</table>

Papermaking fiber

c. influence of pulping processes on fibers

• Mechanical pulping
  – Few chemical changes in fiber
  – Fiber surface chemistry and composition depend on the degree of structural disruption that occurs during pulping

• Chemical pulping
  – Chemical and structural changes during pulping
  – Structural changes: dissolution of lignin and hemicelluloses → more hydrophilic fibers (Table 3.2 Typical chemical composition of kraft pulps)
Fiber fines

• Pulp fines vary widely in morphology, but often are rod–shaped, semicrystalline, fibrilliar particles having widths of 0.1–0.5 \( \mu \text{m} \) and length (several tens of micrometers)

• Primarily fines: occur from pulp fiber

• Secondary fines: generated by refining

• Tertiary fines: generated during the flow of stock
Fiber and fines characteristics important to papermaking chemistry

a. specific surface area

- Smaller particle → have more specific surface area than larger particle
- Surface area of fine: 5–8 times more than that of fiber
- Fines have higher adsorption ability than fiber with higher surface area
- Fines: influence on paper machine drainage performance due to their high water sorption capacity
- Fine retention: crucial to efficient material utilization (40–60% weight of furnish)
Table 3-3. Surface area measurements of pulp fractions.[5]

<table>
<thead>
<tr>
<th>Pulp Fraction</th>
<th>Specific Surface Area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fiber Fraction</td>
<td>9.9</td>
</tr>
<tr>
<td>Fines Fraction (Hydrodynamic)</td>
<td>46.8</td>
</tr>
<tr>
<td>Pulp Blend, 410 CSF</td>
<td>2.1</td>
</tr>
<tr>
<td>Fiber Fraction</td>
<td>1.2</td>
</tr>
<tr>
<td>Fines Fraction (16.5%)</td>
<td>8.0</td>
</tr>
</tbody>
</table>
Table 3-4. Adsorption of wet end additives by fines

<table>
<thead>
<tr>
<th>Additive</th>
<th>Relative Adsorption Intensity</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fibers</td>
<td>Filler Clay</td>
</tr>
<tr>
<td>Cationic Starch</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>Rosin Soap Size</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>Dispersed Rosin Size</td>
<td>1</td>
<td>16</td>
</tr>
<tr>
<td>Alum</td>
<td>1</td>
<td>2</td>
</tr>
</tbody>
</table>
Fiber and fines characteristics important to papermaking chemistry
b. preferential additive adsorption by fines

- Table 3.4—adsorption of wet end addition by fines

- Fines have higher surface area than filler clay or fibers which lead to higher adsorption of cationic starch, rosin soap size, dispersed rosin size and alum
Fiber and fines characteristics important to papermaking chemistry

c. surface charge

• Type of surface charge
  – Table 3.5 Types of ionizable groups in wood
  – Table 3.6 Typical carboxyl group level in virgin and recycled pulps

• The effect of pH on fiber ionization
  – Figure 3.7 The effect of pH on the dissociation of fiber charge–producing groups
Table 3-5. Types of ionizable groups in wood

<table>
<thead>
<tr>
<th>Acid Group</th>
<th>$pK_a\ (25^\circ C)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hemicellulose &amp; Lignin Carboxyl Groups</td>
<td>4-5</td>
</tr>
<tr>
<td>Lignin Phenolic OH Groups</td>
<td>9.5-10.5</td>
</tr>
<tr>
<td>Sugar Alcohol Groups</td>
<td>13.5-15.0</td>
</tr>
<tr>
<td>Hemiacetal OH Groups</td>
<td>12.0-12.5</td>
</tr>
<tr>
<td>Lignosulphonate Groups</td>
<td>100% ionized in water</td>
</tr>
<tr>
<td>Virgin Pulps</td>
<td>Carboxyl Number (meq/100g)</td>
</tr>
<tr>
<td>--------------------------------------------------</td>
<td>----------------------------</td>
</tr>
<tr>
<td>Bleached Softwood Kraft</td>
<td>2-4</td>
</tr>
<tr>
<td>Bleached Hardwood Sulfite</td>
<td>3-8</td>
</tr>
<tr>
<td>CTMP</td>
<td>20-40</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Recycled Fibers</th>
<th>Carboxyl Number (meq/100g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deinked Bl. N. Kraft</td>
<td>7.4</td>
</tr>
<tr>
<td>Deinked Bl. S. Kraft</td>
<td>7.3</td>
</tr>
<tr>
<td>Deinked Tissue</td>
<td>8.6</td>
</tr>
<tr>
<td>Merchant Recycled Pulp</td>
<td>8.9</td>
</tr>
<tr>
<td>Waste Newsblank</td>
<td>19.9</td>
</tr>
</tbody>
</table>
Figure 3-7. The effect of pH on the dissociation of fiber charge-producing groups
and fines characteristics important to papermaking chemistry
d. ion exchange behavior of wood fibers and fines

- Least tightly bound ions
- Most tightly bound ions
- Al\(^{3+}\): more strongly to wood fibers than Ca\(^{2+}\)
- The charge neutralizing power of these cations occurs in similar order.
Summary of this chapter

• Pulp fiber and fines: participate in papermaking process through chemical, colloidal and surface interactions

• Important factor in fiber and fines: composition of surface, size and surface area of particles

• Fiber and fines: have negatively charged surface