Bleaching

- Improved appearance
  - Brightness
  - Shives or dirt specs (largely bark related)
  - Perception of purity - sanitary

- Improved functionality
  - Print readability and impact

- The caveat - the bleach plant is the major source of organic loading (BOD) to the wastewater treatment plant.
What is brightness

• % of incident light reflected by the test specimen relative to a defined white standard.
  – The reference “white” is MgO

• Test is subject to:
  – Optical layout
  – Specimen properties
    • Light absorption
    • Smoothness
    • Opacity
What is opacity?

• Paper backing:
  – The percentage of light reflected by a specimen with a black backing relative to the amount of light reflected by an infinitely thick specimen.

• 89% Reflectance backing:
  – The percentage of light reflected by a specimen backed with a black body relative to the brightness of the specimen when backed by a substance with 89% absolute reflectance.
Fundamental properties

• $k$ = the light absorption coefficient (fraction of incident light adsorbed by the substrate)

• $s$ = the light Scattering Coefficient (fraction of incident light reflected by the substrate)

• Brightness and Opacity are functions of both fundamental properties
  - $R_\infty = 1 + k/s - [(k/s)^2 + (2k/s)]^{0.5}$
  - $R_0/R_\infty = \{\exp[sW(1/R_\infty - R_\infty)] - 1\}/\{\exp[sW(1/R_\infty - R_\infty)] - R_\infty^2}\}$
What controls the fundamentals

- Light absorption is largely controlled by molecular electronic transitions from a ground state to an excited state with a transition energy of 1.5 – 3.5 eV (700-400) nm
- The light active substances in wood pulp is largely lignin which has an adsorption maximum at ~ 200 nm, a distinctive feature at 280 nm and a broad tail that trails into the visible spectrum at 400 nm.
- Brightness is measured with a dominant wavelength of ~ 457 nm
Two standard methods

TAPPI, GE, or Directional  Diffuse Reflectance, or ISO

5°  0°

45°  90°
Bleaching chemicals

• Lignin degrading
  – Alkaline oxygen O
  – Chlorine dioxide D
  – Ozone Z
  – Caustic (extraction) E
  – Pressurized peroxide $P_{HT}$

• Lignin Preserving
  – Sodium hydrosulfite
  • $Na_2S_2O_4$
  – Alkaline peroxide P
Bleach Plants

- Mechanical pulps – one or two stages, hydrosulfite and/or peroxide
- Chemical pulps - typically 3-6 stages
  - Sequence is identified by letter designation, starting from the brown stock end
  - Combined processes/chemicals are placed in parenthesis
  - OD(Eo+p)DPD
  - D(Eo+p)DED
OD(Eo+p)DPD

- Oxygen delignification
- followed by chlorine dioxide
- followed by an alkaline extraction - fortified with oxygen and peroxide
- Followed by a chlorine dioxide stage
- Followed by a peroxide stage
- Followed by a final chlorine dioxide stage.
Why multiple stages?

• Efficiency in the oxidative stages is limited by continuing to react with lignin fragments, and the build-up of the lignin fragments within the pore structure of the fiber wall.

• Alkaline stages (E or P) dissolve the phenolic lignin fragments and reactivate the fiber for further bleaching
Typical bleach stage

![Graph showing the relationship between brightness and chemical charge. The graph starts with a steep increase in brightness as chemical charge increases, followed by a plateau at the brightness ceiling.](image)
## Chemicals

<table>
<thead>
<tr>
<th>Chemical</th>
<th>MW</th>
<th># e⁻</th>
<th>MW/e</th>
<th>Selectivity</th>
<th>$ (rank)</th>
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<tr>
<td>ClO₂</td>
<td>67.5</td>
<td>5</td>
<td>13.5</td>
<td>High</td>
<td>3</td>
</tr>
<tr>
<td>O₂</td>
<td>32</td>
<td>4</td>
<td>8</td>
<td>Low</td>
<td>1</td>
</tr>
<tr>
<td>H₂O₂</td>
<td>34</td>
<td>2</td>
<td>17</td>
<td>High</td>
<td>5</td>
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<tr>
<td>O₃</td>
<td>48</td>
<td>6</td>
<td>8</td>
<td>Medium</td>
<td>6</td>
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</table>
Oxygen Delignification

- Oxygen (typically 10-25 kg/ton ~ 100 psig)
- NaOH (typically 15-30 kg/ton)
- 90 – 100° C
- 20 to 45 minutes
- Three systems
  - Low consistency – 3-4% - unsuccessful
  - Medium consistency ~ 10% - mc mixer
  - High consistency (20-25%)
**Oxygen**

- Wash filtrates are used as wash water in brown stock washing
- Delignification usually limited to 40-50%
- High and medium consistency often add MgSO$_4$ as a viscosity stabilizer
- **Cautions/problems**
  - Low consistency – gas chimney effect
  - Medium consistency – “foam” collapse
  - High consistency – product gas explosions
Chlorine dioxide

• Usually $D_0$ and $D_1$ use about 1% ClO$_2$ on pulp (maybe a bit higher in $D_0$). Generally less on hardwoods

• $D_0$ pH is between 2 and 4, $D_1$ pH is usually about 4
ClO$_2$

- O – six valence electrons
  - It is more electronegative than Cl, so for electron counting it is considered to be O$^{2-}$ and the oxygens have 8 electrons.
- Cl adds 7 valence electrons $2 \times 6 + 7 = 19$
  - it is paramagnetic - a radical oxidant.
ClO$_2$

- An unstable gas
- Produces a low velocity decomposition
  - $2\text{ClO}_2 \rightarrow \text{Cl}_2 + 2\text{O}_2$
  - Referred to usually as a puff. Kind of a euphemism for explosion.
- Sold to the chemical as stable sodium chlorate
- Manufactured on site by:
  - $\text{ClO}_3^- + \text{HCl} \rightarrow \text{ClO}_2 + \frac{1}{2} \text{Cl}_2 + \text{OH}^-$
  - Reaction is carried out in strong sulfuric acid and the by-product is $\text{Na}_2\text{SO}_4$ which is used as makeup.
## ClO₂ Generation: Tons per ton ClO₂

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Mathieson</th>
<th>R3</th>
<th>R7</th>
<th>R8</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaClO₃</td>
<td>1.75</td>
<td>1.68</td>
<td>1.68</td>
<td>1.68</td>
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<tr>
<td>NaCl</td>
<td>-</td>
<td>1.15</td>
<td>0.35</td>
<td>0.025</td>
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<tr>
<td>SO₂</td>
<td>0.65</td>
<td>-</td>
<td>0.4</td>
<td>-</td>
</tr>
<tr>
<td>Methanol</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.14</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>1.17</td>
<td>2.3</td>
<td>1.6</td>
<td>-</td>
</tr>
<tr>
<td>Na₃HS₂O₄</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.3</td>
</tr>
<tr>
<td>Cl₂</td>
<td>-</td>
<td>0.7</td>
<td>0.25</td>
<td>0.04</td>
</tr>
</tbody>
</table>
ClO₂ Generation

- ClO₂ is generated in a strong acid
- ClO₂ gas is swept out of the reactor – either by sparging with air, or placing the system under a vacuum
- ClO₂ gas is then scrubbed in chilled water, producing a ClO₂ solution at 6-10 gpl as ClO₂ (15 – 26 gpl as TAC)
- Becomes unstable at ~ 100 mm Hg partial pressure.
  - At 10° C this is 16 gpl,
  - at 25° C, this is 8 gpl.
**ClO₂** (1000 tpd mill ~700 kg pulp/min)

- **ClO₂**
  - 1.3 m³/min

- **Mixer**
  - Tower
  - Washer

- **Washer**
  - ~2 tons of fresh water per ton of pulp
Optimization

![Graph showing the relationship between pH off, % available chlorine, ClO3-, ClO2-, and Brightness.](image)
ClO₂ Optimization

• Chlorite (ClO₂⁻) forms from a one electron oxidation by chlorine dioxide.
• ClO₂⁻ does not react further but HClO₂ does react with lignin
• Other reactions
  – 2HClO₂ + HClO → ClO₂ + HCl + H₂O
  – 2HClO₂ → H⁺ + HOCl + ClO₃⁻ (Chlorate)
  – Chlorate is stable at bleaching pH
Alkaline Peroxide Bleaching

• Routine Peroxide is not very good at removing lignin.
  – Has some delignification value in the first extraction stage.
  – Generally used to reduce color
  – Has better brightness retention (reduced reversion) than other bleach reagents.
  – Activated &/or pressure P-stage with metals management more effective at removing lignin
Alkaline Peroxide

• Sensitive to trace metal contamination
  – $2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$
  – Catalyzed by surfaces containing iron
  – Catalyzed by manganese

• Control issues
  – Precede by acidic stage
  – Add chelating reagents (EDTA/DTPA ~ 2 kg/ton)
  – Add magnesium sulfate (probably encapsulates Mn(OH)$_2$ in the Mg(OH)$_2$ precipitate 0.5 kg/ton)
  – Add sodium silicate (same basic mechanism as MgSO$_4$ ~ 30 kg/ton)
Alkaline Peroxide

• Typical peroxide charge: 1% on pulp, usually less
  – In late stages, brightness ceiling is usually at about 0.2 to 0.3% on pulp.

• Temperature is usually not an issue

• Retention time from 1 to 12 hours can be handled

• In brightening stages, need to maintain a peroxide residual.
Peroxide – other bleaching uses

- If you don’t have a tower method: High density (high consistency) storage.
  - Low charges – 0.2-0.3% on pulp
  - Low alkali (need to run out of alkali before consuming all the peroxide)
  - Good for ~ 2 points brightness

- Dryer bleaching
  - Flash dryer or on machine
  - Again, low charges
  - Usually uses sodium tripolyphosphate as alkali source.

- These are useful – low capital approaches for 2-3 points in brightness.
Ozone Bleaching

• Under evaluation as a bleaching agent since early 70’s
  – Scott/Impco high consistency
  – IP and others, low consistency

• Low concentration component (3-6%) in air or oxygen.

• Sparingly soluble in water

• Unstable: decomposes to oxygen.

• Aggressive chemical, second to fluorine in oxidation potential (2.07 V relative to SHE)
Ozone in the 90’s

• Has been installed by a few mills in the US and approx half dozen in Europe.

• Two basic designs:
  – High consistency tube conveyor
  – Medium Consistency (High shear mixer) designs
Ozone bleaching

• Usually the first stage – after an oxygen delignification stage.

• Ozone charge is usually small, 0.5-1% on pulp
  – High consistency can handle higher ozone charges than medium consistency
  – High charge MC applications use two mix/tower stages in series.
Ozone

- pH is acidic – 2-3
- Temperature – as low as the mill can achieve. Room temperature is best
- Retention time – usually short, 5-15 minutes
Bleach towers: General considerations

• Retention time (volume)
  – Typically 30 min to 1 hr for $D_0$
  – Typically 1 hr for Extraction stages
  – Typically 2 to 4 hours for $D_1$ and $D_2$

• Plug flow
  – Inlet and discharge design
  – $h/d$
  – Critical vertical velocity (> 0.3-0.5 ft/min)

• Materials of construction
Bleach towers

Upflow
• No control over retention time
• May have a bottom mixer to distribute pulp radially at the bottom

Downflow
• Usually a pre-retention tower of J tube
• Can control retention time
Scrapper: rotates at 2-4 rpm

Dilution

Laundering Ring

Medium Consistency up-flow bleach tower
Medium Consistency down-flow bleach tower
Level is controlled for retention time

Pulp in

Dilution

Pulp out
Materials of Construction

• The issue – increasing chloride content (due to reduced fresh water input) leads to a more corrosive environment.

• Corrosion resistant alloys
  – Titanium (incompatible with peroxide)
  – Hasteloy C (incompatible with peroxide)

• Tile lining
  – Tiles are either acid or base compatible

• The issue – it is hard to change bleach chemistries
Control instrumentation

- Brightness probe
- Residual measurement
- pH
- Temperature
- Production rate
- Normally need about 5-10 minutes retention time before probe.
Environmental issues

• Eutrophication (72/77 – Clean Water Act)
  – Biological oxygen demand

• Toxicity (97/98 – Cluster Rules)
  – Chlorinated organics or AOX (Absorbable organic halogen)
“Solutions”

• BOD
  – reduce volume
  – O₂ delignification
  – add secondary treatment (aeration stabilization basin, or activated sludge)

• AOX
  – O₂ delignification
  – ClO₂ substitution (ECF — Elemental Chlorine Free)
  – O₃ and H₂O₂ (TCF — Totally Chlorine Free)
General Concepts

- Countercurrent wash systems so that final bleach stages do not contend with a build up of process and non-process chemicals.
- Minimize mixing of alkaline and acid streams to minimize pH adjustments, and avoid acid precipitation of lignin.
- Controlled water use to minimize the effluent volume to waste treatment.
Split Stage Washing
3200 gal/T

To Papermachine
Counter Current Washing
2,100 gal/T
To Papermachine