Paper Recycling Technology

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Washers
Washers

- Definition: a separation device that rinses small particulate contaminants away from fibers
- Deinking Washer:
  - Dilute pulp with wash water
  - Disperse small contaminant in water phase
  - Remove contaminant laden water
Washers

- Washers in recycling remove all of the following:
  - fines
  - filler
  - inks
  - dissolved species
- In order for washing to be successful, the intended contaminant must be small.
Thickening vs. Dilution Washing

- **Thickeners**
  - purpose to increase consistency
  - fiber mat formation ok
  - lower yield losses

- **Deinking (Dilution) Washers**
  - purpose is to remove contaminant particles
  - fiber mat formation avoided
  - higher yield losses
### Influence of Pulp Mat Formation on Washing Efficiencies

Pulp mats prevent the removal of small particles in washing.

<table>
<thead>
<tr>
<th>Type</th>
<th>Inlet % K</th>
<th>Outlet % K</th>
<th>Ash Removal %, Theoretical</th>
<th>Ash Removal %, Actual</th>
<th>Pulp Mat Formation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sidehill Scrn</td>
<td>0.8</td>
<td>3</td>
<td>74</td>
<td>60</td>
<td>Minimal</td>
</tr>
<tr>
<td>Grav Decker</td>
<td>0.8</td>
<td>5</td>
<td>85</td>
<td>55</td>
<td>Yes</td>
</tr>
<tr>
<td>Incl. Screw</td>
<td>3.0</td>
<td>10</td>
<td>72</td>
<td>45</td>
<td>Extensive</td>
</tr>
<tr>
<td>Horiz. Screw Press</td>
<td>4.0</td>
<td>28</td>
<td>89</td>
<td>35</td>
<td>Extensive</td>
</tr>
<tr>
<td>Belt Washer</td>
<td>1.0</td>
<td>10</td>
<td></td>
<td>80</td>
<td>Minimal</td>
</tr>
<tr>
<td>Vario Split</td>
<td>0.8</td>
<td>10</td>
<td>85</td>
<td>80</td>
<td>Minimal</td>
</tr>
</tbody>
</table>
Types of Washers

- Low Consistency Washers
- Intermediate Consistency Washers
- High Consistency Washers
Low Consistency Washers

- Up to 8% discharge consistency
  - side-hill screen
  - gravity decker
  - DSM screen
  - Hydrasieve
Sidehill Screen

IN
SIDEHILL
IN

Water

Thick Stock
Gravity Decker

- Pulp enters at 0.8% and leaves at 5%
- Water passes through wire mesh cylinder
- Vacuum created by liquid falling increases water removal
Gravity Decker

Balance arm
Feed
Shower pipe
Couch roll
Doctor blade
Overflow ports
White water outlet
Wire mesh (fine)
Wire mesh (coarse)
Screen plate
Intermediate Consistency Washers

- 8-15% discharge consistency
  - high speed belt washer
    - DNT
    - Vario-split
  - Vacuum filter
  - inclined screw extractors
Double Nip Thickener
Double Nip Thickener

- DNT Washer
  - “double nip thickener”
Disk Filter: increases consistency of pulp
Vacuum Disk Filter for thickening
High Consistency Washers

- Above 15% discharge consistency
  - screw press
  - belt press
Screw Press

Inlet of Material

Filtrate

Outlet of Cake
Pressing

- HC-Press
## Washers Wire Mesh Sizes

<table>
<thead>
<tr>
<th>Mesh Size</th>
<th>Wire Diam, mm</th>
<th>Open Area, %</th>
<th>Opening Size, mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>.254</td>
<td>36</td>
<td>0.425</td>
</tr>
<tr>
<td>60</td>
<td>.191</td>
<td>30.5</td>
<td>0.250</td>
</tr>
<tr>
<td>80</td>
<td>.140</td>
<td>31.4</td>
<td>0.180</td>
</tr>
<tr>
<td>100</td>
<td>0.114</td>
<td>30.3</td>
<td>0.150</td>
</tr>
</tbody>
</table>
Washing Performance

Particle Removal Efficiency

![Graph showing efficiency factors for different particle sizes at various washer discharge consistencies.](image)
Washing Performance

Theoretical Ink Removed In One Washing Stage

Outlet %K

Inlet Consistency, %

Theoretical Ink Removal In One Washing Stage, %
Washing Performance

- Countercurrent washing

Diagram:
- Pulper
- No. 1 Washer
- No. 2 Washer
- No. 3 Washer
- Clarifier

Arrows indicate the flow of pulp and filtrate.
Washing Performance:
Counter Current Flow of Pulp and Water

Theoretical Ink Removed In Multiple Counter Current Washing Stages
A double-wire press is utilized for initial dewatering of the stock to achieve up to 40% bone-dry consistency. The dryness is raised to 48-50% bone-dry by a heavy duty press. The pulp web is then slit and cut into sheets by a rotating knife drum. The sheets drop onto a pallet.
**Flotation**

- **Definition:** a process in which contaminants are preferentially removed from a pulp stock by attachment to air bubbles.

Ink particles attached to air bubble
Flotation

- In 1992, about 80% of the de-inking plants in the US used flotation
- Since the 1950’s flotation cell design has steadily improved
Example Flotation Cell

1. Air bubbles & low consistency stock introduced together.
2. Air bubbles & stock are mixed.
3. Stock travels toward exit of flotation device.
4. Air bubbles rise.
5. Foam removed as rejects.
6. Accepted stock removed from cell.

Voith Paddle Cell, 1960’s technology
Flotation

- **Mechanism:** For successful flotation of a contaminant (e.g., ink) several sub-processes must occur:
  1. The ink must be free from the fibers.
  2. Ink must collide with an air bubble.
  3. A strong attachment must form between the ink & the bubble.
  4. The ink-bubble must rise to the surface.
  5. The ink-bubble must be incorporated into the foam.
  6. The foam must be removed from the system.
What determines the flotation efficiency?

- Contaminant characteristics
- Bubble characteristics
- Process conditions
Given two types of particles suspended in water, which one will attach and be removed by an air bubble?

- Hydrophobicity
- Detachment from fibers
- Size
- Shape
- Density
Contaminant Characteristics: Hydrophobicity

- **Hydrophobic** - lacking affinity for water
- **Hydrophilic** - having a strong affinity for water.

A hydrophobic material suspended in water has a greater tendency to contact and adhere to air bubbles due to its lack of affinity to water.

This causes a preferential separation of hydrophobic material in a flotation process.
Contaminant Characteristics: Hydrophobicity

- **Hydrophobic** - lacking affinity for water
- **Hydrophilic** - having a strong affinity for water.
Contaminant Characteristics: Detachment from Fibers

- **Typical Cases**
  - Fibers attached to toners, sometimes referred to as “hairy particles.”
  - Inks or toners attached to surface of fibers.
  - Pigments from inks lodged into wall of fiber.
Contaminant Characteristics: Ink size

- Ink very small: the ink travels around the bubble in the stream line, does not have enough momentum to cross stream line and attach to bubbles
- Ink very large: ink’s weight and large size promotes detachment from bubble surface due to gravity and fluid forces
Historically, for ONP deinking, salts of fatty acids combined with calcium ions in the flotation cell have been used to collect fine ink particles into agglomerates.

OMG added to provide ash for agglomerates.

The agglomerates, because of their size, are removed at higher efficiency.
Synthetic Collectors

- Non-ionic and ionic surfactants
- Also called displectors because they can disperse in washing and collect in flotation
- Do not require calcium, reduces deposits
- Lower dosages needed (0.2% rather than 0.7% of fatty acids)
**Bubble Characteristics**

- **Size of bubble**:
  - If bubble is *too small* then the buoyancy force may not be large enough to carry particle.
  - If bubble is *too small*, then bubbles tend to adhere to fibers, causing excessive fiber losses.
  - If bubbles are *too large*, then the area of bubble surface is small (compared to smaller bubbles with same total volume) and the probability of collision with contaminant is less.
  - If bubbles are *too large*, then the bubbles tend to rise rapidly, not offering many opportunities for contact with contaminants.
  - The *large, fast rising* bubbles disrupt flow patterns in the flotation cell causing channeling of bubbles and disruption of the foam.
Bubble Characteristics

- Quantity of Bubbles
  - Increased number of bubbles have a higher probability of contacting a contaminant.
  - Too many bubbles may cause agglomeration of the bubbles into larger bubbles, see proceeding slide for problems with large bubbles.
  - Air to stock ratio used depends on the type of equipment, can be 0.3 : 1 or as high as 10 : 1 air : stock
Process Conditions

1. Consistency

The consistency is typically around or less than 1%. If the consistency is too high, then the fibers tend to knock off (or filter) the ink from the bubble surface.

- High consistency also causes a poor mixing/distribution of bubbles in the stock. Bubbles tend to form channels in which bubbles short circuit the flotation cell.
- High consistency can lead to excessive amounts of fibers being rejected with the foam.
2. Foam Generation
   - Foam is generated by adding a foaming agent to the stock before the stock enters the flotation process.
   - Too much foam causes excessive fiber losses, and increased amounts of foam to destroy.
   - Too little foam or an unstable foam will allow contaminants to fall back into the stock and not be removed.
   - The amount of foam is usually controlled by the flowrate of foaming agent.

3. Flow Rate
   - Too high a flow rate through a flotation cell generates large turbulent forces which can detach inks from bubbles. It also can disturb the foam. The required production rate sets a minimum value on the flow rate.
4. Retention Time
   - Longer retention times increase the likelihood of bubble-contaminant collisions. Retention time is limited by production rate demands and volume of existing equipment. **Flotation cells are often put in series to increase retention time.**

5. Quality and Quantity of Air Bubbles

6. Waste Paper Furnish
   - In the past, a certain percent of old magazine or coated material has been added to old news print to enhance flotation.
   - Suspected that the filler acted as a collection site for inks that were more effectively floated.
   - Fillers can also act to consume chemicals and break foam.
Flotation Equipment

- Equipment
  - Voith
  - Fiberprep
  - Sulzer
  - BC
  - Beloit
  - Shinhama
  - Kamyry
  - Wemco
Flotation Cell

- Black Clawson Flotator
Voith-Sulzer Flotation Machine, each pump in series, stock follows: feed->1->2->3>Acc.

Most prominent type of flotation unit with over 200 installations in the early 1990’s.
Trace Lines
Foam
Flotation Cell

- Lamort - Fiberprep Flotation Cell
Flotation Cell

PDM Pressurized Flotation Unit

Feed → Air → Bubble Separation → Accepts

Rejects & Air

Aeration Zone 1  Mixing Zone 2  Separation Zone 3  Foam Separation
Flotation Cell

- Pressurized Deinking Module
Major Parameters Impacting Flotation Efficiency

- Particles: number, size, shape, density, surface chemistry, agglomeration
- Bubble: type of gas, number, size, surface chemistry, nature (dispersed or dissolved)
- Mixing: Nature, intensity, time
- Process Conditions: Recovered paper, type/amt ink, type/amt ash, fiber characteristics, consistency, temp, retention time, cell design, pH, chemical environment, foam characteristics

Secondary Fiber Recycling, Tappi Press, 1993
## Washing vs. Flotation

<table>
<thead>
<tr>
<th></th>
<th>Flotation</th>
<th>Washing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemistry-Sensitive</td>
<td>more</td>
<td>less</td>
</tr>
<tr>
<td>Water Use</td>
<td>lower</td>
<td>higher</td>
</tr>
<tr>
<td>Yield</td>
<td>higher</td>
<td>lower</td>
</tr>
<tr>
<td>Ash Removal</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Tensile Str.</td>
<td>Lower</td>
<td>Higher</td>
</tr>
<tr>
<td>Opacity</td>
<td>Higher</td>
<td>Lower</td>
</tr>
</tbody>
</table>
Dispersion of Contaminants in Recovered Paper Stock

- **Definition:** The use of mechanical action to decrease the particle size of contaminants and release the contaminants from the fiber surfaces (below, an example of pulp before and after dispersion).
Dispersion of Contaminants in Recovered Paper Stock

- Contaminants: inks, toners, coatings, wax, bitumen, varnish, hot melts, glues
- Dispersion assisted by heating, contaminants soften from 60 – 120 C
- Visible size (40 microns) to sub-visible size
Disk Dispersion

- **How does it work?**
  - Pulp at high consistency is passed between disks that have bars or teeth protruding from the surface.
  - Rotation of one of the disks causes intense shearing action on the fibers breaking down the contaminants.

- **Typical Conditions**
  - Consistency = 30% K
  - Temperature = 95 °C
  - Retention Time = 2 seconds
  - RPM = 1200-1800
  - Gap between disks = 0.5-1.5 mm
  - 1.6-4.0 hp days / ton
Dispersion

- Teeth
- Rotating Shaft
- Feed
- Exit
Dispersion

- Dispersing System:
  - Process stock is dewatered to 30%K
  - Clods of stock are broken in the breaker screw
  - Steam introduced into a heating screw to increase temperature to 85-120 °C (above 120 °C damages fibers)
  - Stock fed to dispersing unit
  - Stock is diluted and agitated for further processing
Screw press
Steam Preheater
Kneading

- **How does it work?**
  - Pulp at high consistency is mixed between moving bars on a slow-rotating shaft and stationary bars attached to the housing.
  - Strong shear forces (mainly fiber-fiber rubbing) break the contaminants.

- **Typical Conditions**
  - Consistency = 30% K
  - Temperature = 40-50 C
  - Retention Time = 10-60 seconds
  - RPM = 100-900
  - Gap between bars = 10-40 mm
  - 3.0-4.5 hp days / ton
Single Shaft Kneader

- Process stock is dewatered to 30% K
- Stock enters a feed screw, steam or bleaching chemical may be added
- Stock is kneaded
- Stock is discharged, diluted and agitated for further processing
Double Shaft Kneader

- Operation principles the same as the single shaft kneader
- Contains two shafts rotating in different directions at slightly different speeds (20% difference in RPM)
- The different speeds and directions of the shafts generate intense shearing action.
Double Shaft Kneader
Drawbacks to Kneading

- Energy intensive: 3.0-4.5 hp day/ton
- High initial capital cost
- Requires thickening equipment
- Does not reduce sticky size (this may be an advantage)
- Rotors can wear out (1-2 years)
# Kneading vs. Dispersion

Methods to decrease contaminant size.

<table>
<thead>
<tr>
<th></th>
<th>Dispersion</th>
<th>Kneading</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Mechanism</strong></td>
<td>Shear</td>
<td>Rub</td>
</tr>
<tr>
<td><strong>Consistency</strong></td>
<td>30%</td>
<td>30%</td>
</tr>
<tr>
<td><strong>Temp.</strong></td>
<td>95</td>
<td>50</td>
</tr>
<tr>
<td><strong>RPM</strong></td>
<td>1200-1800</td>
<td>100-900</td>
</tr>
<tr>
<td><strong>Retent. Time</strong></td>
<td>2 s</td>
<td>10-60 s</td>
</tr>
<tr>
<td><strong>Gap, mm</strong></td>
<td>.5-1.5</td>
<td>10-40</td>
</tr>
</tbody>
</table>
## Kneading vs. Dispersion

Methods to decrease contaminant size.

<table>
<thead>
<tr>
<th>Effect</th>
<th>Dispersion</th>
<th>Kneading</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tappi Dirt Reduct.</td>
<td>75%</td>
<td>85%</td>
</tr>
<tr>
<td>Toner Reduct.</td>
<td>yes</td>
<td>better</td>
</tr>
<tr>
<td>Stickies Reduct.</td>
<td>better</td>
<td>no effect</td>
</tr>
<tr>
<td>Fiber Cutting</td>
<td>substantial</td>
<td>none</td>
</tr>
<tr>
<td>Fines Generation</td>
<td>yes</td>
<td>no</td>
</tr>
</tbody>
</table>
Bleaching

- Bleaching is the chemical process applied to cellulosic materials to destroy chromophores, increasing the brightness and reducing color.
Bleaching

- Dye and Fluorescent Whitening Agents (FWA) Destruction
- Destruction/modification of lignin from wood-containing fibers
- Does not affect pigments, which have color due to the lattice structure of molecules

“Chromophore Absorbs Light”
Brightness Measurement

- **Tappi Method T452**
  - Specifies illuminating light at 45° to the sample and the reflected light measurement at 90° to the sample. Reflectance compared to magnesium oxide powder.
  
  *Units: % GE brightness*

- **Technical Section, CPPA Method E1**
  - Specifies the sample should be diffusely illuminated using a highly reflecting integrating sphere. Reflected light measurement is at 90° to the sample. Reflectance is compared to absolute reflectance from an imaginary, perfectly reflecting diffusing surface.

  *Units: %ISO brightness*
Brightness Scales
Several color coordinate systems

$L, a, b$ color space
  - $L$: light or dark
  - The $a$ coordinate: red or green
  - The $b$ coordinate: yellow or blue

Dye removal index uses $L^*, a^*, b^*$ coordinates to determine dye removal effectiveness
Fluorescence Measurement

- Fluorescent whitening agents: ultraviolet energy is absorbed and re-emitted as visible light, increasing the brightness
- Fluorescence: Brightness w/o UV filter – Brightness with UV filter
Paper Fibers

- Cellulose and hemicellulose:
  - white, colorless, do not absorb light
- Lignin and extractives:
  - have some color, when modified
  - alkaline environments increase the color producing groups
Anthocyanidine

Chalcone

Flavone

Flavanone

Conjugated aldehyde

Quinone
Dyes and printing inks contribute to the color of fibers. Often contain aromatic, carbonyl, or azo groups. It is the conjugated double bonds that cause color.
Types of Papers

• Chemically pulped and bleached fibers:
  ■ have 0% lignin
  ■ white

• Chemically pulped unbleached fibers (linerboard):
  ■ have 5% lignin
  ■ Brown
  ■ Condensed lignin, extended conjugated structures, aromatic groups, several double bonds of carbon
  ■ Electrophilic agents such as oxygen, chlorine dioxide, chlorine can oxidize, interrupting conjugation and color

• Mechanically pulped fibers (newsprint):
  ■ Have 20-25% lignin
  ■ Lignin is in natural, non-condensed condition
  ■ Are brighter than chemically-pulped, unbleached fibers
  ■ Carbonyl groups are responsible for the yellowing
  ■ Can be bleached with non-degrading, lignin preserving chemicals
Bleaching

- If the color is due to conjugated carbonyl groups, lignin preserving chemicals should be used
  - Peroxide, dithionate, FAS
Bleaching

- If the color is due to azo groups, conjugated carbon-carbon double bonds or condensed aromatic structures, only lignin degrading chemicals can be used.
  - Oxygen, ozone, chlorine, chlorine dioxide, sodium hypochlorite.
Peroxide Bleaching (P)

- The most important bleaching agent for mechanical recovered paper pulps
- A clear, colorless liquid soluble in water at any concentration
- HOO(-), perhydroxyl anion acts as a nucleophilic bleaching agent
- $\text{H}_2\text{O}_2 + \text{H}_2\text{O} \leftrightarrow \text{HOO}(-) + \text{H}_3\text{O}(+)$
- $\text{H}_2\text{O}_2 + \text{OH}(-) \leftrightarrow \text{HOO}(-) + \text{H}_2\text{O}$
Peroxide Bleaching (P)

- The most important bleaching agent for mechanical recovered paper pulps
- Bleaches in a non delignifying manner by destroying the chromophore
Peroxide Bleaching

- NaOH is added to increase the perhydroxyl anion concentration, the active bleaching agent, HOO(-):
- $\text{H}_2\text{O}_2 + \text{H}_2\text{O} \leftrightarrow \text{HOO}(-) + \text{H}_3\text{O}(+)$
- $\text{H}_2\text{O}_2 + \text{OH}(-) \leftrightarrow \text{HOO}(-) + \text{H}_2\text{O}$
Peroxide Bleaching

- There is an optimized amount of NaOH to add,
  - too little and not enough activation,
  - too much and the alkali yellows the pulp
Peroxide Bleaching Process Conditions

- Application: 1-3% on solids, typically less than 2%, bleaching result improves with increased application
- Time: 30-90 minutes
- Consistency: 10+%  
  - Higher consistency increases concentration of chemicals and reduces interfering substance quantities in the liquid
- Temperature: 60-90 C
- pH: 9.0-11.5
- Good mixing
Peroxide Bleaching Process Conditions: Consistency

![Graph showing the relationship between consistency and ISO brightness.](image-url)
Peroxide Bleaching

- Heavy metal ions can decompose the peroxide
- \( \text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O}^* \rightarrow \rightarrow \text{H}_2\text{O} + \frac{1}{2}\text{O}_2 \)
- Must stabilize the peroxide:
  - Sodium Silicate, water glass, Na\text{2SiO}_3
  - Forms a colloidal structure with metal ions and deactivates them
  - Also added to pulper as a surfactant, penetrant and anti-corrosion agent
  - 2-3% is normal

**Figure 7.** Effect of water glass on brightness.\(^5\)
Peroxide Bleaching

- Heavy metal ions or enzymes (catalases) can decompose the peroxide
  
  \[ \text{H}_2\text{O}_2 \rightarrow 2\text{HO}^* \rightarrow \rightarrow \text{H}_2\text{O} + \frac{1}{2}\text{O}_2 \]

- Must stabilize the peroxide:
  - Chelating agents: form complexes with the heavy metal ions to deactivate them
  - Most common: EDTA and DTPA
Peroxide Bleaching: Chelating Agents

\[
\text{Na}_6\text{DTPA} \quad \text{Pentasodium salt of Diethylenetriaminepentaacetic acid}
\]

\[
\text{Na}_4\text{EDTA} \quad \text{Tetrasodium salt of Ethylenediaminetetraacetic acid}
\]
Peroxide Bleaching: Decomposition of Peroxide

- Causes of hydrogen peroxide decomposition
  - Metal Ions
  - Catalase:
    - an enzyme produced by microorganisms and animal and vegetal cells to destroy peroxide which is toxic to the cell
    - Must thermally denature the catalase of use a biocide
- High pH
- High temperature
Peroxide Bleaching: Pulper

- Not used as a true bleaching chemical in the pulper
- Used to actually compensate for the darkening due to alkali in the pulper
- Used to decolorize chromophores in groundwood generated by alkaline pH – prevents alkali darkening
Peroxide Bleaching: Disperser

- Used to compensate for graying of pulp due to the dispersion of the ink

- Advantages
  - Newly exposed fiber surfaces
  - High consistency
  - Good mixing
  - High temperature

- Disadvantages:
  - Short residence time
  - Too high a temperature can degrade pulp
  - Must use chelating agent as silicate may build up on disks
Peroxide Bleaching: Tower

- More efficient than pulper
- Added to suction of medium consistency pump to upflow tower
- Caustic and silicate added to conveyor to medium consistency standpipe
Peroxide Bleaching: Post-bleaching

- In the high density storage chest/tower
- Pulp is thickened and heated with steam to 60°C
- High shear mixer with chemicals added at one addition point a preparation
- 1-3 hrs at 15% consistency
- If market pulp, must be neutralized to pH of 7 to avoid degradation
Dithionite Bleaching (Y)

- Common reductive bleaching chemical that can be used for wood containing pulps
- Often called hydrosulfite bleaching, which is the incorrect term
- \( \text{Na}_2\text{S}_2\text{O}_4 + \text{H}_2\text{O} \rightarrow 2\text{Na}(+) + \text{S}_2\text{O}_4(-2) \)
- Sodium Hydrosulfite, \( \text{Na}_2\text{S}_2\text{O}_4 \)
- Dithionate ion \( \text{S}_2\text{O}_4(-) \) is active
- Oxygen decomposes the bleaching agents
- Calcium or magnesium precipitates the bleaching agent, need to add chelant
Dithionite Bleaching (Y)

- Can be done in the pulper
- Added to disperser at 30% consistency, 80-100°C, then diluted and pumped to an upflow tower
- Added to a MC pump feeding an upflow tower at 10-12% consistency

- Application: 0.5-1.0%, 50-70°C, 30-90 min, pH = 5.5-6.5, consistency 3-5%
FAS Bleaching

- Formamidine Sulphinic Acid
- Low odor, crystalline reducing agent used only for wood containing pulps
- Effective decolorizing for colored paper and carbonless paper
- Decomposes with oxygen
- Stronger than dithionite
- Slightly soluble in water
- Must be used soon or else decomposes in water
FAS Bleaching

- Application: 0.3-1%, 30-90 min, 3.5-12 %K, 40-65°C, pH=8-11
- Need 1 part FAS to 0.5 parts NaOH
- Initial pH=9, Final pH=7-8 is optimum
- High filler content, calcium carbonate, requires less NaOH
- Can be applied in a disperser or in post bleaching
FAS: Post bleaching

- DIP
- Thickening (4% - 12%)
- FAS, NaOH
- MC high-shear mixer or pump (50°C - 80°C)
- Reaction tower
- Bleached DIP
FAS Disperser Bleaching
Sodium Hypochlorite (H) Bleaching

- Oxidative bleaching that degrades lignin
- Advantages: inexpensive, very effective, can be added to pulper to remove color
- Disadvantage:
  - no chlorine free label,
  - prepared by dissolving chlorine gas in caustic solution,
  - generates chloroform (carcinogen),
  - can not be used for pulps with greater than 10% mechanical pulp, causes coloring
Sodium Hypochlorite (H)
Bleaching

- $2\text{NaOH} + \text{Cl}_2 \rightarrow \text{NaOCl} + \text{NaCl} + \text{H}_2\text{O}$
- NaOCl is sodium hypochlorite
- HOCl $\Leftrightarrow$ H(+) + ClO(-), pKa = 7.5
- Need pH greater than 9.5 for ClO-
- If pH 6-7 hypochlorous acid HOCl, which attacks and degrades cellulose
- If pH less than 3 generate chlorine Cl2
Sodium Hypochlorite (H) Bleaching
Sodium Hypochlorite (H) Bleaching

- Application: 0.5-2.5%
- Time, 30-90 min
- Consistency: 3-12%
- Temperature: 35-70°C
- pH = 9.5-11.0
Chlorine Dioxide Bleaching (D)

- Oxidative bleaching with excellent color stripping and large brightness gains
- Disadvantages: no chlorine free label
- Process Conditions
  - Application: 0.2-1.0%
  - Time: 60-180 minutes
  - Consistency: 10-15%
  - Temp: 55-70 C
  - pH: 6.5-9.5, with 6.0 optimum
Oxygen Bleaching (O)

- Oxidative bleaching that improves brightness, lowers chemical costs, removes color, detackifies stickies
- Disadvantages: will not tolerate mechanical pulps, need pressurized vessel of 60-115 psig
- Oxygen produces radicals that degrade lignin and also form peroxide which reacts with the chromophores
- Only system is Oxypro, patented by Air Products
- Conditions
  - 1.0 % application, 60 min, 10-15 %K, 85-95 C, 1.0 % H2O2, 0.7-1.0 % NaOH, Na2SiO3 1.5-2.0%, DTPA 0.2%, pressure 60 psig
Ozone Bleaching (Z)

- Destroys dyes and optical whiteners
- Toxic and high capital cost
- Not frequently used
- Ozone decomposed by metal ions
- Uses low pH to solubilize and remove metal ions and chlorating agents used to remove metal ions
- Conditions: 0.25-3.0%K, 1-5 min, 10-40 %K, 20-60 C, pH=2.5-10, Ozone concentration: 2-12% in gas applied to pulp
- Ozone: most effective TCF bleaching reagent for removing fluorescence
Bleaching Sequences:

- Single stages are not effective in reaching 80% ISO brightness on MOW furnish
- Need two stages for MOW
- Variable incoming recovered paper requires multiple stages
- Combination of oxidative followed by reductive bleaching is most successful
- Must be careful to remove oxidative bleaching chemical so it does not consume the reductive bleaching chemical
- Not common to do reductive bleaching first as the reductive products are susceptible to being oxidized
- Common 2 stage processes: Peroxide-Peroxide, Peroxide-dithionate, Peroxide-FAS, FAS-Peroxide
The generation of acceptable recycled pulp is accompanied with significant waste streams.
<table>
<thead>
<tr>
<th>Mill</th>
<th>Yield %</th>
<th>Sludge OD Tons/day</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFR</td>
<td>65</td>
<td>340</td>
</tr>
<tr>
<td>GLPF</td>
<td>70</td>
<td>220</td>
</tr>
<tr>
<td>SF</td>
<td>75</td>
<td>60</td>
</tr>
<tr>
<td>FUF</td>
<td>72</td>
<td>140</td>
</tr>
</tbody>
</table>

### Types of waste from recovered paper mills:

<table>
<thead>
<tr>
<th>Stock Prep. Rejects</th>
<th>Sludges</th>
<th>Inciner. Waste</th>
<th>Other Waste</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ragger Tails</td>
<td>Deinking Sludges</td>
<td>Ashes</td>
<td>Chemicals</td>
</tr>
<tr>
<td>Drum Rejects</td>
<td>Clarifier Sludges</td>
<td>Cinders (slags)</td>
<td>Used Oils</td>
</tr>
<tr>
<td>Screening Rejects</td>
<td>Biological Sludges</td>
<td>Flue Ashes</td>
<td>Cleaners</td>
</tr>
<tr>
<td>Cleaner Rejects</td>
<td></td>
<td>Gypsum</td>
<td>Wires</td>
</tr>
<tr>
<td></td>
<td></td>
<td>....</td>
<td>Felts</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Hazard. Waste</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>....</td>
</tr>
</tbody>
</table>
Amount of Rejects and Sludges for Production of Paper Grades

<table>
<thead>
<tr>
<th>Produced paper</th>
<th>Recovered paper grade</th>
<th>Amount of total waste [% by dry weight]</th>
<th>Amount of waste [% by dry weight]</th>
<th>Rejets</th>
<th>Sludges</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Graphic paper</td>
<td>News, magazines</td>
<td>15–20</td>
<td>1–2</td>
<td>3–5</td>
<td>8–13</td>
</tr>
<tr>
<td></td>
<td>Superior grades</td>
<td>10–25</td>
<td>&lt; 1</td>
<td>≤ 3</td>
<td>7–16</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2–5</td>
</tr>
<tr>
<td>Hygienic paper</td>
<td>Files, office paper, ordinary, medium grades</td>
<td>28–40</td>
<td>1–2</td>
<td>3–5</td>
<td>8–13</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>15–25</td>
</tr>
<tr>
<td>Market DIP</td>
<td>Office paper</td>
<td>32–40</td>
<td>&lt; 1</td>
<td>4–5</td>
<td>12–15</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>15–25</td>
</tr>
<tr>
<td>Liner, fluting</td>
<td>Sorted mixed recov. paper, supermarket waste</td>
<td>4–9</td>
<td>1–2</td>
<td>3–6</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0–(1)</td>
</tr>
<tr>
<td>Board</td>
<td>Sorted mixed recov. paper, supermarket waste</td>
<td>4–9</td>
<td>1–2</td>
<td>3–6</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0–(1)</td>
</tr>
</tbody>
</table>
# Amount of Rejects and Sludges for Production of Paper Grades

## Table 2. Solid waste from different stages in recovered paper processing\(^2\).

<table>
<thead>
<tr>
<th>Source of waste</th>
<th>Composition of waste</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pulper, drum pulper</td>
<td>Larger objects such as plastic bags, bookbinders, textiles, bottles, shoes, strings, tools, toys, wires, wood pieces, wet strength paper, ...</td>
<td>nonhazardous</td>
</tr>
<tr>
<td>High-density cleaning</td>
<td>Glass, nails, paper clips, textiles, pins, staples, ...</td>
<td>nonhazardous</td>
</tr>
<tr>
<td>Pre-screening</td>
<td>Long, thin and wide contaminants, plastic, polystyrene, stickies, ...</td>
<td>nonhazardous</td>
</tr>
<tr>
<td>Flotation deinking</td>
<td>Fillers, fibers, fines, printing ink, stickies</td>
<td>nonhazardous</td>
</tr>
<tr>
<td>Forward cleaning</td>
<td>Small compact particles with high density such as sand, shives, hard particles from UV-colors, coating colors, varnish, ...</td>
<td>nonhazardous</td>
</tr>
<tr>
<td>Fine screening</td>
<td>Plastic fragments, light-weight contaminants, hot melts, stickies</td>
<td>nonhazardous</td>
</tr>
<tr>
<td>Process water clarification</td>
<td>Colloidal material, fillers, fibers, fines, ink particles</td>
<td>nonhazardous</td>
</tr>
</tbody>
</table>
Composition of Reject Samples

Newspaper:
- Metallic compounds: 7%
- Wood: 7%
- Flakes/fibers: 27%
- Plastic (hard): 24%
- Textiles: 7%
- Plastic foils: 28%
- Adhesive tapes: 28%

Packaging Paper:
- Metallic compounds: 7%
- Flakes/fibers: 13%
- Plastic (hard): 13%
- Textiles: 6%
- Plastic foils: 61%
- Adhesive tapes: 28%
Composition of De-inking Sludge Samples

Printing Paper (Flotn)
- Clay and other fillers: 37%
- Calcium carbonate: 19%
- Fines and printing inks: 29%
- Fibers: 7%

Tissue (Washing)
- Fibers: 11%
- Calcium carbonate: 20%
- Clay and other fillers: 26%
- Fines and printing inks: 40%
- Extractable compounds: 3%
De-inking Sludges
Treatment of Wastewaters

- Pulper
- No. 1 Washer
- No. 2 Washer
- No. 3 Washer
- Clarifier
- Pulp
- Filtrate
- Sludge
Water Treatment

- Re-use filtrates (often from thickening or washing process) to conserve water
- Clarifier objective: take filtrate and make a sludge and a filtrate
- Filtrate to Clarifier: 2000 ppm suspended solids
- Clarified water: 100 ppm suspended solids
- Sludge: 3-7% solids
- No change in colloidal or dissolved species
DAF Clarifier

- Raw Water
- Chemicals
- Settled Sludge
- DAF Clarifier
- Floated Sludge
- Scoop
- Air
- Clarified Water
Clarifier
Clarifier Rejects Scoop
DAF Clarifier

- DAF = dissolved air flotation
- most common clarifier for recycling
- raw water is treated with chemicals to form flocs of suspended solids
- tiny air bubbles are mixed with the water and attach to the flocs
- the flocs rise to the surface and are scooped out
- some of the flocs settle to the bottom and are also removed
## Dewatering Processes

<table>
<thead>
<tr>
<th></th>
<th>Heavy-weight &amp; coarse rejects</th>
<th>Light-weight &amp; fine rejects</th>
<th>Deinking sludges</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Composition</strong></td>
<td>Glass, nails, sand, stones, paper clips, pins, staples, textiles, wood pieces, wet strength paper</td>
<td>Sand, textiles, fibers, coating colors, plastic fragments, hot melts, stickies</td>
<td>Fillers, pigments, fibers, fines, printing ink, stickies</td>
</tr>
<tr>
<td><strong>Dewatering facilities</strong></td>
<td>Screens, Vibrating screens, Screw classifiers, Rake classifiers</td>
<td>Screens, Disk thickeners, Dewatering drums, Gravity tables, Screw presses</td>
<td>Dewatering drums, Gravity tables, Belt filter presses, Screw presses, Chamber filter presses, Centrifuges</td>
</tr>
<tr>
<td><strong>Achievable dry solids contents</strong></td>
<td>60%–80%</td>
<td>50%–65%</td>
<td>one-stage operation: &lt;15%, two-stage operation: &lt;65%</td>
</tr>
</tbody>
</table>
Dewatering of Sludges

- Ragger and rejects from pulper system not dewatered
- Sludges use 2 step process:
  - Gravity table or drum or disk thickener
  - Followed by belt filter press or screw press
Dewatering of Sludges

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Dewatering of Sludges

- Sludges use a 2-step process:
  - Gravity table or drum or disk thickener
  - Followed by belt filter press or screw press
Screw Press
Example of Sludge Combustion

- Combustion:
  - Volume Reduction
  - Inert organics
  - Immobilize harmful material in ashes and slags
  - Generate energy
- Increased interest:
  - Increased cost of fuel and purchased power
  - Landfill costs
  - Environmental regulations
  - New combustion techn. With flue gas cleaning
Sludge Final Fates:

- Final disposition
  - landfill
  - incineration
  - composting
  - Cement, brick, concrete, mortar and lime brick, road construction
  - others
Summary: Paper Recycling Waste

- Recycling Generates significant waste
- Many different types of waste
  - Rejects
  - Sludge
- Sludge from clarifier must be dewatered
- Several modes of disposal
  - Landfilling
  - Incineration
  - others
High Density Storage Tower
Papermachine wet end
Paper roll storage
Paper Recycling Operations
Additional/Alternative Paper Recycling Operations used in Producing Recycled Printing Grades: Review Quiz

- Match the following:
  - kneader: same purpose as dispersion
  - flotation: more fiber-fiber rubbing
  - washing: use chemicals to brighten pulp
  - bleaching: removes hydrophobic particles
  - high consistency pulping: removes small particles
Paper Recycling Systems

- Learning objectives
  - Appreciate the strategies involved in designing a recycle process
  - Recognize the relative number and types of sub-operations in each type of recycle process
  - Understand rejects, sludge and water management in a recycle system
Paper Recycling Operations: A Balancing Act

- Production
- Yield
- Safety
- Profit
- Quality
- Environment
# Key Parameters for Cleanliness

<table>
<thead>
<tr>
<th></th>
<th>White System</th>
<th>Brown System</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Product Quality Parameters</strong></td>
<td>Optical Properties</td>
<td>Stickies</td>
</tr>
<tr>
<td></td>
<td>Brightness</td>
<td>Flakes</td>
</tr>
<tr>
<td></td>
<td>Dirt Specks</td>
<td>Sand</td>
</tr>
<tr>
<td></td>
<td>Color</td>
<td>Fines</td>
</tr>
<tr>
<td></td>
<td>Stickies</td>
<td>Ash Content</td>
</tr>
<tr>
<td></td>
<td>Ash Content</td>
<td></td>
</tr>
<tr>
<td><strong>Process Water Management</strong></td>
<td>Susp. and Colloidal solids</td>
<td>Susp. and Colloidal solids</td>
</tr>
<tr>
<td></td>
<td>COD</td>
<td>COD</td>
</tr>
<tr>
<td></td>
<td>Cationic Demand</td>
<td>Cationic Demand</td>
</tr>
<tr>
<td></td>
<td>Conductivity</td>
<td>Conductivity</td>
</tr>
<tr>
<td></td>
<td>pH</td>
<td>Biological Activity</td>
</tr>
</tbody>
</table>
# Amount of Rejects and Sludges for Production of Paper Grades

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<th>Recovered paper grade</th>
<th>Amount of total waste [% by dry weight]</th>
<th>Amount of waste [% by dry weight]</th>
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<th>Sludges</th>
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<td></td>
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<td>2–5</td>
</tr>
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<td>1–5</td>
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<td>Market DIP</td>
<td>Office paper</td>
<td>32–40</td>
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<td>15–25</td>
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<td>Liner, fluting</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Light-weight &amp; fine</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Flotation deinking</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>White water clarification</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Recovered Paper Prices

- Sorted White Ledger
- ONP
- OCC
- Mixed Paper

$/ton vs. Year

Year

System Design Considerations

- There are several objectives of a recycling mill:
  - Profitable
  - Meet product quality specifications
  - Environmentally acceptable
  - Reliable and safe operations

- There are many variables that can be adjusted to meet the objectives:
  - Type of wastepaper furnish
  - Type and number of unit operations
  - Order of operations

- There are several variables that impact a recycle mill that are largely uncontrollable:
  - Price and availability of raw materials
  - Price of products
  - Changing governmental regulation

- The optimization of this multiple-input, multiple-objectives problem is non-trivial -- in the 1990’s several deinking plants went out of business
Other System Design Considerations

- Raw Material
  - availability
  - cost
  - suitability for process
  - Usable fiber content
- Product Desired
  - optical properties
  - strength properties
- Environmental Constraints
  - Solid waste
  - Water effluents
  - Gas effluents
- Space Requirements
- Capital Costs
- Operating Costs
The following concepts or strategies are often implemented in system design:

- Keep out unremovable contaminants from the process
- Ensure that contaminants are well separated from the fibers
- Remove contaminants early in the process
- Keep contaminants large to enhance removal
- Repeat inefficient unit operations
- Save fiber by cascading unit operations
- Avoid excessive changes in consistency
Major Recycling Systems

- Can be categorized by the products they produce
  - Packaging Materials
    - Typically, OCC materials are recycled back into linerboard, medium, tube stock, and solid board products
    - Mixed waste can be used in lower quality applications
  - Newsprint
    - Old newspapers and magazines are converted into newsprint
  - Tissue
    - Bleached printing and writing wastes are converted into tissue
    - Wood containing papers can be used for lower quality applications
  - Printing and Writing Materials
    - Bleached printing and writing wastes are converted into new printing and writing grades
Recovery of Major Recovered Paper Categories, 2003

Recovered Paper Statistical Highlights, 2004 Edition, AF&PA
Where Old Corrugated Containers Go

- Containerboard: 62%
- Recycled Paperboard: 16%
- Net Exports: 18%
- Pkging/Industr Converting: 1%
- Tissue: 1%
- Other: 2%
Where Old Newspapers Go

- Recycled Paperboard: 13%
- Tissue: 8%
- Newsprint: 30%
- Other (Molded Products): 18%
- Printing/Writing: 3%
- Net Exports: 28%
Where Printing and Writing Papers Go

- Net Exports: 38%
- Recycled Paperboard: 19%
- Tissue: 22%
- Newsprint: 2%
- Printing/Writing: 11%
- Other: 8%

 Recovered Paper Statistical Highlights, 2004 Edition, AF&PA
Production of Newsprint
ONP-OMG Recycling

- Used to produce recycled newsprint
- May have batch, continuous tub or drum pulping
- Note the strategy:
  - 1st remove coarse contaminants
  - 2nd remove smaller contaminants, deinking
  - 3rd disperse unremoved contaminants
- Often bleaching is used to increase brightness
- Problems with stickies may be caused by OMG
Newsprint Recycle Process

Product: Newsprint, and improved grades, approx. 40-90 g/m²
Furnish: News, magazines
Yield: Approx. 83%
Effluent: Approx. 8 L/kg
Ash: Feed approx. 22 %, finished paper approx. 13 %
Brightness: Finished paper approx. 63-66% ISO
Newsprint Recycle Process: Consistency
Newsprint Recycle Process: Ash
Newsprint Recycle Process: Stickies
Newsprint Recycle Process: Dirt Speck Area
Newsprint Recycle Process: Brightness
Newsprint Recycle Process: Rejects and Sludge Components

- Coarse rejects:
  - Flakes
  - Plastics
  - Wood
  - Wires
  - Metal

- Small heavy particles:
  - Sand
  - Staples
  - Glass

- Fine rejects:
  - Plastics
  - Flakes

- Sludge, fine rejects

Stock preparation

Approach flow

PM
Production of High-Grade Printing and Writing Grades
Deinking of Printing Grades for Printing/Writing

- Used to produce new printing and writing grades
- May use mixed or sorted waste ($ vs production trade-off)
- Note the strategy:
  - 1st remove coarse contaminants
  - 2nd remove smaller contaminants, deinking
  - 3rd disperse unremoved contaminants
  - 4th bleach to high brightness
- Most complex system to produce highest standard pulp
High Grade Printing and Writing Grades

Diagram showing the process flow for High Grade Printing and Writing Grades, including stages such as MC screen, Flotation, Press, and DAF treatment.
Production of Tissue Grades
Deinking of Printing-Writing Grades for Tissue

- Use sorted or non-sorted office waste to make tissue
- For tissue making, filler level must be low for creping (1-1.5%) (see 2 stages of washing)
- Yield can be as low as 60%
- Depending on quality of tissue, brightness and dirt count also important
- Lower grade tissue pulp production omits 1 stage of cleaners, bleaching and washing. May also omit flotation.

Wastepaper

High Consistency Pulper
High Density Cleaning
Coarse Screening (Holes)
Cleaning
Fine Screening (slots)

Washing I
Thickening
Dispersion
Bleaching (Oxidative)

Flotation
Washing II
Cleaning
Fine screening

Storage
High Grade Tissue: Wood Free
Low-Grade Tissue: Wood Containing
Production of Packaging Grades
Simple Repulping System for Packaging Product

- Used in filler systems in recycled-fiber boxboard mills
- Easy to operate, low capital cost, very high yield
- No capability to remove contaminants, must be removed before pulping
- Product quality is simply a function of the input furnish
Crude Cleaning System for Packaging Product

- Used to produce liner, medium or tube stock
- Simple, high yield process
- Ability to remove only coarse contaminants
- Often used with a continuous pulper
Multi-ply Board Packaging Product

- Folding Boxboard
- Stiff, have plybond strength, clean on outside
- Top layer can be bleached chemical pulp or de-inked white grade
- Underliner can be de-inked wood containing pulp
- Filler layer has mixed waste
- Back layer uses kraft unbleached pulp
- Quality indicated by number
- Excess water from each loop goes to inferior layer

Top Liner, 1

___________________________

Underliner, 3

Filler, 4

___________________________

Back Liner, 2
OCC Recycling for Higher Grades

- Used to produce linerboard or medium
- Often have a continuous pulper with cleaning system
- Note the strategy:
  - 1st remove coarse contaminants
  - 2nd remove smaller contaminants
  - 3rd disperse unremoved contaminants
- Use alkali to swell fibers and regenerate strength
- Problems with stickies necessitate extra cleaning steps
Test Liner Production
Test Liner Production: Macro-Stickies
Paper Recycling Systems: Summary

- **Learning objectives**
  - Appreciate the strategies involved in designing a recycle process
    - Cleanliness/strength, production rate, yield
  - Recognize the relative number and types of sub-operations in each type of recycle process
    - Depends on the quality of product and the incoming raw material
    - Need different operations to deal with inks, large junk, stickies, fillers and brightness
  - Understand rejects, sludge and water management in a recycle system
    - Counter-current flow water-pulp to improve quality
    - Thickening to isolate water loops
    - Large rejects easily drained
    - Sludges are dewatered and pressed
Paper Recycling Systems
: Review Quiz

Build your own recycling mill.