Lecture:

Wash Deinking



Deinking Washers

- Definition: a separation device that rinses small particulate contaminants away from fibers (opposite of screening)
- Deinking Washer:
  - Dilute pulp with wash water
  - Disperse small contaminant in water phase, sometimes aided with a dispersant chemical
  - Remove contaminant laden water

Deinking Washers

- Washers in recycling remove all of the following small contaminants
  - fines
  - filler
  - inks
  - dissolved species
- In order for washing to be successful, the intended contaminant must be small and must be detached from the fibers

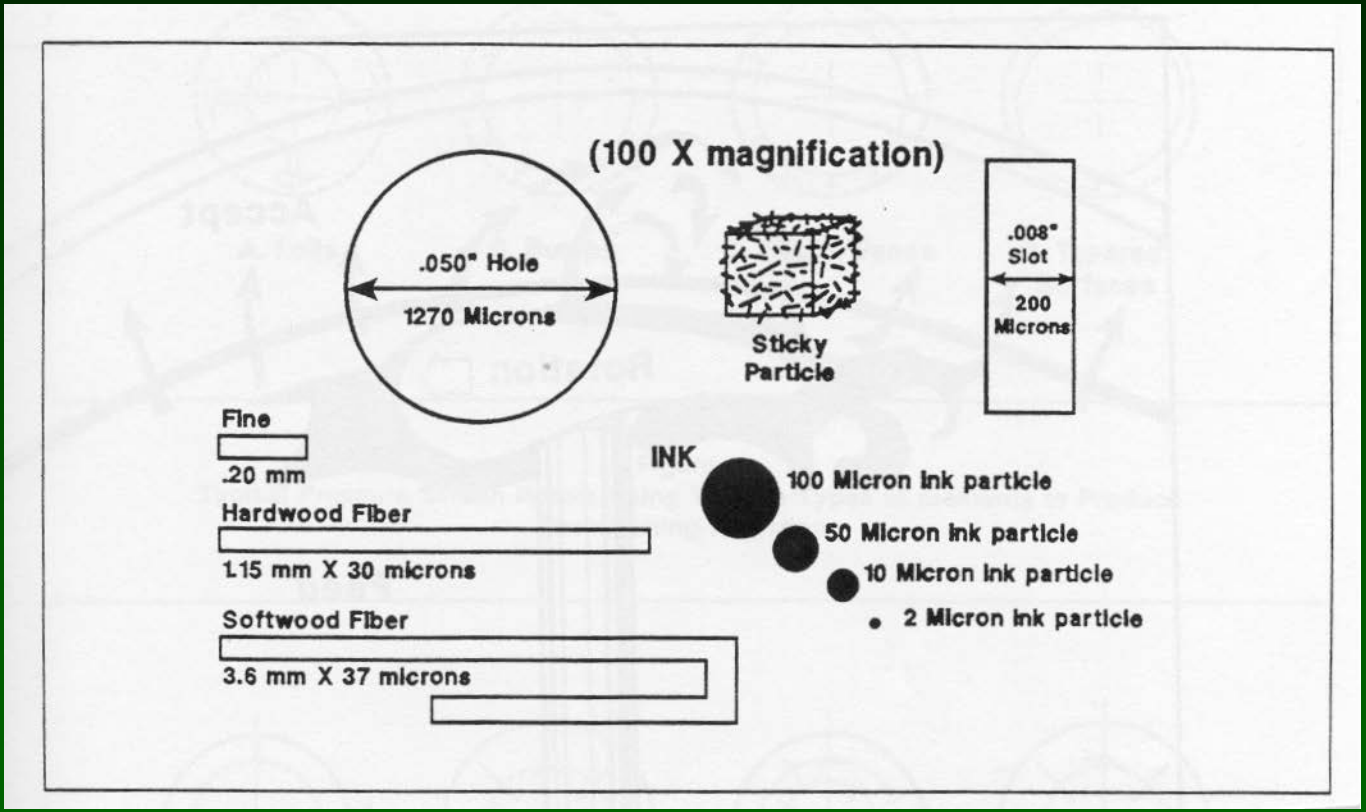
Washers Wire Mesh Sizes

Mesh Size	Wire Diam, mm	Open Area, %	Opening Size, mm
40	.254	36	0.425
60	.191	30.5	0.250
80	.140	31.4	0.180
100	0.114	30.3	0.150

Inks & Toners
Note: wash wires around 250 micron openings

Type	Component	Drying System	Ink Resin Film	Particle Size (microns)	End Products
Simple Letter Press	Pigment + Mineral Oil	Absorption into Web	Weak	1-15	Letterpress Early Newsprint
Newsprint and Offset	Pirgment + Soft Resin & Mineral Oil	Penetration of Vehicle into Web + Resin Oxidation	Soft Film Hard Film	2-30	Newsprint, Books We Offset, Letter Press
Rotogravure	Pigment +Hard Resin & Solvent	Solvent Evaporation	Hard Film	2-250	Magazines, Catalogues
Flexographic	Pigment + Resin & Water Emulsification	Amine Absorption, Evaporation	Water Resistant Film	N/A	Newsprint inserts, Corrugated
UV Cured	Pigment +Monomer	UV Photopolymeri zation	Non swelling, Non saponif. Hard Film	50-100	High Speed Coated Papers
Specialty	Various Pgiments and Rosins	Heat set or Other	Hard, Coherent Films	40 **-500**	Xerography Laser Printers Electronic Forms

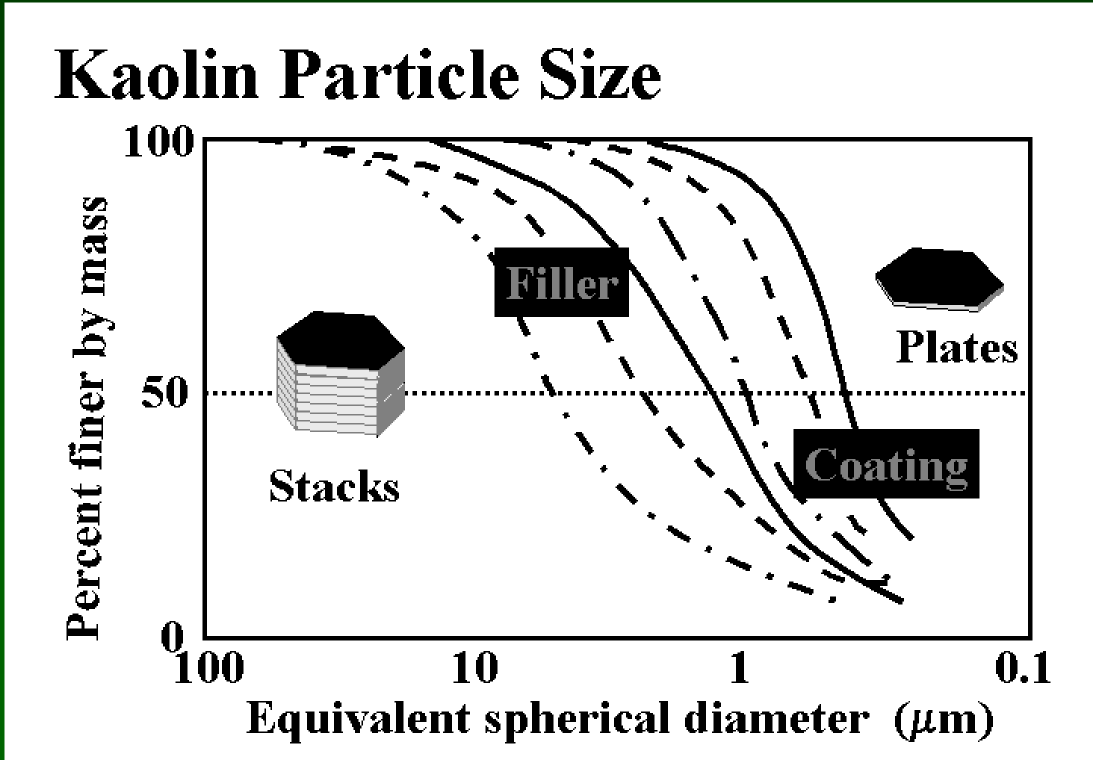
Sizes of fibers and inks:
Note: wash wires around 250 micron openings



0.001 inch = 1 Mil = roughly 25 microns = .025 mm

Sizes of Clay Fillers
Note: wash wires around 250 micron openings

- Clay, from Hubbe (left). Clay particles magnified by an electron microscope. drainchem.com.au (right)
-



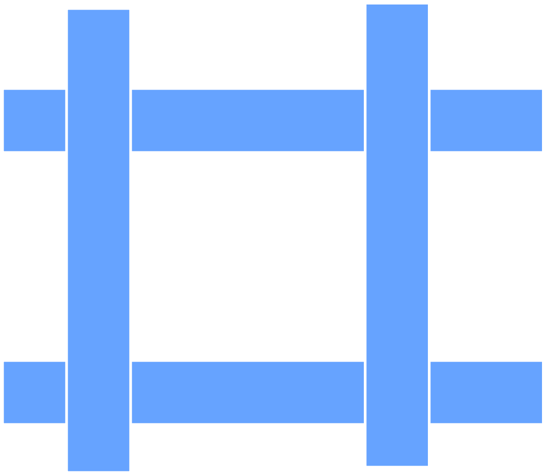
Hagemeyer, *Pigments for Paper*, 1984, adapted

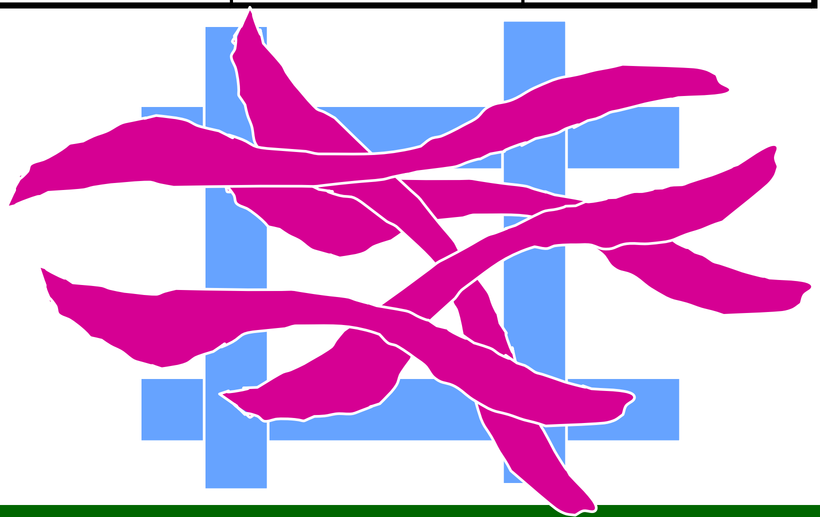
Thickening vs. Dilution Washing

- 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

Pulp mats prevent the removal of small particles in washing.

Type	Inlet % K	Outlet % K	Ash Removal %, Theoretical	Ash Removal %, Actual	Pulp Mat Formation
Sidehill Scrn	0.8	3	74	60	Minimal
Grav Decker	0.8	5	85	55	Yes
Incl. Screw	3.0	10	72	45	Extensive
Horiz. Screw Press	4.0	28	89	35	Extensive
Belt Washer	1.0	10		80	Minimal
Vario Split	0.8	10	85	80	Minimal





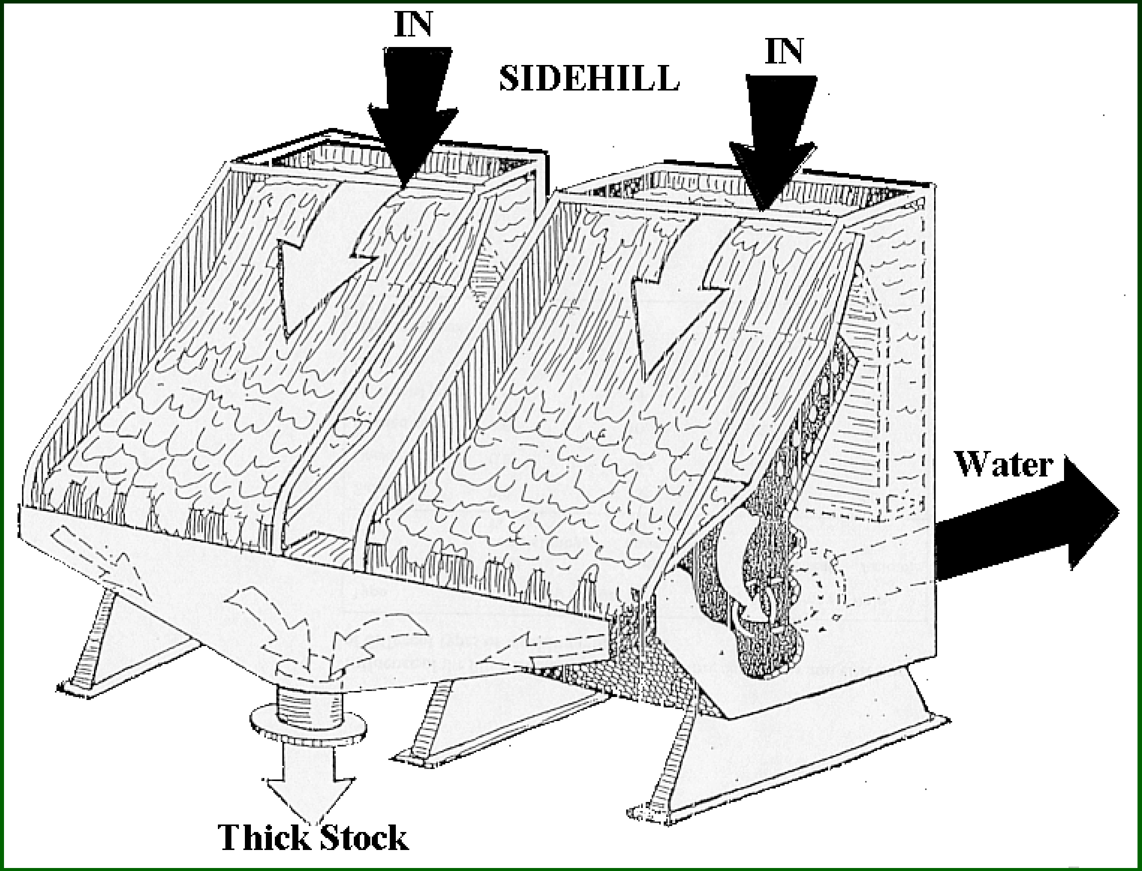
Types of Washers

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

Low Consistency Washers

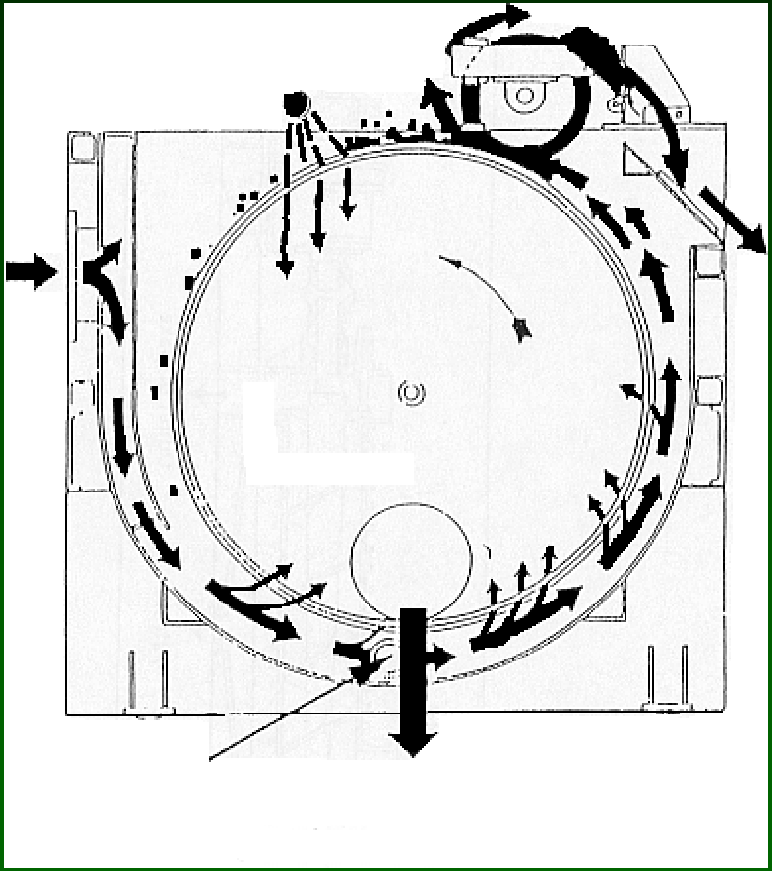
- Up to 8% discharge consistency
  - side-hill screen
  - gravity decker
  - DSM screen
  - Hydrasieve

Sidehill Screen

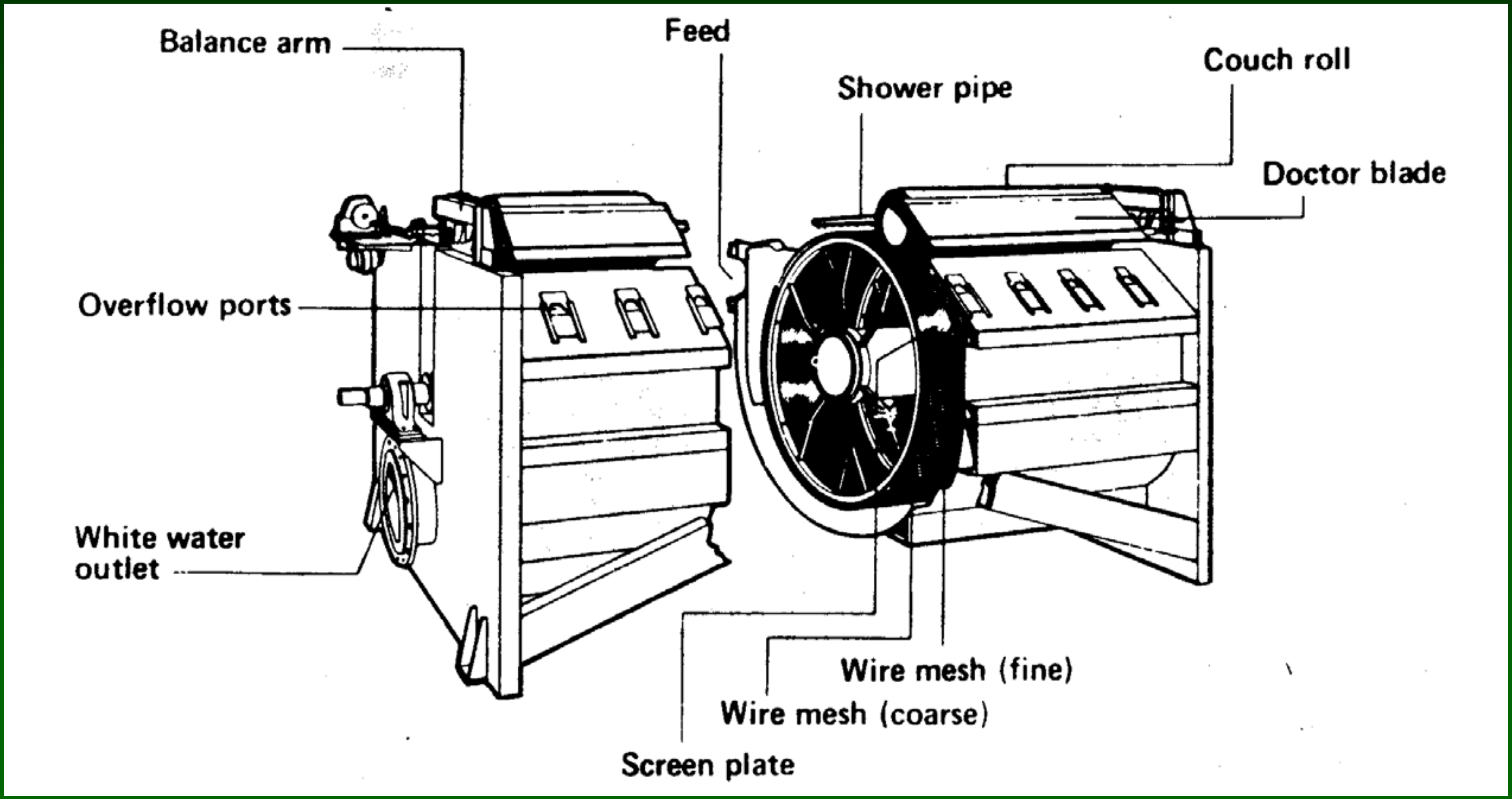


Gravity Decker

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



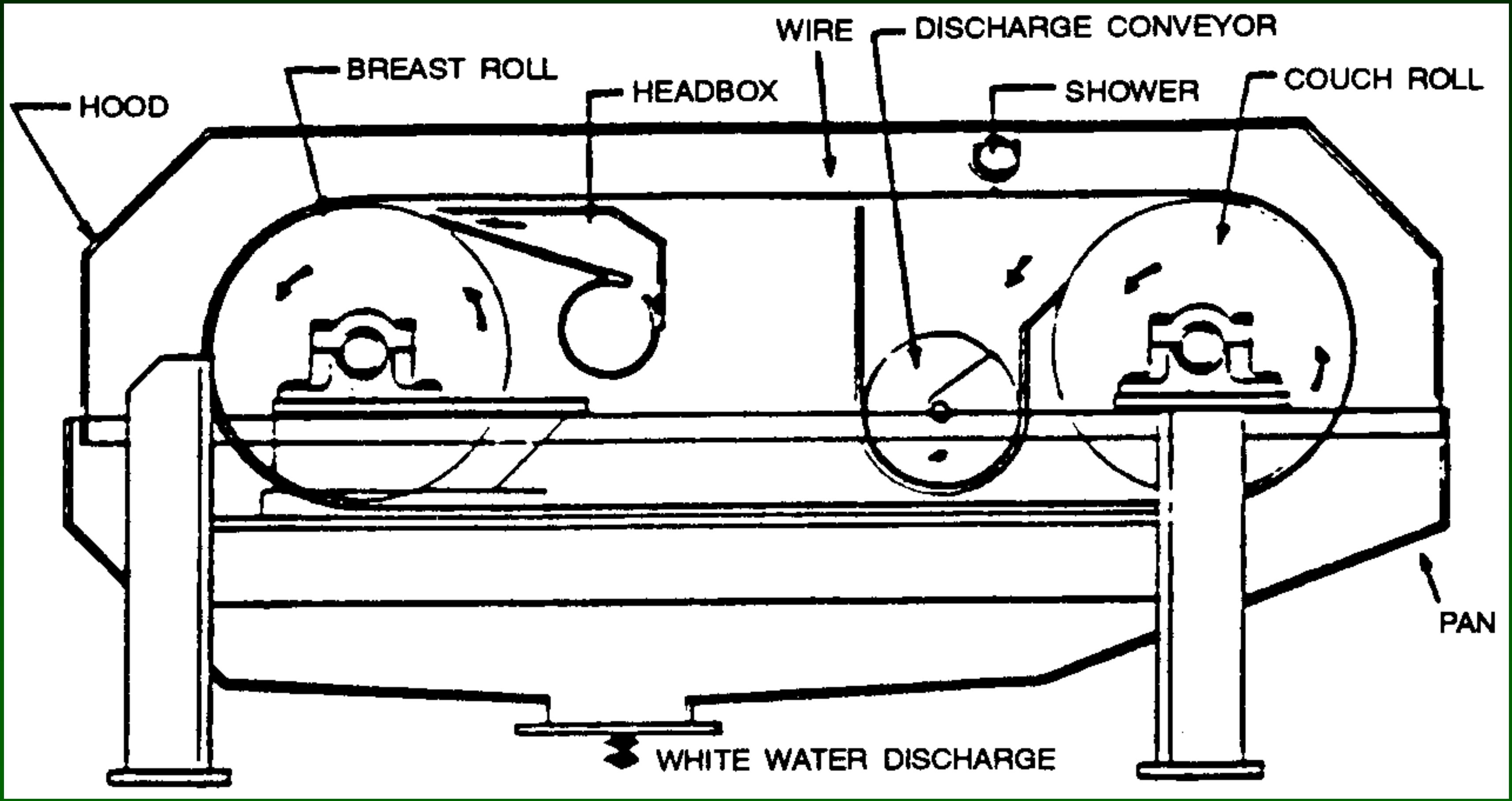
Gravity Decker



Intermediate Consistency Washers

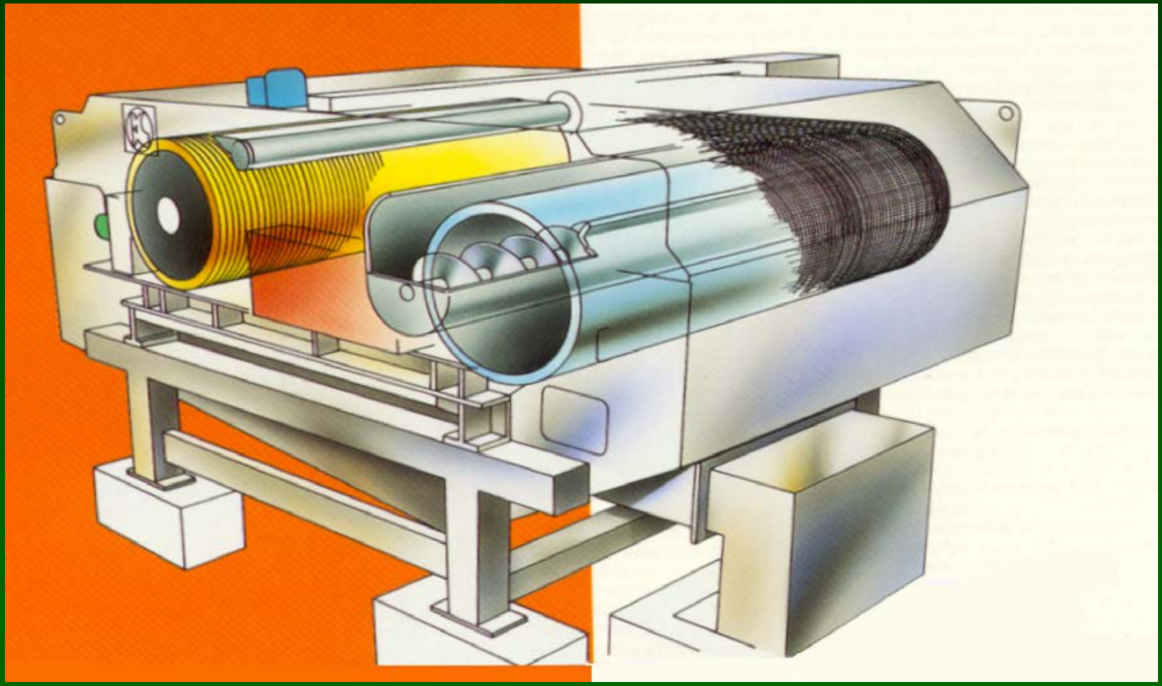
- 8-15% discharge consistency
  - high speed belt washer
    - DNT
    - Vario-split
  - Vacuum filter
  - inclined screw extractors

Double Nip Thickener

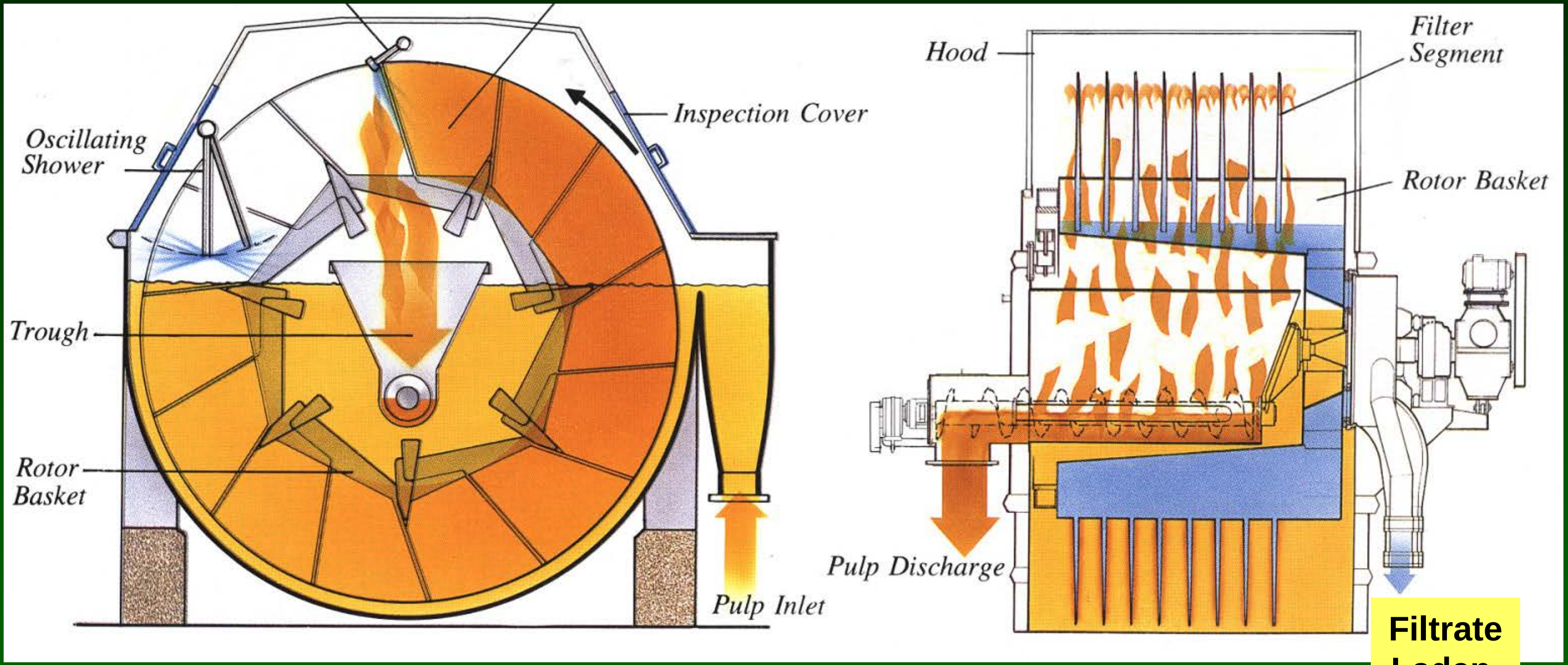


Double Nip Thickener

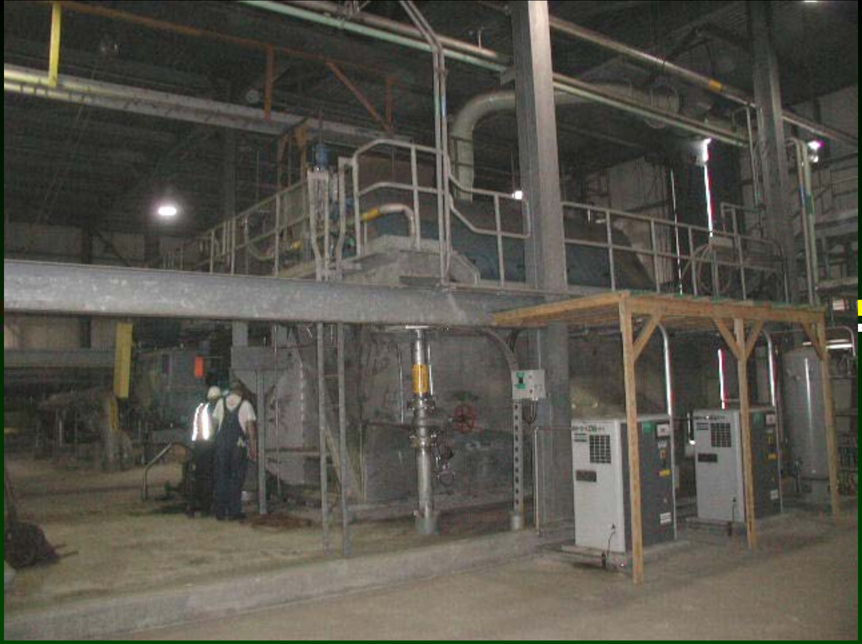
- DNT Washer
  - "double nip thickener"



Disk Filter:



Filtrate Laden With Ink



Vacuum Disk Filter
Mainly for thickening

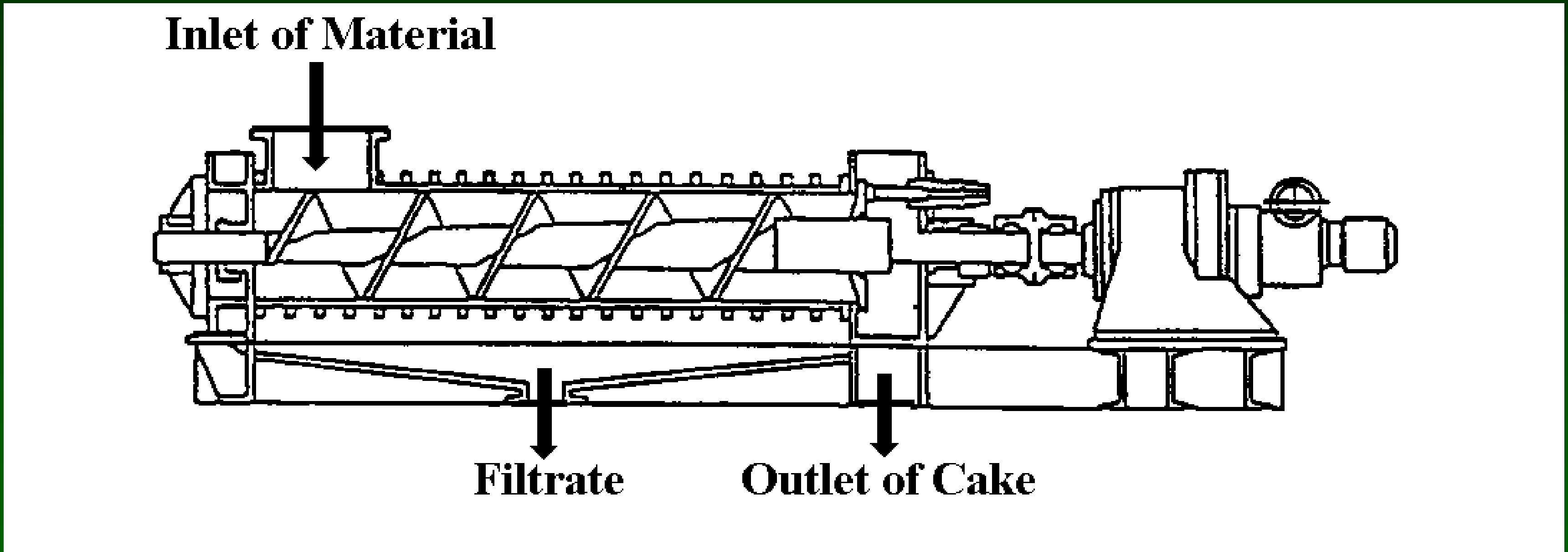
Overview

Disks

High Consistency “Washers”

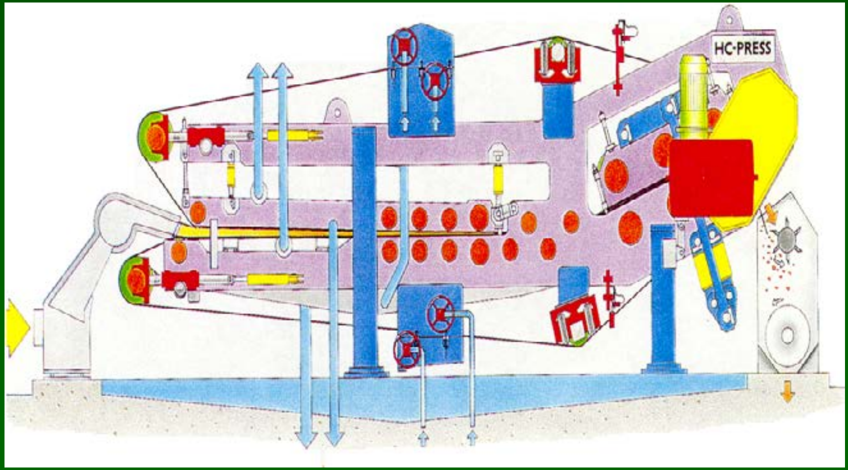
- Not really designed as washers, but more designed to thicken
- Above 15% discharge consistency
  - screw press
  - belt press
  - Wet lap pulp machine
- Low to small contaminant (ink) removal efficiency

Screw Press

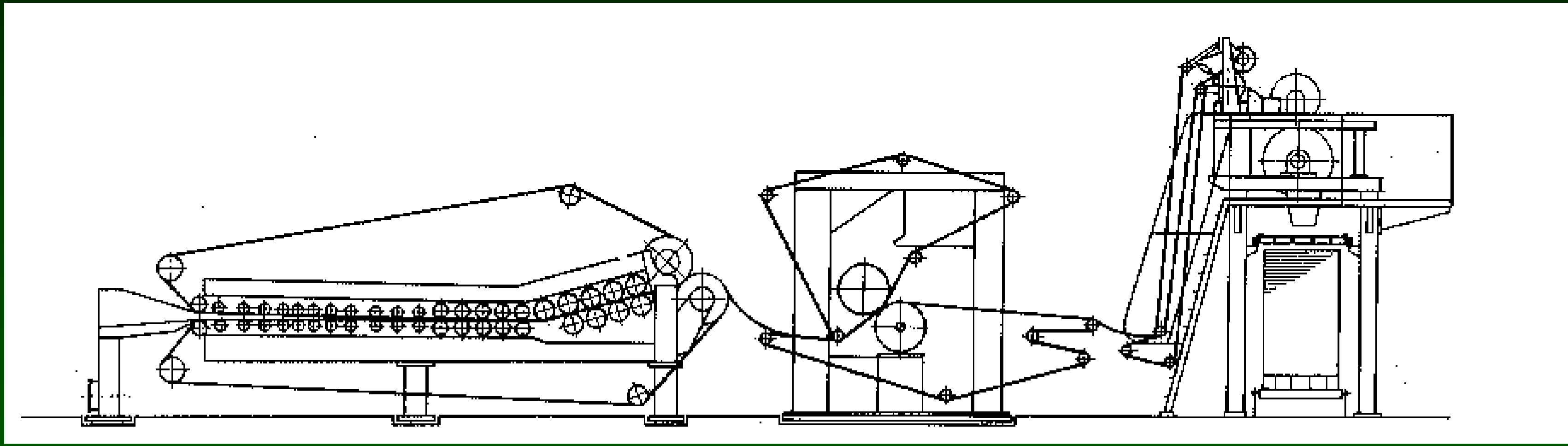


Pressing

- HC-Press



Wet-Lap Pulp Machine



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.

General concepts in washing:

- There are several equipment variables and operating variables that determine the washing efficiency

Washers Wire Mesh Sizes

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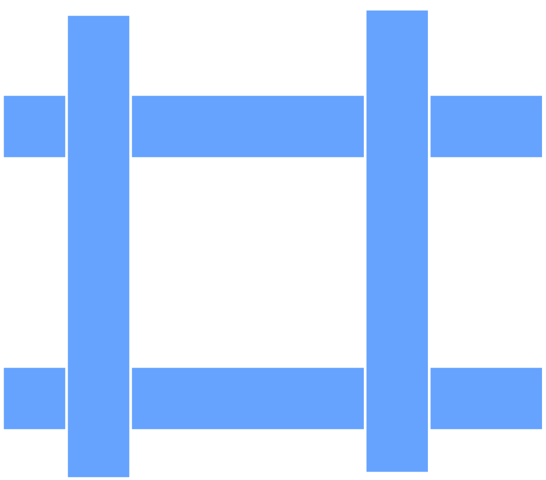
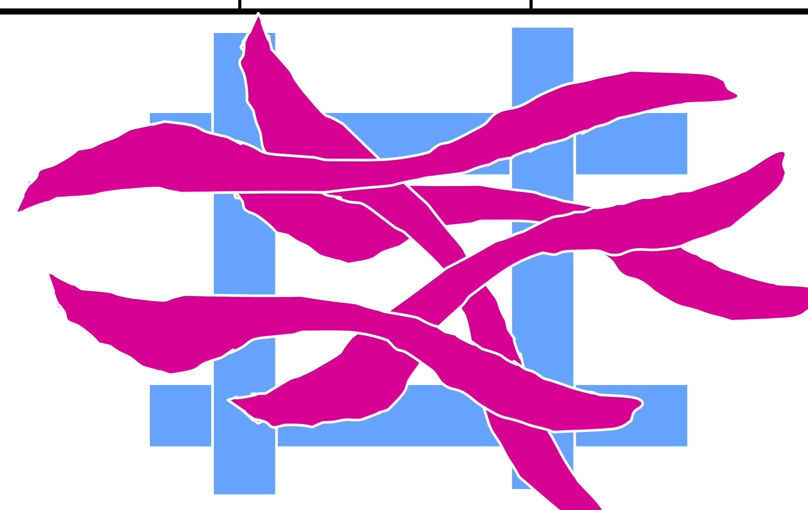
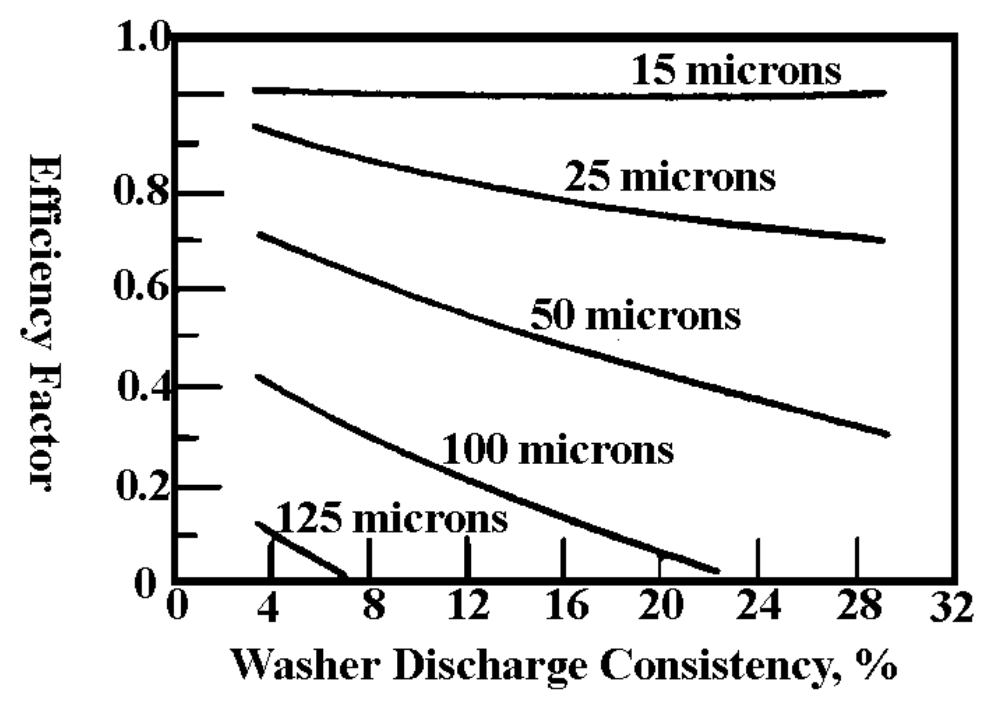




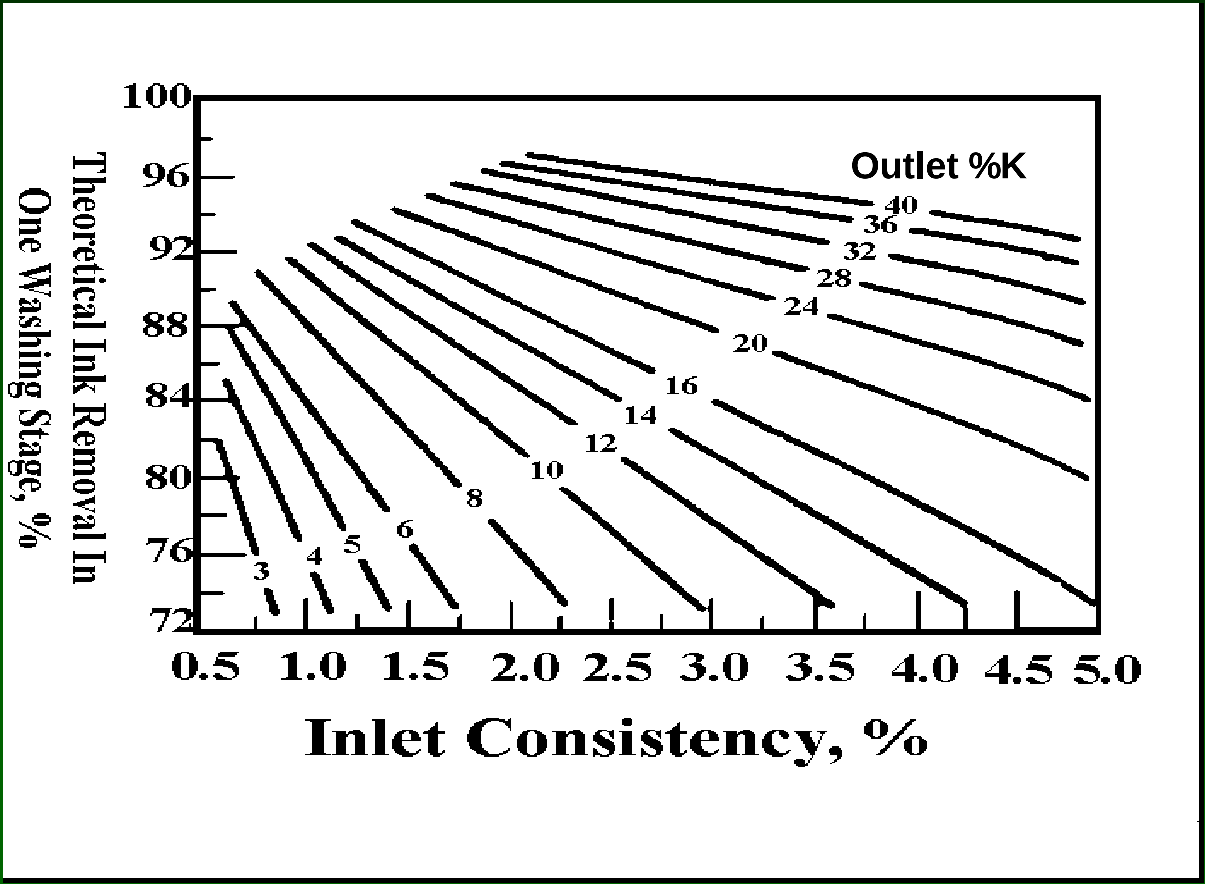
Washing Performance:

Particle Removal Efficiency



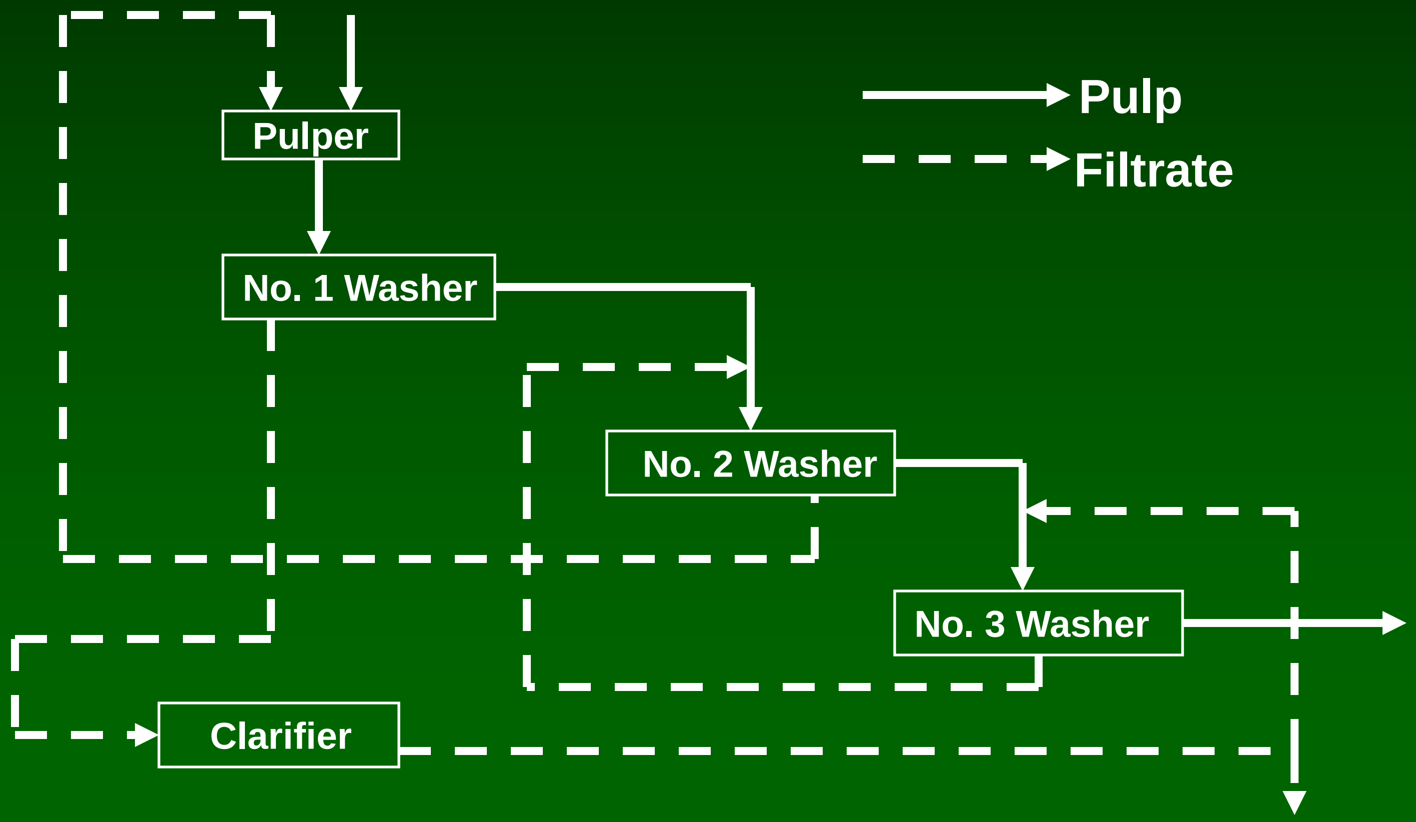
Washing Performance

Theoretical Ink Removed In One Washing Stage



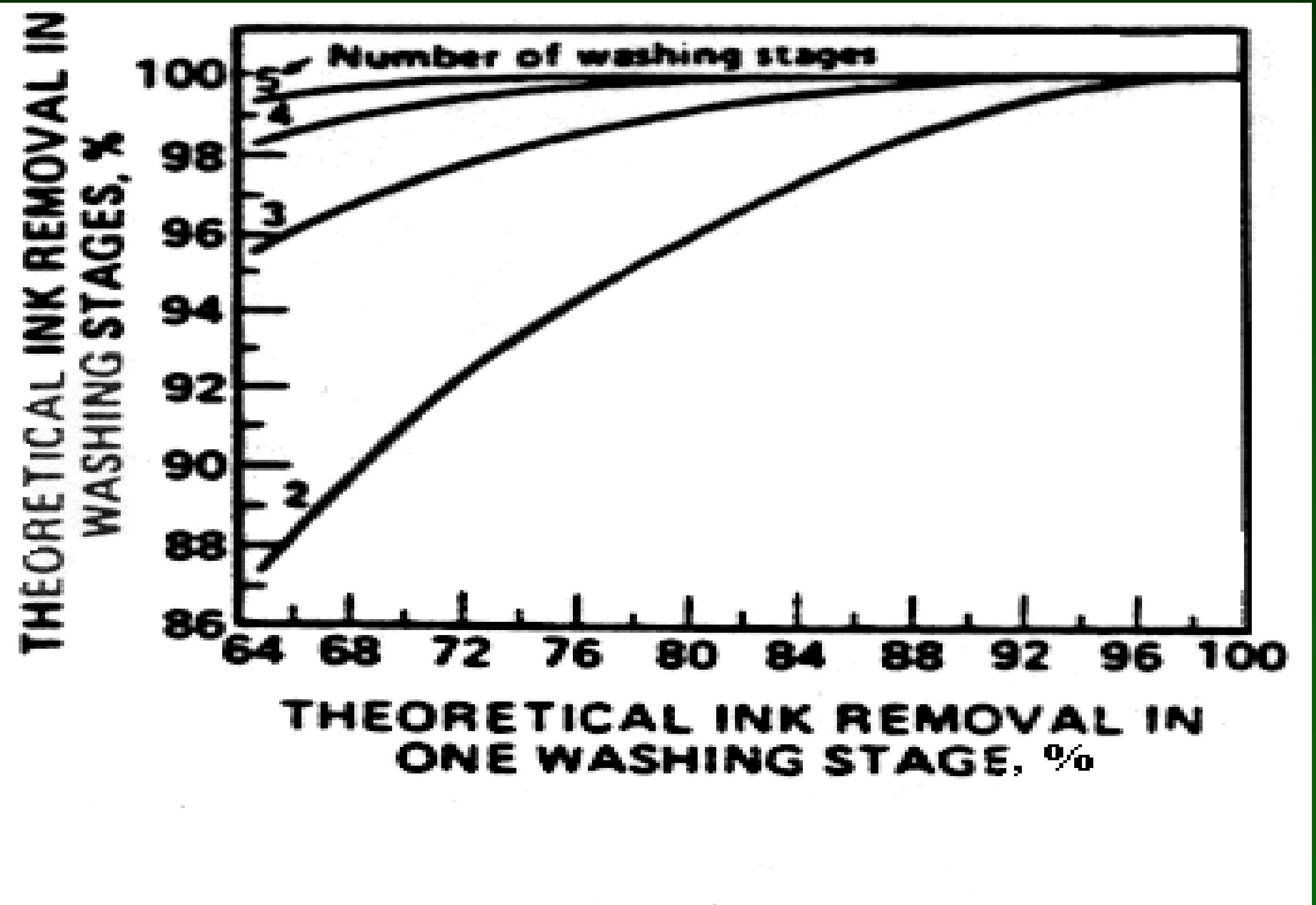
Washing Performance

- Countercurrent washing



Washing Performance:
Counter Current Flow of Pulp and Water

Theoretical Ink Removed In Multiple Counter Current Washing Stages



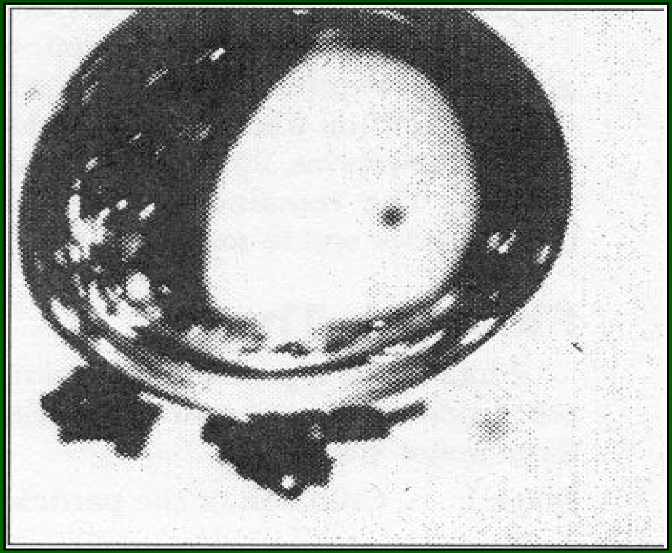
Lecture:

Flotation



Flotation

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



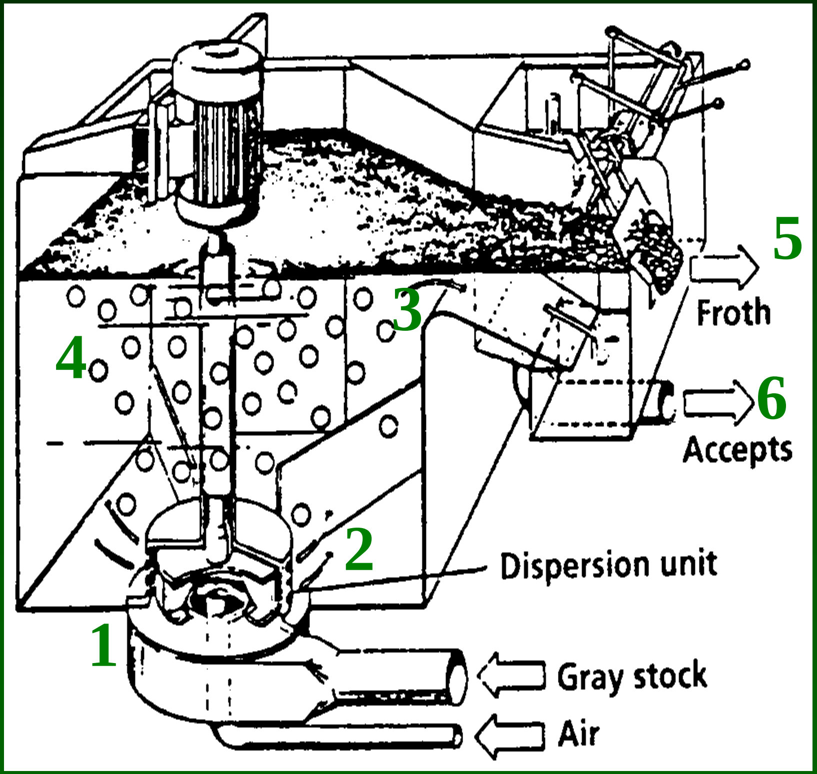
Ink particles attached to air bubble

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.

Flotation

- What determines the flotation efficiency?
  - Contaminant characteristics
  - Bubble characteristics
  - Process conditions

Effect of Contaminant Characteristics on Flotation Efficiency

- 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

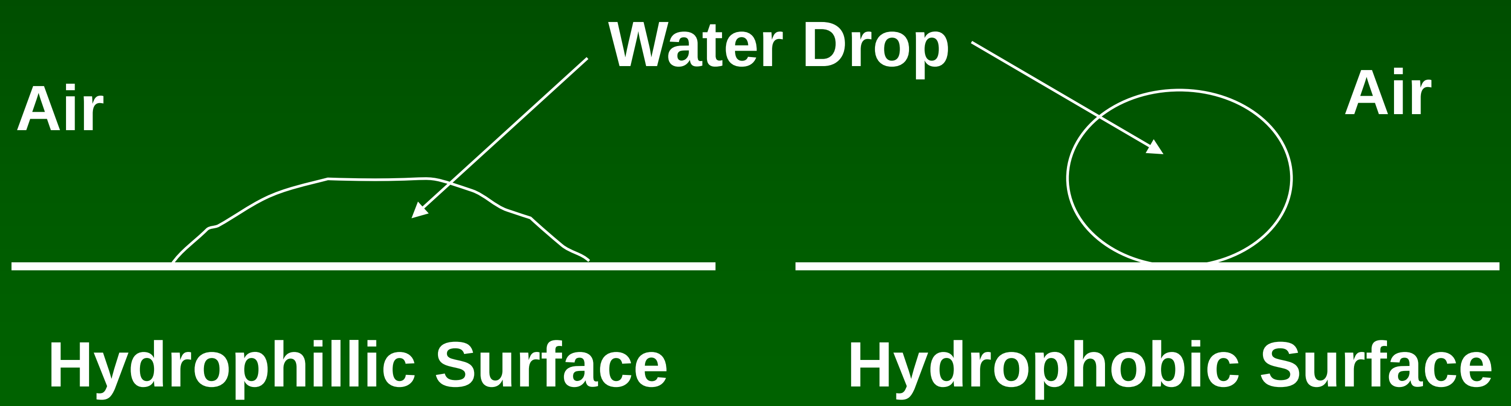
- Hydrophobic - lacking affinity for water
- Hydrophilic - having a strong affinity for water.

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.

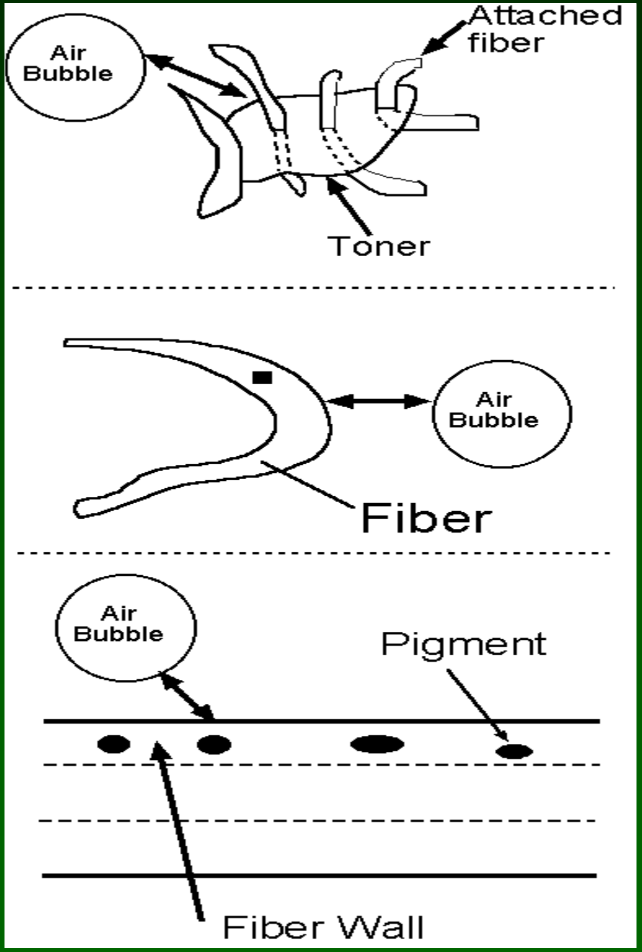
Contaminant Characteristics: Hydrophobicity

- 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

Collector Soaps

- 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.

Process Conditions

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.

Process Conditions

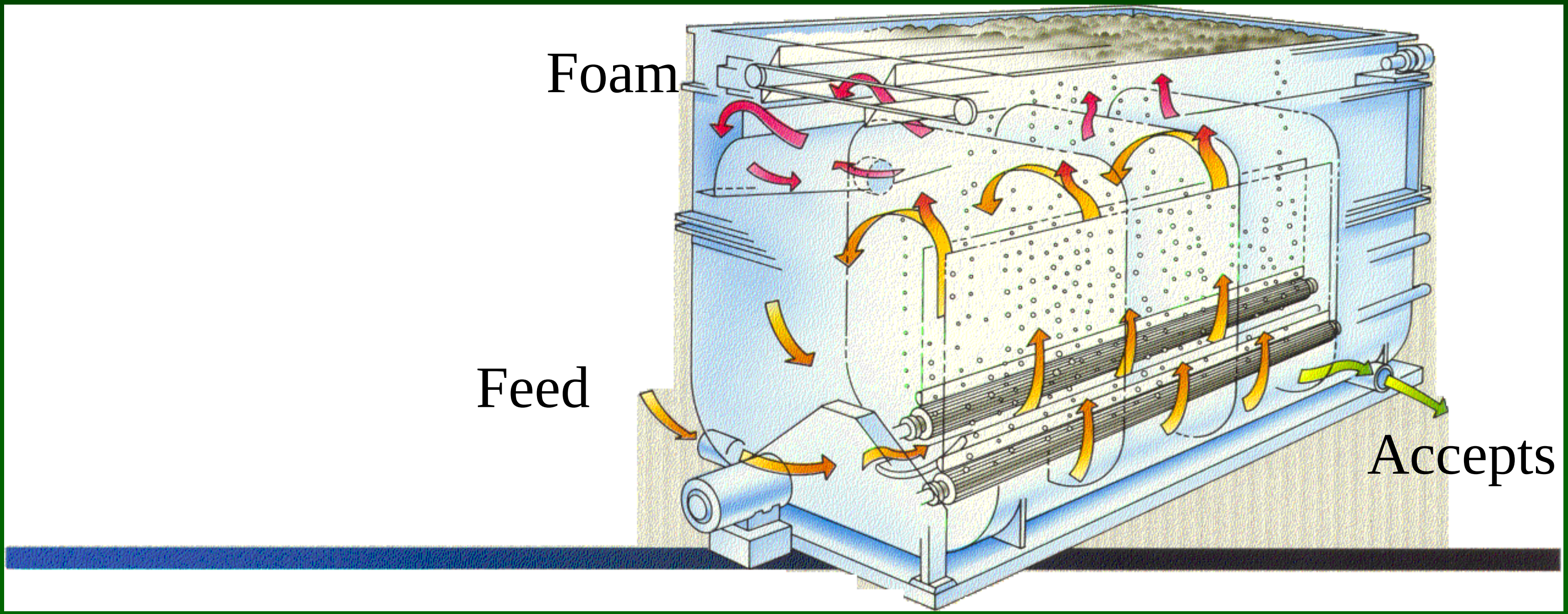
4. Retention Time
   - Longer retention times increase the likelihood of bubble-contaminant collisions. Retention time is limited by production rate demands and volume of existing equipment. Flotation cells are often put in series to increase retention time.
5. Quality and Quantity of Air Bubbles
6. 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**
  - **Kamyr**
  - **Wemco**

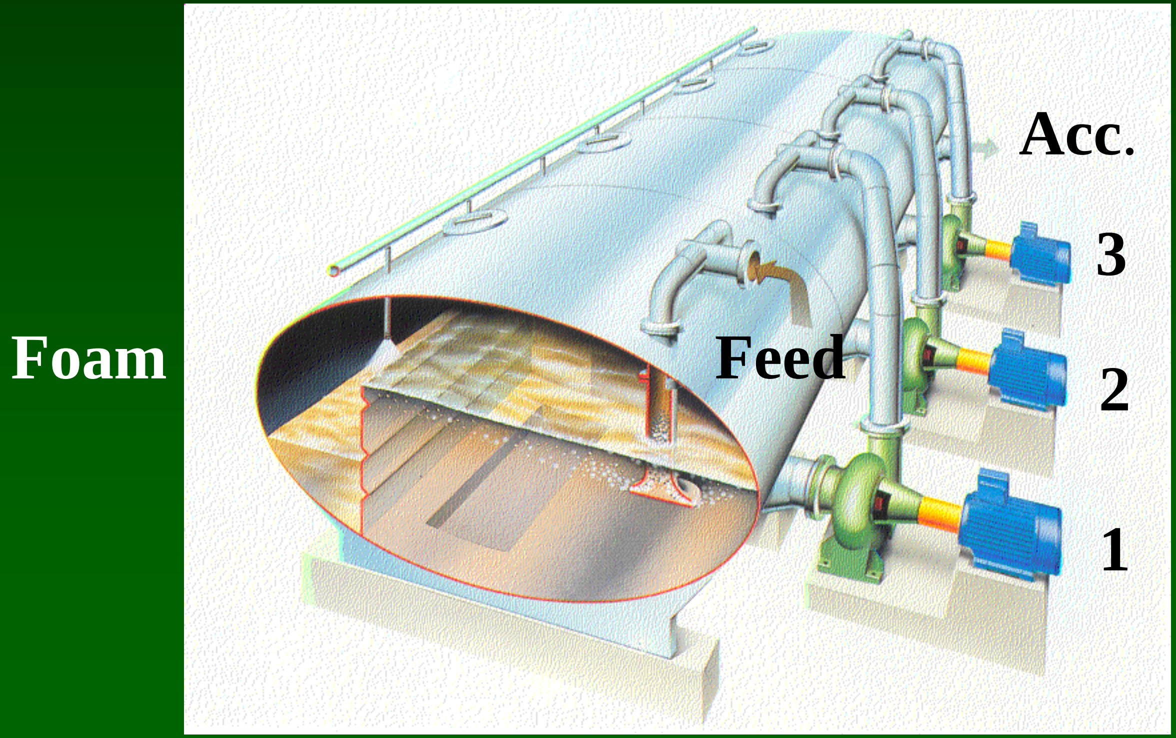
Flotation Cell

- Black Clawson Flotator



Flotation Cell

- 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.

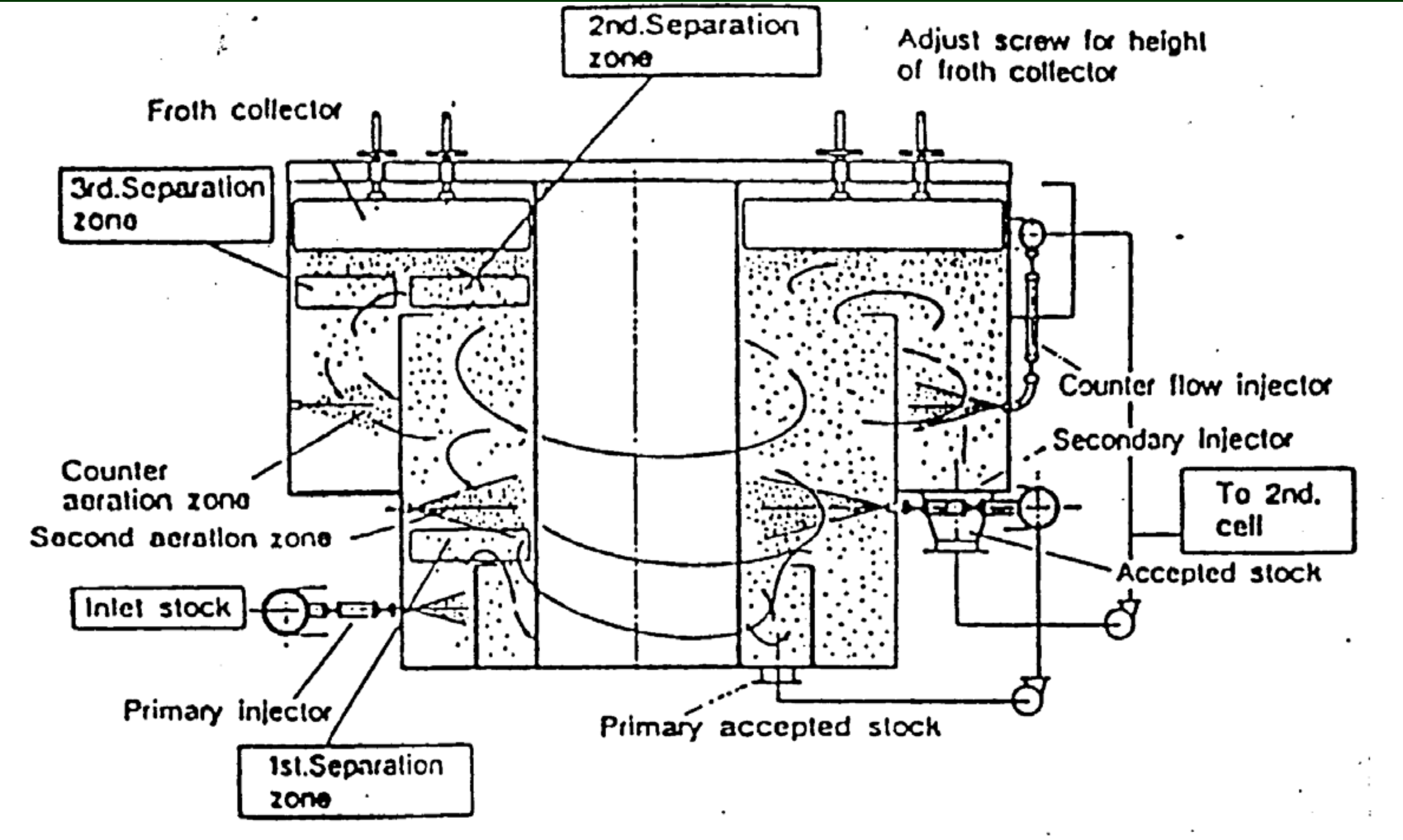
Overview

Trace Lines

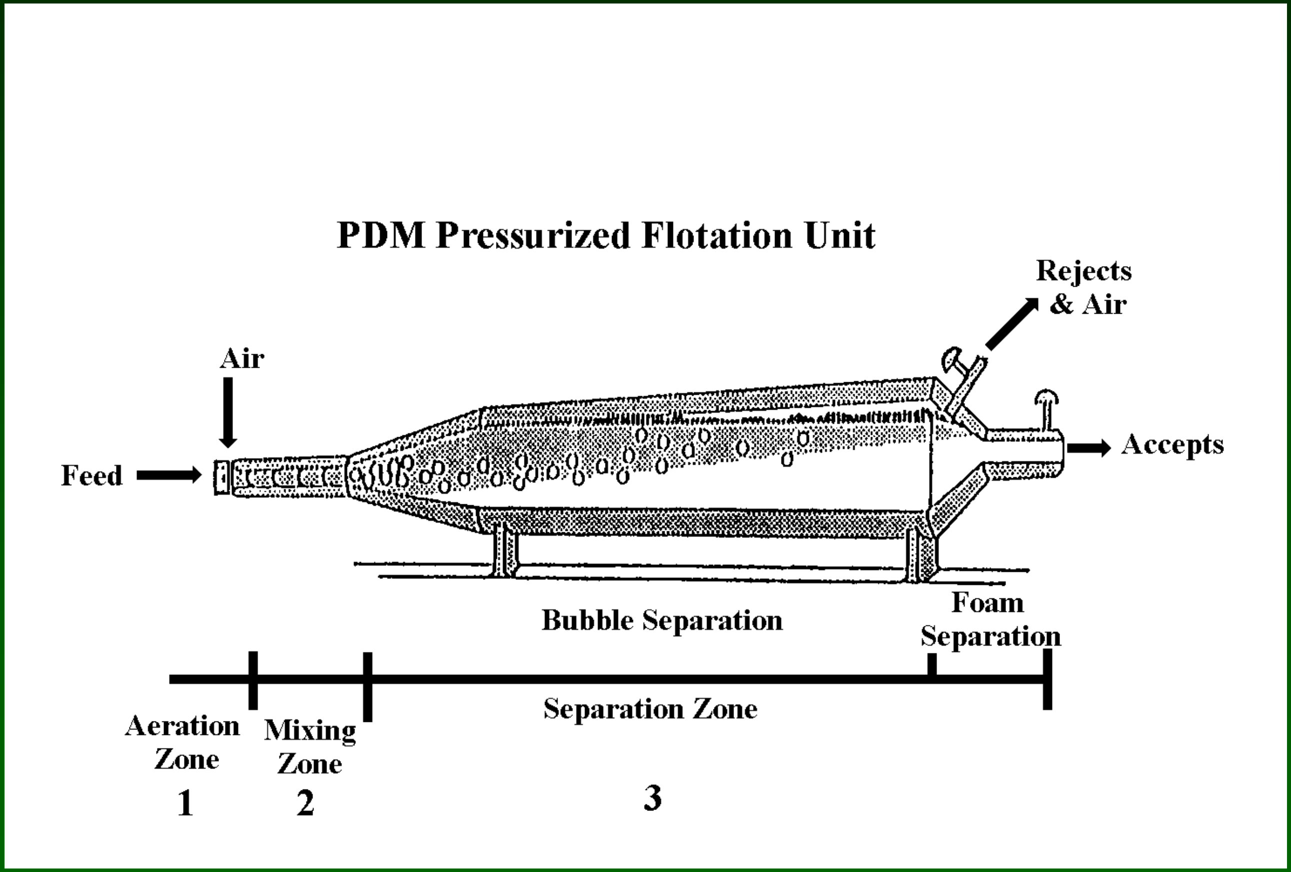
Foam

Flotation Cell

- Lamort - Fiberprep Flotation Cell

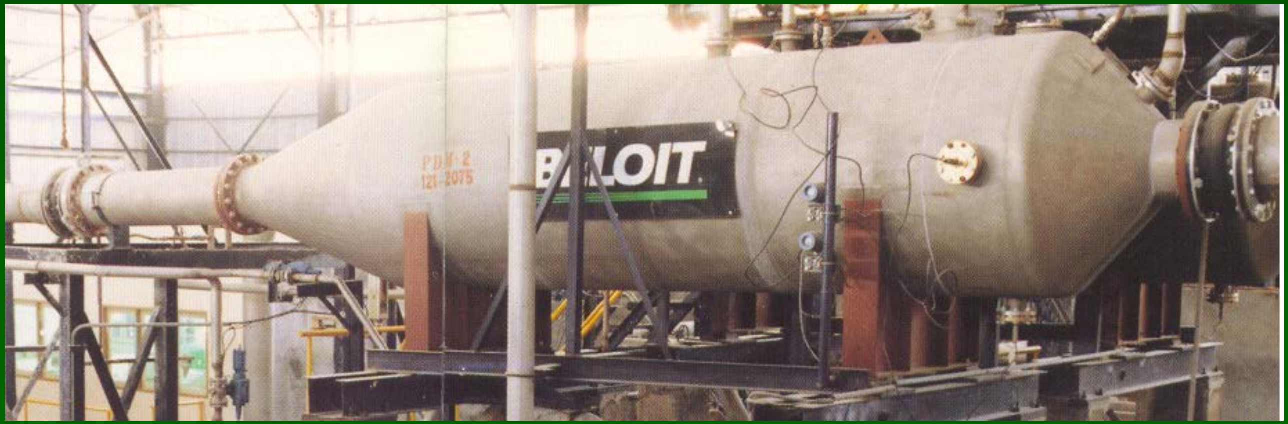


Flotation Cell



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

	Flotation	Washing
Chemistry-Sensitive	more	less
Water Use	lower	higher
Yield	higher	lower
Ash Removal	No	Yes
Tensile Str.	Lower	Higher
Opacity	Higher	Lower

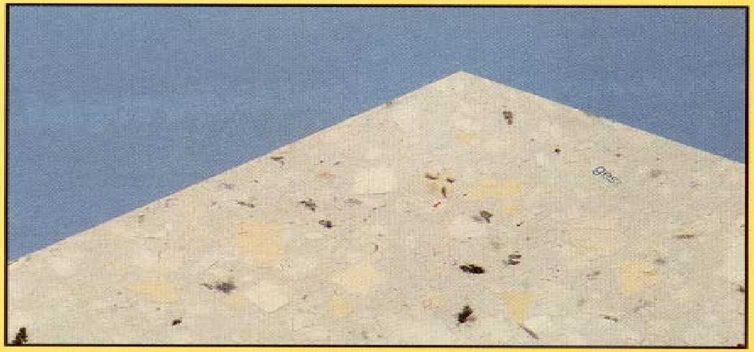
Lecture:

Dispersion and kneading

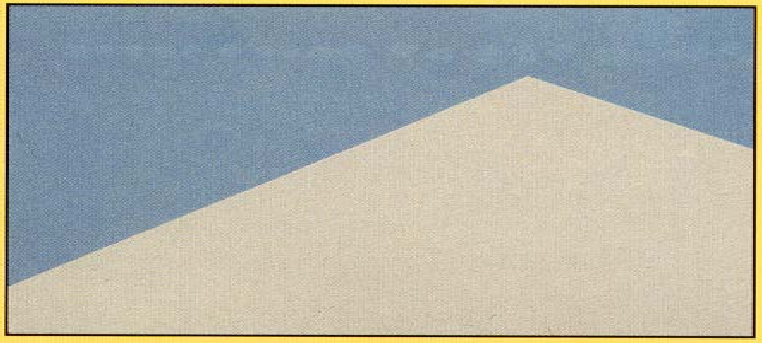


Dispersion of Contaminants in Recovered Paper Stock

- 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).



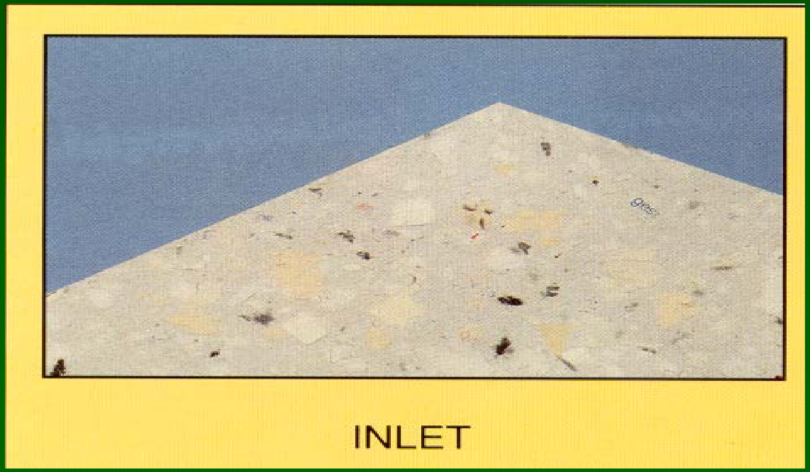
INLET

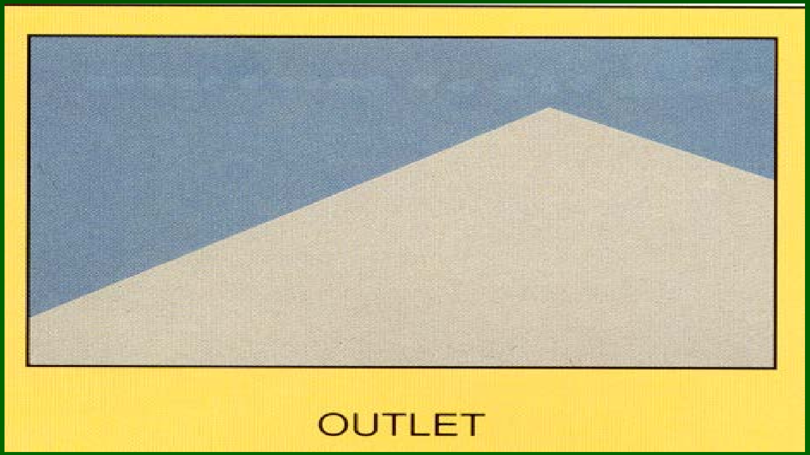


OUTLET

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

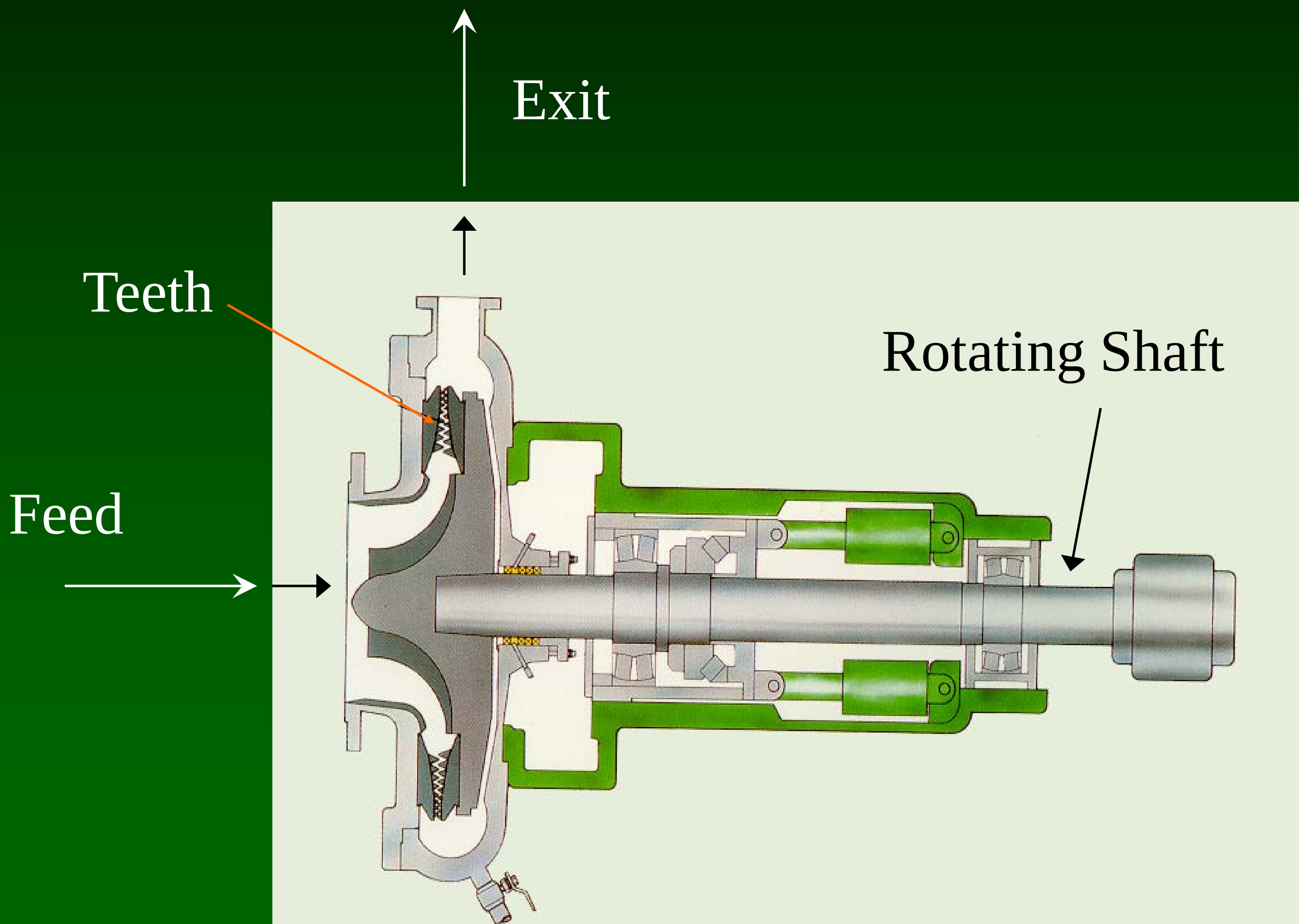


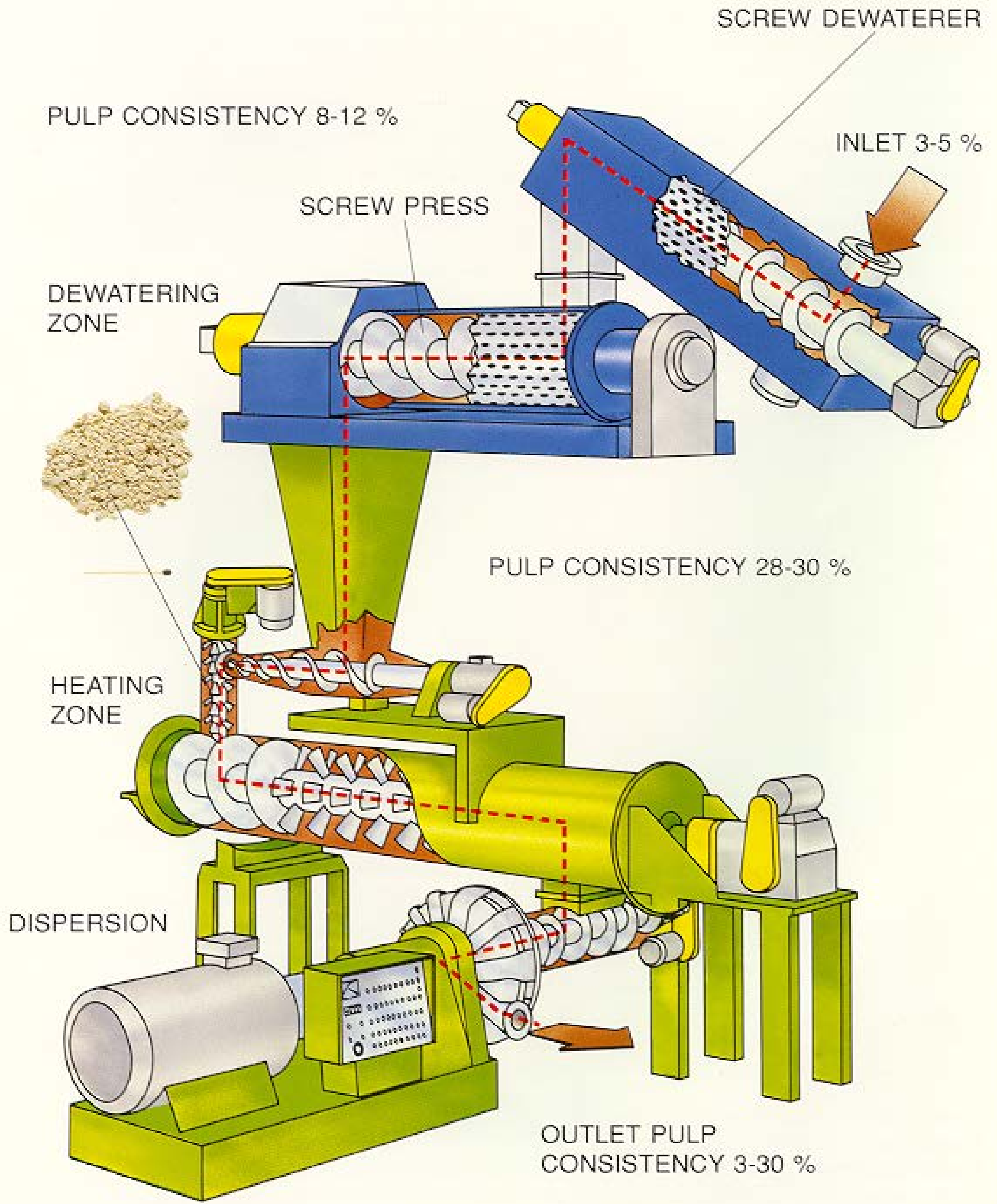


Disk Dispersion

- 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



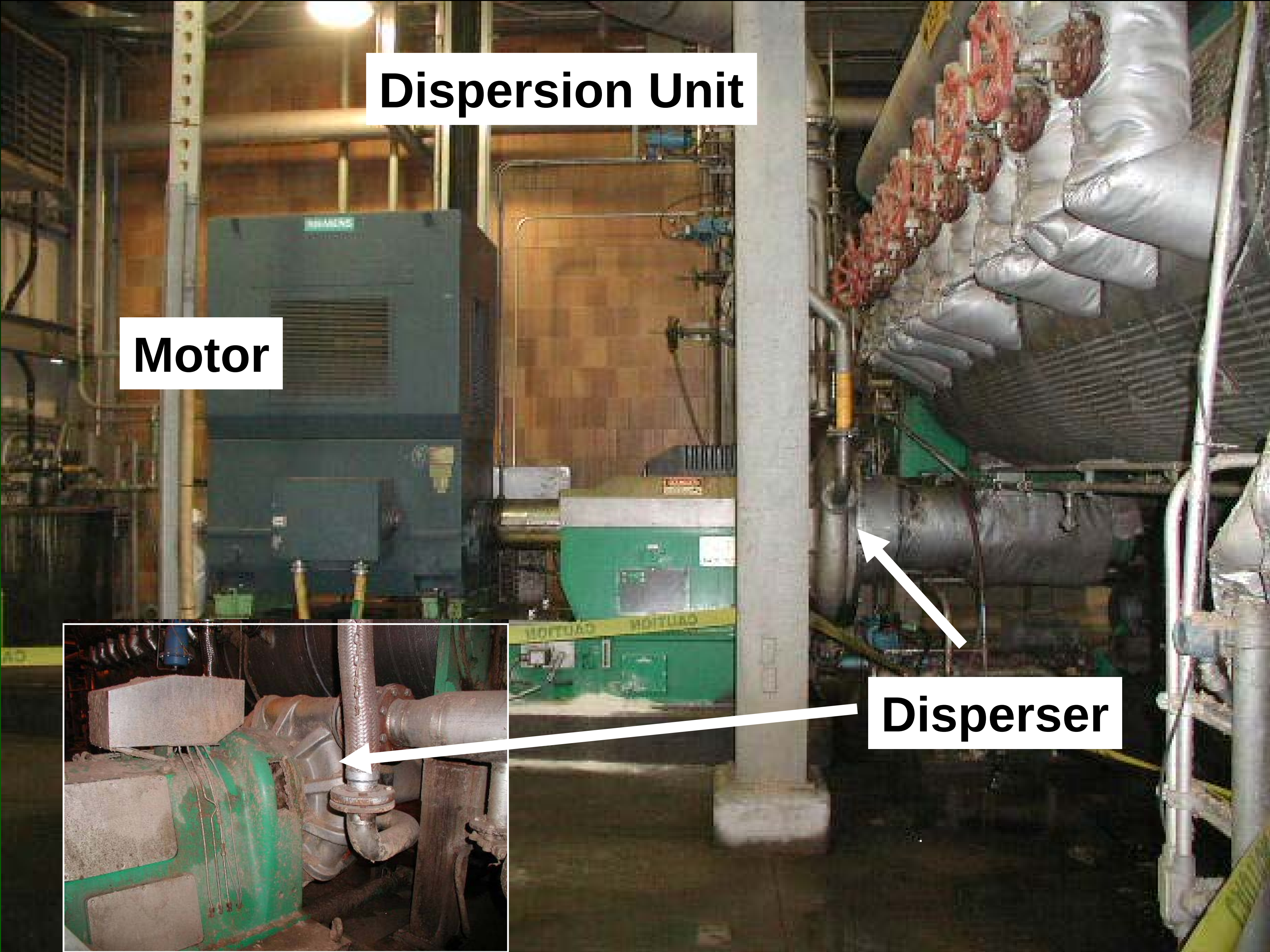


Dispersion

- 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


Dispersion Unit
Motor
Disperser
CAUTION

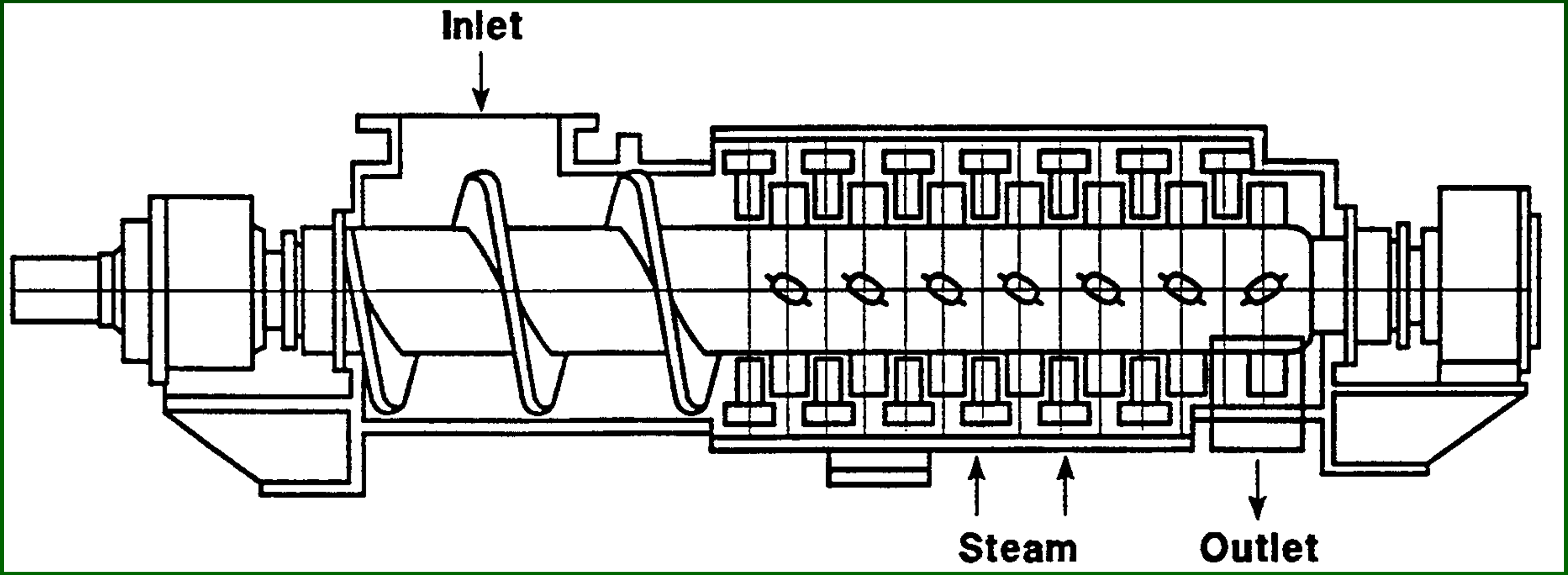
Kneading

- 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 (compare to dispersion at 1 mm gap)
  - 3.0-4.5 hp days / ton

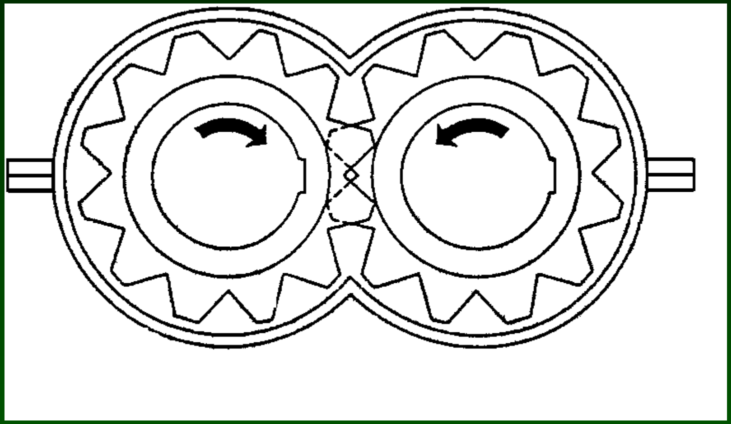
Single Shaft Kneader

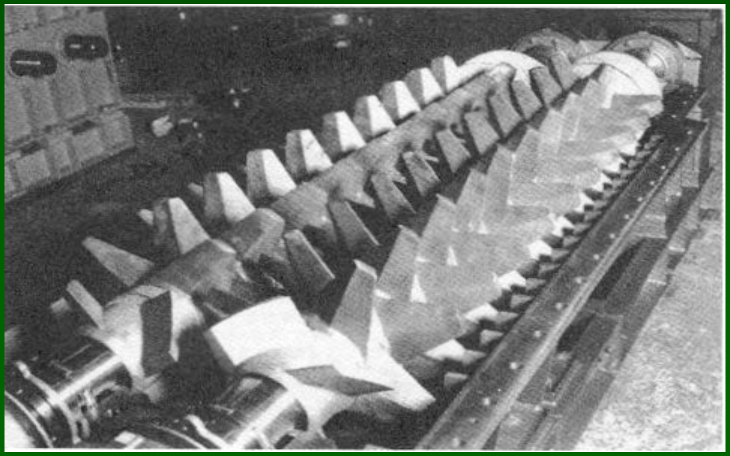
- Process stock is dewatered to 30% K
- Stock enters a feed screw, steam or bleaching chemical may be added
- Stock is kneaded
- Stock is discharged, diluted and agitated for further processing



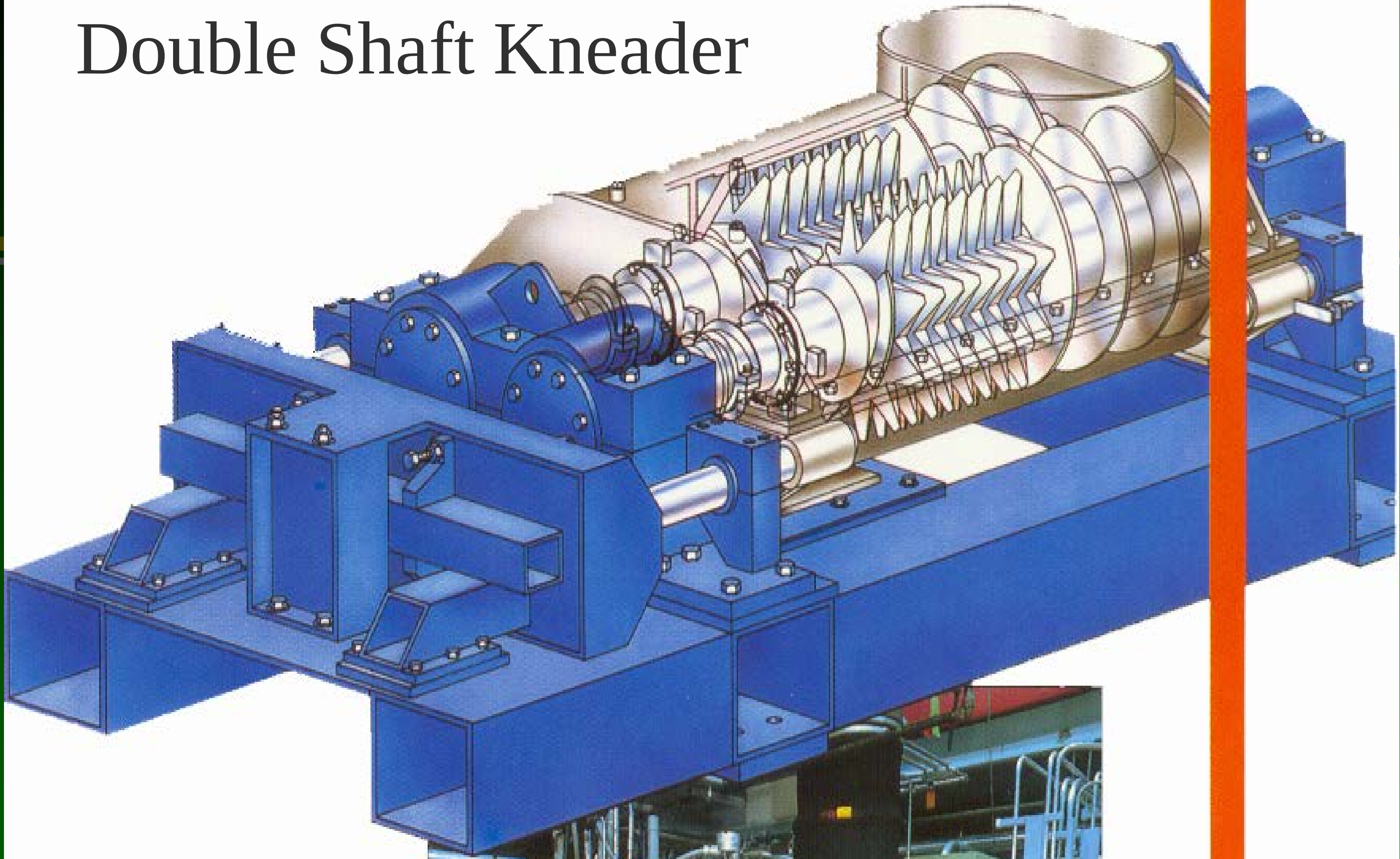
Double Shaft Kneader

- 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.

	Dispersion	Kneading
Mechanism	Shear	Rub
Consistency	30%	30%
Temp.	95	50
RPM	1200-1800	100-900
Retent. Time	2 s	10-60 s
Gap, mm	.5-1.5	10-40

Kneading vs. Dispersion

Methods to decrease contaminant size.

Effect	Dispersion	Kneading
Tappi Dirt Reduct.	75%	85%
Toner Reduct.	yes	better
Stickies Reduct.	better	no effect
Fiber Cutting	substantial	none
Fines Generation	yes	no

Lecture:

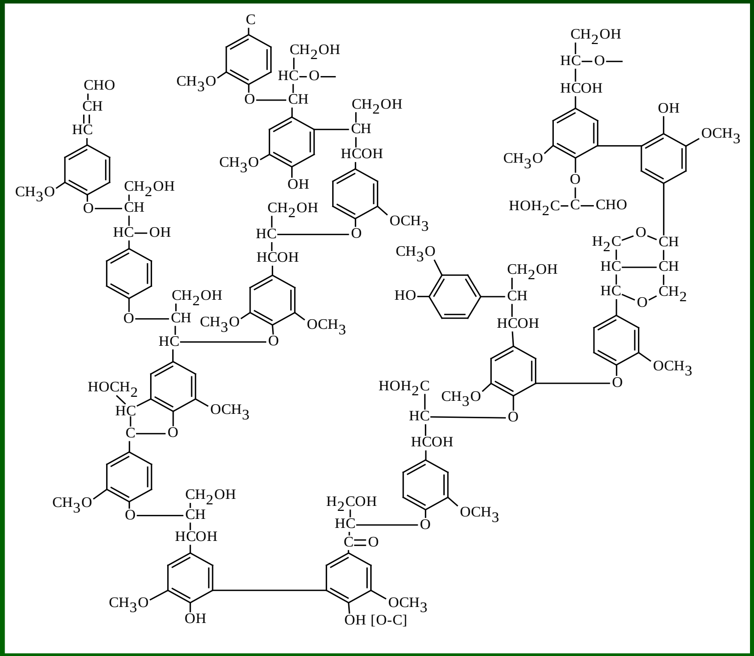
Bleaching

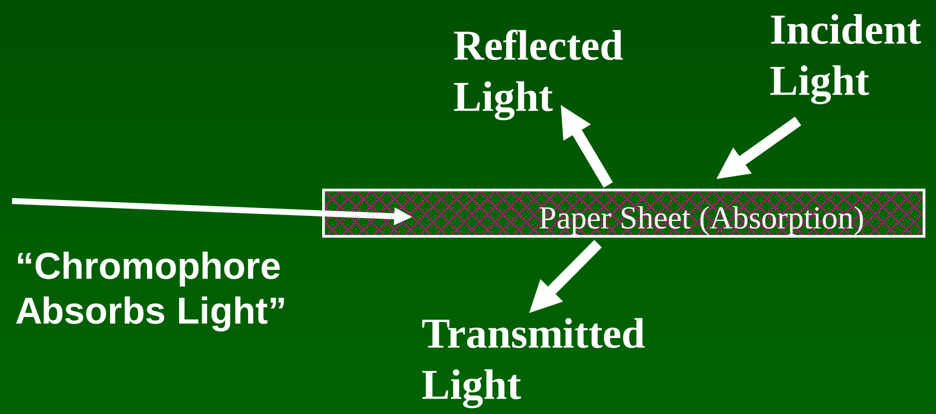
Bleaching

- Bleaching is the chemical process applied to cellulosic materials to destroy chromophores, increasing the brightness and reducing color
- Chemical reactions
  - Oxidative, like peroxide
  - Reductive, like Sodium hydrosulfite and FAS

Bleaching

- Dye destruction
- Fluorescent Whitening Agents (FWA) Destruction
- Destruction/modification of lignin from lignin-containing fibers
- Does not affect pigments, which have color due to the lattice structure of molecules (like carbon black or titanium dioxide)





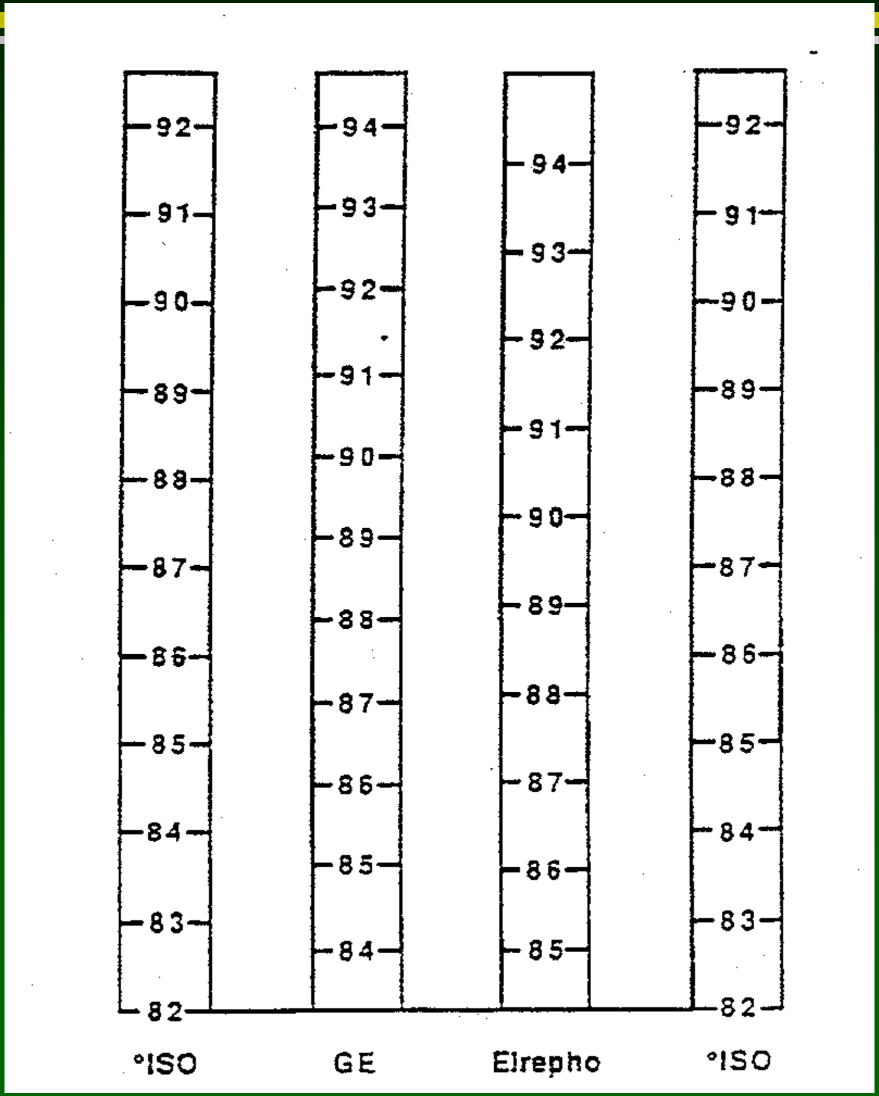
Brightness Measurement

- Tappi Method T452
  - Specifies illuminating light at 45º to the sample and the reflected light measuremement at 90º 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 90o to the sample. Reflectance is compared to absolute reflectance from an imaginary, perfectly reflecting diffusing surface.

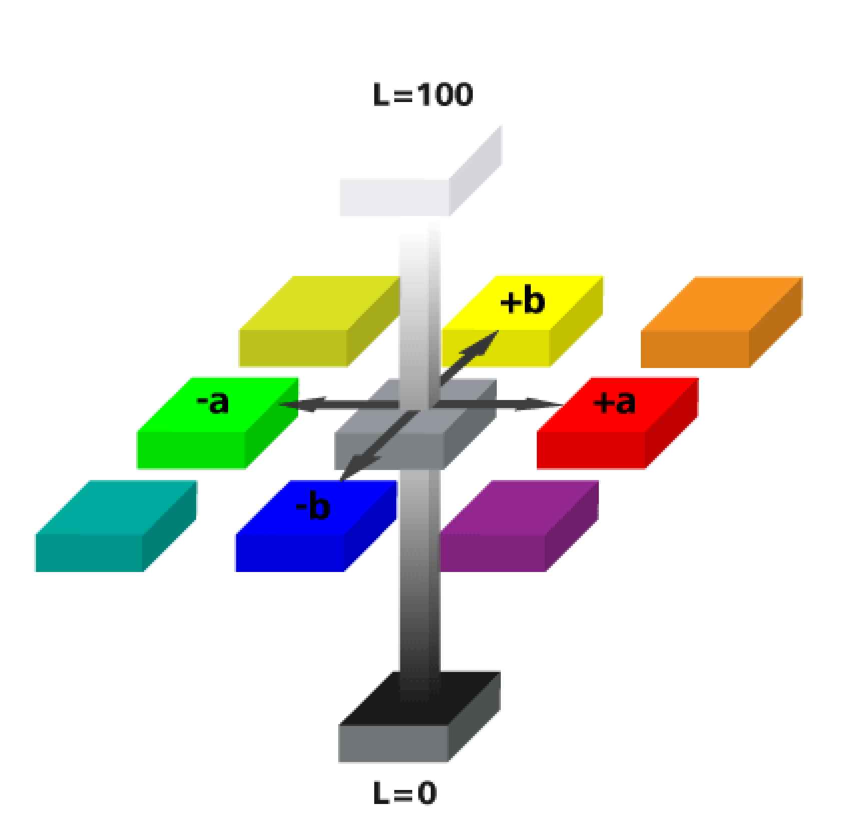
    Units: %ISO brightness

Brightness Scales



Color Measurement

- *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*
- *http://www.zeiss.de*



Fluorescence Measurement

- *Fluorescent whitening agents: ultraviolet energy is absorbed and re-emitted as visible light, increasing the brightness*

- *To measure Fluorescence:*
  - *Measure Normal Brightness with UV light shining on sample*
  - *Measure Brightness with UV filter that blocks the UV light from shining on the sample*
  - *If there is a difference in the two brightnesses, there is FWA present*

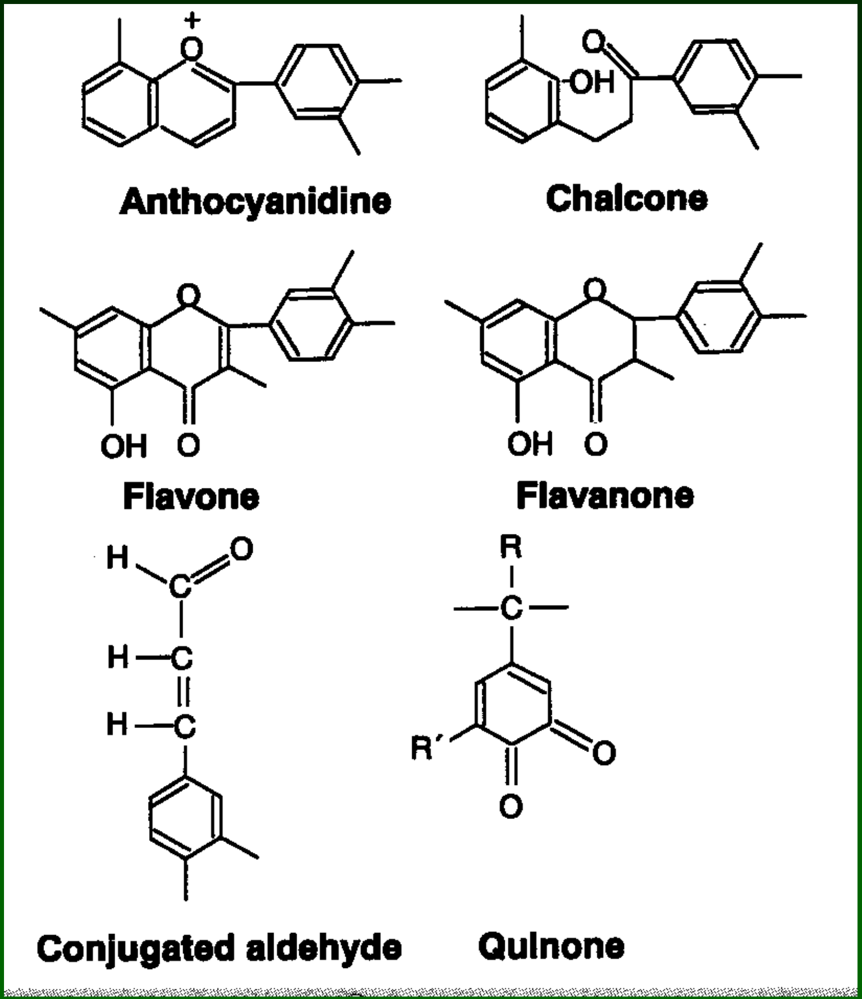
Paper Fibers

- Cellulose and hemicellulose:
  - white, colorless, do not absorb light
- Lignin and extractives:
  - have some color, especially when modified
  - alkaline environments increase the color producing groups in lignin
    - kraft chemical pulping
    - Semi-chemical pulping
    - Alkali used in ONP recycling to liberate inks and swell fibers
- Dyes absorb light causing color and decreasing brightness

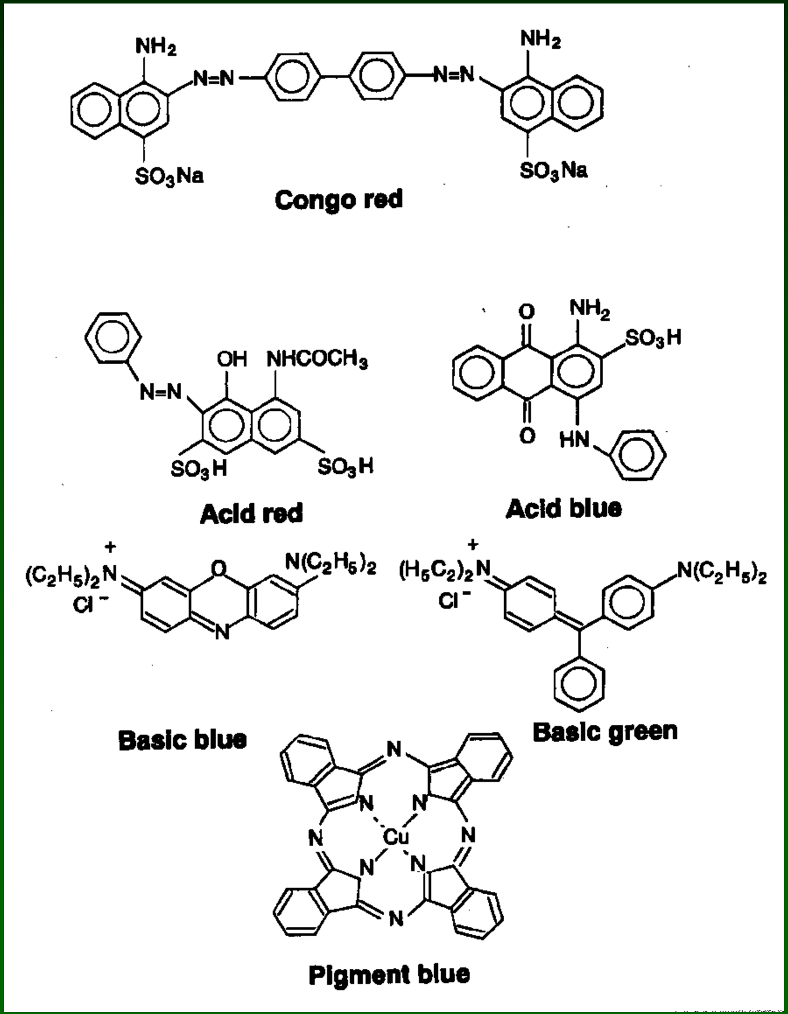
Chemical structure of colored extractives and groups in wood and lignin

- It is the conjugated double bonds (alternating single and double bonds) that cause color

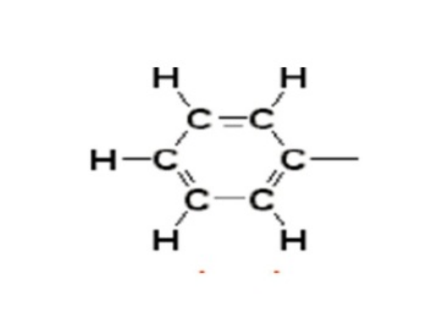
- Ref: Papermaking Science and Technology, Book 7, Recyled Fiber and Deinking, Tappi Press.



Dyes



- Dyes and printing inks contribute to the color of fibers
- It is the conjugated double bonds that cause color



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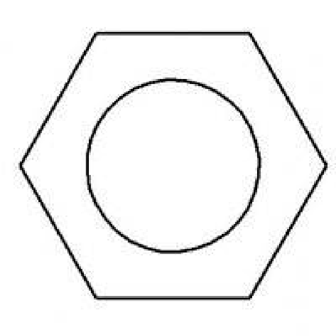
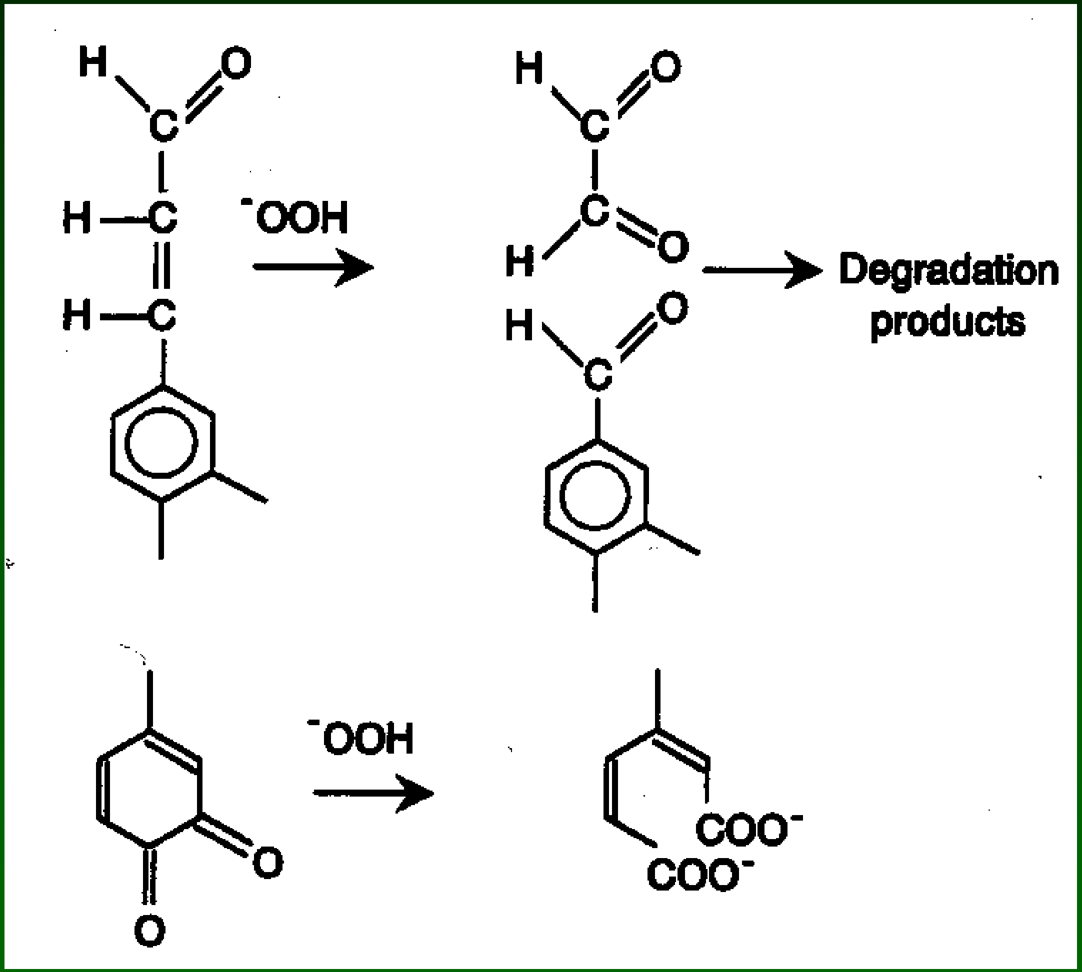


Peroxide Bleaching (P)

- 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
- $H_2O_2 + H_2O \leftrightarrow HOO^{-} + H_3O^{+}$
- $H_2O_2 + OH^{-} \leftrightarrow HOO^{-} + H_2O$
- Oxidation reactions are irreversible

Peroxide Bleaching (P)



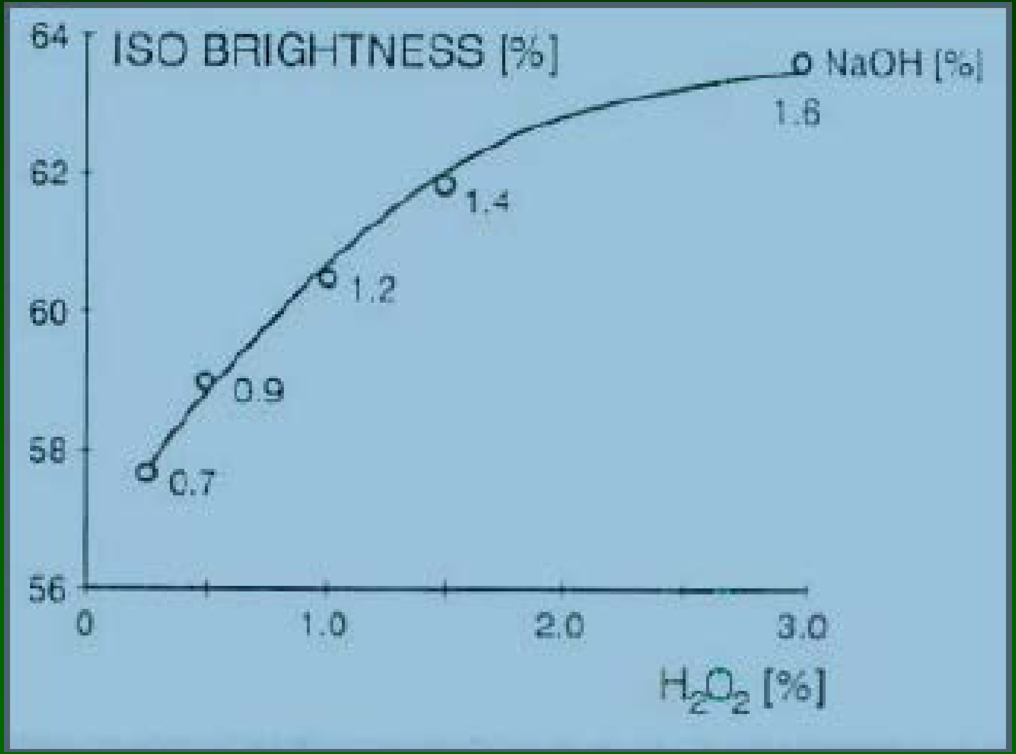
- The most important bleaching agent for mechanical recovered paper pulps
- Bleaches in a non delignifying manner by destroying the chromophore
- Irreversible

Peroxide Bleaching

- Sodium hydroxide (NaOH) is added to increase the perhydroxyl anion concentration, the active bleaching agent, HOO(-):

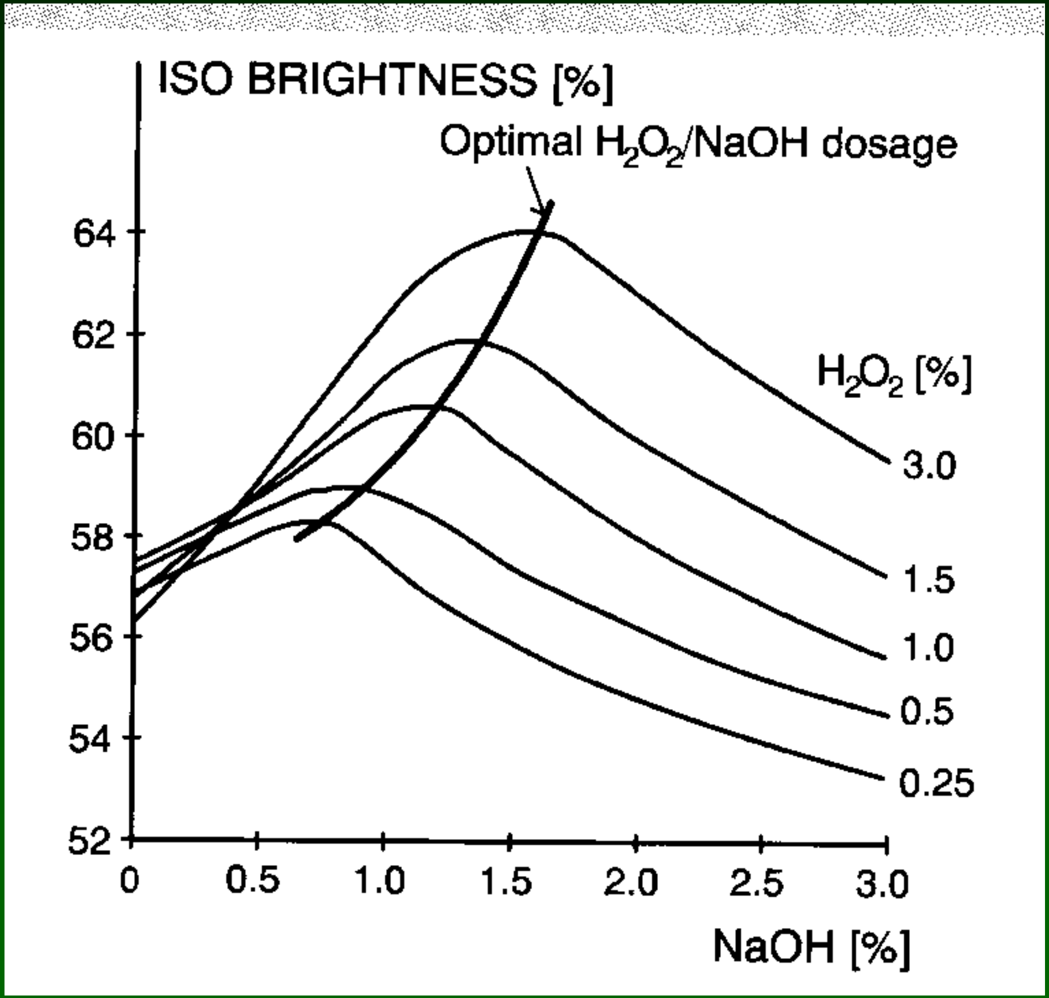
- $H_2O_2 + H_2O \leftrightarrow HOO^{-} + H_3O^{+}$
- $H_2O_2 + OH^{-} \leftrightarrow HOO^{-} + H_2O$

Peroxide Bleaching



- There is a non linear relationship between H2O2 and bleaching performance

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

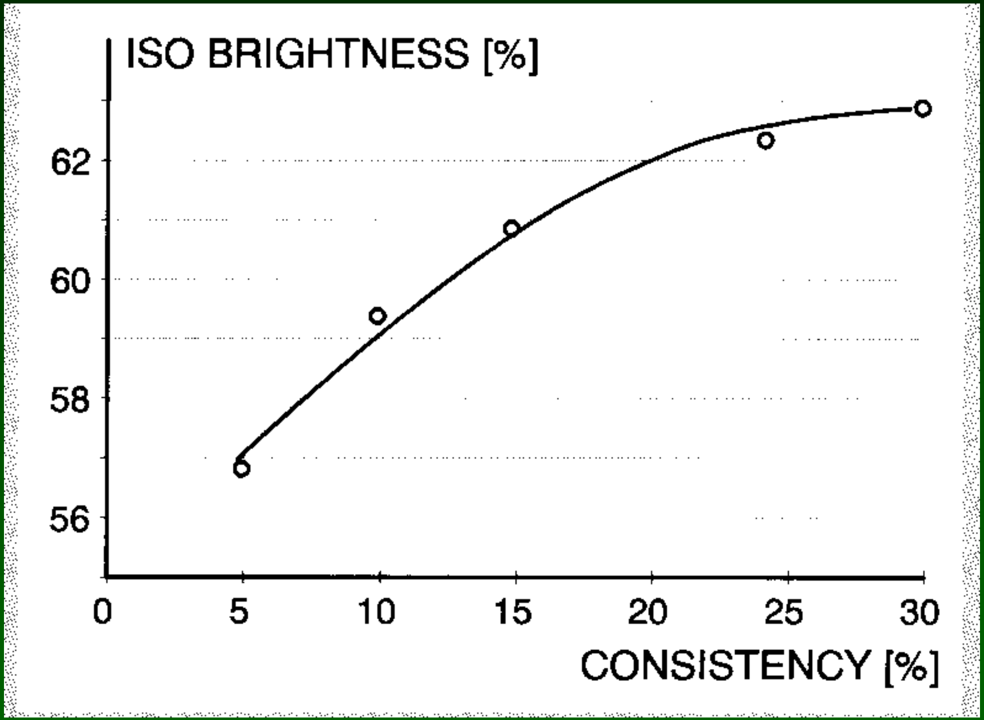
- Application: 1-3% on pulp solids, typically less than 2%
- Time: 30-90 minutes
- Consistency: 10+%
- Temperature: 60-90 C
- pH: 9.0-11.5
- Good mixing

Peroxide Bleaching Process Conditions: Consistency

Two reasons

Higher concentration of bleaching chemical

Less liquid phase, less trash to interfere with bleaching



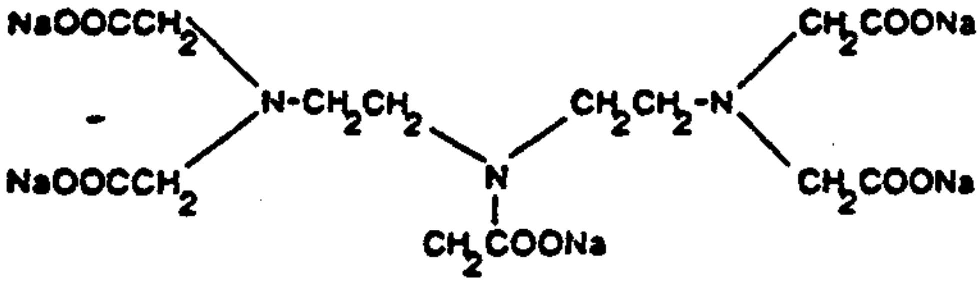
Peroxide Bleaching

- Heavy metal ions or enzymes (catalases) can decompose the peroxide
- H202 -> 2H0* -> -> H2O + ½O2
- Must stabilize the peroxide so it won't form HO*:
  - Chelating agents: form complexes with the heavy metal ions to deactivate them
  - Most common: EDTA and DTPA
- HO* does two bad things
  - Its generation decreases the available bleaching agent
  - Can damage the cellulose in the fibers

Peroxide Bleaching: Decomposition of Peroxide

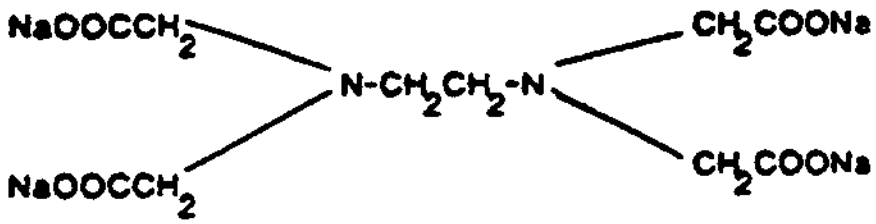
- Causes of hydrogen peroxide decomposition
  - Metal Ions
  - Catalase:
    - an enzyme produced by microorganisms and animal and vegetal cells to destroy peroxide which is toxic to the cell
    - Must thermally denature the catalase by use of a biocide
  - Too High pH
  - Too High temperature

Peroxide Bleaching: Chelating Agents



Na_5DTPA

Pentasodium salt of Diethylenetriaminepentaacetic acid



Na_4EDTA

Tetrasodium salt of Ethylenediaminetetraacetic acid

Peroxide Bleaching: Sodium Silicate

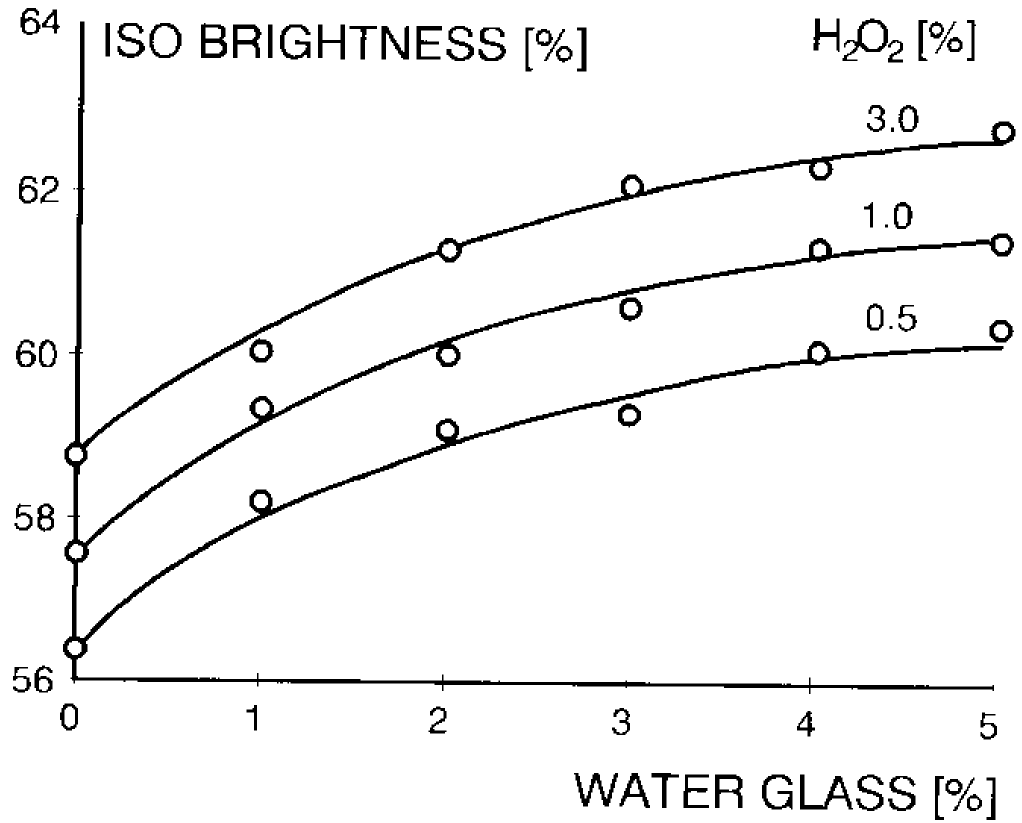
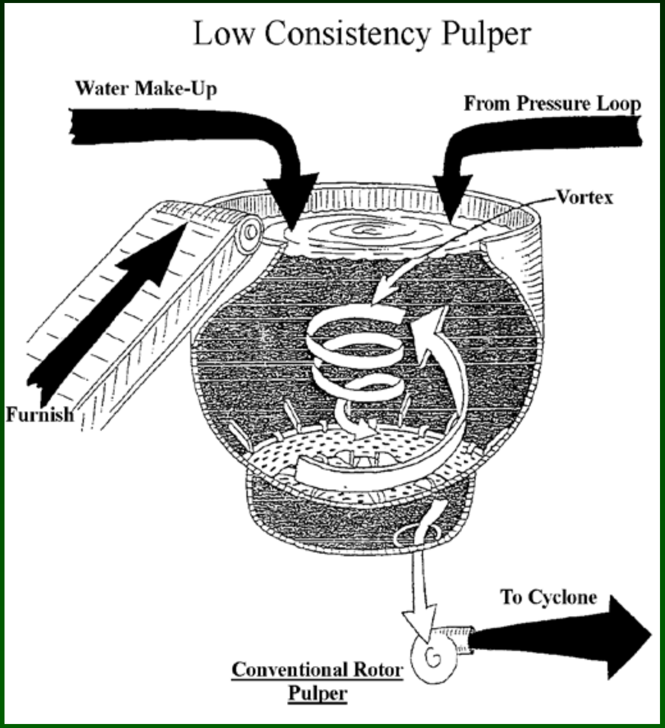


Figure 7. Effect of water glass on brightness[5].

- Heavy metal ions can decompose the peroxide
- H202 -> 2H0* -> -> H2O + ½O2
- Where HO* is a radical, not the bleaching chemical desired
- Must stabilize the peroxide so it won't form HO*:
  - **Sodium Silicate** or water glass, Na2SiO3
  - 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

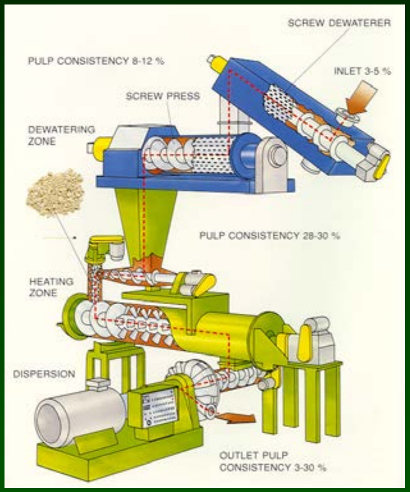
Peroxide Bleaching: Pulper

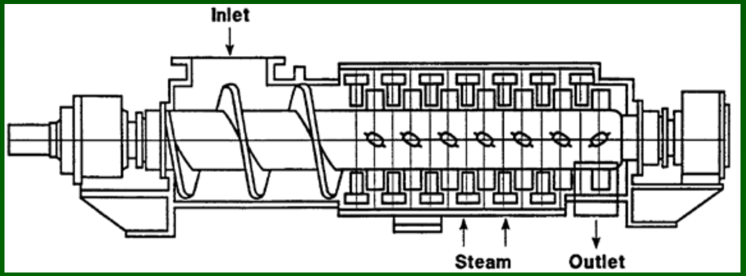
- Not used as a true bleaching chemical in the pulper
- Used to actually compensate for the darkening due to alkali in the pulper
- Used to decolorize chromophores in groundwood generated by alkaline pH – prevents alkali darkening
- Much of the contaminants in pulper render the bleaching action poor



Peroxide Bleaching: Disperser or Kneader

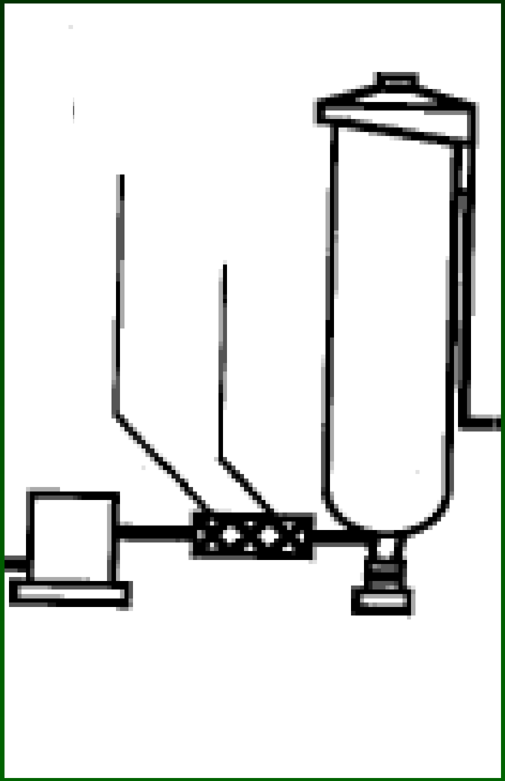
- Used to compensate for graying of pulp due to the dispersion of the ink
- Advantages
  - Newly exposed fiber surfaces
  - High consistency
  - Good mixing
  - High temperature
- Disadvantages:
  - Short residence time
  - Too high a temperature can degrade pulp
  - Must use chelating agent as silicate may build up on disks





Peroxide Bleaching: Tower

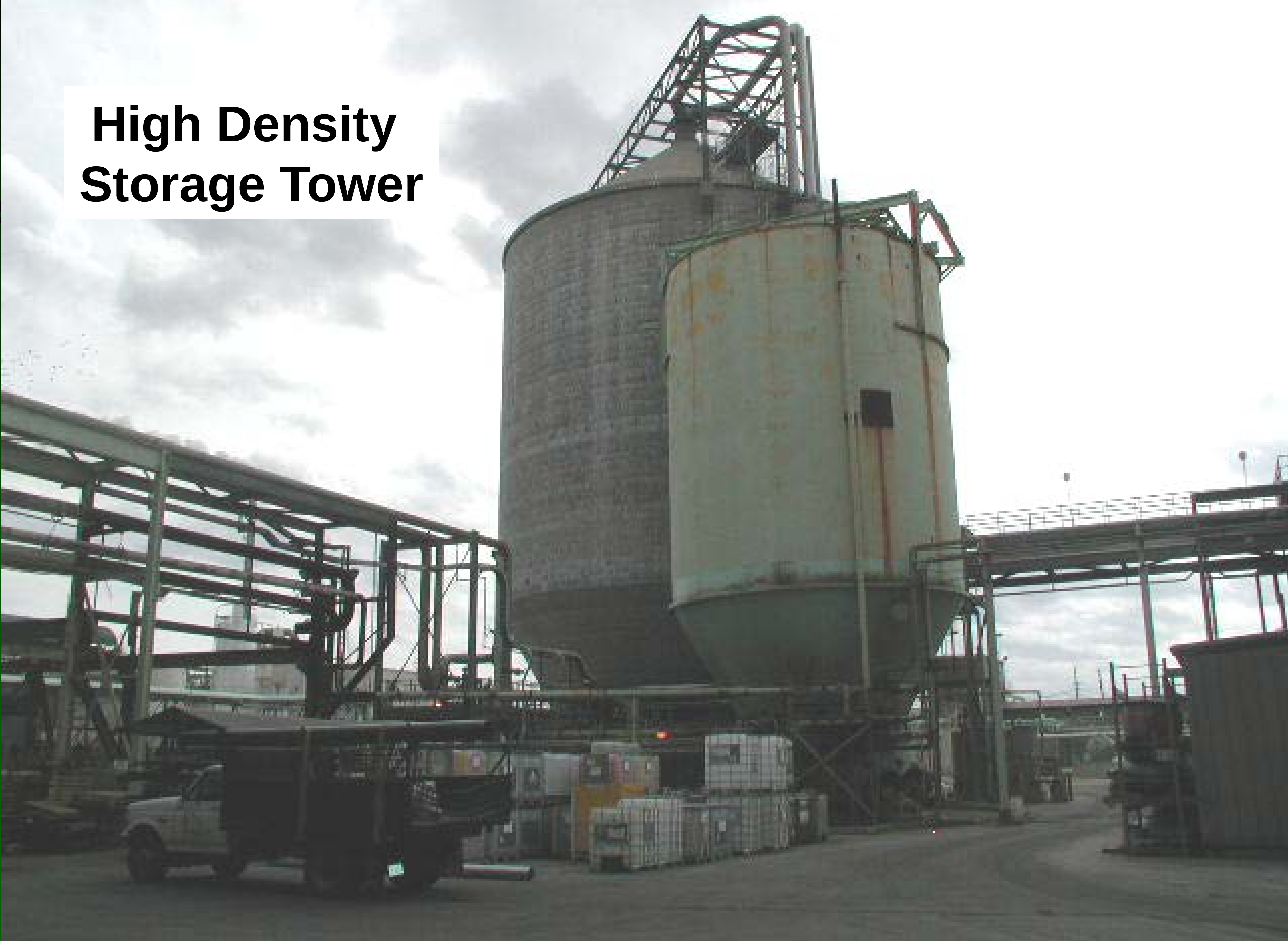
- More efficient than pulper
- Controlled reaction time
- Added to suction of medium consistency pump to upflow tower
- Caustic and silicate added to conveyor to medium consistency standpipe



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

High Density Storage Tower



Dithionite Bleaching (Y)

- Common reductive bleaching chemical that can be used for wood containing pulps
- Good at color stripping dyes
- Often called hydrohydrosulfite bleaching, which is the incorrect term
- $Na_2S_2O_4$ + H2O -> 2Na(+) + S_2O_4(-2)
- Sodium Hydrosulfite, $Na_2S_2O_4$
- Dithionate ion S_2O_4(-) is active
- Reductive reactions are reversible
- Oxygen decomposes the bleaching agents, need to keep air out
- 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 up-flow tower at 10-12 % consistency

- Application: 0.5-1.0% on pulp, 50-70 C,

 30-90 min,pH =5.5-6.5 (acidic), consistency 3-5%, must be oxygen free

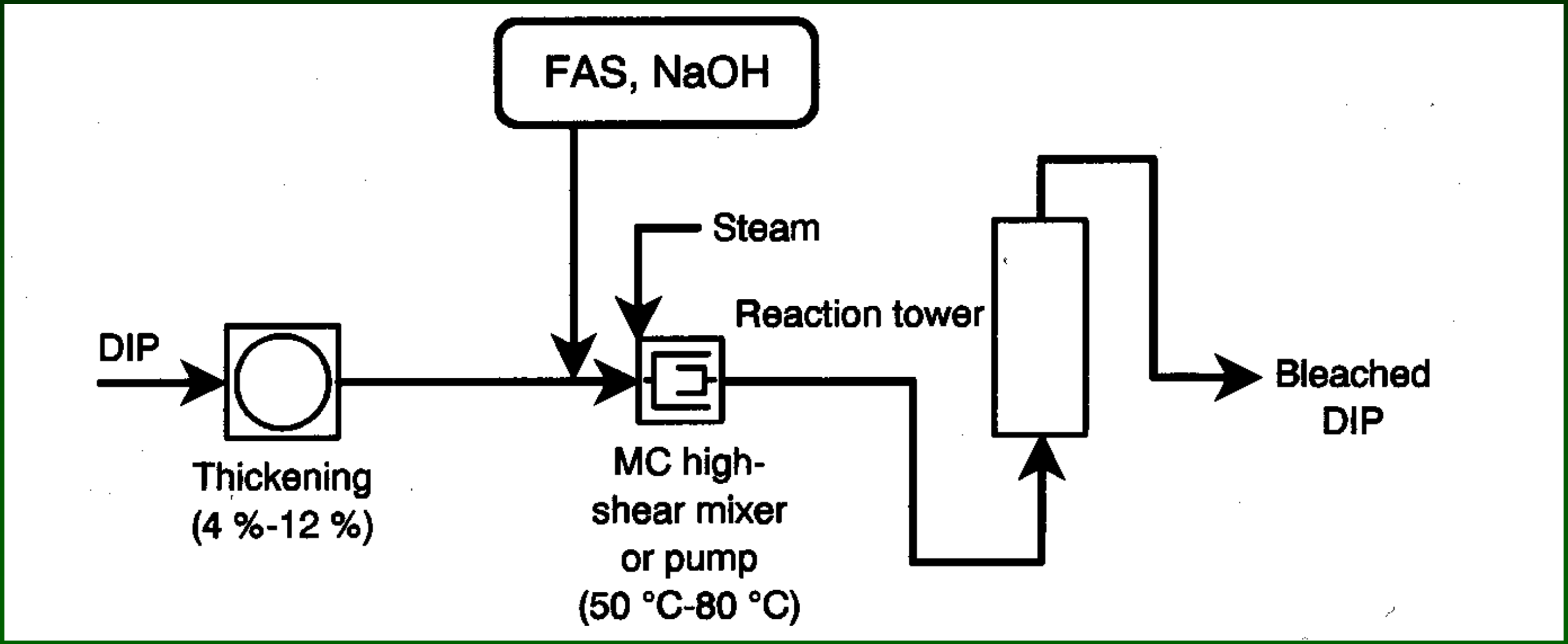
FAS Bleaching

- Formamidine Sulphinic Acid
- Low odor, crystalline powerful reducing agent
- Effective decolorizing for colored paper and carbonless paper
- Excellent dye stripping
- Decomposes with oxygen
- Used in place of and is stronger than dithionite
- Slightly soluble in water
- Must be used soon or else decomposes in water

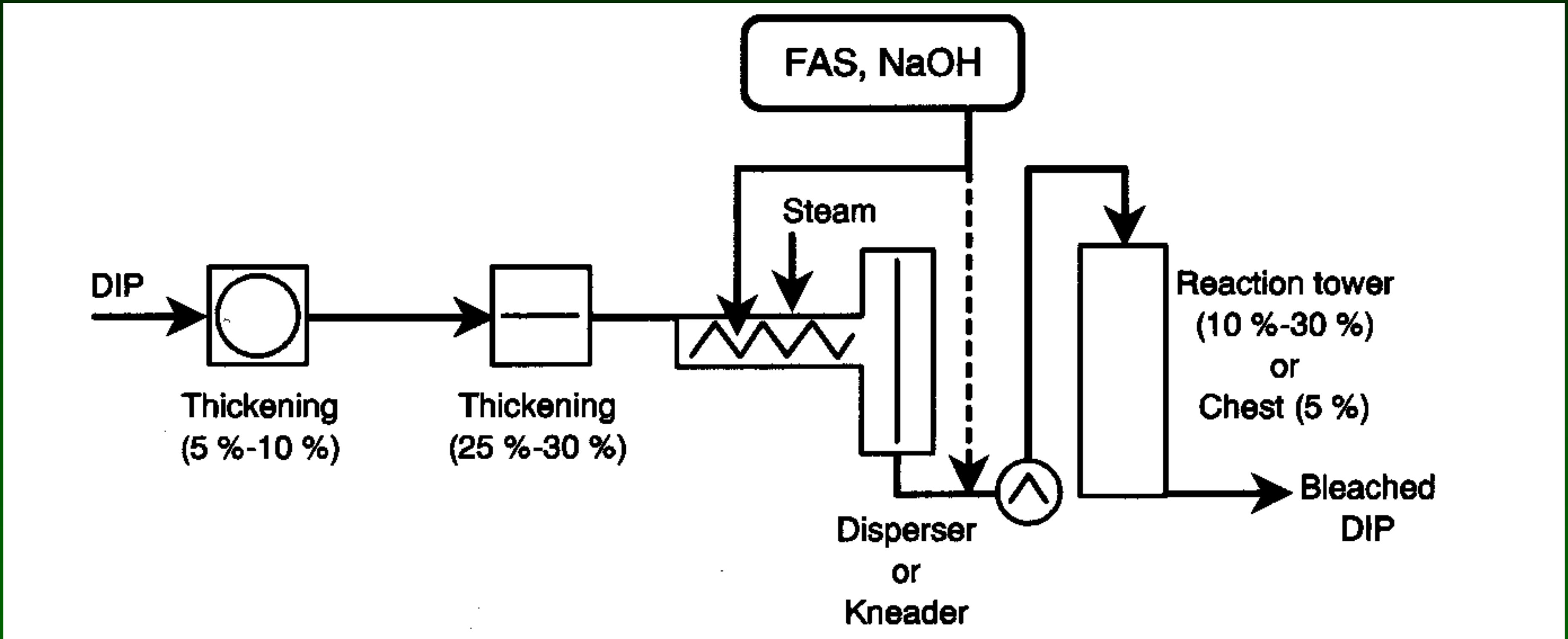
FAS Bleaching

- Application: 0.3-1%, 30-90 min, 3.5-12 %K, 40-65C, pH=8-11, must be oxygen free
- 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



FAS Disperser Bleaching



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-dithionite, Peroxide-FAS

Lecture:

Treatment of waste streams from paper recycling operations

Paper Recycling Mill Waste

- The generation of acceptable recycled pulp is accompanied with significant waste streams

DI Pulp Solid Waste Generation

Mill	Yield %	Sludge OD Tons/day
AFR	65	340
GLPF	70	220
SF	75	60
FUF	72	140

Most sludge is around 50% MC, so wet sludge flows are double this.

Progr. Paper Recycling 6(1), 1996.

Types of waste from recovered paper mills:

Stock Prep. Rejects	Sludges	Inciner. Waste	Other Waste
Ragger Tails Drum Rejects Screening Rejects Cleaner Rejects	Deinking Sludges Clarifier Sludges Biological Sludges	Ashes Cinders (slags) Flue Ashes Gypsum ….	Chemicals Used Oils Cleaners Wires Felts Hazard. Waste ….

Ref: Papermaking Science and Technology, Book 7, Recyled Fiber and Deinking, Tappi Press.

Amount of Rejects and Sludges for Production of Paper Grades

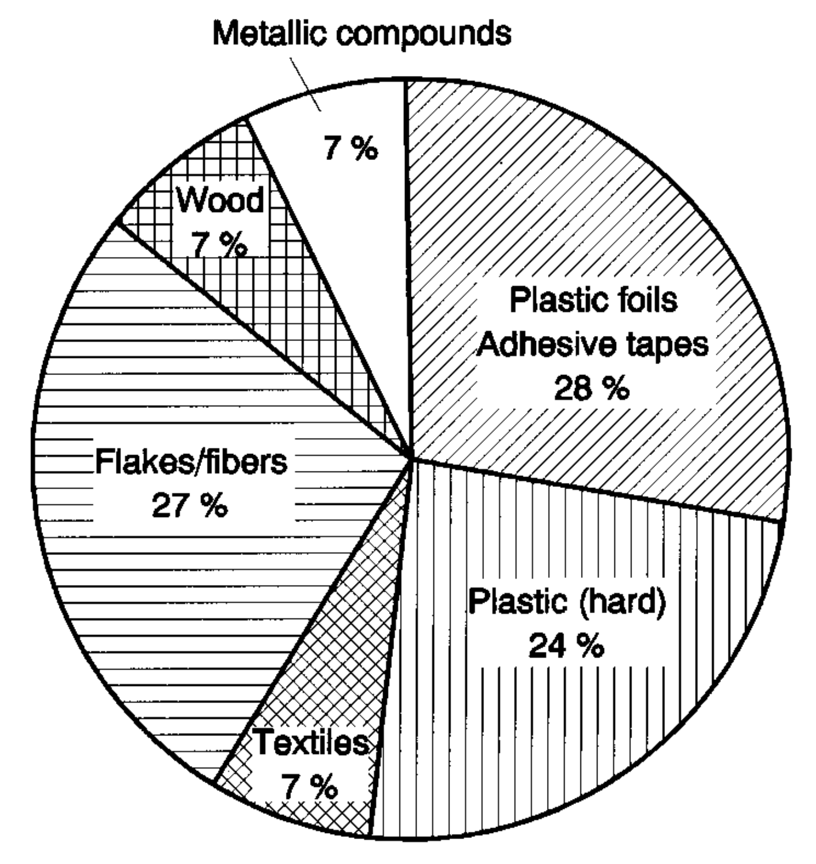
Produced paper	Recovered paper grade	Amount of total waste	Amount of waste [% by dry weight]			
			Rejects		Sludges	
		[% by dry weight]	Heavy-weight & coarse	Light-weight & fine	Flotation deinking	White water clarification
Graphic paper	News, magazines	15–20	1–2	3–5	8–13	2–5
	Superior grades	10–25	< 1	≤ 3	7–16	1–5
Hygienic paper	Files, office paper, ordinary, medium grades	28–40	1–2	3–5	8–13	15–25
Market DIP	Office paper	32–40	< 1	4–5	12–15	15–25
Liner, fluting	Sorted mixed recov. paper, supermarket waste	4–9	1–2	3–6	–	0–(1)
Board	Sorted mixed recov. paper, supermarket waste	4–9	1–2	3–6	–	0–(1)

Amount of Rejects and Sludges for Production of Paper Grades

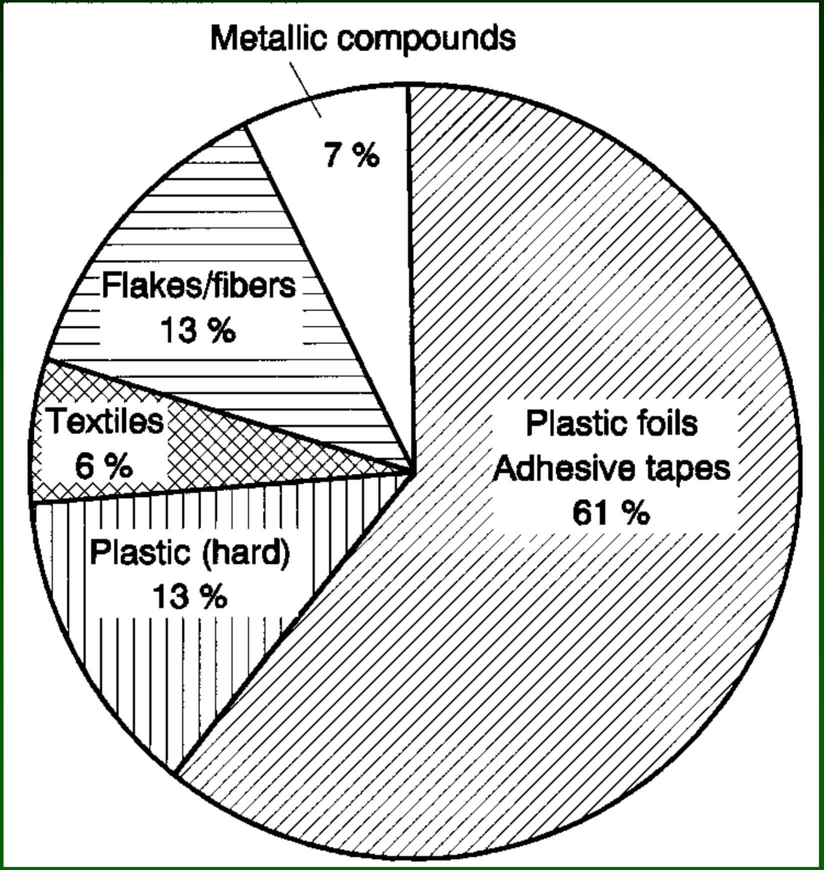
Table 2. Solid waste from different stages in recovered paper processing[2].

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

Composition of Reject Samples

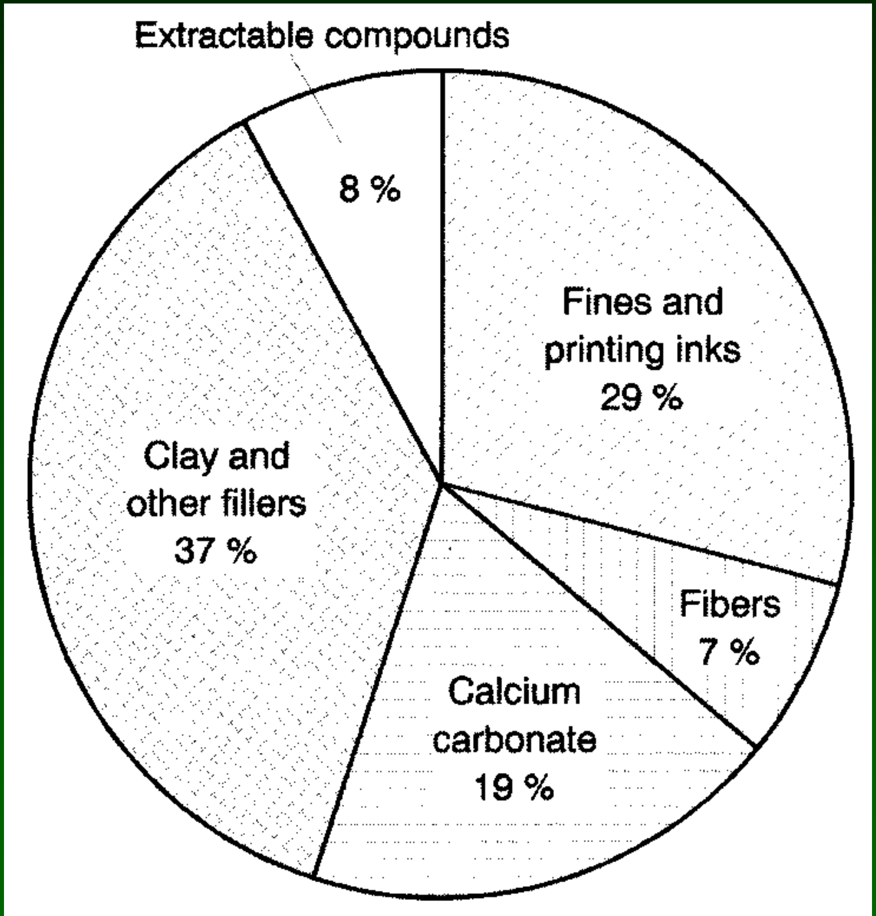


Newsprint

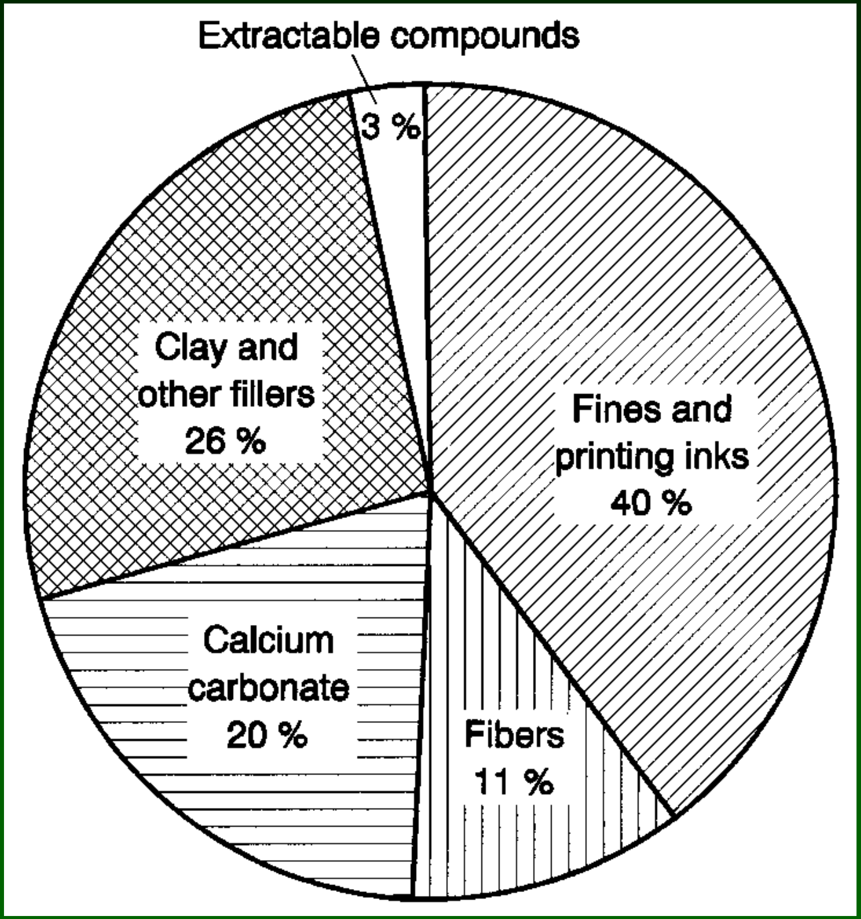


Packaging Paper

Composition of De-inking Sludge Samples



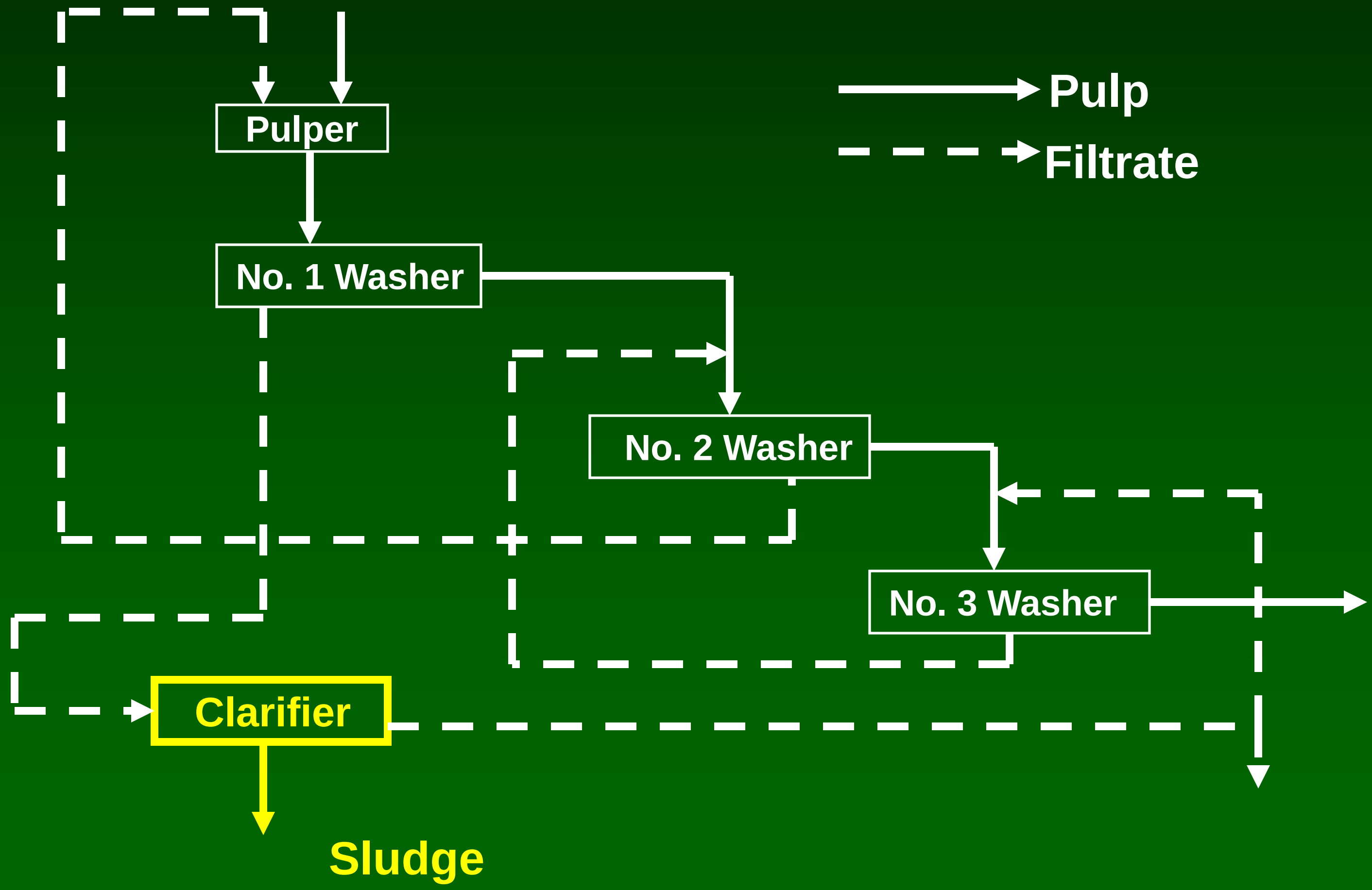
Printing Paper (Flotn)



Tissue (Washing)

De-inking Sludges

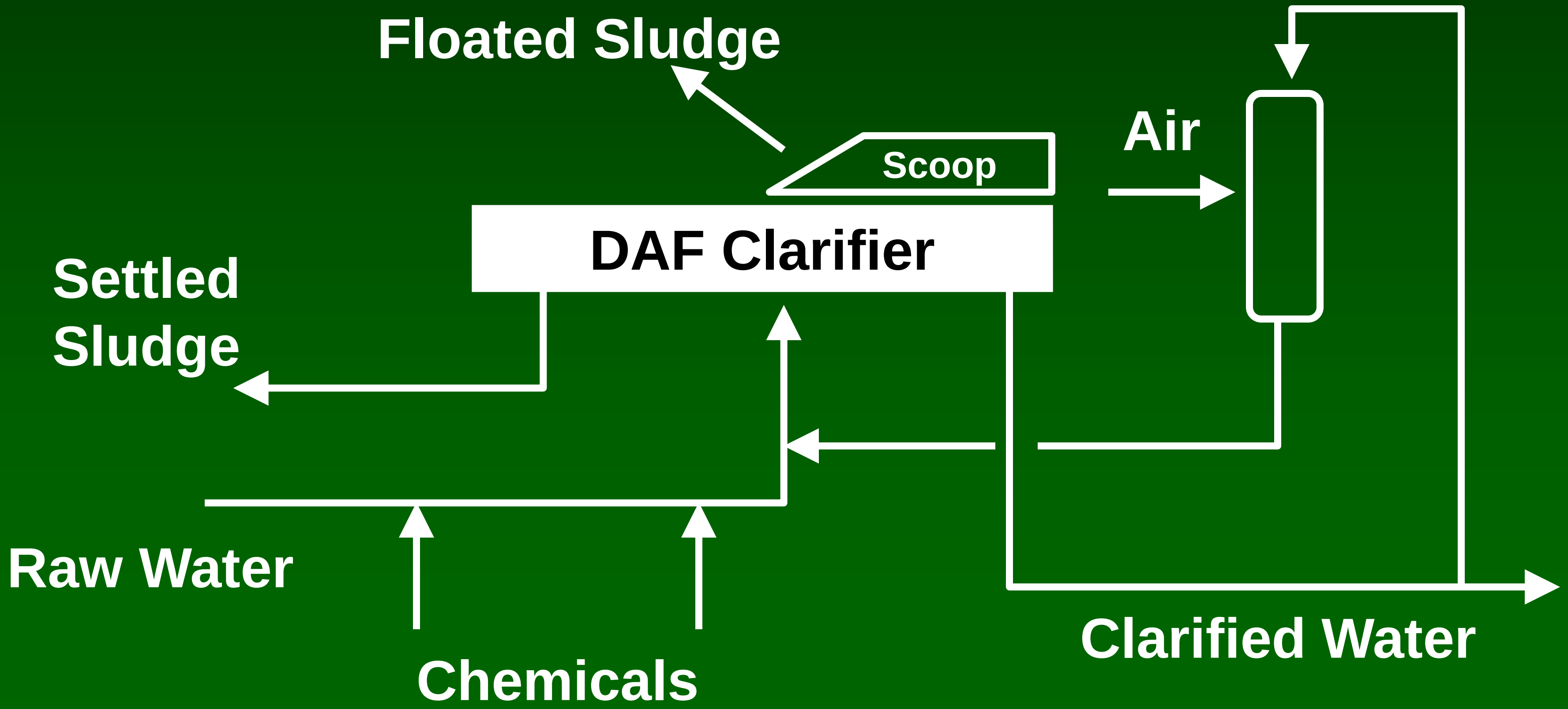
Treatment of Wastewaters



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




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

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

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

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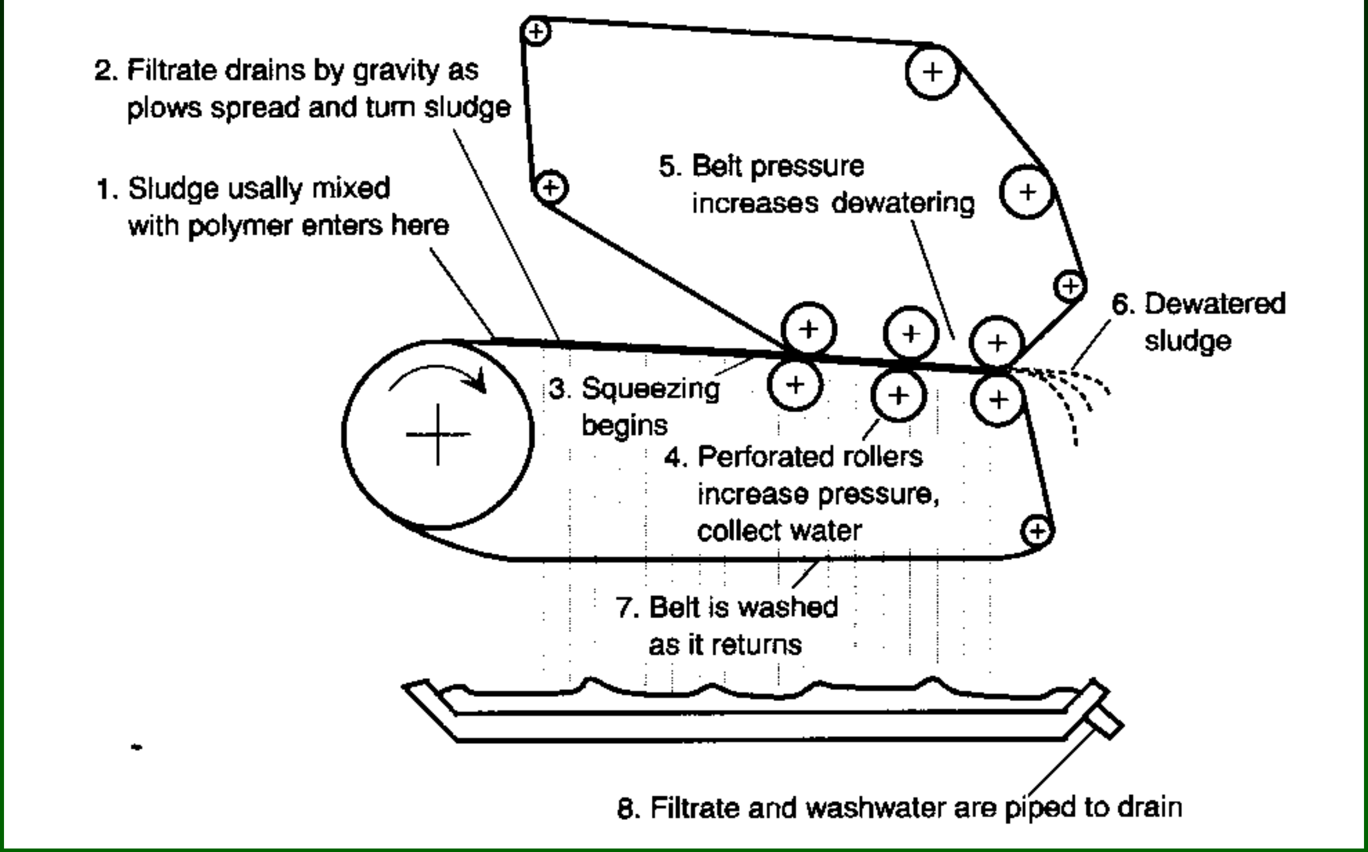
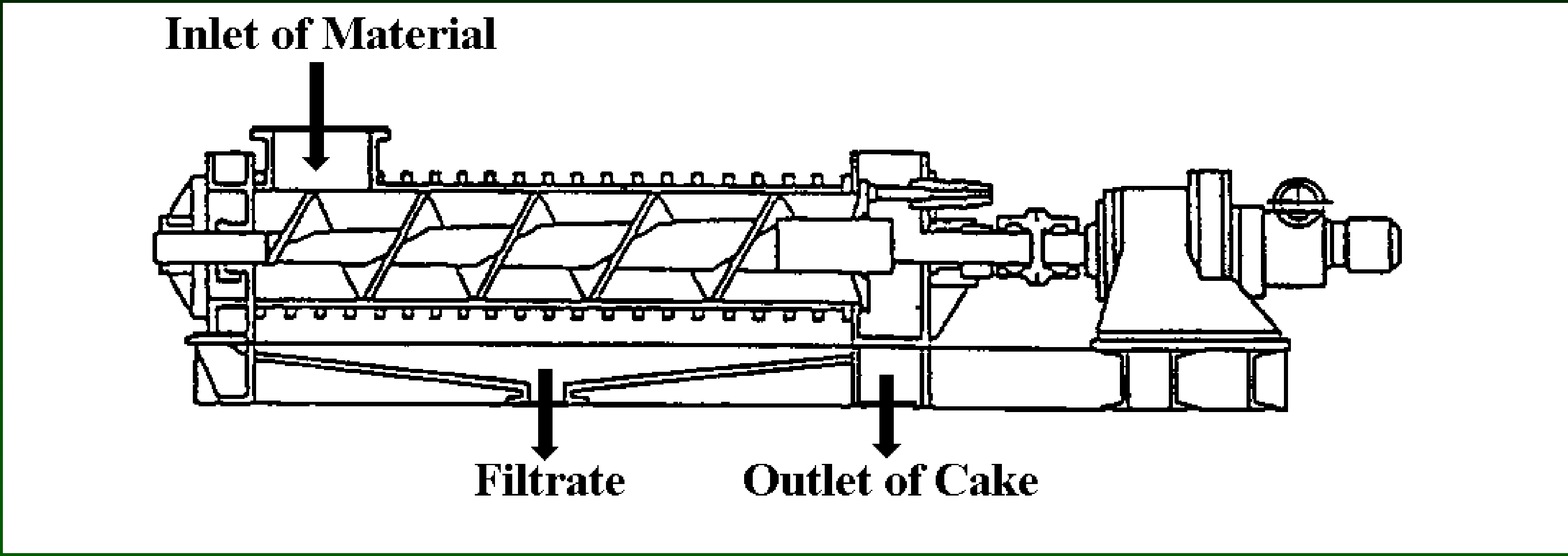
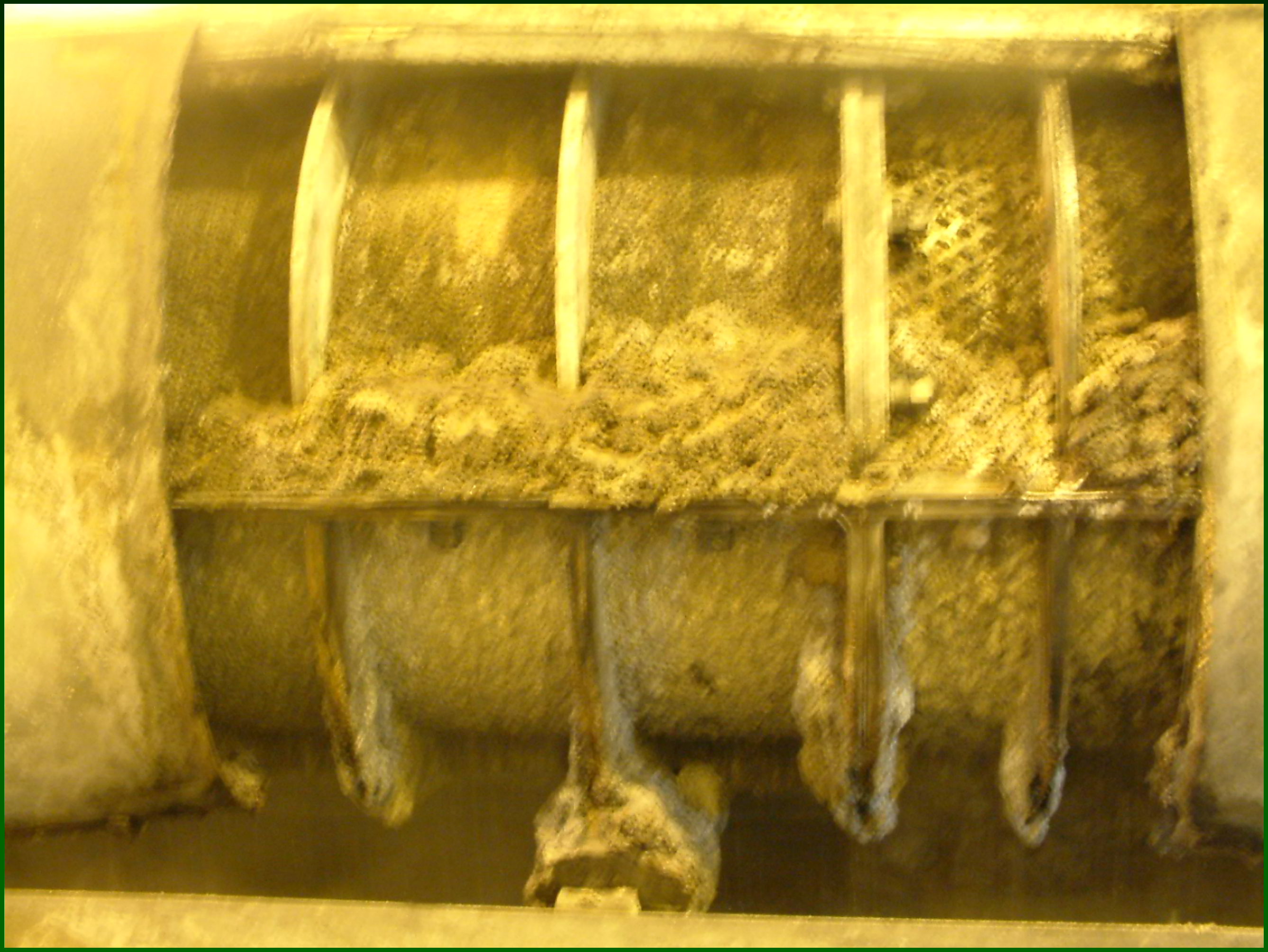


Dewatering of Sludges



- Sludges use 2 step process:
  - Gravity table or drum or disk thickener
  - Followed by belt filter press or screw press

Screw Press



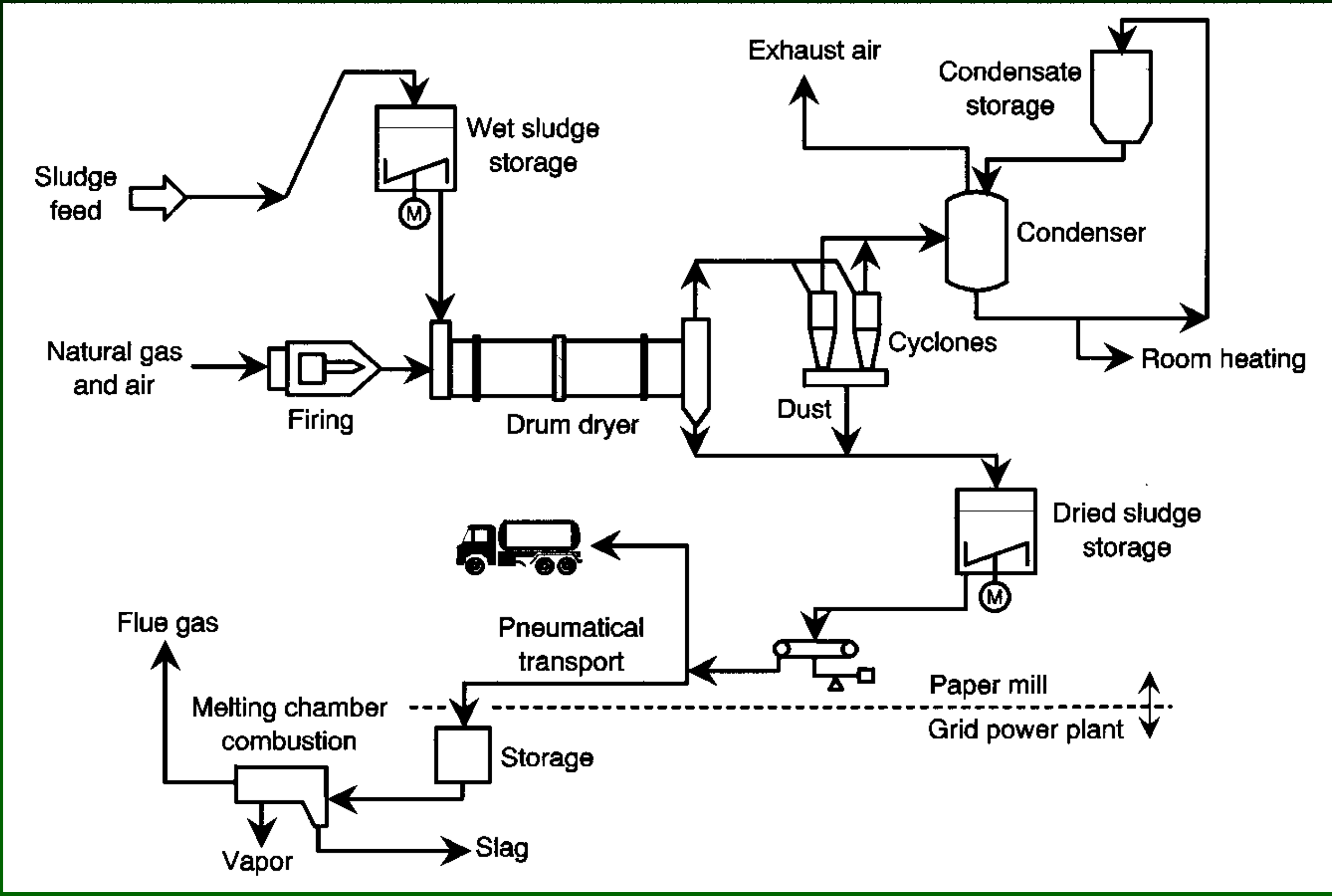
De-watered sludge dumped into truck

Sludge Final Fates:

- Final disposition
  - landfill
  - incineration
  - composting
  - Cement, brick, concrete, mortar and lime brick, road construction
  - others

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



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

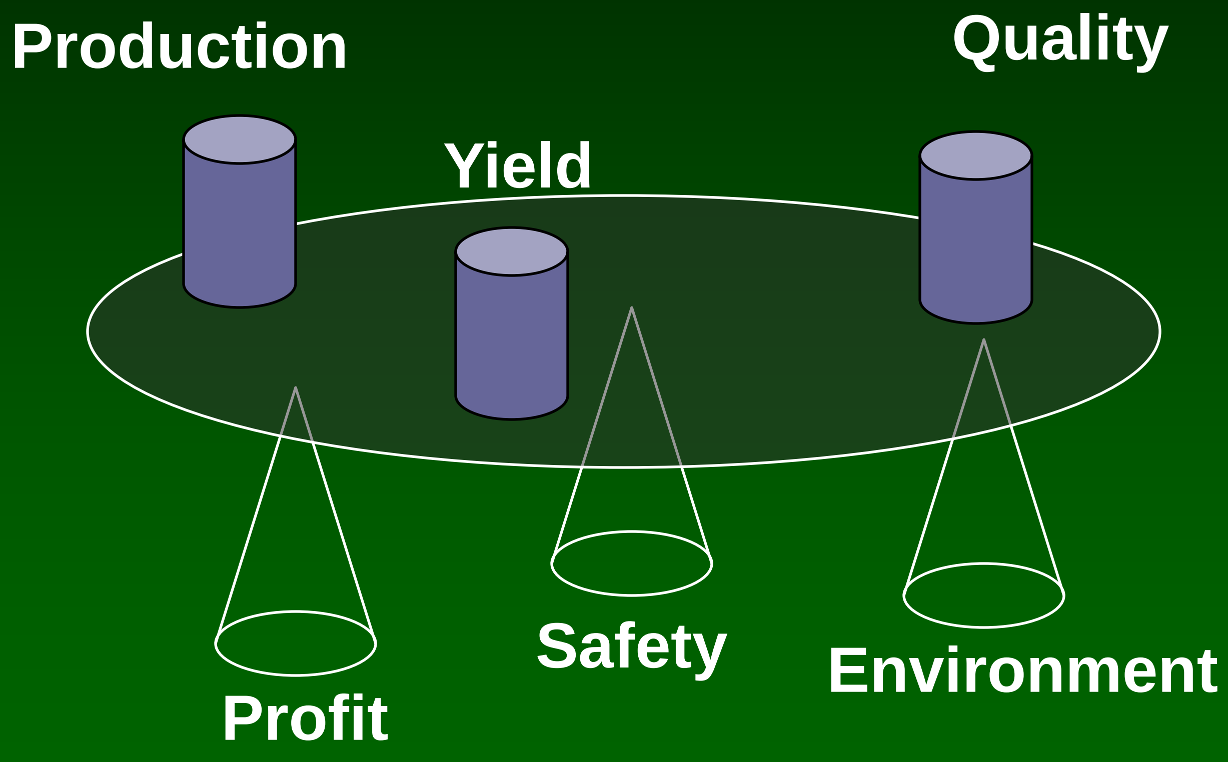
Lecture:

Paper recycling system design strategies

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

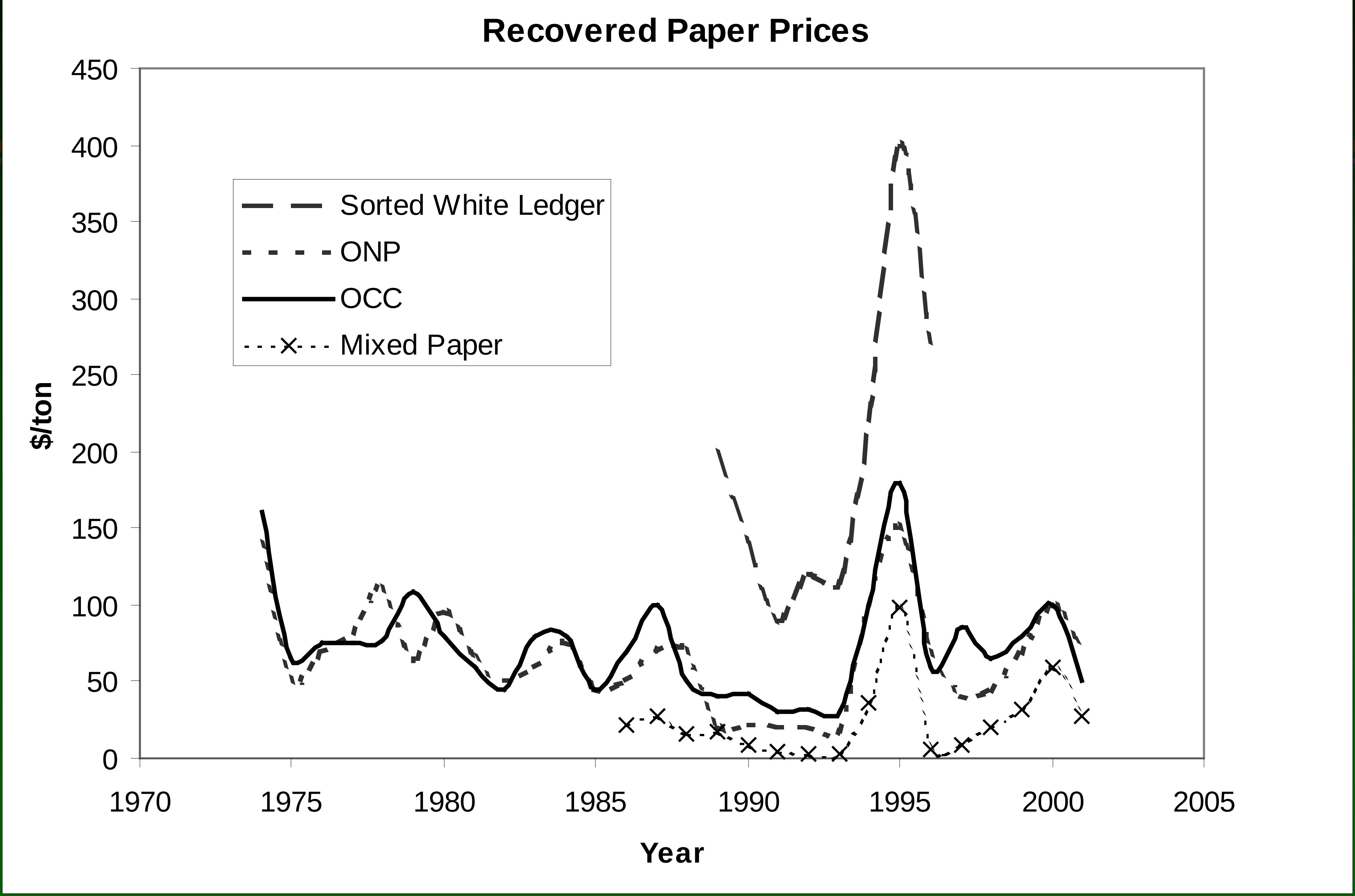


Key Parameters for Cleanliness

	White System	Brown System
Product Quality Parameters	Optical Properties Brightness Dirt Specks Color Stickies Ash Content	Stickies Flakes Sand Fines Ash Content
Process Water Management	Susp. and Colloidal solids COD Cationic Demand Conductivity pH	Susp. and Colloidal solids COD Cationic Demand Conductivity Biological Activity

Amount of Rejects and Sludges for Production of Paper Grades

Produced paper	Recovered paper grade	Amount of total waste [% by dry weight]	Amount of waste [% by dry weight] Rejects: Heavy-weight & coarse	Rejects: Light-weight & fine	Sludges: Flotation deinking	Sludges: White water clarification
Graphic paper	News, magazines	15–20	1–2	3–5	8–13	2–5
	Superior grades	10–25	< 1	≤ 3	7–16	1–5
Hygienic paper	Files, office paper, ordinary, medium grades	28–40	1–2	3–5	8–13	15–25
Market DIP	Office paper	32–40	< 1	4–5	12–15	15–25
Liner, fluting	Sorted mixed recov. paper, supermarket waste	4–9	1–2	3–6	–	0–(1)
Board	Sorted mixed recov. paper, supermarket waste	4–9	1–2	3–6	–	0–(1)


Recovered Paper Prices
450
400
350
300
250
200
150
100
50
0
$/ton
Sorted White Ledger
ONP
OCC
Mixed Paper
1970
1975
1980
1985
1990
1995
2000
2005
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 and continue to put pressure on the recycling industry

Other System Design Considerations

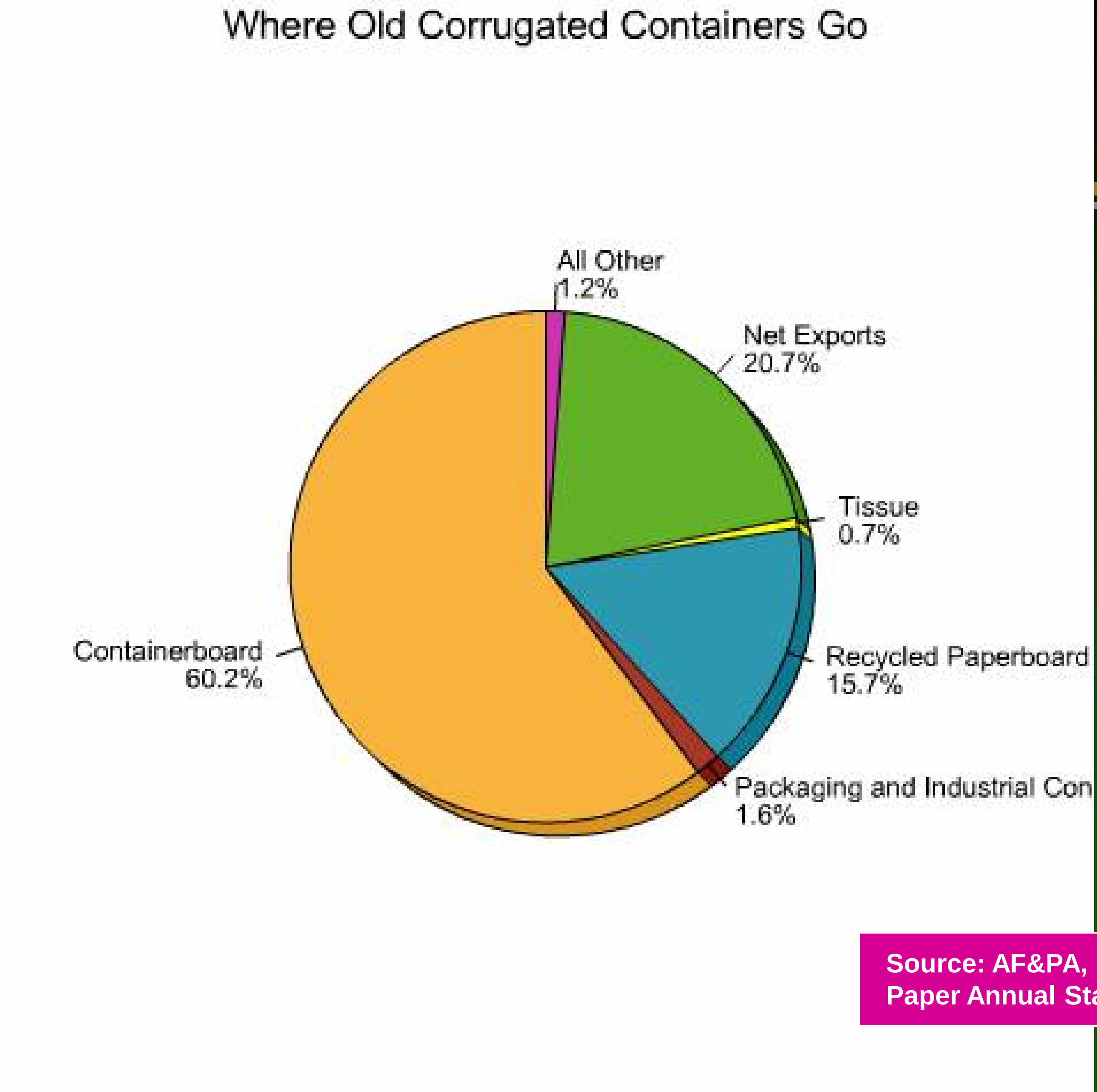
- Raw Material
  - availability
  - cost
  - suitability for process
  - Usable fiber content
- Product Desired
  - optical properties
  - strength properties
- Environmental Constraints
  - Solid waste
  - Water effluents
  - Gas effluents
- Space Requirements
- Capital Costs
- Operating Costs

General Process Strategies

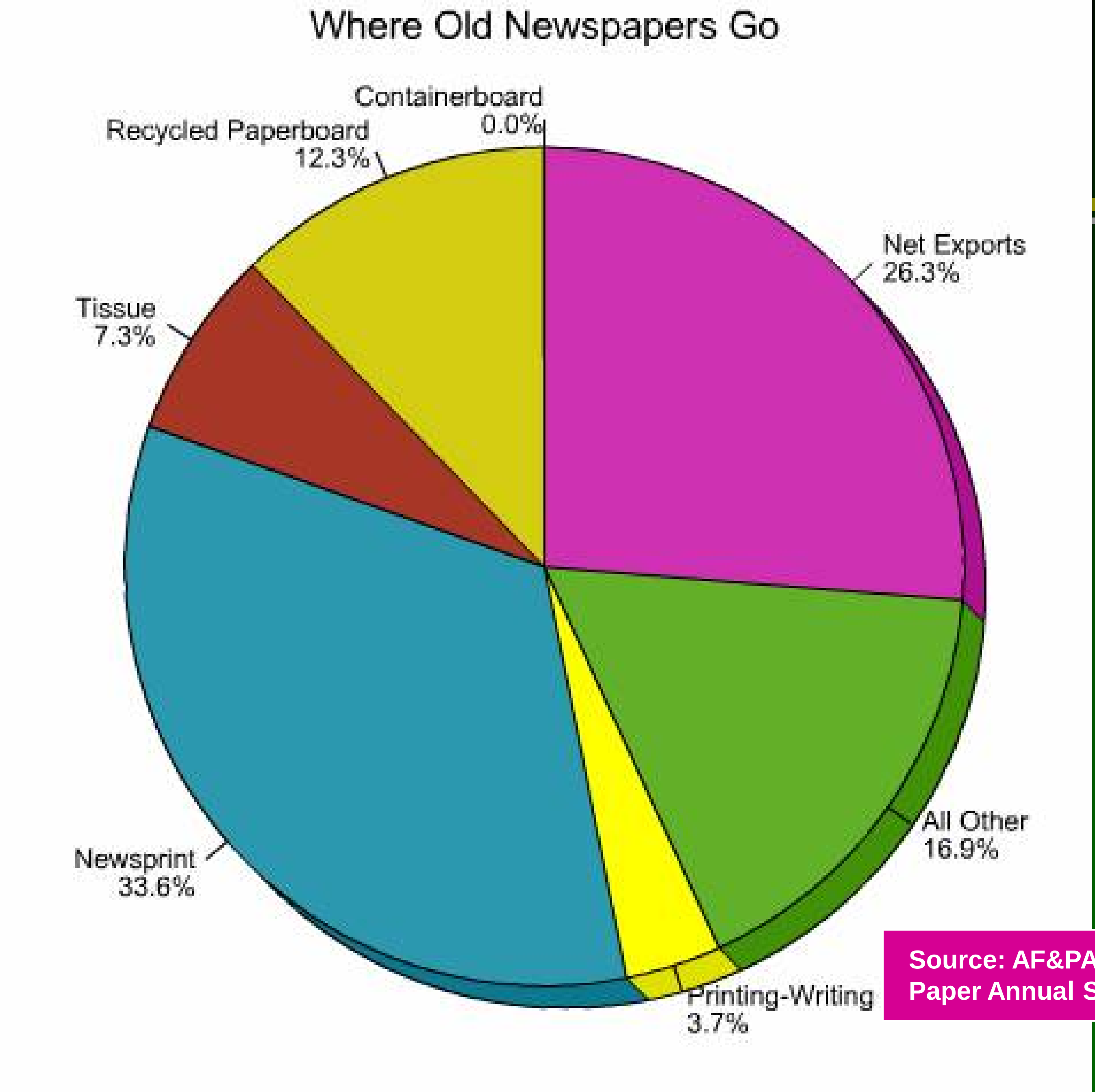
- The following concepts or strategies are often implemented in system design :
  - Keep out unremovable contaminants from the process
  - Ensure that contaminants are well separated from the fibers
  - Remove contaminants early in the process
  - Keep contaminants large to enhance removal
  - Repeat inefficient unit operations
  - Save fiber by cascading unit operations
  - Save water by using counter current operations and by clarifying the water effectively
  - Avoid excessive changes in consistency

Major Recycling Systems

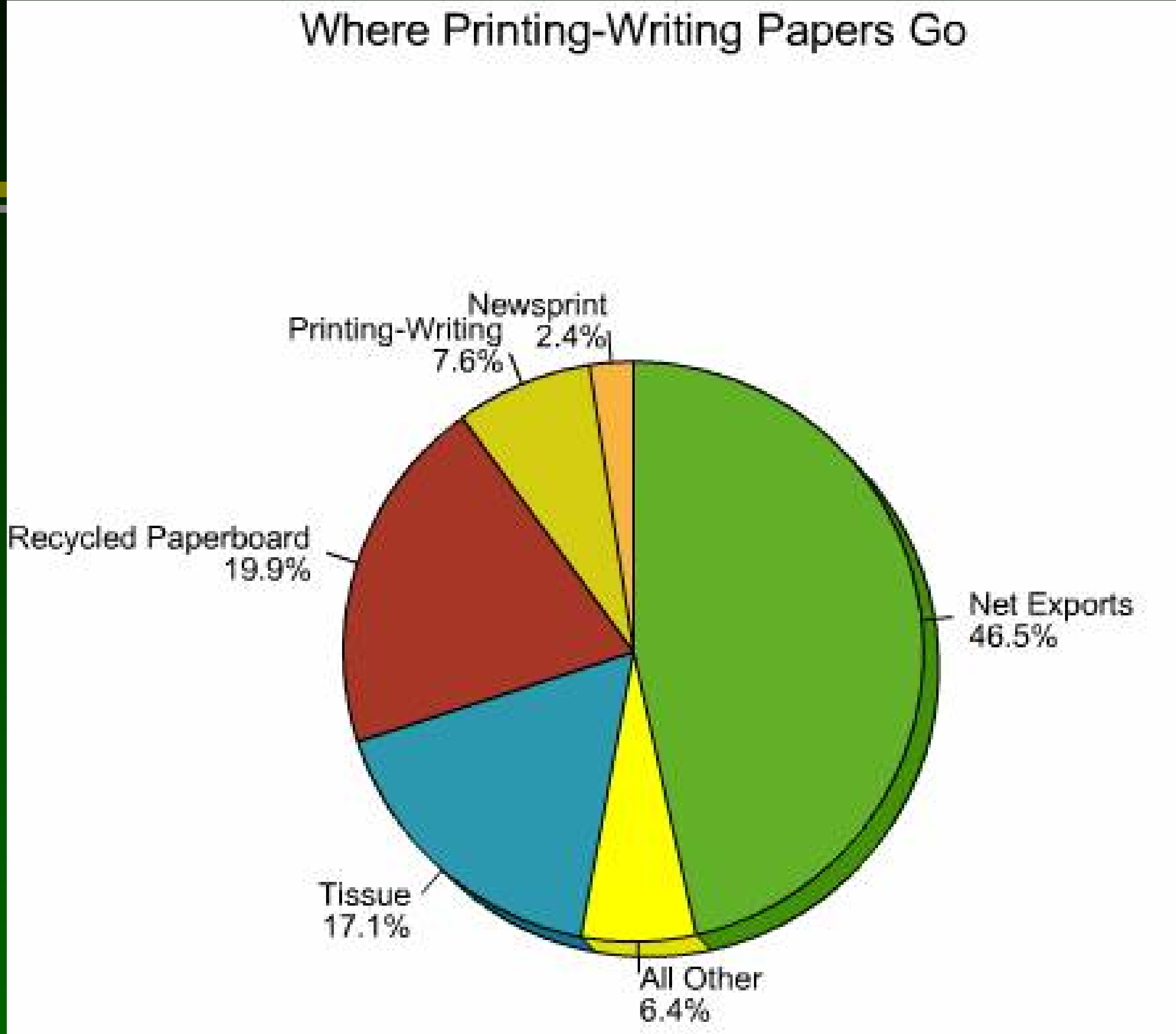
- Can be categorized by the products they produce
  - Packaging Materials
    - Typically, OCC materials are recycled back into linerboard, medium, tube stock, and solid board products
    - Mixed waste can be used in lower quality applications
  - Newsprint
    - Old newspapers and magazines are converted 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



Source: AF&PA, 2006 Recovered Paper Annual Statistics



Source: AF&PA, 2006 Recovered Paper Annual Statistics



Source: AF&PA, 2006 Recovered Paper Annual Statistics

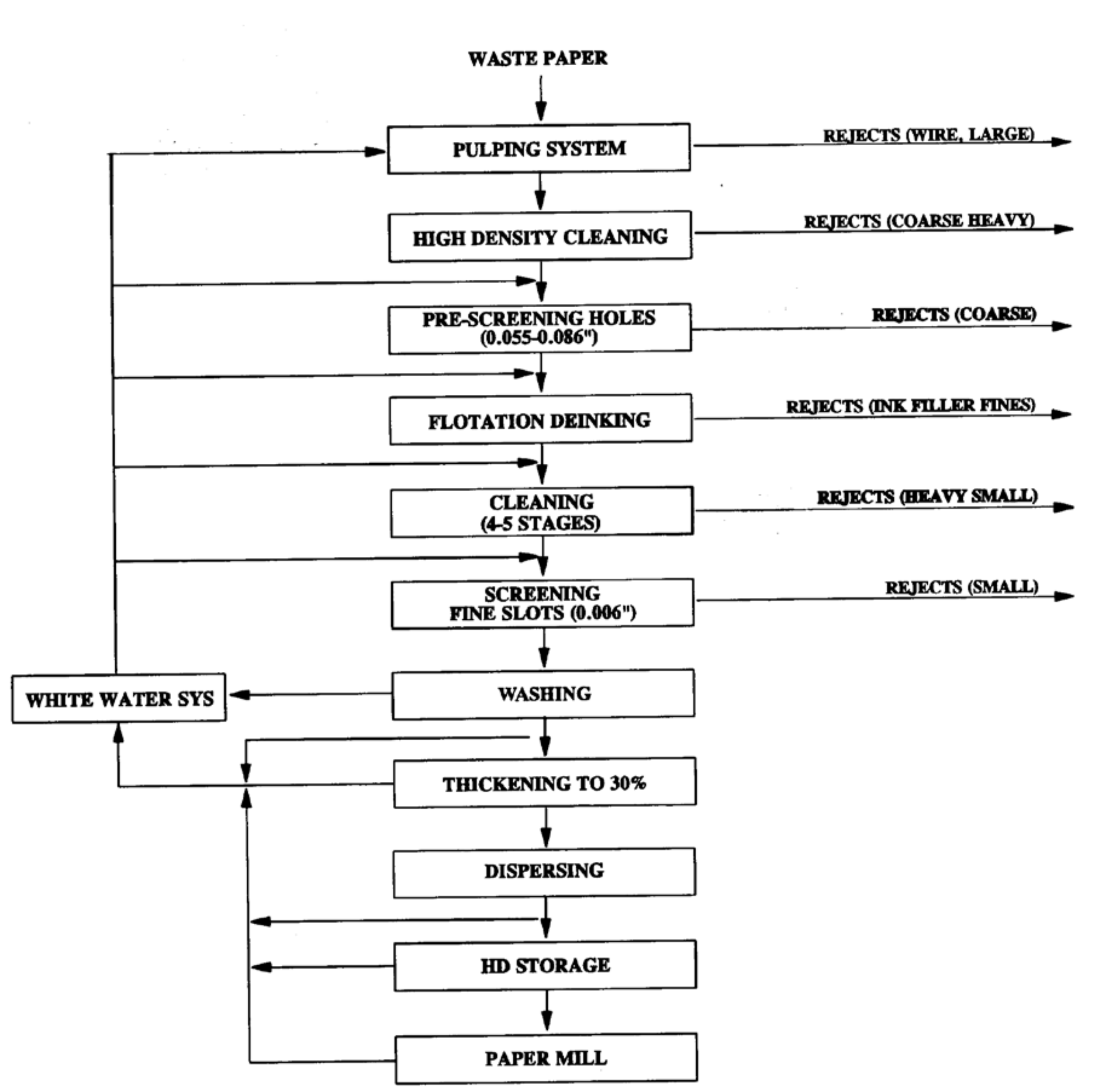
Lecture:

Paper recycling systems

Production of Newsprint

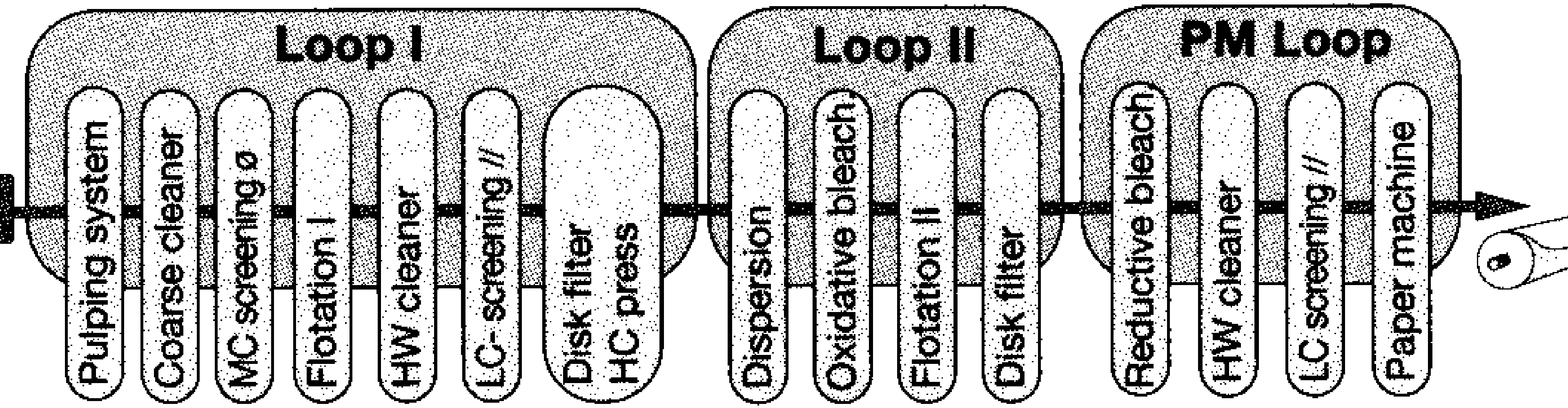
ONP-OMG Recycling

- Used to produce recycled newsprint
- May have batch, continuos 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



Ref: Secondary Fiber Recycling, Tappi, 2003.

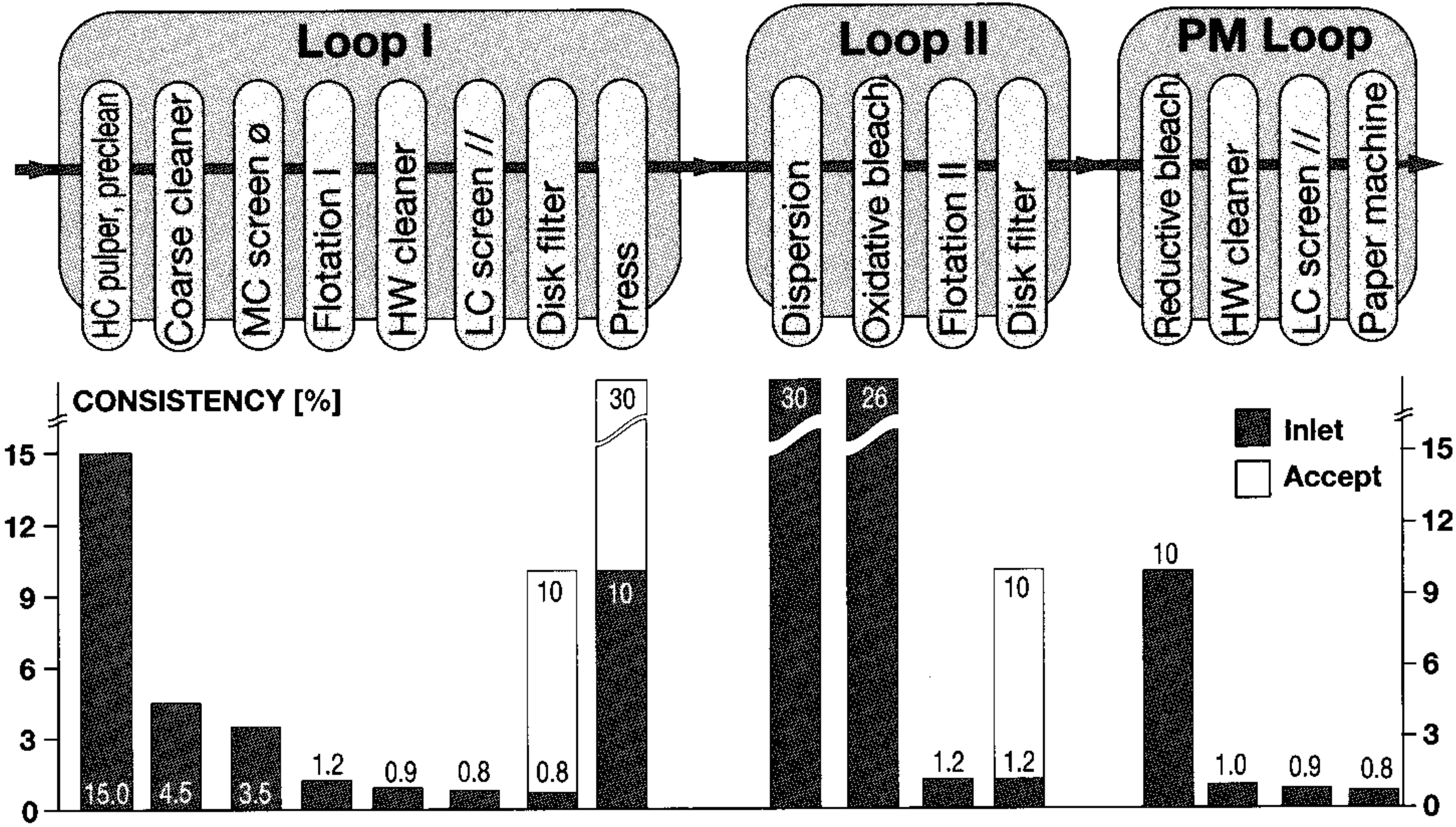
Newsprint Recycle Process



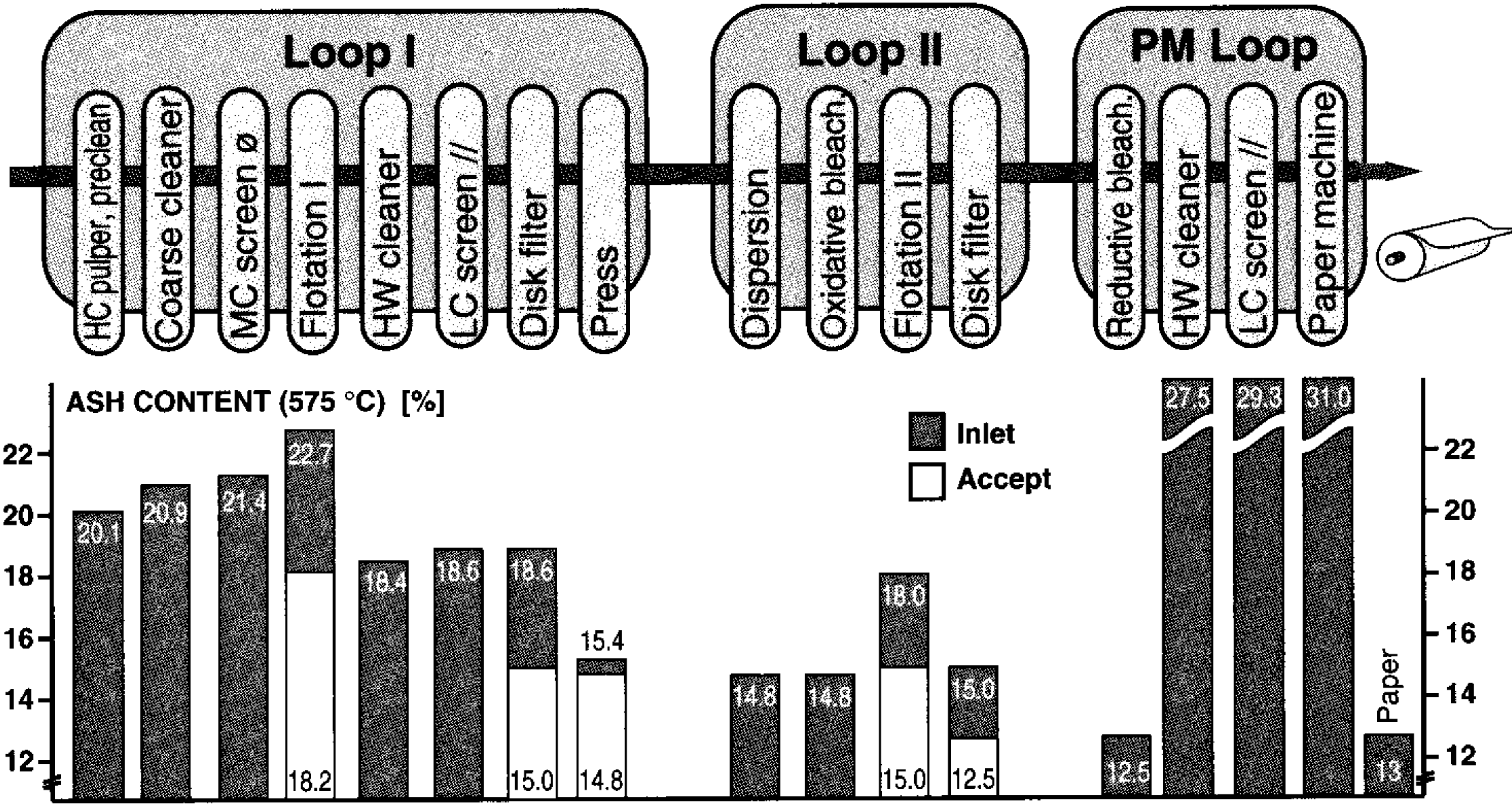
Product:	Newsprint, and improved grades, approx. 40-90 g/m^2
Furnish:	News, magazines
Yield:	Approx. 83 %
Effluent:	Approx. 8 L/kg
Ash:	Feed approx. 22 %, finished paper approx. 13 %
Brightness:	Finished paper approx. 63-66% ISO

Ref: Papermaking Science and Technology, Book 7, Recyled Fiber and Deinking, Tappi Press.

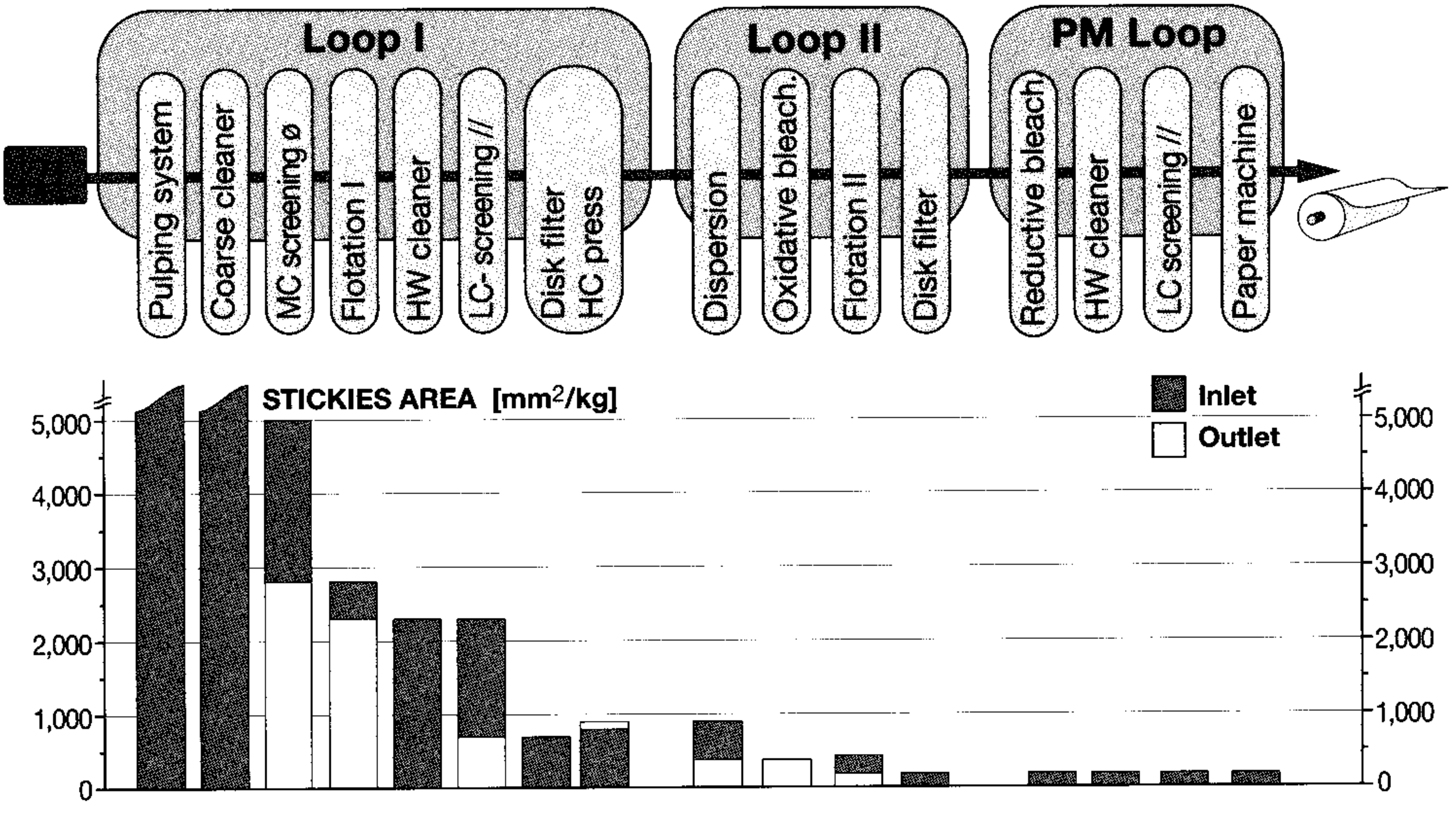
Newsprint Recycle Process: Consistency



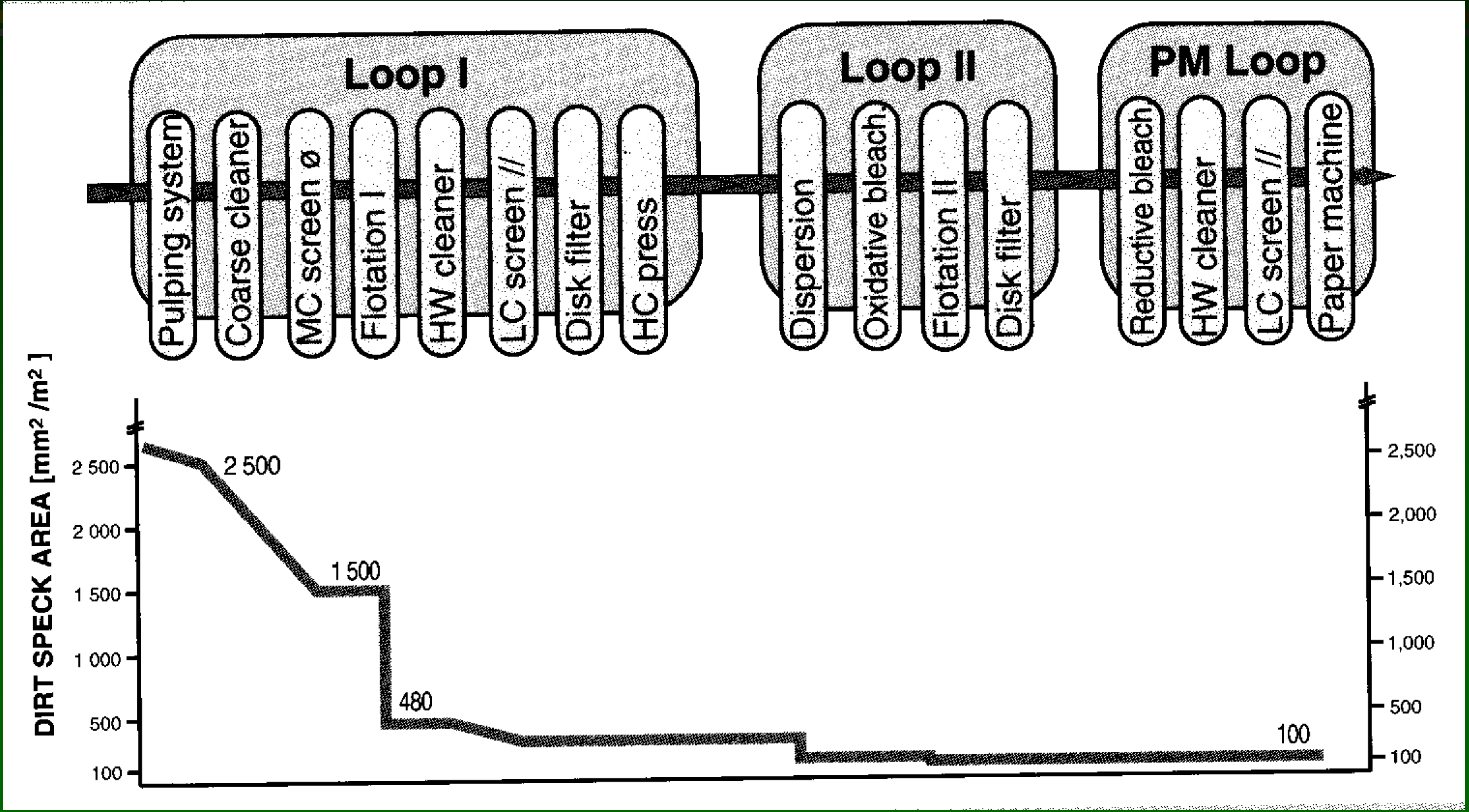
Newsprint Recycle Process: Ash



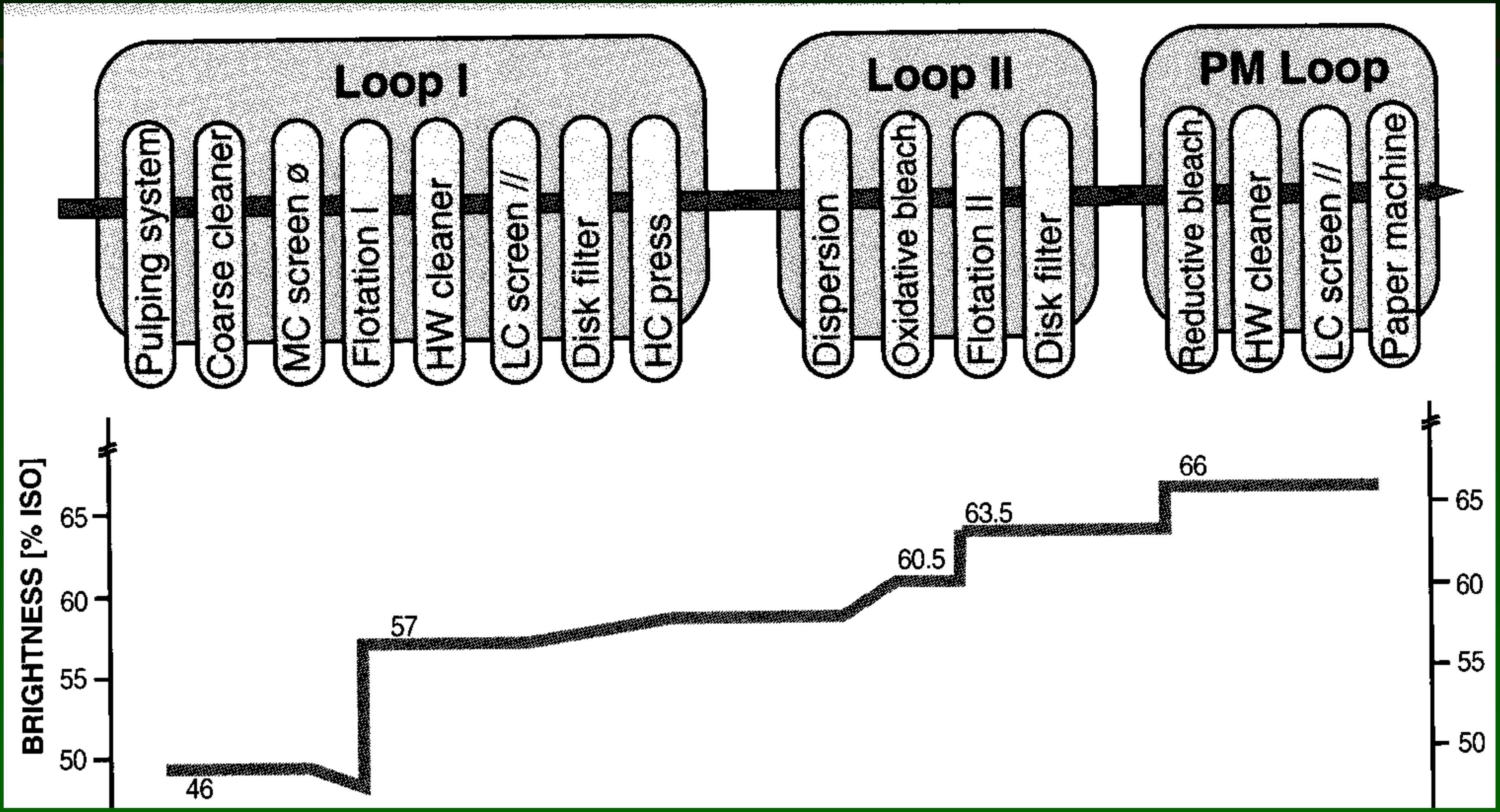
Newsprint Recycle Process: Stickies



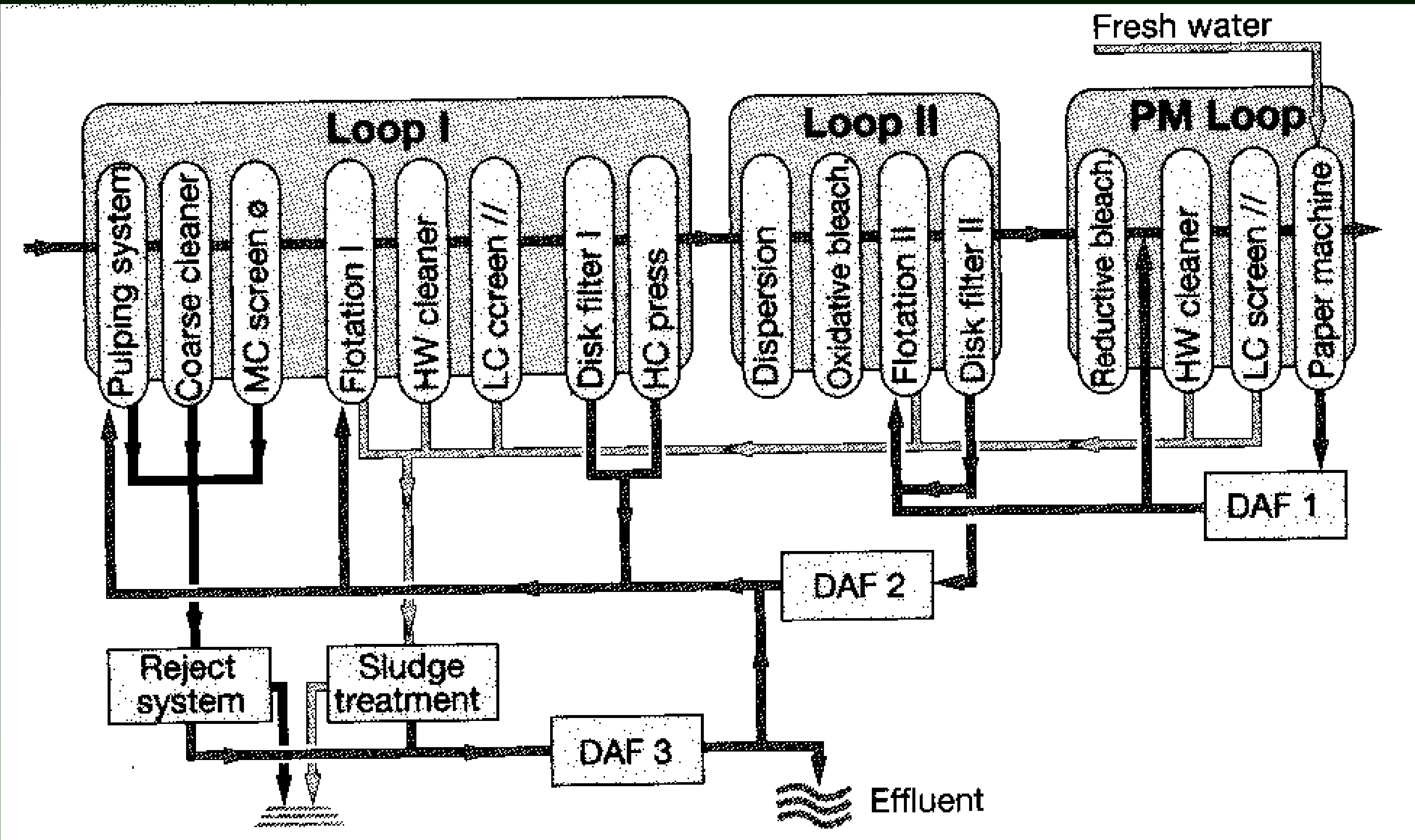
Newsprint Recycle Process: Dirt Speck Area



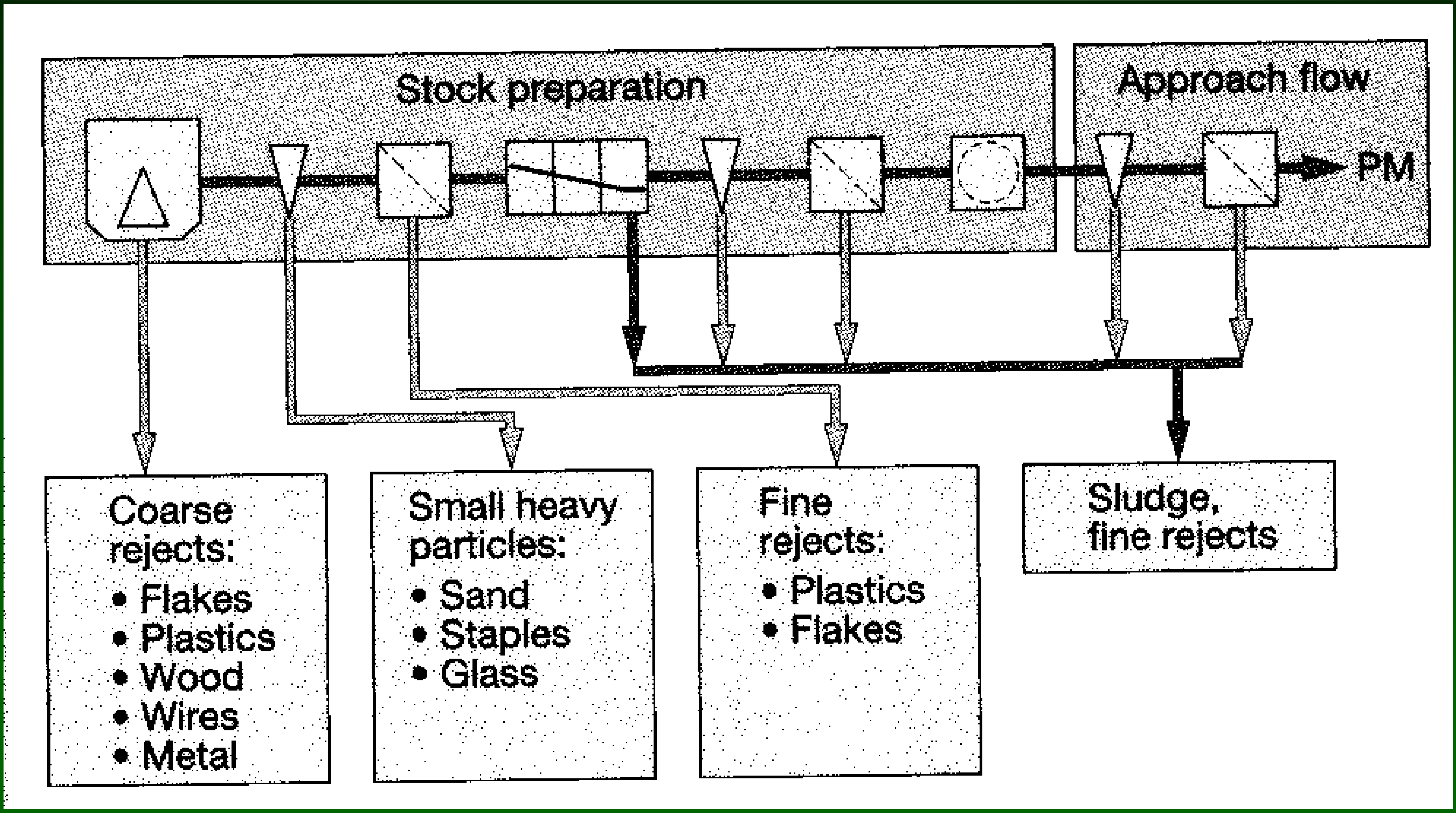
Newsprint Recycle Process: Brightness



Newsprint Recycle Process: Rejects, Sludge Water Systems



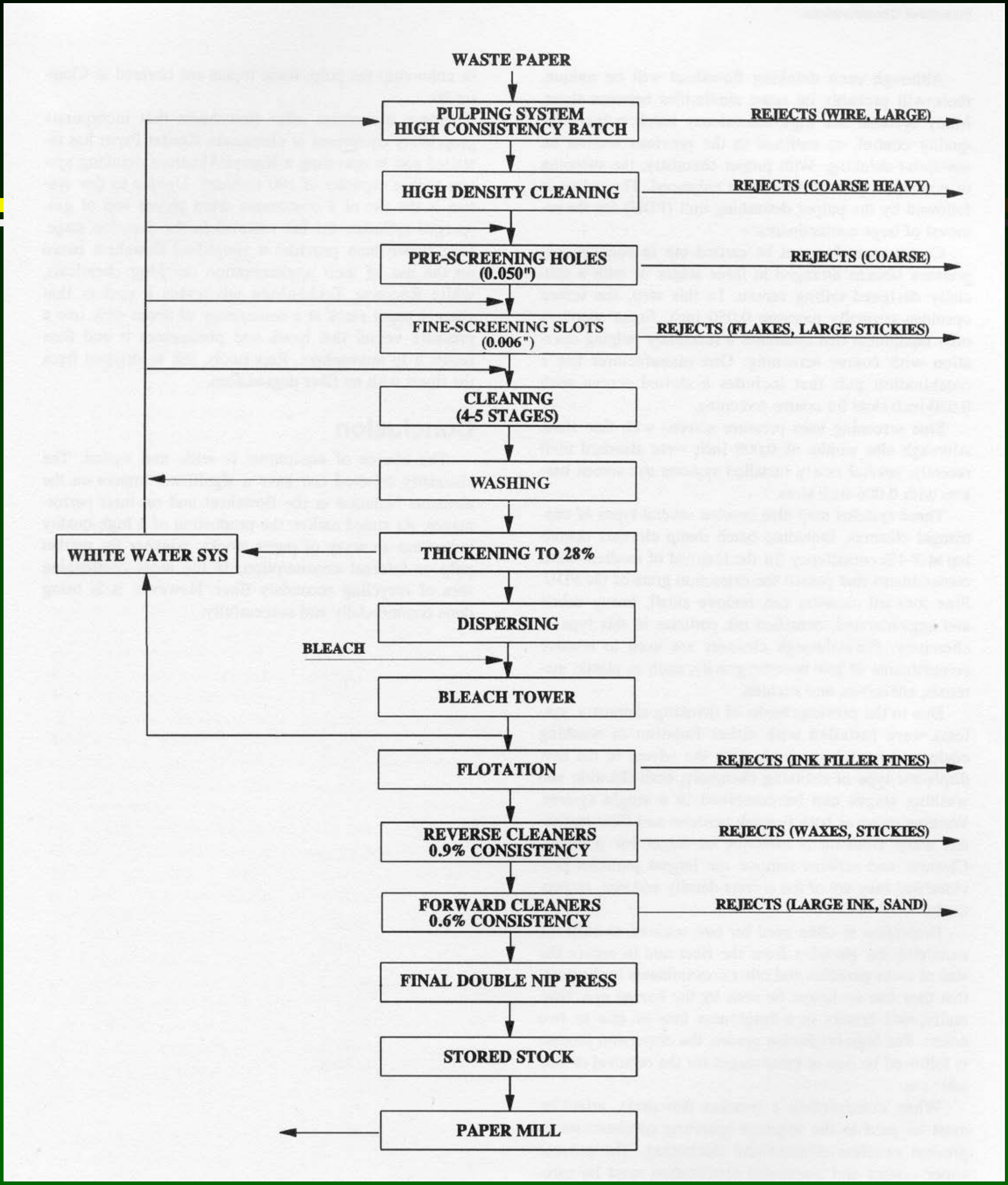
Newsprint Recycle Process: Rejects and Sludge Components



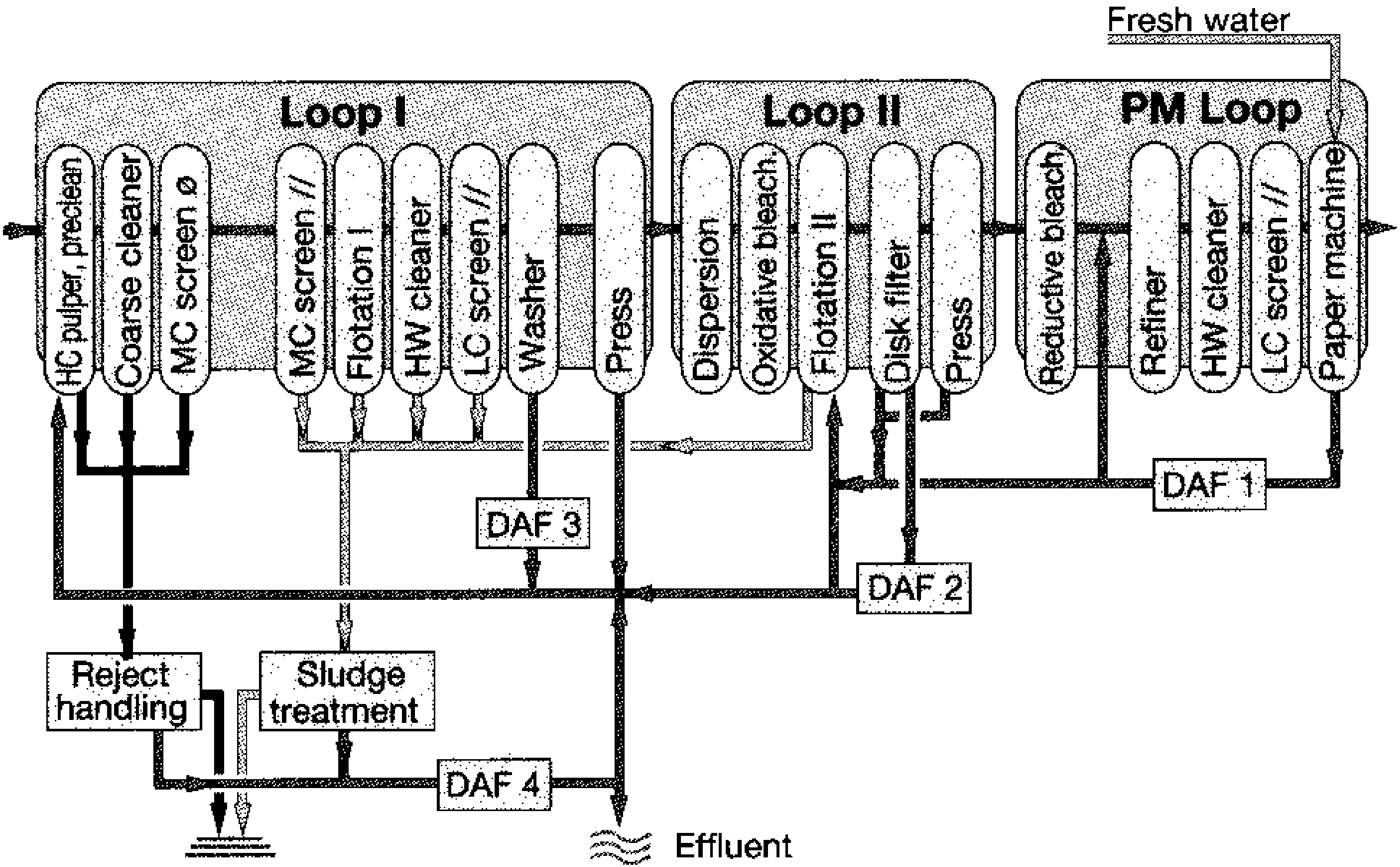
Production of High-Grade Printing and Writing Grades

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



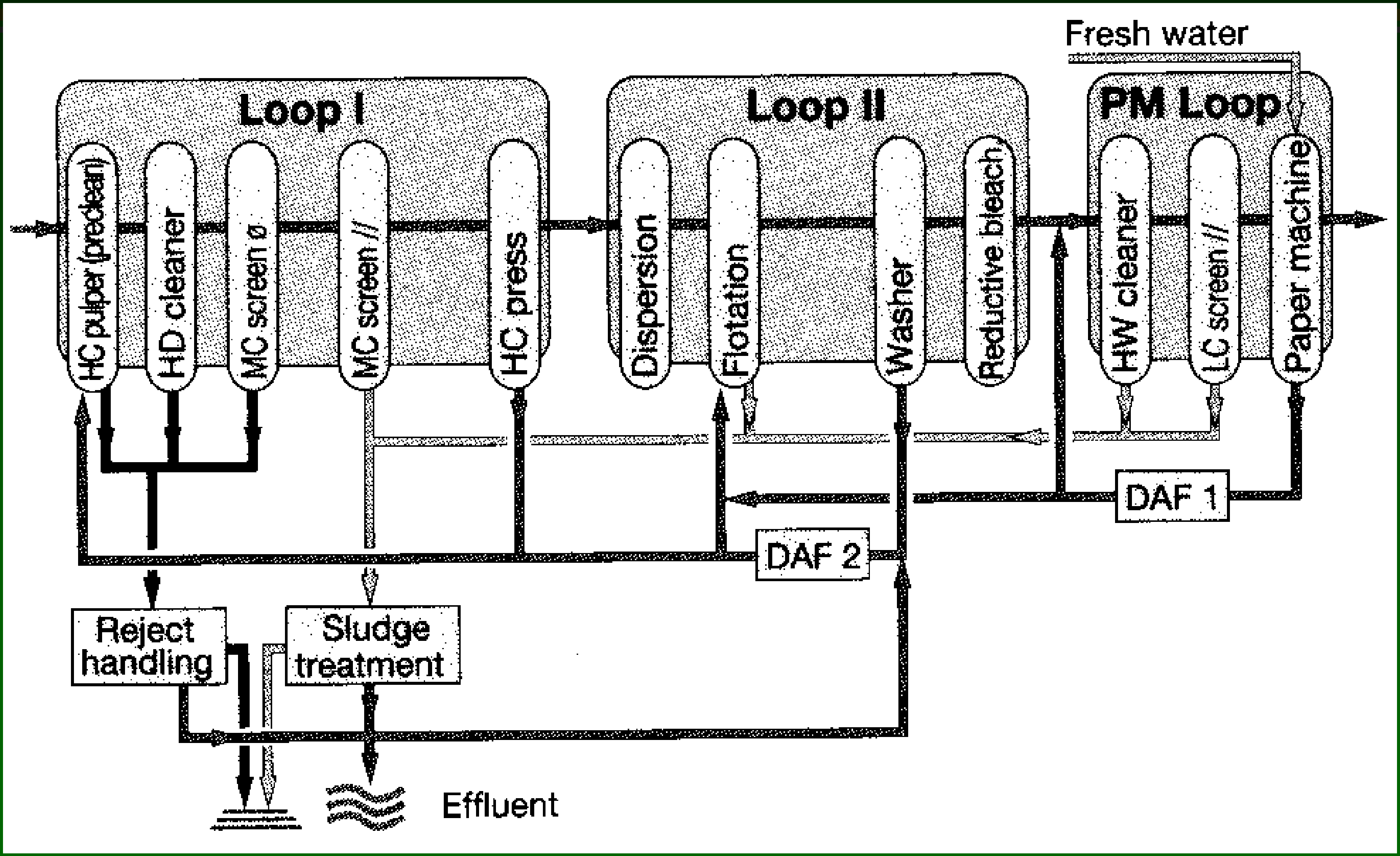
Production of Tissue Grades

Deinking of Printing-Writing Grades for Tissue

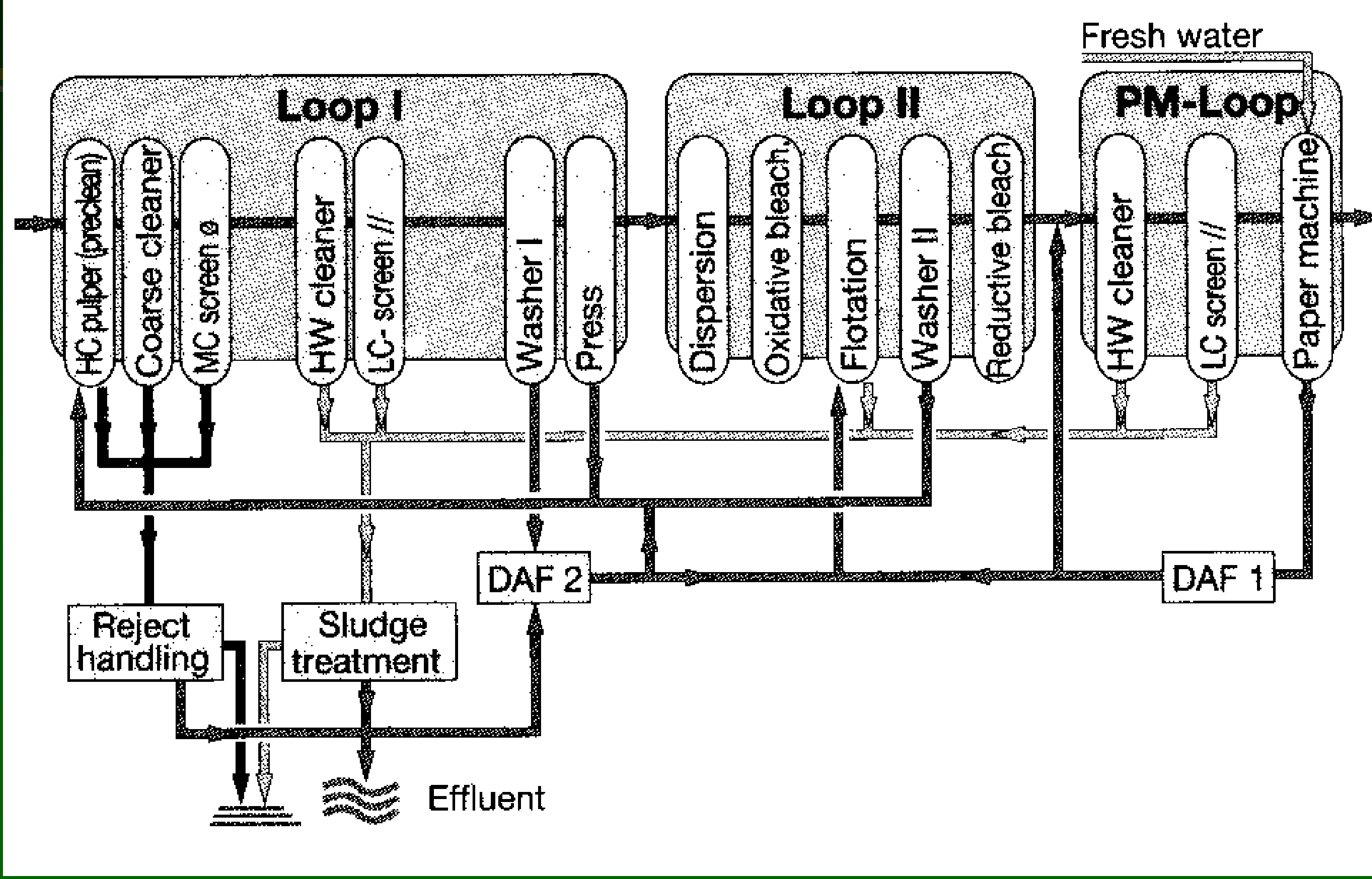
- Use sorted or non-sorted office waste to make tissue
- For tissue making, filler level must be low for creping (1-1.5%) (see 2 stages of washing)
- Yield can be as low as 60%
- Depending on quality of tissue, brightness and dirt count also important
- Lower grade tissue pulp production omits 1 stage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

Ref: Tappi deinking short course, 1995.

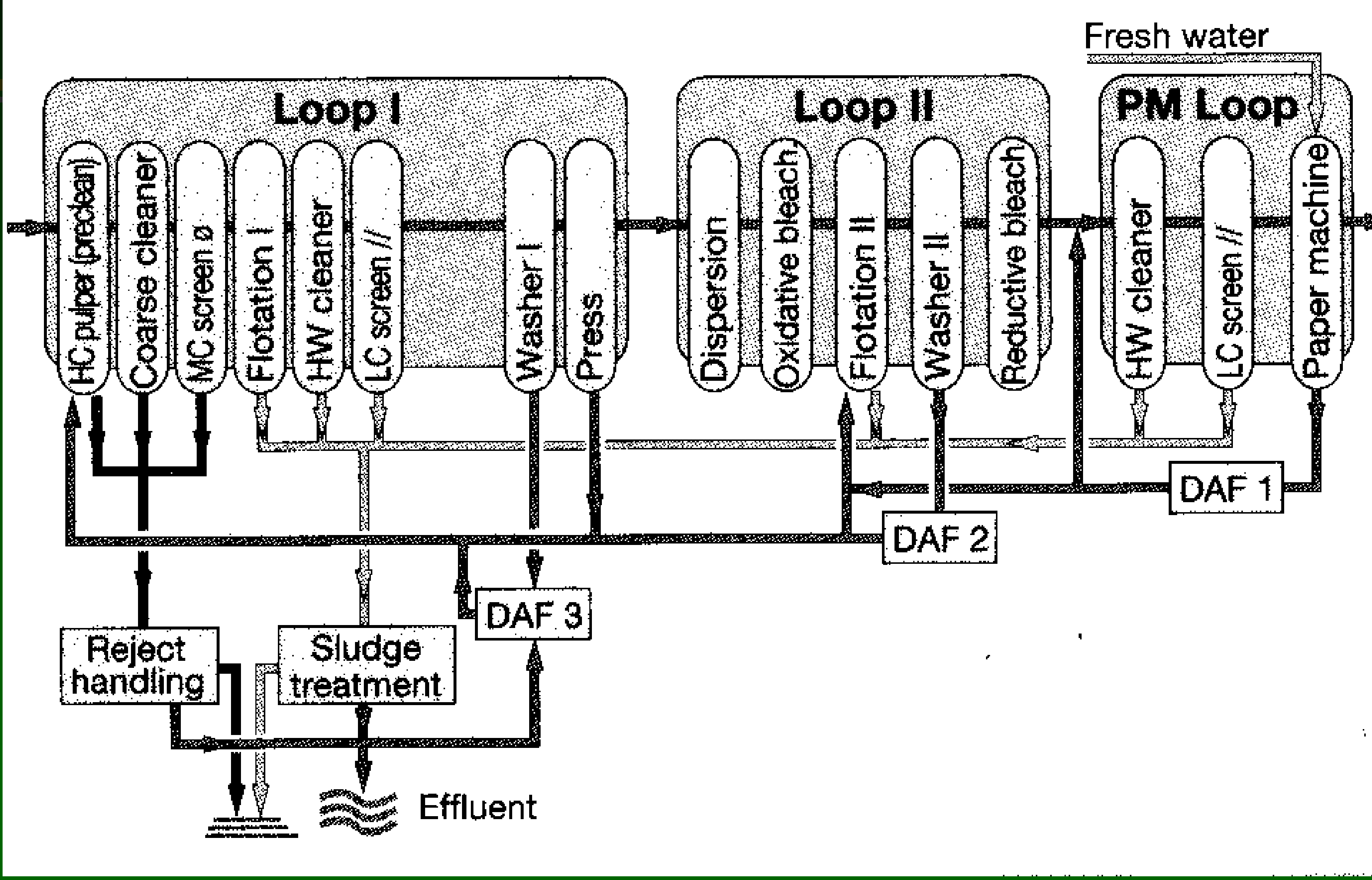
Low grade Tissue



High Grade Tissue: Wood Free



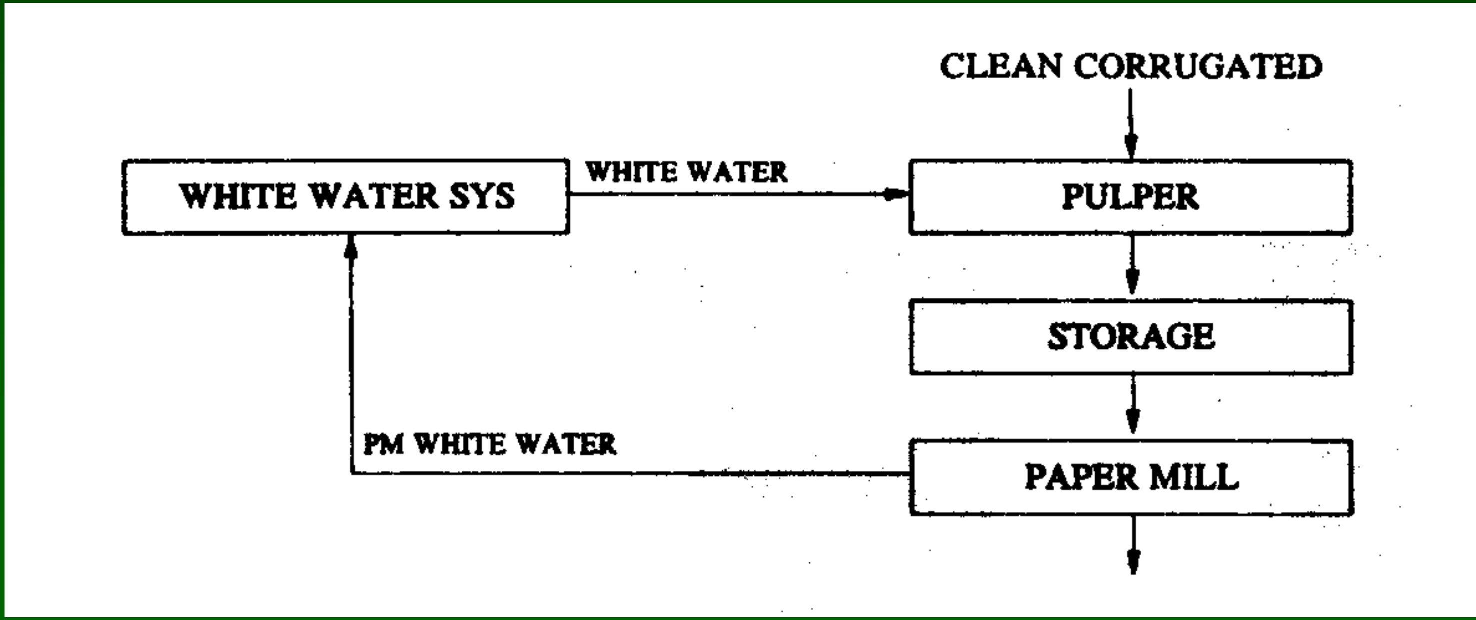
Low-Grade Tissue: Wood Containing



Production of Packaging Grades

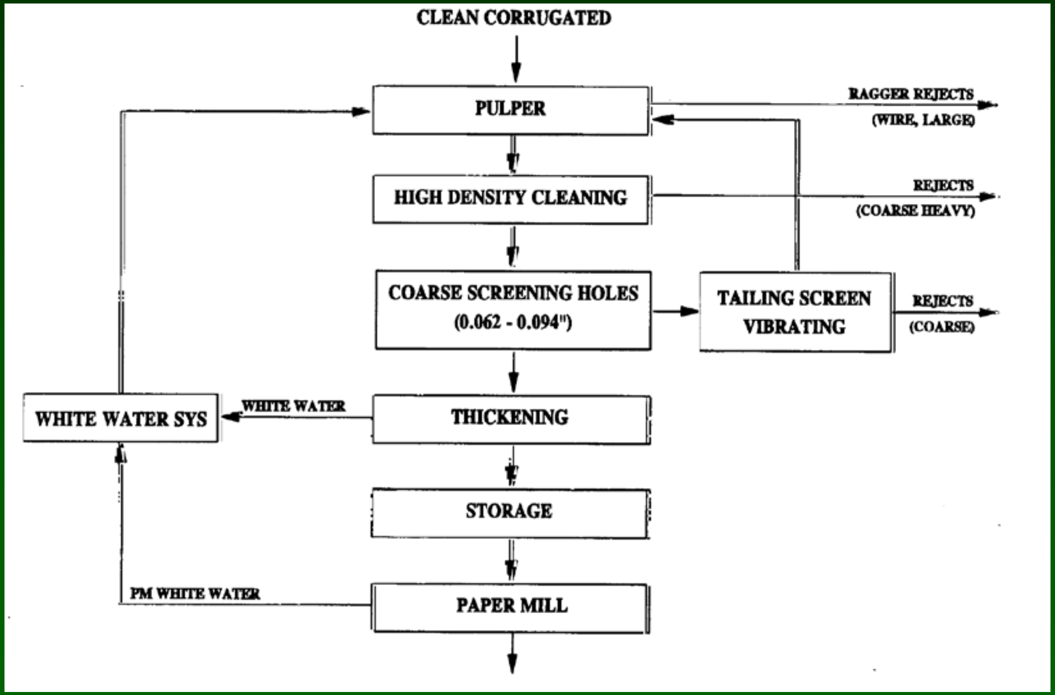
Simple Repulping System for Packaging Product

- 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



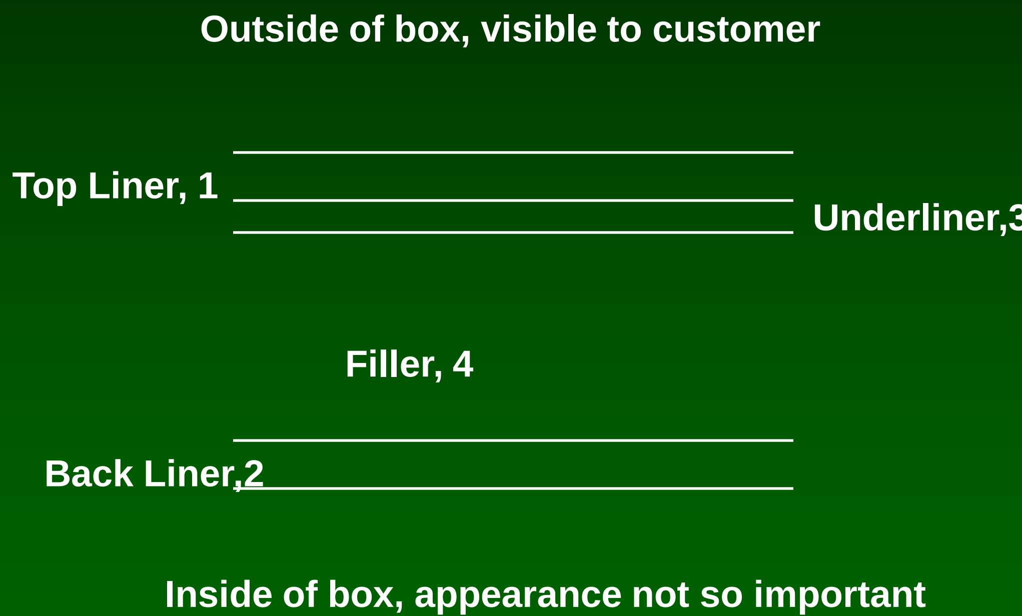
Crude Cleaning System for Packaging Product

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



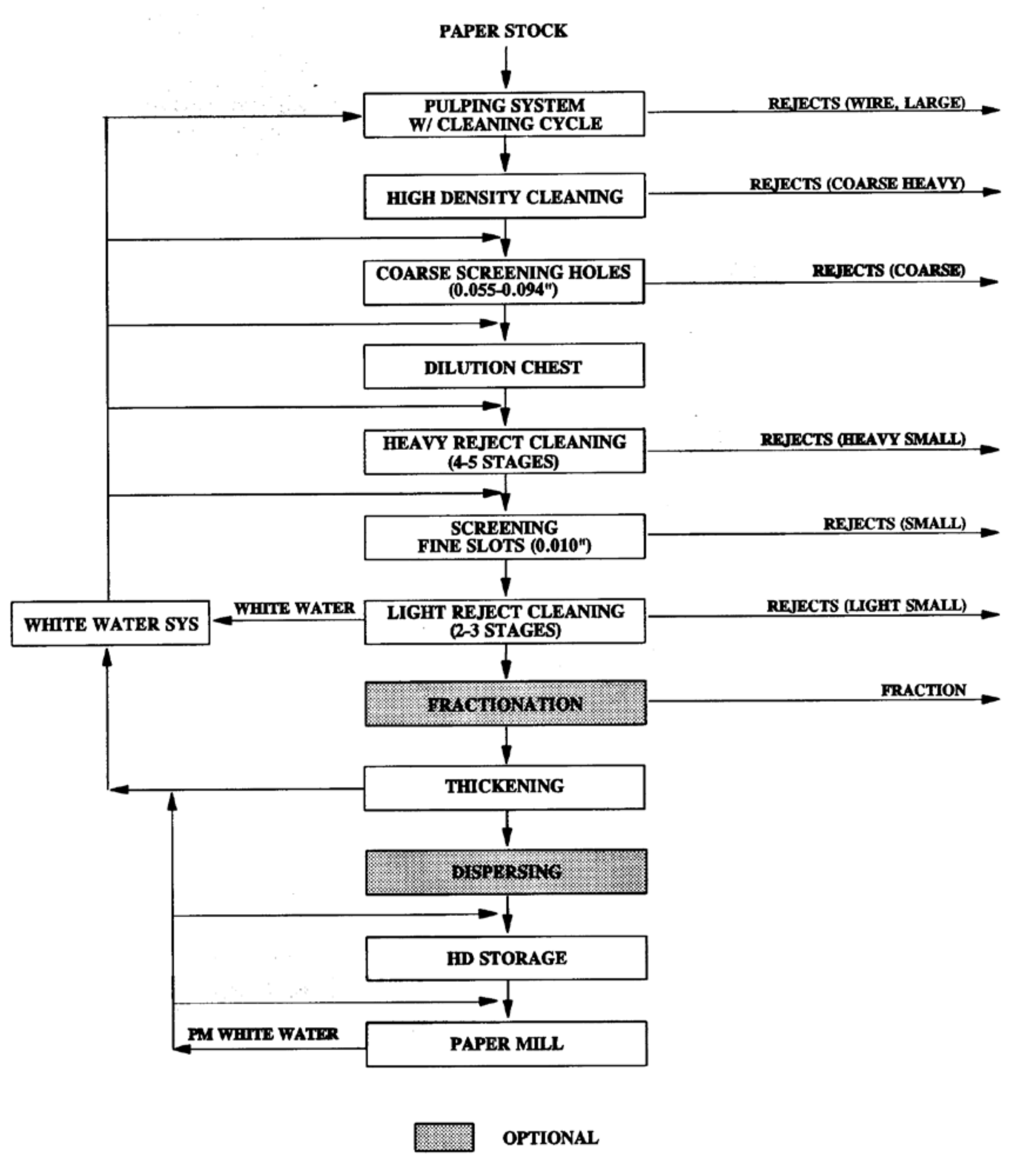
Multi-ply Board Packaging Product

- 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, 1 highest quality
- Excess water from each loop goes to inferior layer

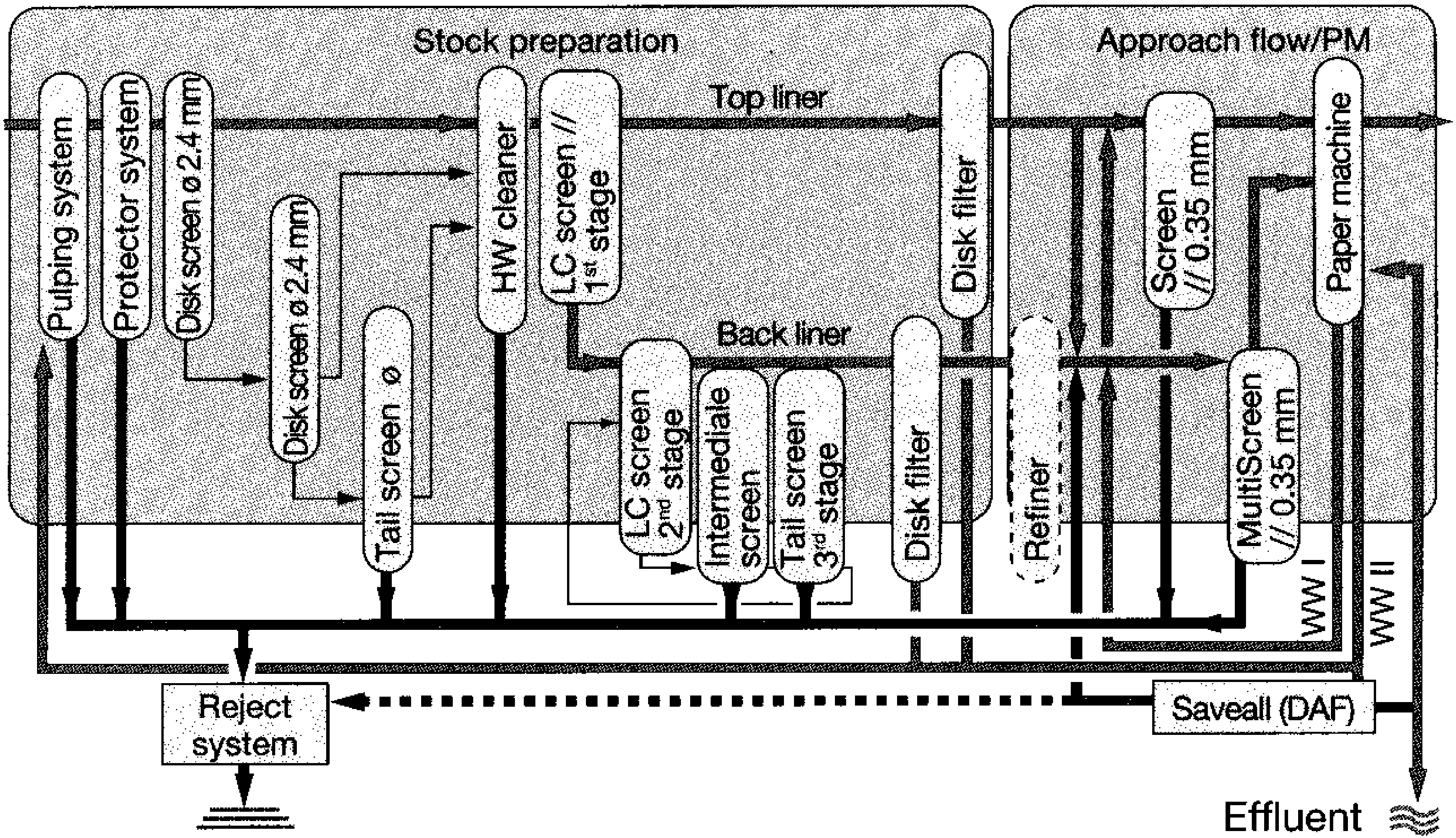


OCC Recycling for Higher Grades

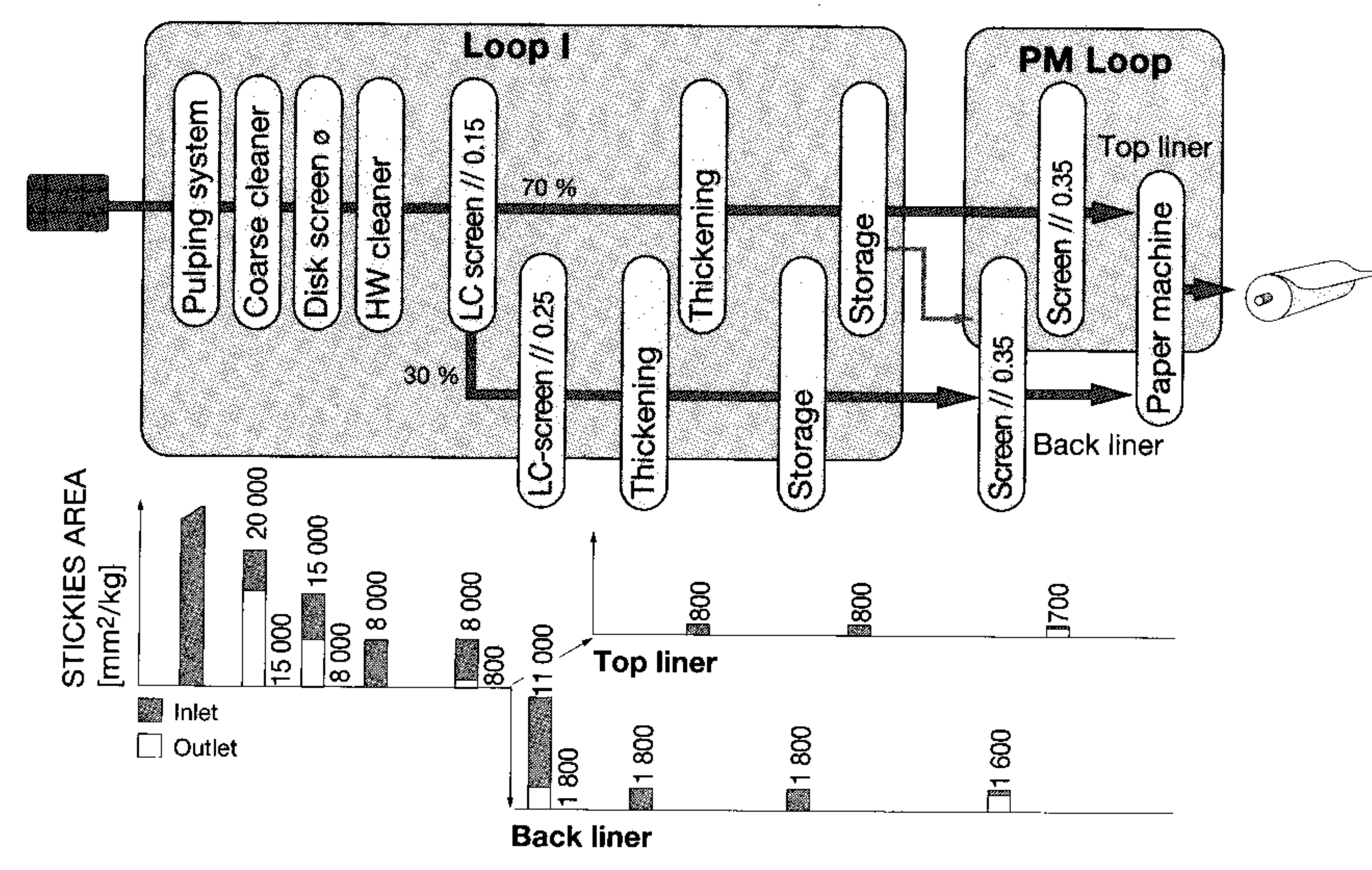
- Used to produce linerboard or medium
- Often have a continuous pulper with cleaning system
- Note the strategy:
  - 1st remove coarse contaminants
  - 2nd remove smaller contaminants
  - 3rd disperse unremoved contaminants
- Use alkali to swell fibers and regenerate strength
- Problems with stickies 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

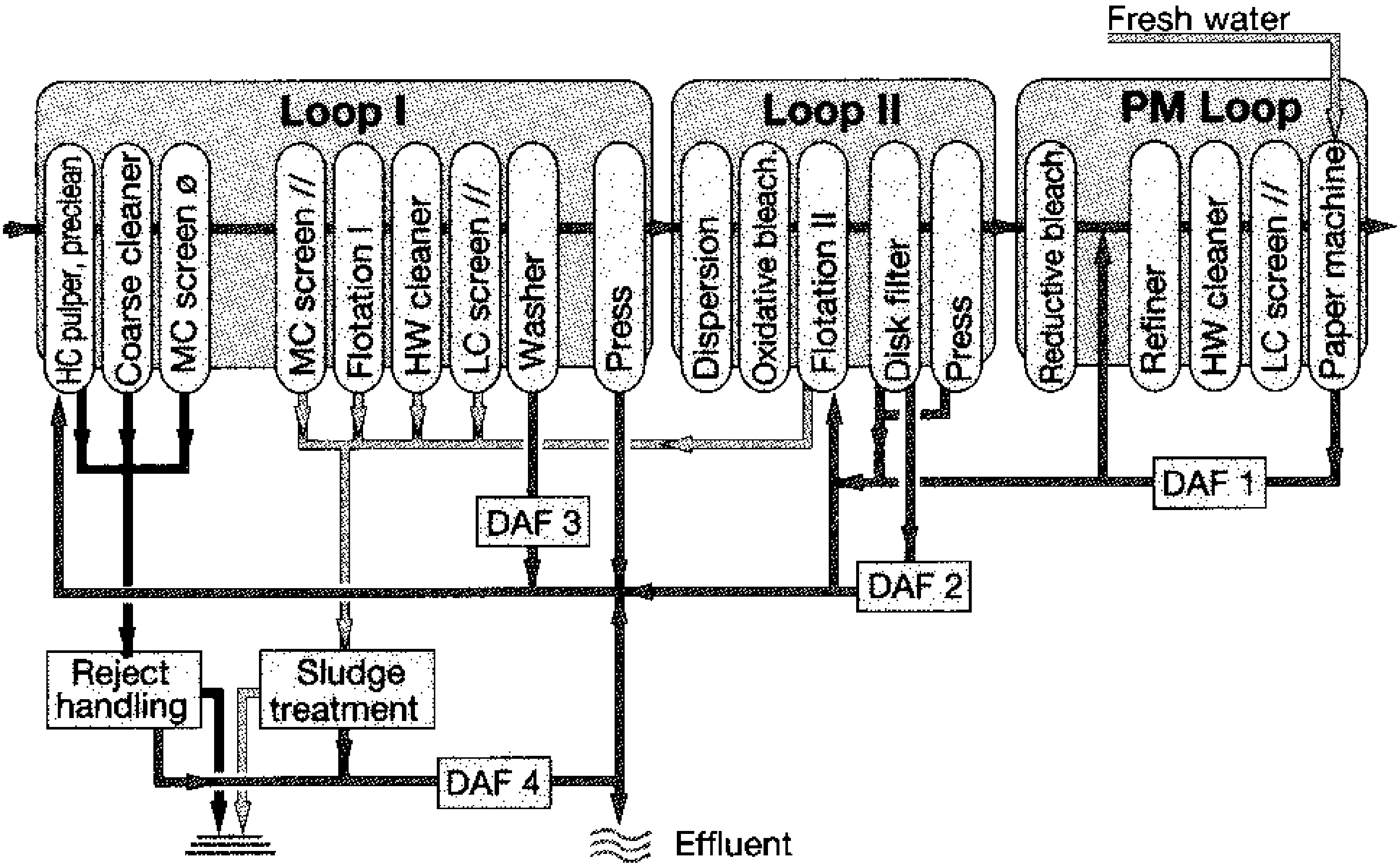
Lecture:

Cost to produce deinked pulp

Cost of Deinked Pulp (DIP)

- System
  - MOW to deinked, bleached pulp (DIP)
  - Flotation (2), washing, oxidative bleaching, complementary processes
  - Produce 200 ODTPD
  - Yield = 67%
- Total Capital Cost Installed= $42 MM
- $6 MM/yr depreciation for 7 years
- MOW Cost =$220/ton delivered

High Grade Printing and Writing Grades



Cost of DIP: Variable Costs

Description	Quantity	Unit	Unit Cost, $	Contribution, $/ton
Fiber	1.5	ton	220	330
NaOH	0.024	ton	400	9.6
Peroxide	0.024	ton	600	14.4
Sodium Silicate	0.022	ton	500	11.0
Flotation Aid	0.0027	ton	1000	2.7
Sludge Dewater Polymer	0.00115	ton	1200	1.4
Clarifier Flocculant	0.00014	ton	1600	0.2
Clarifier Bentonite	0.00085	ton	1600	1.4
Electricity	310	kWhr	0.045	14.0
Steam 790 kPa	0.25	mton	6	1.5
Waste Water Treatment	1.236	m3	0.53	0.7
Waste Disposal	0.984	mton	36	35.4
Process Water	4.8	m3	0.53	2.5
Total Variable Prod. Cost				424.8

Cost of DIP: Fixed Costs

Fixed Costs	$ Per Year	$ / ton
Maintenance	4,000,000	57
Labor	2,000,000	29
Operating Materials	1,700,000	24
Depreciation (7 yr straight line)	6,000,000	86
Business Overhead	1,100,000	16
Total Fixed Costs, $/ton		211

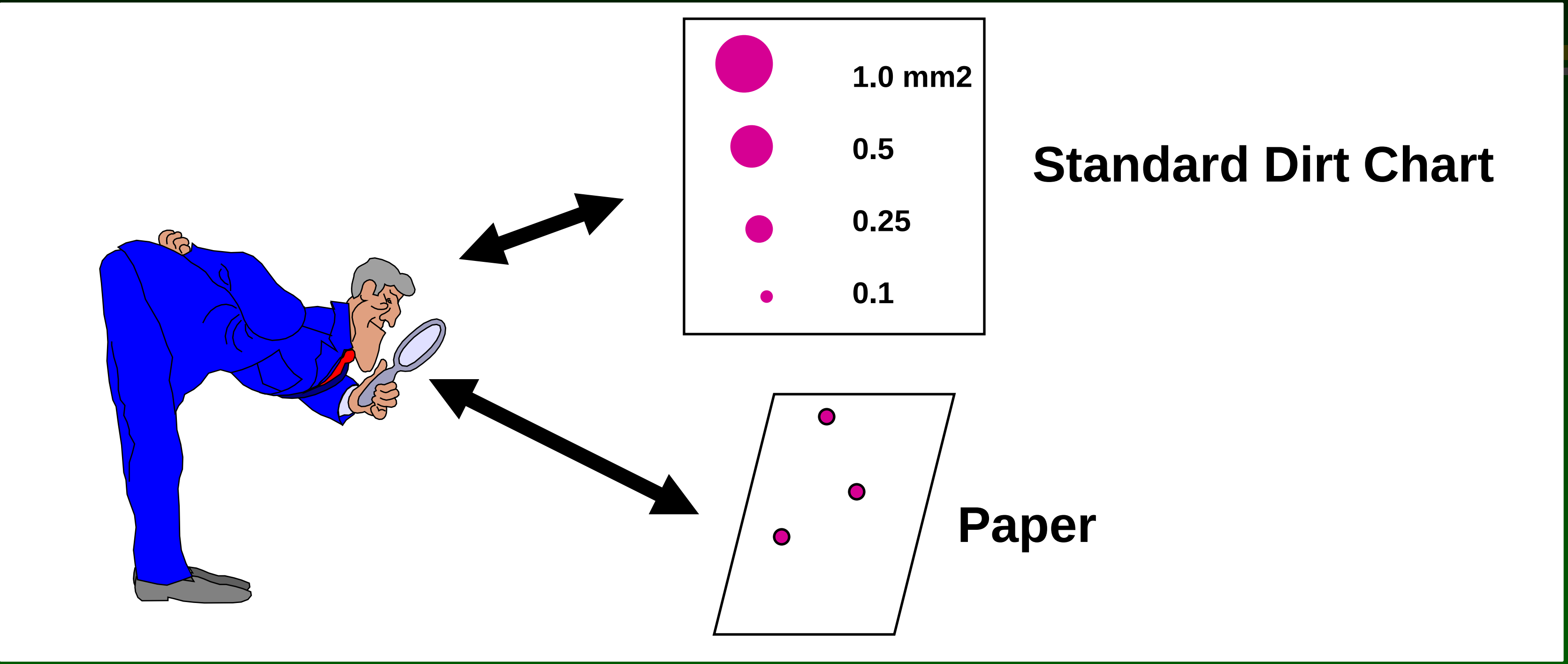
Cost of DIP: ROI

Total Costs, $/ton produced	636
Total Costs per year, $	44,532,716
Selling Price of ton DIP, $/ton	600
Income, $/yr	42,000,000
Profit before taxes, $	-2,532,716
Taxes (25%)	-399,537
Profit after taxes, $	-2,133,179
ROI (%)	Slightly negative!

Lecture:

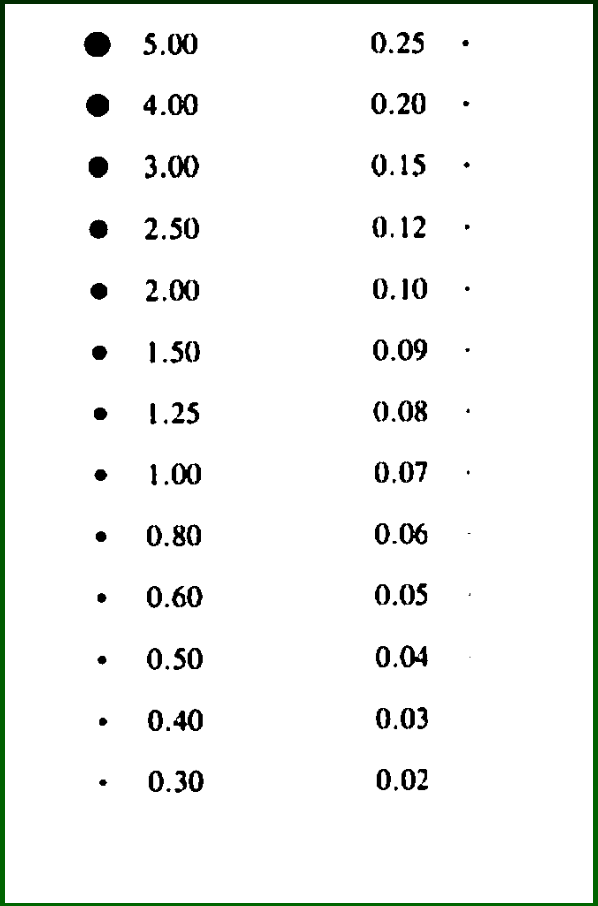
Automated Image Analysis of Paper to Detect Contaminants

Tedious Manual Method to Detect Dirt:



- In the past, a technician would inspect paper samples for dirt specks. The technician would match the size of the speck to a calibrated chart and record the number and sizes of all the specks.
- Dirt Count reported as **parts per million**, **PPM**
- **PPM** = 10^6* (area covered by dirt) / (analyzed area)

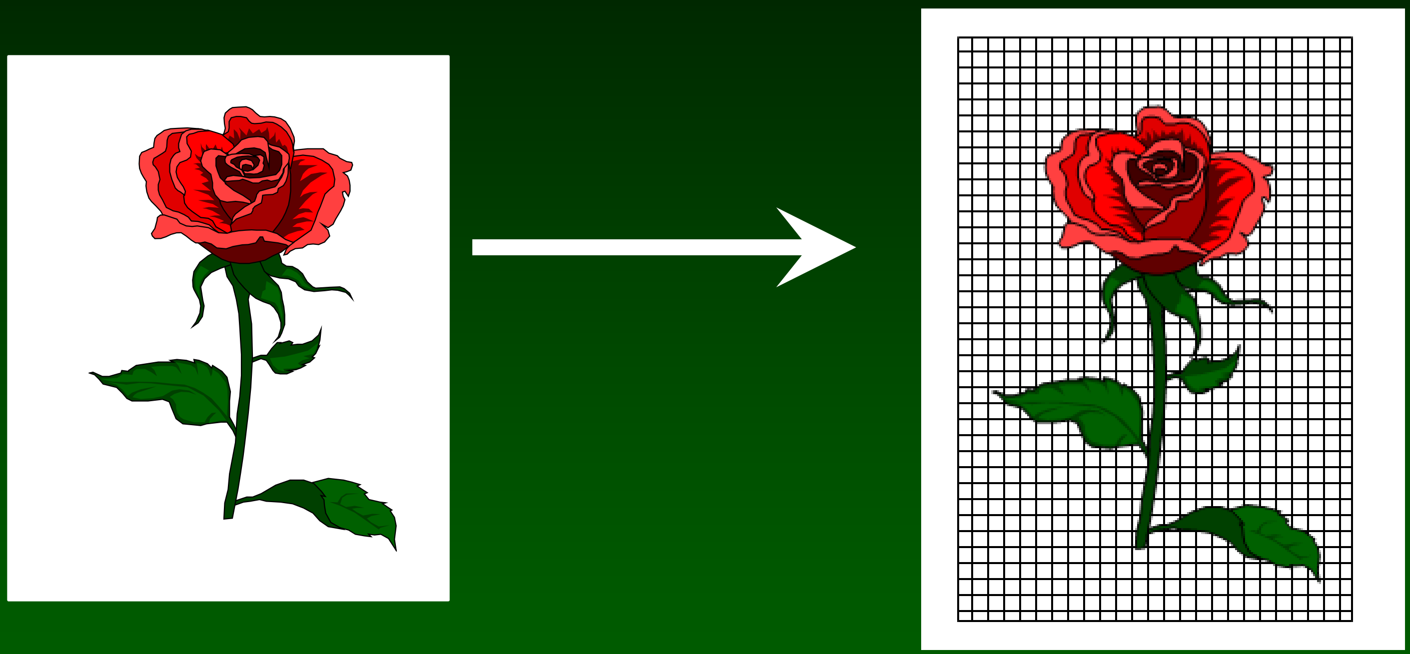
Tappi Dirt Estimation Chart (mm2)



Automatic Image Analysis (IA) to Detect Contaminants

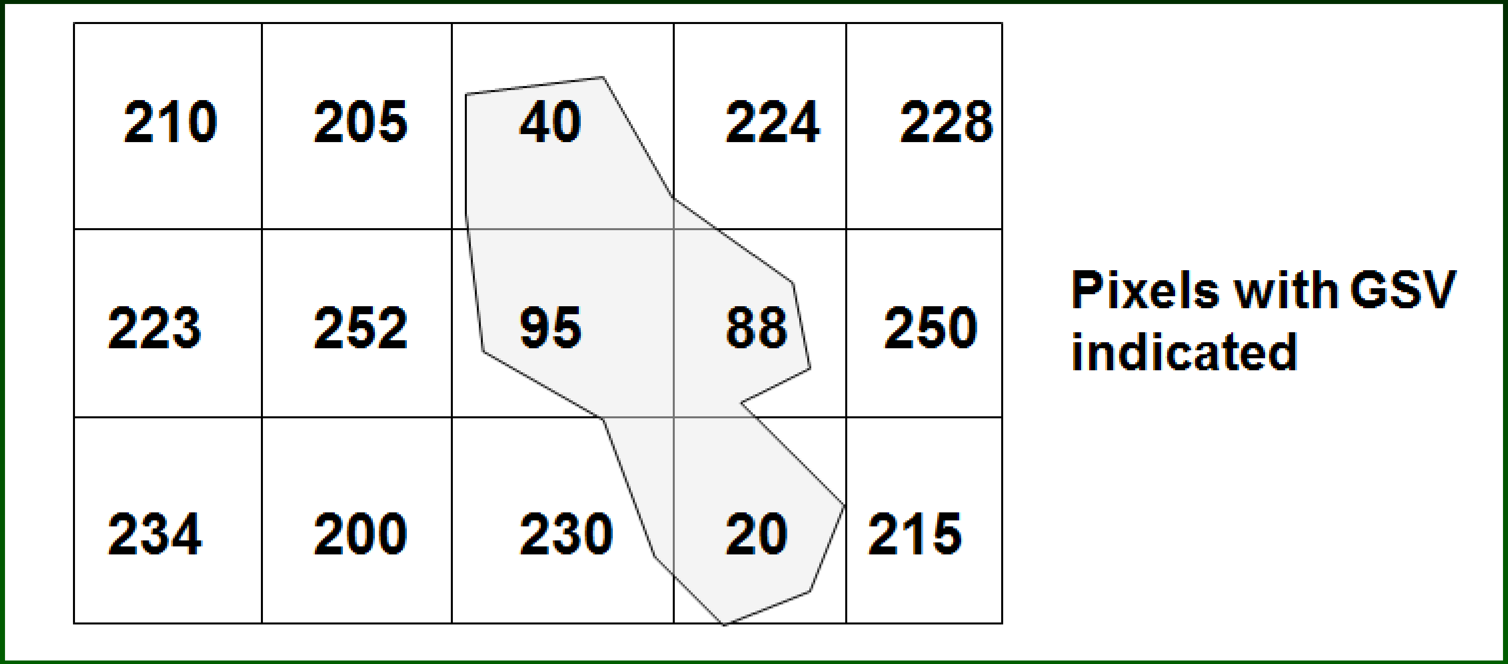
- Scanner: Eyes
- Computer: Brain
- Software Program: Rules for Decision Making

IA: How it works



- Scanners digitize an image; the image is broken down into an array of pixels
- The size of the pixels depends on the resolution
- Resolution often reported as dots per inch (DPI)
- 600 dots per inch square is equal to a square with edge of 0.04 mm or area of .018 mm^2
- The smallest size human sight can detect is an object with 0.05 mm longest axis

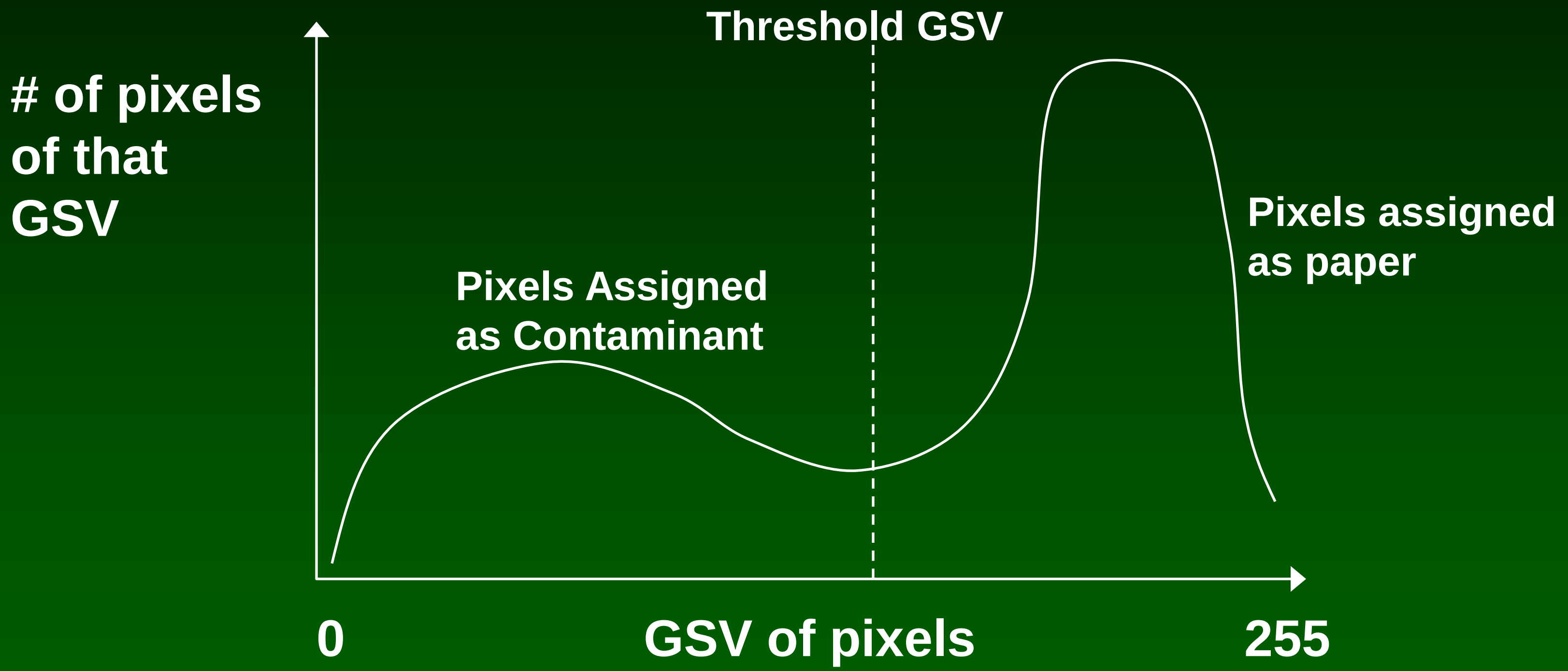
IA: How it works



- Each pixel is assigned a grey scale value (GSV) depending on how dark it is
- Black = 0
- White = 255

- Why go from 0 to 255 ?

IA: How it works



- A threshold GSV is input into the computer by the operator
- If pixel GSV < threshold GSV computer recognizes it as contaminant
- If pixel GSV > threshold GSV computer recognizes it as clean paper

Real life: bleached white paper with black specks

Apogee Systems, Inc.
Spec*Scan 2000 - V.2.2r

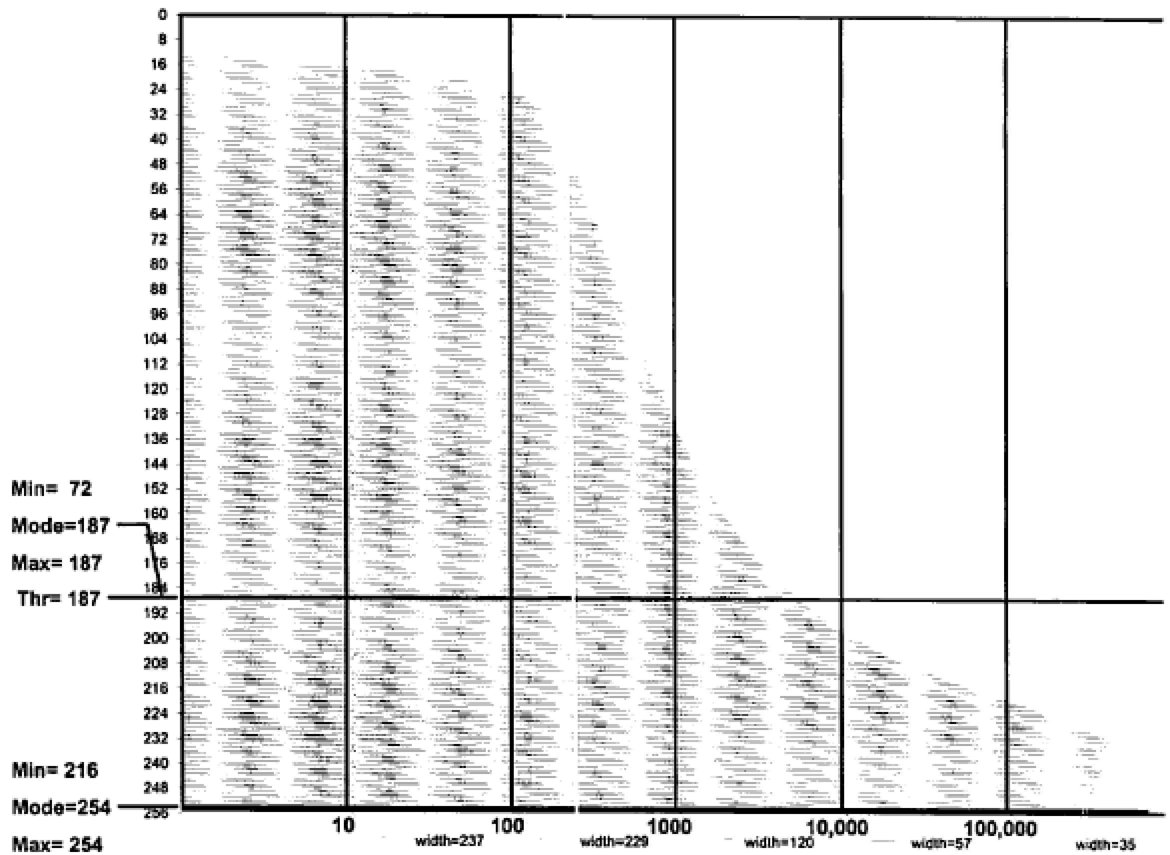
Fri 8-Jun-2007 11:50

Scanner Settings: Tappi Count, 600 dpi, 6" rd
Grade Identification:
Load / Reel Number:

Resolution: 600 dots/inch
Threshold: 187 (80.0%+ 0.0)
256-shade Grayscale mode
Normal Image Mode
Scan-to-Screen

2 sheets 6-inch round
Total Area Scanned: 0.027536 sq.m.

Sheet Number	Speck Data			Overall Gray		Dirt Grayscale				Fiber Grayscale			
	Count	Area	PPM	Ave.	StdDev	2σ Min	Mode	2σ Max	Ave.	2σ Min	Mode	2σ Max	Ave.
1	1117	84.21	6116.7	231.89	16.22	74	187	187	149.2	212	235	254	233.4
2	464	44.13	3205.4	240.62	12.14	66	187	187	145.1	223	254	254	241.2
Sample	1581	128.34	4661.0	236.26	14.98	72	187	187	148.2	216	254	254	237.3



Max= 254
Overall Grayscale Brightness = 236.3 = 92.6%
Overall Grayscale Std Deviation = 15.0 = 5.9%

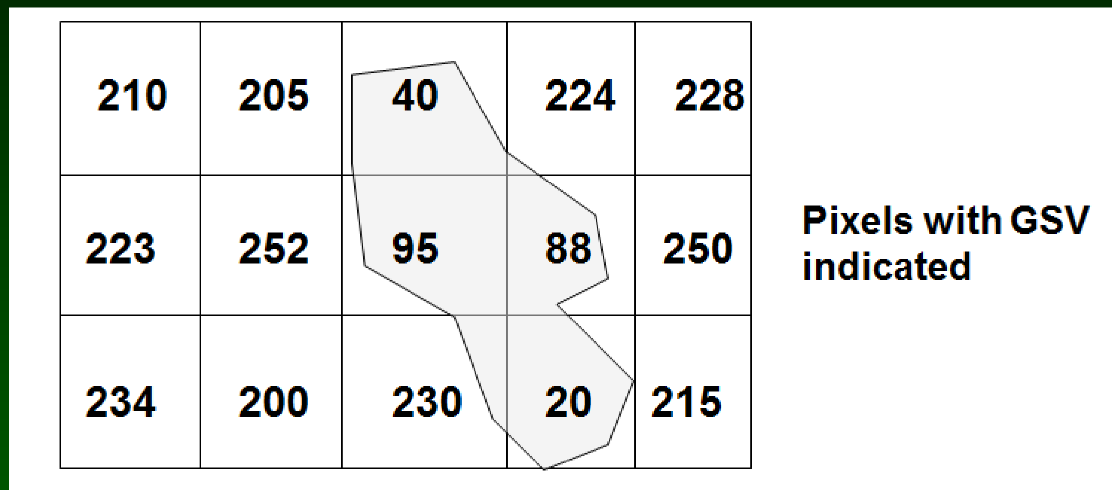
IA: How it works

210	205	40	224	228
223	252	95	88	250
234	200	230	20	215

Pixels with GSV indicated

- Computer groups adjacent pixels with GSV < threshold together and then can determine size of dirt specks and total area covered by dirt and PPM

IA: How it works



- If the threshold GSV for the above sample is set to 175, then what is the PPM of the sample?
- Area covered by dirt = 4
- Area analyzed = 15
- PPM = 1,000,000 * 4/15 =

Real life: bleached white paper with black specks

Categories:	Min Avg. Gray	Max Avg. Gray	Min Meas. Area	Max Meas. Area	Count	Area (sq.mm)	---- Calculated ---- Count (in 1 sq.meter)	PPM	Average Grayscale	Darkest Grayscale	Average Size (sq.mm)
0-39 GSV	0	39	0.020	99999							
40-79 GSV	40	79	0.020	99999	4	1.493	145	54.2	76.25	13.00	0.373
80-119 GSV	80	119	0.020	99999	716	43.072	26729	1564.2	107.63	14.00	0.059
120-129 GSV	120	129	0.020	99999	471	22.165	17105	804.9	124.58	22.00	0.047
130-139 GSV	130	139	0.020	99999	516	26.134	19829	949.1	134.48	25.00	0.048
140-149 GSV	140	149	0.020	99999	519	26.894	19938	976.7	144.54	27.00	0.049
150-159GSV	150	159	0.020	99999	1	0.550	36	20.0	152.00	0.00	0.550
160-169GSV	160	169	0.020	99999	331	15.416	13837	559.8	164.31	67.00	0.040
170-255 GVV	170	255	0.020	99999	125	5.638	4540	204.8	175.66	102.00	0.045
Total > 0.02 sq mm	0	255	0.020	99999	131	12.711	5847	461.6	165.04	26.00	0.079

Sample Grayscale Brightness Analysis:

	99% Min	Mode	99% Max
Dirt Content:	35	187	187
Fiber Content:	203	254	254
Overall	182	254	254

Overall Grayscale Brightness = 236.3 = 92.6%
Overall Grayscale Std Deviation = 15.0 = 5.9%
Std.Dev. of Sheet Overall Ave. = 6.2 = 2.4%

Dirt Count Summary:

	All Sizes	>=0.040
Number of Specks:	1581	1581
Avg. Speck Area:	0.0812	0.0812
Median Speck Area:	0.0603	0.0603
Total Area (sq.mm):	128.34	128.34
Parts Per Million:	4661.0	4661.0
StdDev of Sheet PPM:	2058.60	2058.60
Count in 1 sq.m:	57416	57416
Counting Precision:	2.51	2.51

Real life: bleached white paper with black specks

Apogee Systems, Inc.
Spec*Scan 2000 - V.2.2r

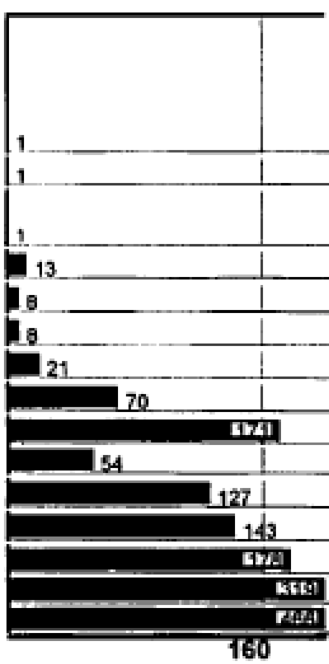
Fri 8-Jun-2007 11:50

Scanner Settings: Tappi Count, 600 dpi, 6" rd
Grade Identification:
Load / Reel Number:

Resolution: 600 dots/inch
Threshold: 187 (80.0%+ 0.0)
256-shade Grayscale mode
Normal Image Mode
Scan-to-Screen

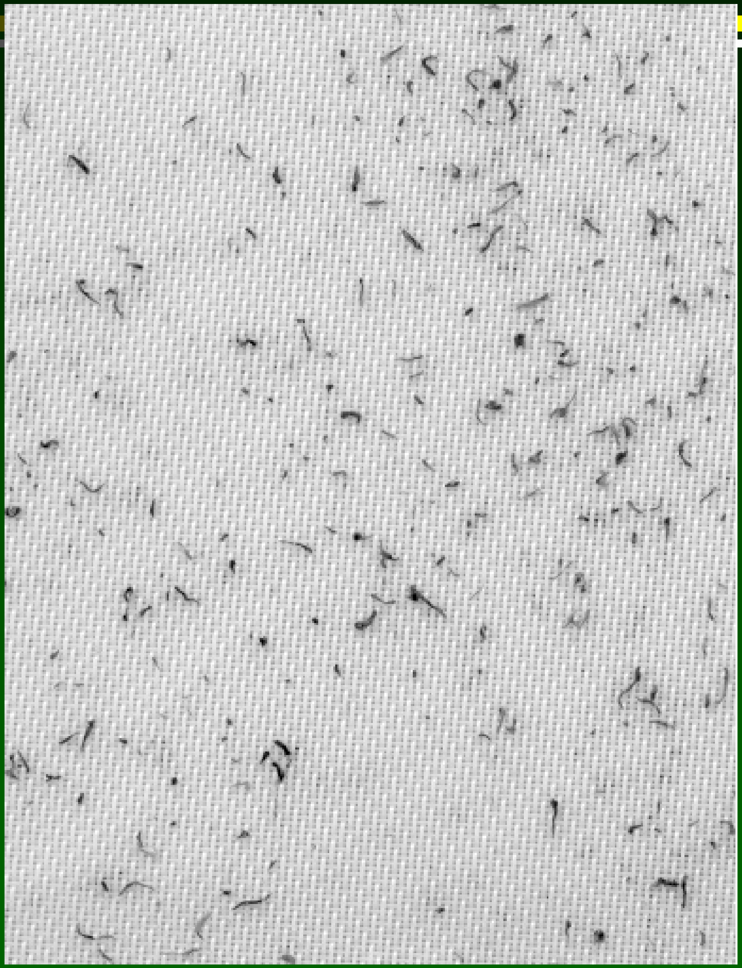
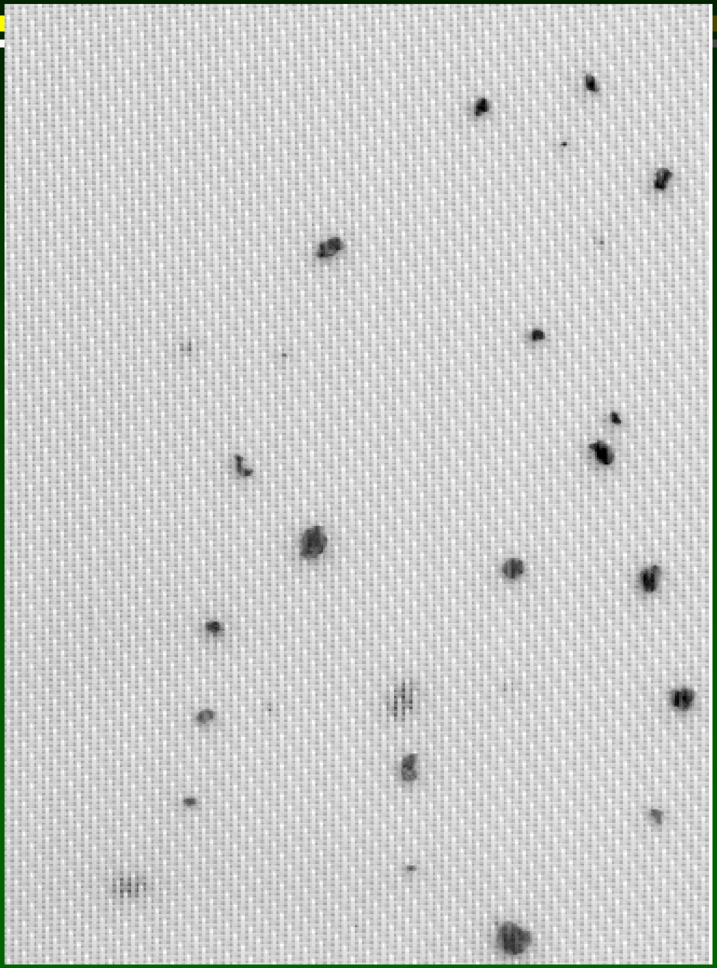
2 sheets 6-inch round
Total Area Scanned: 0.027536 sq.m.

Dirt Content Histogram



Dirt Spot Size	---- Sample ---- Count	Area (sq.mm)	---- Sample ---- Count (in 1 sq.meter)	PPM	---- Cumulative ---- Count	Area (sq.mm)	Cum. PPM
>= 5.000	0						
3.00	0						
2.50	0						
2.00	0						
1.50	1	1.756	36	63.8	1	1.756	63.8
1.00	1	1.025	36	37.2	2	2.781	101.0
0.80	0						
0.60	1	0.747	36	27.1	3	3.529	128.1
0.40	13	6.326	472	229.7	16	9.855	357.9
0.30	8	2.735	291	99.3	24	12.590	457.2
0.25	8	2.188	291	79.5	32	14.778	536.7
0.20	21	4.823	763	175.1	53	19.600	711.8
0.15	70	11.957	2542	434.2	123	31.557	1146.1
0.10	171	20.500	6210	744.5	294	52.057	1890.5
0.09	54	5.113	1961	185.7	348	57.170	2076.2
0.08	127	10.765	4612	391.0	475	67.936	2467.2
0.07	143	10.744	5193	390.2	618	78.679	2857.4
0.06	178	11.627	6464	422.3	796	90.307	3279.6
0.05	319	17.332	11585	629.4	1115	107.638	3909.0
0.04 TAPPI	466	20.706	16923	752.0	1581	128.344	4661.0
Totals ->	1581	128.344	57416	4661.0			

Example of Other Uses of IA:
Adhesive Deposits on Paper Machine Wires

Following slides did not appear in presentations.

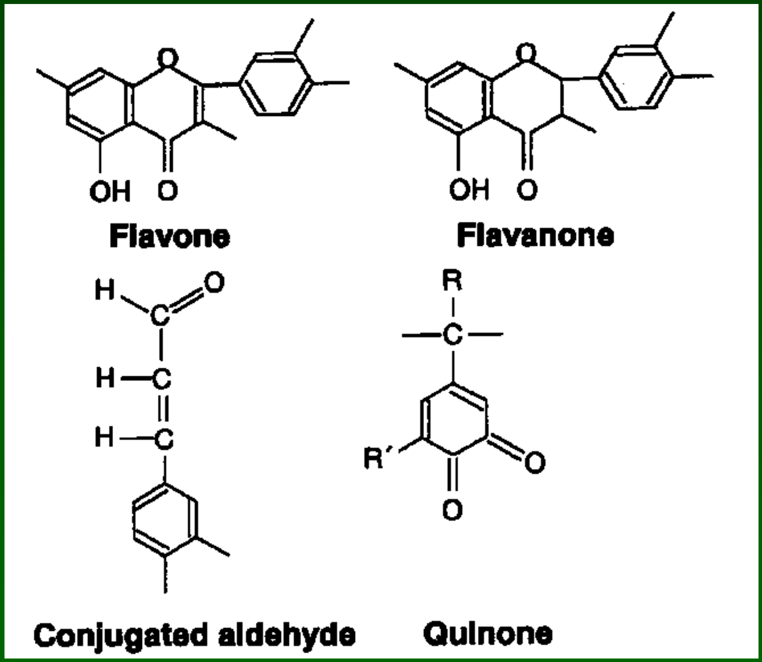
- Left them here to not lose them.

Types of Papers

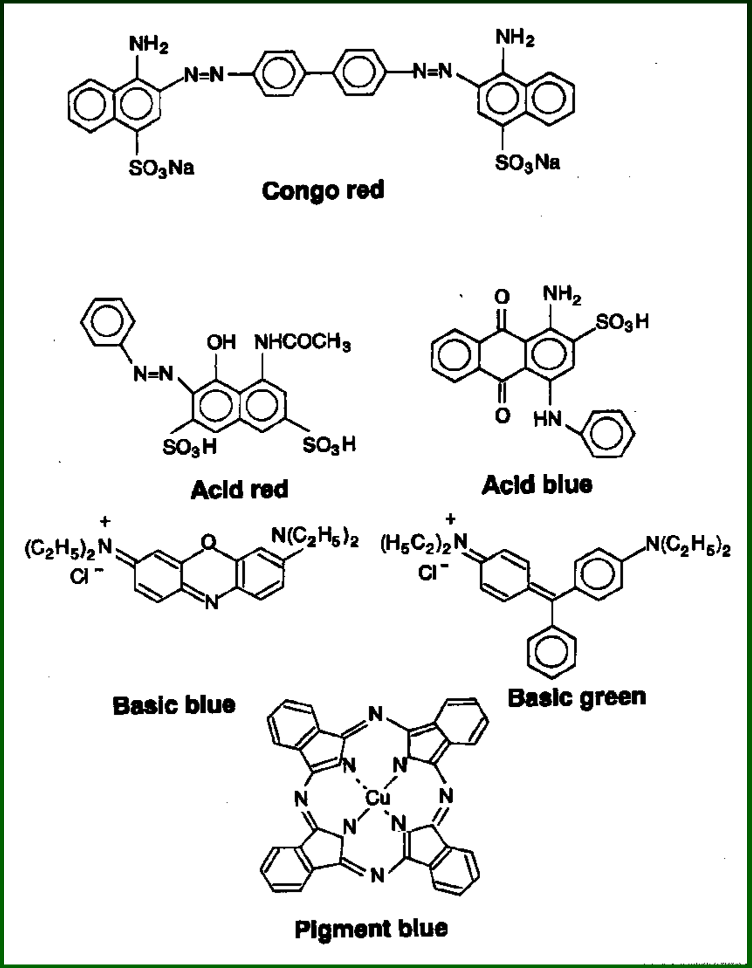
- Chemically pulped and bleached fibers:
  - have 0% lignin
  - Only cellulose and hemicellulose, white
- Chemically pulped unbleached fibers (linerboard):
  - have 5-15% lignin
  - Brown
  - Condensed lignin, extended conjugated structures, aromatic groups, several double bonds of carbon
  - Electrophilic agents such as oxygen, chlorine dioxide, chlorine can oxidize, interrupting conjugation and color
- Mechanically pulped fibers (newsprint):
  - Have 20+ % 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, as in mechanical fibers, 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

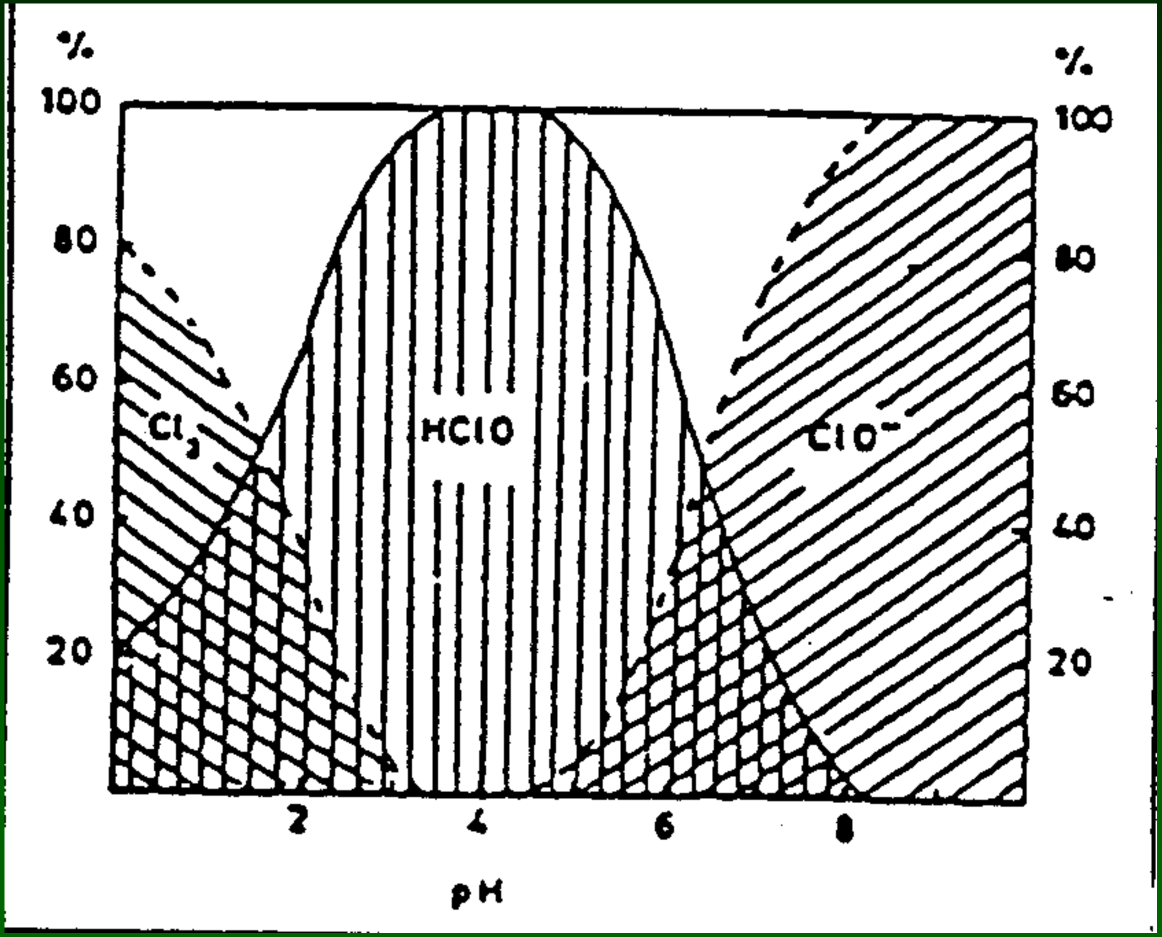
Sodium Hypochlorite (H) Bleaching

- 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
- Has been mostly phased out due to environmental concerns

Sodium Hypochlorite (H) Bleaching

- $2NaOH + Cl_2 \rightarrow NaOCl + NaCl + H_2O$
- 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 gas, Cl_2

Sodium Hypochlorite (H) Bleaching



Sodium Hypochlorite (H) Bleaching

- Application: 0.5-2.5% on pulp
- 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% on pulp
  - 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 % on pulp application, 60 min, 10-15 %K, 85-95 C, 1.0 % H_2O_2, 0.7-1.0 % NaOH, Na_2SiO_3 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 chlating agents used to remove metal ions
- Conditions: 0.25-3.0% on pulp, 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