Pulp and Paper Mill

Environmental Standards

- LARGE PULP AND PAPER/NEWS PRINT/ RAYON GRADE PULP PLANTS OF CAPACITY 24000 TONNE/ANNUM: WASTEWATER DISCAHRGE STANDARDS

Parameter/ Flow	**Concentration not to exceed**
Large pulp and paper	200 cum/ tonne of paper
Large rayon grade/news print	175 cum/ tonne of paper
pH	6.5 to 8.5
SS	100 mg/l
BOD at $27^{o}C$ for 3 days	30 mg/l
COD	350 mg/l
TOCL*	2.0 kg tonne of paper produced

*The standards for total organic chlorine (TOCL) are applicable from January, 1992.

TOCL – Amount of organically bound chlorine that has carried over from the bleaching process into the wastewater. This specific test is carried out on samples of wastewater to determine TOCL content.

Environmental Standards

- **SMALL PULP AND PAPER INDUSTRY: STANDARDS FOR LIQUID EFFLUENTS**

Mode of disposal	Parameter	Concentration not to exceed, mg/l (except for pH and SAR)
Inland Surface Water	pH Suspended solids BOD at 27^{o}C, 3 days	5.5 to 9.0 100 30
Land	pH Suspended solids BOD at 27^{o}C, 3 days Sodium absorption ratio	5.5 to 9.0 100 100 26

Sodium adsorption ratio (SAR)

- It is a measure of the suitability of water for use in agricultural irrigation, as determined by the concentrations of solids dissolved in the water. It is also a measure of the **sodicity** of soil, as determined from analysis of water extracted from the soil.
- The formula for calculating sodium adsorption ratio is:
- $SAR = Na^{+} / \sqrt{(½(Ca^{++} + Mg^{++}))}$

  where sodium, calcium, and magnesium are in milli equivalents/liter.
- Although SAR is only one factor in determining the suitability of water for irrigation, in general, the higher the sodium adsorption ratio, the less suitable the water is for irrigation.
- If irrigation water with a high SAR is applied to a soil for years, the sodium in the water can displace the calcium and magnesium in the soil. This will cause a decrease in the ability of the soil to form stable aggregates and a loss of soil structure and tilth.

Environmental Standards

- **Small pulp and Paper Industry: Wastewater Discharge Standards**

- **CATEGORY A: Agrobased**
  - Before 1992 = 200 cum/tonne of paper produced
  - From 1992 = 150 cum/tonne of paper produced

- **CATEGORY B: Waste Paper Based**
  - Before 1992 = 75 cum/tonne of paper produced
  - From 1992 = 50 cum/tonne of paper produced

Pulp and Paper Mill Waste

- It is a materials industry.
- One of the major industries which contributes to water pollution.
- Few mills produce pulp alone and most of the mills produce paper and pulp.
- Pollution potential of paper mill is negligible compared to pulp mill.

Manufacturing Process and Sources of the Waste

- Manufacturing process two stage:
  - Pulp making
  - Paper production

Pulp Making

- When wood is received – bark is removed (either mechanically or hydraulically)
- Wood is reduced to chips for cooking.

- **Mechanically prepared pulp** (e.g. news paper)

  – Grinding of wood
  – carrying it by water through screens.
  – This produced coloured paper, **low grade**, non-durable.

- **Chemically prepared pulps**

  – Chipped cellulosic raw materials are **digested** with different chemicals under high temperature and pressure.
  – The process **loosens cellulose fibers** and dissolves the lignin, resin and other non–cellulosic materials in the raw material.

Pulp Making

- **Kraft Process (**or sulphate process)
  - Sodium sulphate, sodium hydroxide, sodium sulphide and carbonate (Na_2CO_3) are chemicals used for digestion.

- **Sulphite process**
  - Magnesium or calcium bisulphite and sulphurous acid are used.
  - Temperature 300 ^oF (150 ^oC) and 70 lb pressure, 5 to 6 hr.

- **Alkali Process**
  - Sodium hydroxide or lime is used (or mixture of Na_2CO_3 and $Ca(OH)_2$) for soft wood.

Pulp Making

- After digestion (by any of the process) the **black liquor** is allowed to drain from chemically prepared pulp.
- This spent liquor called as '**black liquor**' is rich in lignin content and unutilized chemicals, therefore treated separately for chemicals recovery.
- 'Black liquor' from sulphite process is not treated for chemical recovery.
- The **cellulosic fibers** after separation from 'black liquor' are **washed** and then partially **dewatered** in a cylindrical screen called '**Decker**'.
- Concentrated wash water is sent for chemical recovery, dilute wash water forms wastewater.

Pulp Making

- **Bleaching**
  - Washed cellulosic fibers are bleached in three stages using **chlorine, caustic and hypochlorite** in successive stages.
  - Wastewater from **first and last stage is yellow in colour**, while from the **caustic extraction stage it is highly coloured**.
  - The dried, bleached pulp is ready for sale or use in paper mill.

Paper Mill

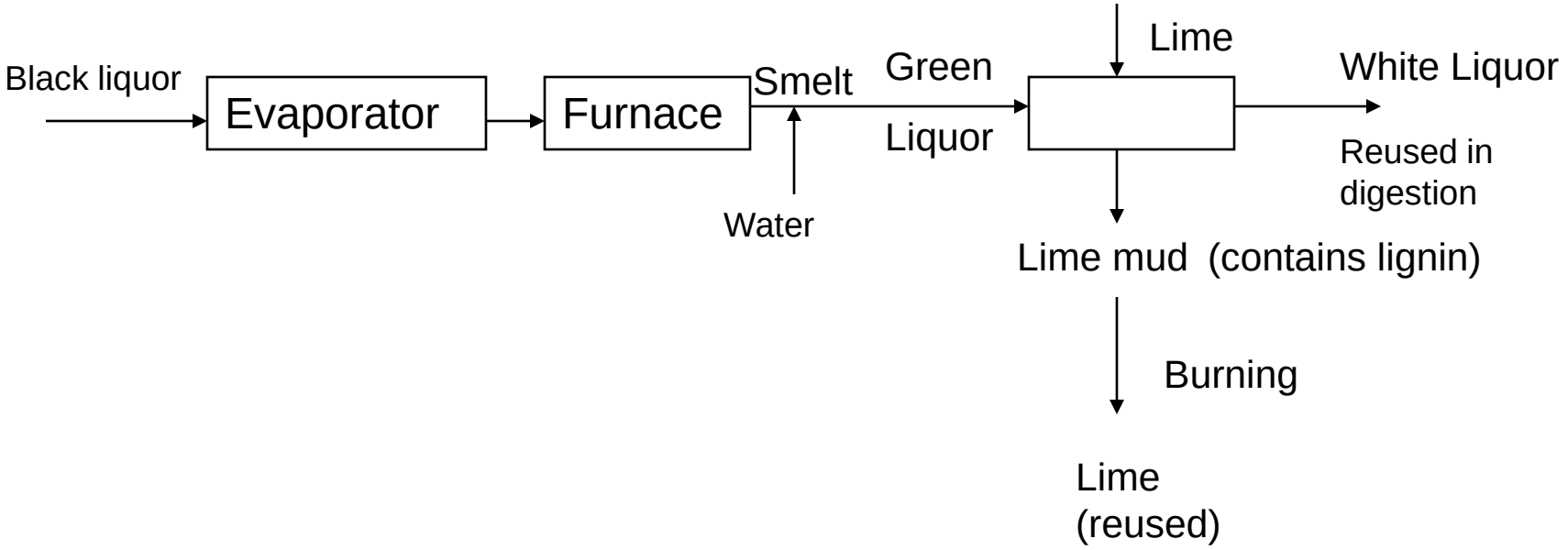
- Beater
  - The pulp is **disintegrated**, and mixed with **various filler materials** such as alum, talc etc. and dyes, in a special tank called as '**beater**'.
  - Beater is designed **to break up the knotted or bunched fibers** and cause a thorough mixing.
  - This is carried out with help of drum with knives attached to its wall and rotation.
- Jordan
  - After beating the pulp is **refined** in a machine known as 'Jordan'.
  - This **cuts the fibers to the final size** desired. (with help of conical drums with knives)

Paper Mill

- Screens
  - The **pulp is then diluted** to proper consistency for paper making and **passed through the screen** to remove lumps or knots.

- Rolls
  - This pulp is carried by traveling belt of fine screen to series of ‘Rolls’ where the paper is produced.
  - The drain water called ‘**white water**’ forms the wastewater from the paper mill section. This contains fine fibers, alum and talc.
  - Usually fibers are recovered and rest liquid is reused for the wet chipping process.

Recovery of chemicals from black liquor



Recovery of chemicals from black liquor

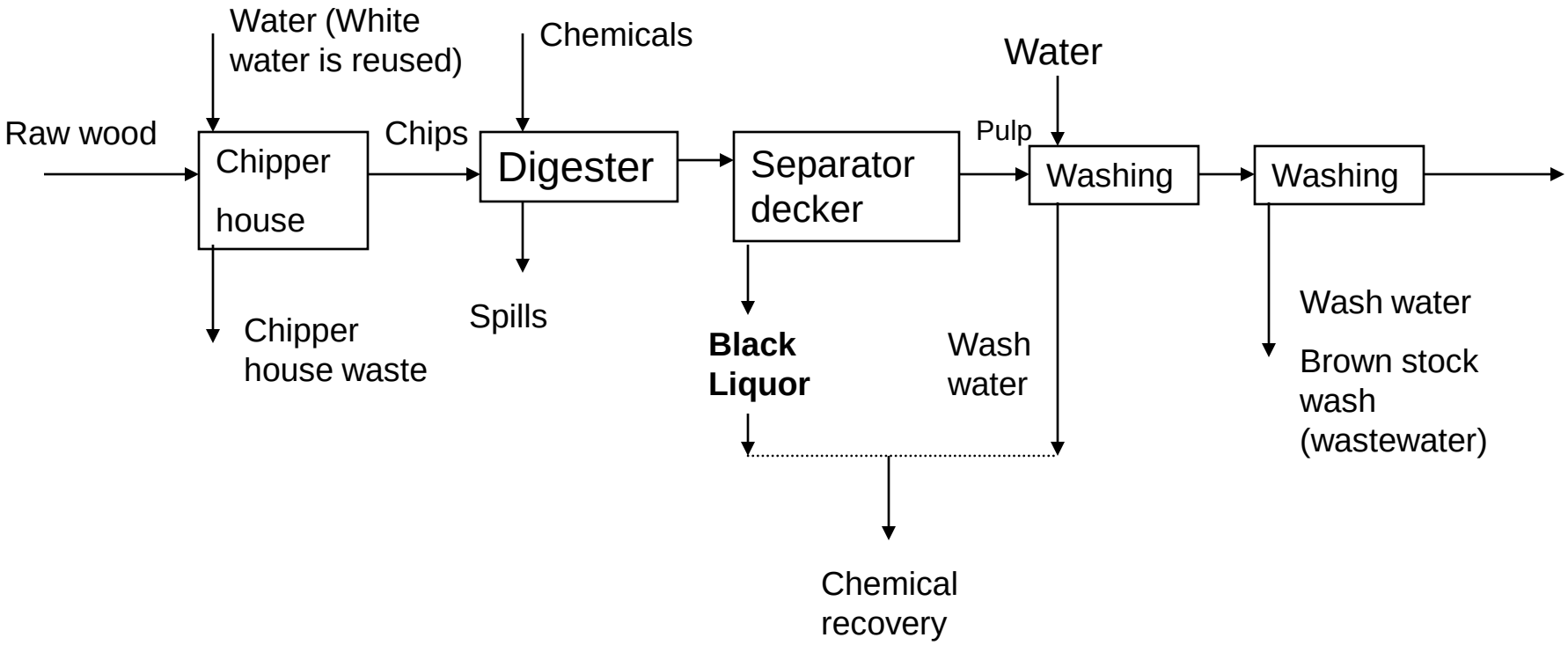
- ‘Black liquor’ from kraft process
  - Concentrated by evaporation and incinerated.
  - The smelt is dissolved in water. This is called as ‘**Green liquor**’.
  - Lime is added to form ‘**white liquor**’ and lime mud
  - White liquor contains desired digestion chemicals and used in digestion.
  - Lime mud is calcined (by burning) to form $Ca(OH)_2$ which is reused in green liquor treatment.
- Small amount of wastewater is generated during wet chipping and bark removal.

- Some **toxic waste material** may develop during chemical recovery from black liquor e.g. Dimethyne Sulphide, Methyl Mercaptan and after condensation form colourless wastewater.

Semichemical pulping

- Use of hard wood for paper manufacturing is increased due to scarcity of soft wood.
- Semi-chemical pulping is used for this hard wood.
- Cooking under **neutral pH with sodium sulphite**
- Some times slightly acidic or basic pH values may be used.
- **This softens the wood but does not fully pulp the wood.**
- Pulping is carried out by mechanical means.
- Used for hard/ coloured packing paper.

Production Process



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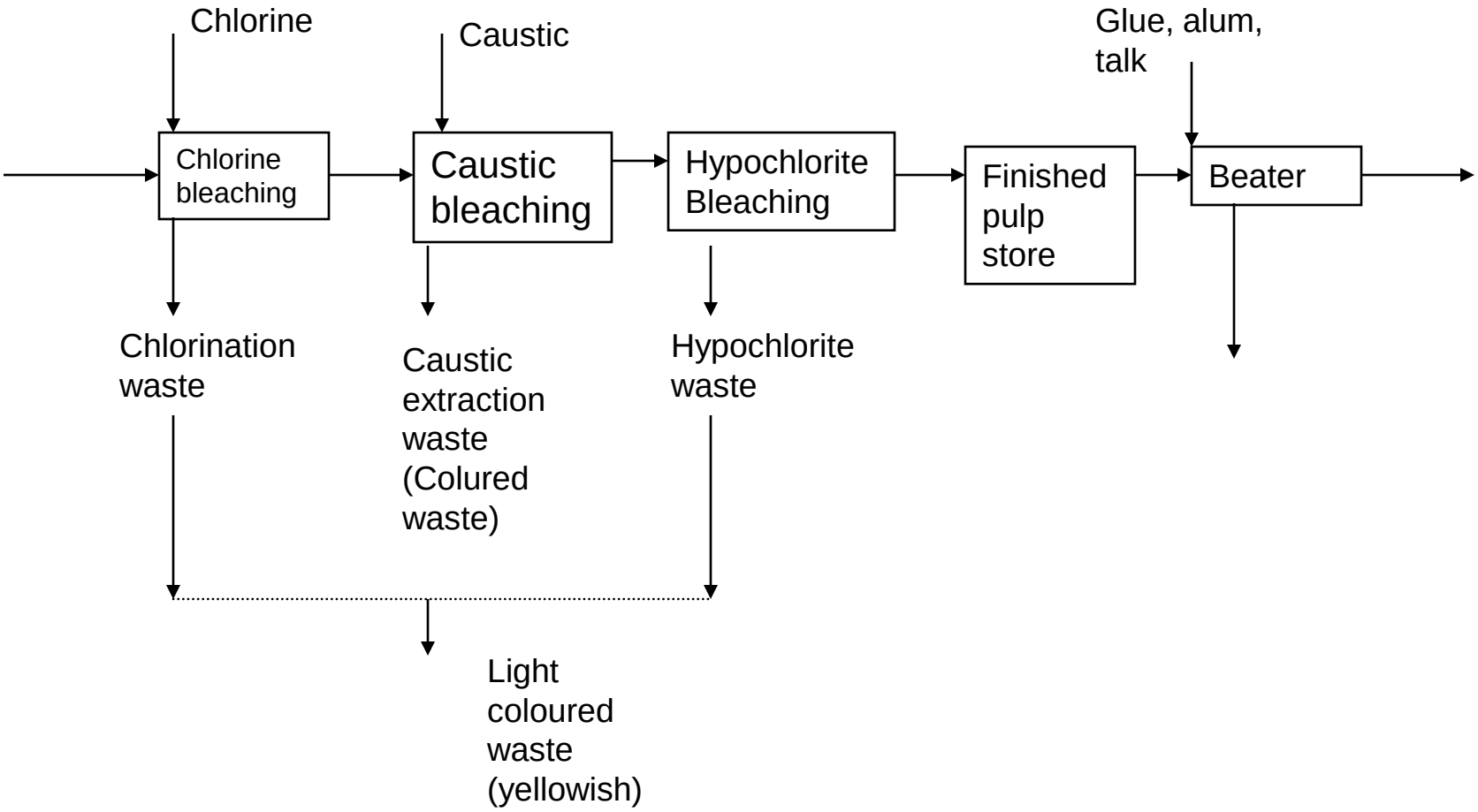

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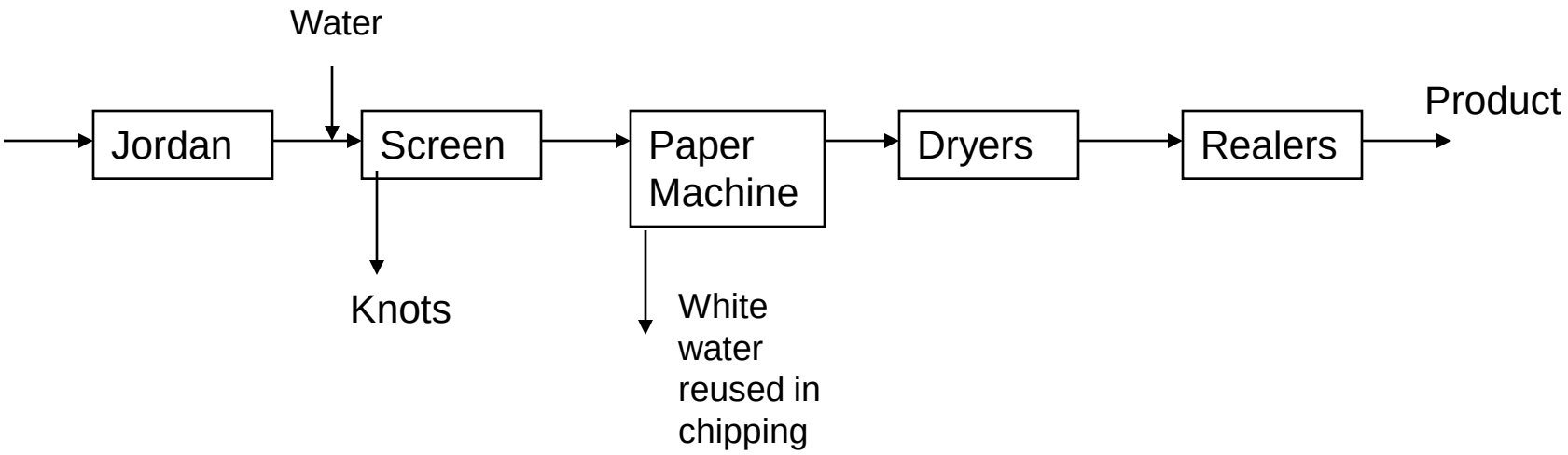


Characteristics of pulp and paper mill wastes

- Volume depends on manufacturing procedure and water economy adopted.
- Most of the Indian pulp mill operates on the Kraft process.
- Waste characteristics depend on size of plant, process used for pulping, and material recovery adopted.
- Chemical recovery is not practiced in small mills due to economic reasons.
- Wastewater is characterized as strong colour, high BOD, high SS high COD/BOD ratio.

Characteristics of the combined effluent

Item	Small mill, 20 tonnes paper per day	Large mill, 2000 tonnes of paper per day	Large mill with chemical recovery
Flow	330 m^3 / t	222 m^3 /t	
Colour	NA	7800 units	(100 -500)
pH	8.2 - 8.5	8.5 – 9.5	7.6 – 9.5
Total Solids, mg/l	NA	4410	800 – 2000
SS, mg/l	900 – 2000	3300	75 – 300
COD, mg/l	3400 – 5780	716	
BOD, mg/l	680 – 1250	155	(100 – 350)
COD/BOD ratio	3.9 – 5.0	4 - 6	

- Low values in large mills are due to chemical recovery from black liquor.
- Also, use of more quantity of water for washing of pulp.

The Effects on Receiving Water

- Pollution is extended to long stretch of river (> 80 km) due to presence of slow decomposing component (lignin).
- **Fine fibers** often clog the water intake screen.
- **Toxic effect** may be induced on aquatic life due to **sulphites and phenols**.
- Deposition of lignino–cellulosic material at discharge point undergo slow decomposition and may lead to DO depletion.
- Normally **not allowed to discharge in sewers** due to strong nature of waste.

Treatment of pulp and paper mill waste

- Pollution load can be reduced by lignin recovery from ‘black liquor’.
- Instead of incineration, where lignin is destroyed
  - Black liquor $\xrightarrow[CO_2 \text{ or } H_2SO_4]{\text{acidification}}$ precipitation of lignin
- Separated lignin
  - Can be used as dispersing agent in various suspension
  - Raw material for polyacrylonitrile fibers
  - Production of activated carbon
- Fibers from ‘white water’ can be recovered by sedimentation or floatation.

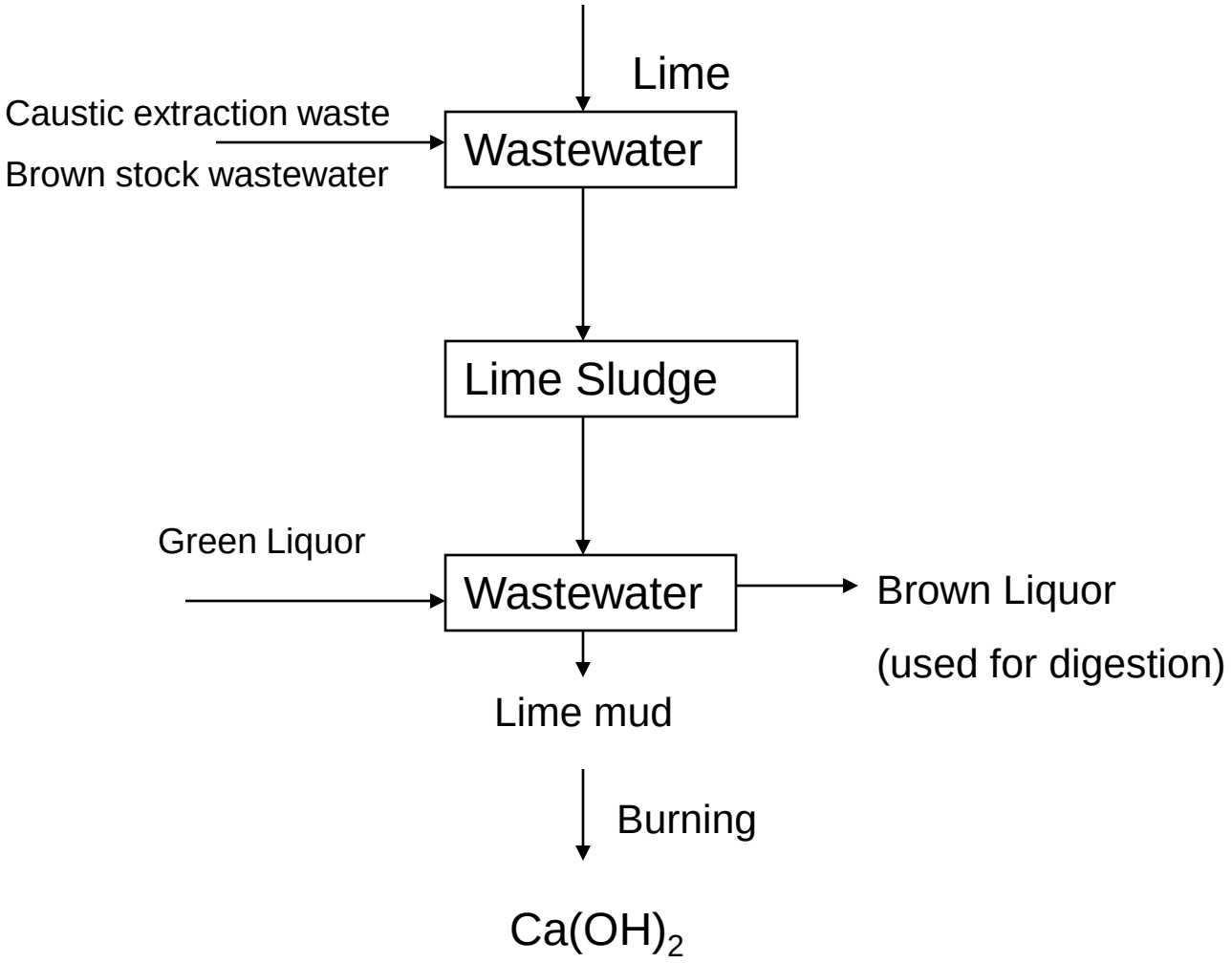
Treatment of pulp and paper mill waste

- **Chemical treatment for colour removal**
  - Chemical coagulation for colour removal is **uneconomical**

- **Massive Lime Treatment:** 90% colour and 40- 60% BOD removal

  - The quantity of lime required for green liquor is allowed to react with coloured waste effluent.
  - The colour is absorbed by the lime, sludge after settling is used for addition to ‘green liquor’ to form white liquor.
  - After treatment it will form dark brown liquor instead of white liquor.
  - This contain desired cooking chemicals and used in digester liquid.
  - The **coloured waste stream can be brown stock + caustic extraction waste** *and* **black liquor**, if no chemical recovery.
  - After digestion, the lignin present in the liquid will be destroyed along with ‘spent black liquor’ during incineration.

Treatment of pulp and paper mill waste



Treatment of pulp and paper mill waste

- **Activated carbon:** can remove 94% colour at pH 3.0

- **Clarification:**
  - 70 – 80 % of suspended solids can be removed from combined waste.
  - BOD reduction is small 25 – 40 %, COD removal 50%.
  - Sludge can be dewatered mechanically.

- **Biological Treatment:**

  - Both conventional and low cost treatment methods can be used

  - Some are even effective in colour removal.

Treatment of pulp and paper mill waste

- **Waste stabilization pond:** 0.9 – 1.5 m depth, DT = 12 to 30 days, 85% BOD removal.
- **Aerated lagoon:** DT = 3 to 20 days up to 95% BOD reduction. At loading 670 to 1340 kg BOD / hectare. Day.
- Nitrogen and phosphorous addition may be necessary for biological treatment.
- **Anaerobic lagoon:** DT= 6 – 20 days, 0.05 to 0.02 kg BOD/m^3.d; 70 to 77 % BOD removal
- **Activated sludge process:**
  - Most effective, surface aerator works better than diffuser due to problem of clogging.
  - 80 to 90% BOD removal (F/M = 0.2 to 0.3); DT = 3 – 9 hr. N & P addition is necessary.
- Trickling filter has limited use due to clogging of filter bed by fibers.

Treatment of pulp and paper mill waste