

### 33 PULP AND PAPER MILLS

#### Processes

A number of processes, grouped by type as **mechanical**, **chemical**, and **semi-chemical** (or **hybrid**), are used in the preparation of wood pulp. In 1990 (according to Lockwood's Directory) the distribution of pulp mills in Ontario and Quebec was as follows:

	Process Type				Total
	Chemical Processes		Semi-chemical	Mechanical	
	Kraft	Sulphite			
Ontario	9	4	2	15	30
Quebec	10	8	2	41	61

Figure 22.1: Number of pulp mills by type in Ontario and Quebec

In chemical pulping, the wood chips are cooked, using heat and a chemical solution that depends on the type of process being used. The lignin binder, a natural glue that holds the wood cells (fibres) together, is dissolved.

The two common forms of chemical pulping are  
 1) the dominant "alkaline" or "kraft" process, and  
 2) the "acid pulping" or "sulphite" process.

Acid pulping has generally declined but is still in use. The digester liquor is a solution of sulphurous acid,  $H_2SO_3$ , mixed with lime (CaO) or other base (magnesium, sodium, or ammonium) to form bisulphites.

Mechanical processes produce the highest yield from the wood, but have high energy demands. Mechanical pulping generally incorporates thermal or chemical pre-softening of the wood chips, resulting in lower energy requirements.

Some chemical processes include mechanical features. The division is not distinct and is generally based on efficiency of production from dry wood.

Figure 22.2 provides a flow diagram for a semi-chemical pulp mill.

Of the **chemical processes**, alkaline pulping – the kraft or sulphite process – is the most common and is shown in Figure 22.3.

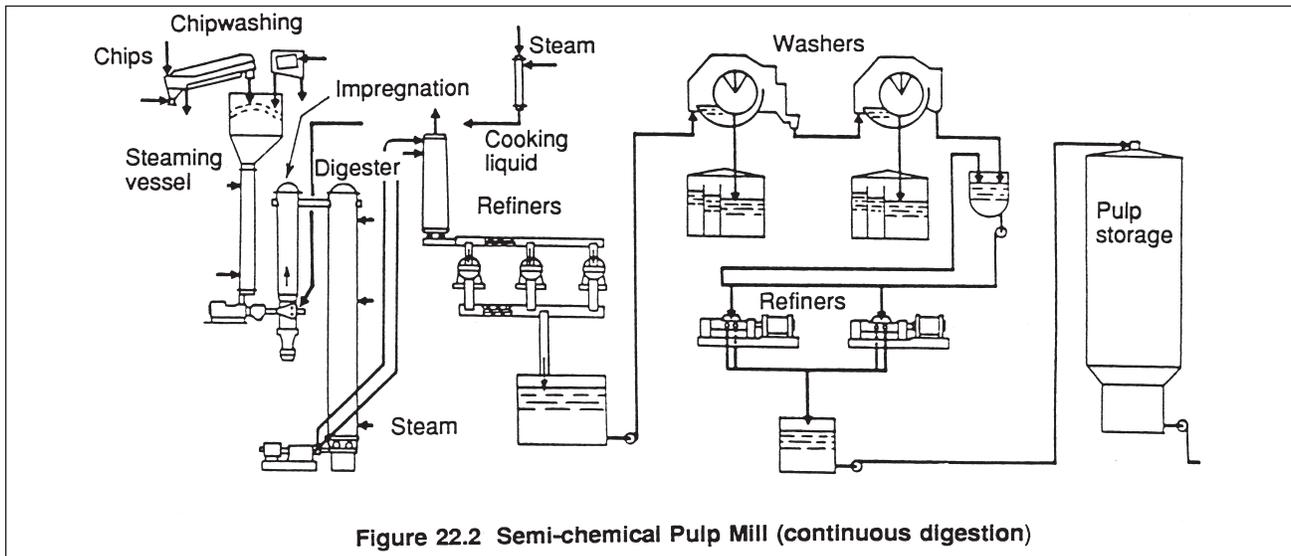


Figure 22.2 Semi-chemical Pulp Mill (continuous digestion)

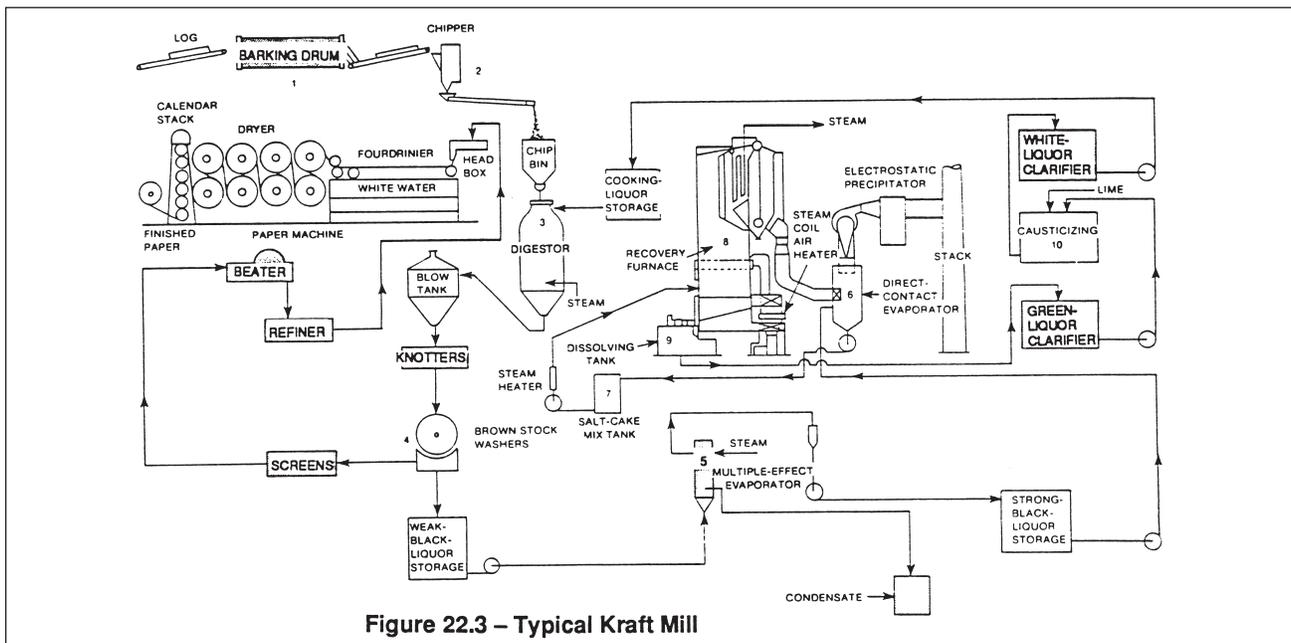


Figure 22.3 – Typical Kraft Mill

## Kraft Process

The kraft process consists of three principal operations:

- 1) cooking and washing
- 2) evaporation and alkali recovery
- 3) causticizing and lime recovery.

Following debarking and chipping, the chipped wood is "cooked" or digested with steam at a pressure of approximately 150 psig (1034.1 kPa) in the digester with a solution of sodium hydroxide (NaOH) and sodium sulphide (NaS<sub>2</sub>) known as white liquor. After cooking for about six hours, the lignin binder is dissolved and the cellulose fibres, now called pulp or "brown stock," are separated from the spent cooking liquor (black liquor) in the pulp washers. The kraft process is associated with strong-smelling gases – organic sulphides – which are an environmental concern.

The dilute or "weak" black liquor (10-15% solids) comes from the washers. After concentration by removal of water in the multiple-effect evaporator using steam, the resulting "heavy" black liquor usually goes through further concentration in a direct-contact evaporator.

The concentrated black liquor then goes to the mix tank where the sodium sulphate (salt cake) is mixed with the liquor to make up the chemical losses in the system. The "heavy" black liquor (60-70% solids), with its salt cake burden, is heated to lower its viscosity and pumped to the recovery furnace where it is sprayed on the walls for dehydration prior to final combustion of the dried "char" on the hearth. Sodium sulphate dust in the boiler gases is removed by an electrostatic precipitator.

The intense heat in the furnace fuses the inorganic elements of the black liquor (mainly sodium carbonate and sodium sulphide) to form what is known as smelt. The smelt is tapped from the furnace and runs into a dissolving tank where it is mixed with water to form "green liquor."

Carbon and other impurities in the green liquor are settled out in a clarifier, filtered, and sent to landfill. The clarified green liquor is subjected to a causticizing treatment with hot lime, Ca(OH)<sub>2</sub>, in a lime slaker to convert sodium carbonate into sodium hydroxide. The insoluble calcium carbonate mud produced is settled out and reused. The resulting sodium of sodium hydroxide and sodium sulphide, now called "white liquor", is reused as cooking liquor for the wood chips in the digester.

The bleaching of brown pulp to white pulp is usually accomplished with chlorine, followed by extraction with sodium hydroxide, then calcium or sodium hypochlorite, and finally a chlorine dioxide treatment.

## Hazards

Maintenance work in operating pulp and paper mills can present a number of special hazards to construction workers. In addition to the trade hazards associated with what is commonly encountered in new construction, there are other hazards:

- 1) hazardous process chemicals
- 2) piping systems
- 3) heat

- 4) noise
- 5) pinchpoints and moving equipment.

The following information is provided to help construction crews recognize, assess, and control these hazards in pulp and paper mills.

### 1) Hazardous Process Chemicals

#### General

Of the many different hazardous chemicals used, most are found in the parts of the mill that digest or break down the wood fibres. The cooking liquors described above (white liquor, green liquor, and black liquor) all tend to be very corrosive and may contain several different toxic or hazardous ingredients.

Extreme precautions should be taken when working in tanks or vessels used for these liquors or when working on related piping. Hazardous chemicals may be encountered in storage tanks, process piping, process equipment, waste handling systems, and environmental control systems.

In addition to these "contained" sources, some processes may emit gases, vapours, or dusts that may be hazardous. Always be aware of potential emissions or leaks from adjacent operating or apparently isolated equipment or storage facilities.

Harmful residues may also be left as potential exposures to maintenance and construction personnel. Extreme precautions should be taken when working in tanks or vessels. During maintenance or repair operations inside production equipment, confined space procedures must be established and followed strictly.

#### Process Exposures

Following are some of the potential exposures from various parts of the process.

#### Digester

Potential exposures include organic sulphur compounds, primarily methyl mercaptan, ethyl mercaptan, dimethyl sulphide and dimethyldisulphide, in addition to hydrogen sulphide and sulphur dioxide.

#### Evaporator and Recovery

Evaporators are sources of hydrogen sulphide and sulphur dioxide and require precautions, especially during maintenance. When they become plugged, precautions must be taken while cleaning them with nitric acid solutions. Repair and maintenance around digesters, evaporators, and furnaces also offer potential exposure to caustic liquors and asbestos. Air emissions associated with recovery boilers contain sulphur dioxide, sodium sulphate particulate, and salt cake (basically a nuisance dust). Duct systems, electrostatic precipitators for particulates, and wet scrubbers for SO<sub>2</sub> require appropriate precautions during repairs.

#### Causticizing and Lime Recovery

In addition to exposure to caustics, potential exposures include calcium oxide (quicklime) and calcium hydroxide dusts, particularly during cleanups.

#### Bleaching

Potential exposures include chlorine and chlorine dioxide

(ClO<sub>2</sub>) which is a severe pulmonary irritant even at low concentrations – usually encountered only during upsets or leaks.

**Paper Machines**

Potential exposures include dusts from cleaners, slimicides, pH control chemicals, and off-gassing of formaldehyde and ammonia.

**Specific Process Chemical Hazards**

Although the kraft, or alkaline, process is the most common, there are other pulping processes. The sulphite process involves acid cooking in which the digester liquor is a solution of sulphurous acid mixed with lime or other

base to form bisulphites.

Figure 22.4 lists some of the major chemicals used or encountered in different processes. It is not intended as a comprehensive reference to all of the major chemicals or intermediate chemicals used in pulp and paper mills. The precise chemicals, quantities, and processes may vary from one facility to another.

Construction crews should obtain and review the Material Safety Data Sheets (MSDSs) for these and other hazardous materials in use at the plant where work is scheduled to take place. MSDSs should be readily available from the client/operator of the mill.

Figure 22.4: Hazardous Process Chemicals in Pulp Processing

Chemical	Uses and Characteristics	Hazards
Acids: • sulphurous (H <sub>2</sub> SO <sub>3</sub> ) • sulphuric (H <sub>2</sub> SO <sub>4</sub> ) • nitric (HNO <sub>3</sub> )	<ul style="list-style-type: none"> <li>• in sulphite cooking liquor</li> <li>• clear &amp; oily, biting acrid odour</li> <li>• used in cleaning evaporators</li> <li>• yellow colour, biting acrid odour</li> </ul>	<ul style="list-style-type: none"> <li>• reactive and corrosive</li> <li>• dehydrates skin, causes reddening, skin then turns black</li> <li>• severe burns – turns skin yellow.</li> </ul>
Ammonia	<ul style="list-style-type: none"> <li>• used to digest pulp in some processes</li> </ul>	<ul style="list-style-type: none"> <li>• very irritating to eyes, nose and throat</li> <li>• overexposure can cause choking and difficulty in breathing</li> </ul>
Black liquor	<ul style="list-style-type: none"> <li>• liquid alkali, thick and slippery like molasses when concentrated</li> <li>• in weaker concentrations is a brown-to-black, watery liquid</li> <li>• slightly sickening smell, with odour of sulphides</li> </ul>	<ul style="list-style-type: none"> <li>• corrosive burns</li> <li>• reddening of skin, burning sensation</li> </ul>
Calcium bisulphite	<ul style="list-style-type: none"> <li>• used in cooking pulp in the "sulphite process"</li> </ul>	<ul style="list-style-type: none"> <li>• primarily a skin irritant</li> <li>• corrosive</li> </ul>
Calcium sulphate	<ul style="list-style-type: none"> <li>• used in finishing stages to impart special properties to paper</li> </ul>	<ul style="list-style-type: none"> <li>• nuisance dust</li> <li>• non-corrosive</li> </ul>
Caustic soda	see <b>sodium hydroxide</b>	
Calcium oxide (CaO)	see <b>lime</b>	
Chlorine (Cl <sub>2</sub> )	<ul style="list-style-type: none"> <li>• toxic gas with characteristic acrid odour, like bleach, sweet-tasting</li> <li>• used in bleaching pulp</li> <li>• gasifies immediately on contact with air</li> <li>• yellow-green coloured gas-cloud</li> </ul>	<ul style="list-style-type: none"> <li>• acute exposures cause irritation, stinging of eyes, nose and throat</li> <li>• exposure causes coughing, chest pain, and difficulty in breathing</li> <li>• overexposure can be fatal</li> <li>• delayed acute response to overexposure is fluid build-up in the lungs</li> </ul>
Chlorine dioxide (ClO <sub>2</sub> )	<ul style="list-style-type: none"> <li>• produced on site and used in the bleaching process dissolved in water</li> <li>• liquid - yellow, green colour</li> <li>• biting, acrid odour like bleach, releases ClO<sub>2</sub> gas</li> </ul>	<ul style="list-style-type: none"> <li>• the gas is a severe pulmonary irritant even at low concentrations</li> <li>• choking sensation, followed by coughing and, in heavy concentrations, nausea and insensibility</li> <li>• skin burns on contact, reddening of the skin</li> </ul>
Green liquor	<ul style="list-style-type: none"> <li>• alkali</li> <li>• green colour, no odour</li> <li>• slippery or soapy feeling</li> </ul>	<ul style="list-style-type: none"> <li>• corrosive burns - less corrosive than white liquor, but is scalding hot when handled in the plant</li> <li>• reddening of skin, burning sensation</li> </ul>
Hydrogen peroxide (H <sub>2</sub> O <sub>2</sub> )	<ul style="list-style-type: none"> <li>• liquid, clear and colourless</li> <li>• slight pungent odour</li> </ul>	<ul style="list-style-type: none"> <li>• strong oxidizer, will react with organic materials and cause fire</li> <li>• concentrations: mild 3-5%-no danger; moderate 6-10%-minor burns, eye damage; medium 10-50%-minor burns, eye damage; high over 70%-major burns</li> <li>• explosion risk if mixed with strong acids or caustics</li> </ul>
Hydrogen sulphide (H <sub>2</sub> S)	<ul style="list-style-type: none"> <li>• colourless, toxic gas, byproducts</li> <li>• rotten-egg odour at low concentrations</li> <li>• biting acrid odour</li> </ul>	<ul style="list-style-type: none"> <li>• rotten egg smell at very low concentrations (below 100 ppm)</li> <li>• as concentration rises, the sense of smell is rapidly deadened</li> <li>• nausea, dizziness, and disorientation</li> <li>• toxic gas: 500-700 ppm can be instantly fatal</li> <li>• explosive at high concentrations</li> </ul>

<b>Chemical</b>	<b>Uses and Characteristics</b>	<b>Hazards</b>
Lime: • quicklime, calcium oxide (CaO) • slaked lime, calcium hydroxide(Ca(OH) <sub>2</sub> )	• white powder • used in sulphite pulping	• corrosive, alkali burns • dehydrates skin
Methanol (CH <sub>3</sub> OH)	• methyl alcohol or wood alcohol • colourless • when pure, has slight alcoholic odour; other grades have oily odour	• harmful to inhale vapour, or to allow repeated or prolonged skin contact • affects central nervous system; signs of poisoning include headache, nausea, vomiting, aimless erratic movement, and dilated pupils • flammable liquid and vapour-air mixture can be explosive
Methyl mercaptan (CH <sub>3</sub> SH)	• colourless gas	• irritant causing watering of eyes and nose • headaches and nausea • high concentrations can be fatal
Sodium Carbonate, soda ash: (Na <sub>2</sub> CO <sub>3</sub> )	• used in some processes to digest pulp	• primarily irritates eye, nose, throat • corrosive
Sodium Chlorate (NaClO <sub>3</sub> )	• used in some bleaching processes • liquid – normally clear, colourless, odourless • in white crystalline form when dry • used or found in some bleaching processes	• harmless when wet, <b>except</b> when in contact with acid – then a <b>violent flammable reaction</b> • irritating to eyes nose and throat • when sodium chlorate solutions dry to crystals, the dry form is very unstable and can be ignited by spark or friction. Fire cannot be put out by water except by total immersion
Sodium Hypochlorite	• used in bleaching processes	• dust may cause irritation of eyes nose and throat • contact with water can release chlorine gas
Sodium Hydroxide <b>Caustic Soda</b> or Lye - (NaOH)	• used in digesting pulp • slippery or soapy to touch on skin • clear to milky white, odourless	• very corrosive material, can cause chemical burns on exposed skin • can cause irritation of skin, eyes, nose and throat • overexposure to mists or dusts containing sodium hydroxide can lead to fluid build-up in the lungs
Sodium Sulphate (Na <sub>2</sub> SO <sub>4</sub> )	• make-up chemical for cooking liquor	• minor irritation of eyes, nose and throat possible • low toxicity based on animal studies • reacts dangerously when melted with aluminum
Sodium Sulphide (NaS <sub>2</sub> )	• component of white liquor used in digesting (cooking) pulp in the kraft process	• inhalation of dust can cause irritation of nose, throat and lungs • corrosive – can cause skin burns • may react with moisture to release hydrogen sulphide gas • repeated skin contact may cause allergic skin reaction
Sulphur (S)	• yellow solid • used in some processes to produce sulphur dioxide gas, which is used in digesting pulp	• burns to produce sulphur dioxide
Sulphur Dioxide (SO <sub>2</sub> )	• used in digesting pulp • clear and colourless gas, biting acrid odour	• very irritating gas: causes irritation of eyes, nose and throat • exposure can cause choking and difficulty in breathing • delayed response to overexposure can result in fluid build-up in the lungs
White liquor	• alkali • golden colour, no odour • slippery or soapy feeling	• corrosive burns • reddening of skin, burning sensation, like caustic but at a higher temperature

**2) Piping Systems**

The contents of piping systems, storage bins, or other components should be determined. If clearly worded content labels do not exist, WHMIS regulations require that some other warning system be in place. This may vary from one facility to another. For example, one plant may use a coded number system; another may use colour coding or symbols. Construction crews working in these facilities must become familiar with the warning system in use.

**MSDSs**

MSDSs for materials that may be encountered should be reviewed with the crew to ensure that everyone is aware of the location and nature of the hazard(s).

**Confined Spaces**

Entry into vats, maintenance holes, or other enclosed work spaces must be done in accordance with the regulations for confined spaces (refer to the chapter on Confined Spaces in this manual). Requirements include

testing atmospheres for toxic or explosive conditions as well as oxygen deficiency or excess.

### **Leaks**

When working on pumps, pipes, or valves where there is a danger from squirting liquids, always follow three precautions:

- 1) wear goggles, a face shield, or both
- 2) have a hose immediately available to deliver water for immersion
- 3) know the location of the nearest emergency shower and eyewash station.

### **Emergency Systems**

In addition, construction crews in pulp and paper mills should be made aware of any emergency procedures that are in place. For example, the plant may have some kind of alarm system to warn people of a gas leak or process problem. If there is an evacuation plan involving special assembly areas or the use of self-rescue equipment such as respirators, these precautions must be fully explained to all construction workers at the project.

### **Pressurized Systems**

Construction crews must ensure that work on process piping or other components is done with the system de-energized. Many processes rely on pressurized feed lines or may have pressure vessels in the process system. All components should be brought to atmospheric pressure before attempting to disconnect or open them. Contents must be determined beforehand, since some of the process materials or byproducts can be very toxic or very corrosive. Small leaks under pressure can present serious health and safety hazards.

### **3) Heat**

Heat is used or generated in many parts of pulp and paper mills. Refer to the chapter on Heat Stress in this manual.

### **4) Noise**

Noise is a hazard inherent in many pulp and paper mills. In many cases, the ambient noise level may require the wearing of earmuffs and/or ear plugs. The noise hazard should be identified by warning signs in the facility. Additional noise sources from tools and equipment used by the construction or maintenance crew will increase the total noise exposure. Hearing protection is advised for all trades working under these conditions.

### **5) Pinch Points and Moving Equipment**

Conveyors, rollers, and other pieces of moving machinery present common hazards in pulp and paper mills. Wherever possible, de-energize systems before working on components with moving parts.

Exposed pinch points should be guarded. Where permanent guards have been removed in order to carry out repairs or modifications, temporary guards should be installed during the work. All permanent guards must be replaced after completion.

In high traffic areas, where plant personnel are moving equipment or where construction equipment may endanger plant personnel, use signallers or lane barricades to keep people away from moving equipment.