

# Chemical Pulp Mills

Pulping is the term used for the process which separates wood fibers. Chemical pulping, dissolving the lignin in the wood to create a pulp, is the most commonly used pulping process. Chemical pulping creates higher sheet strength than mechanical pulping; however, yields 40 to 50 percent pulp, where mechanical pulping yields 95 percent pulp.

The two main types of chemical pulping are the more common sulfate pulping (most commonly known as Kraft pulping) and sulfite pulping. Kraft pulping accommodates a variety of tree species, recovers and reuses all pulping chemicals, and creates a paper with a higher sheet strength. Sulfite pulp, however, is easier to bleach, yields more bleached pulp, and is easier to refine for papermaking. The major difference between the two types of chemical pulping is the types of chemicals used to dissolve the lignin. This report will focus mainly on these two types of chemical pulping and bleach plants.

Pulp mills are one of the largest emission sources in Washington and a large toxic pollutant emission producer. There are eight pulp mills in Washington: six Kraft (sulfate) mills and two sulfite mills (one sulfite mill has recently closed).

EPA formally adopted MACT in April 1998 for certain pulping processes. Sources will have between 3 and 8 years to come into compliance with the provisions of the MACT. Emissions estimations made after MACT has become effective should be sure to take emissions limitations due to MACT into account. The MACT provisions are found in Part 63, Subpart S, sections 63.440 - 63.459 of the Code of Federal Regulations. MACT requirements for combustion sources at pulp and paper mills will be subject to a separate MACT.

## Kraft (Sulfate) Pulping

The Kraft process was developed in Germany in 1879 and was first applied to a Swedish mill in 1885. The resulting paper was much stronger than any paper previously made, and therefore the process was named “Kraft”, (German and Swedish for “strength”). (MacDonald, 349) Kraft pulping creates dark brown paper which is used for boxes, paper bags, and wrapping paper. Kraft pulp can also be used for writing paper and paperboard when bleached, and for diapers when fluffed.

The three main steps involved in Kraft pulping are:

1. Digestion: wood chips are cooked
2. Washing: black liquor is separated from the pulp
3. Chemical recovery: chemicals are recovered from the black liquor for reuse

Turpentine and tall oil may also be recovered for use or resale. This process is covered briefly in the Digestion section.

## Description of Process

### 1. Digestion

The first step in pulping wood is to “cook” the wood chips. A digester, heated by steam, “cooks” the wood chips in *white liquor* (a mix of sodium hydroxide (NaOH) and sodium sulfide (Na<sub>2</sub>S)) until done. The cooking process dissolves most of the *lignin*<sup>1</sup> and only some of the *hemicellulose*<sup>2</sup>, leaving mostly *cellulose*<sup>3</sup> to hold the fibers together. The digester system may be a batch or a continuous process.

Relief gases are vented continuously from the digester, which helps remove air and other non-condensable gases and reduce the pressure at blow, when the pulp is discharged to the blow tank. After the cooking process, the pulp and *black liquor* (the chemical mix left after the cooking process) are discharged to a blow tank.

By-products can be recovered from the digestion process. For example, turpentine distills with water out of the blow tank and the evaporators and is separated to be used. The resin acids and fatty acids dissolved from the wood form sodium soaps which are skimmed off the black liquor from storage tanks, evaporators, and black liquor oxidation tanks, and then acidified with sulfuric acid to form tall oil.

Before the washing process, the pulp is usually sent to deknotters, screens used to remove knots (large pieces of fiber not completely broken down in the digester).

### 2. Brownstock Washing

Pulp from the blow tank and deknotter is washed with water in a process commonly called *brownstock washing*. Washing removes weak black liquor from the pulp which is sent to the chemical recovery process. This also prevents contamination during subsequent processing steps. Types of washers used include rotary vacuum washer (most common type of washer), diffusion washers, rotary pressure washers, horizontal belt washers, wash press, and dilution/extraction.

All the washer types use water (fresh or recycled) and are usually placed in series to achieve higher removal efficiency.

The rinsed pulp is screened for oversize particles and then excess water is removed. This is done in a gravity thickener (more commonly known as a *decker*).

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<sup>1</sup> “Lignin are essentially substituted phenylpropane three-dimensional polymers with the phenylpropane units held together by ether and carbon-carbon bonds.” (MacDonald, 36) Lignin makes up 20-35 percent of the wood substance and holds the wood fibers together, giving the wood rigidity.

<sup>2</sup> *Cellulose* and *hemicellulose* are polysaccharides, which make up 60-80 percent of the wood substance. Polysaccharides are high molecular weight carbohydrates. Cellulose is the major component of polysaccharides and is alkali resistant, therefore it is resistant to Kraft chemicals. Hemicellulose is the other portion of polysaccharides and can be dissolved by alkali.

<sup>3</sup> See footnote 2.

### 3. Chemical Recovery

The reason Kraft pulping is economically successful is that the used cooking liquor can be recovered and reused in the chemical recovery process.

The first step in recovering the chemicals from the black liquor is evaporation. This removes excess water from the black liquor and maximizes the fuel value for the recovery furnace.

There are two types of evaporators generally used in the chemical recovery process: direct (DCE) and indirect (NDCE) contact evaporators. Some types of DCE include the multiple-effect evaporator (most common), flash evaporation and thermocompressor evaporation. DCE use heat from direct contact with the recovery furnace flue gases, while NDCE uses indirect contact.

Black liquor oxidation is needed after DCE, but not after NDCE. After DCE, the black liquor is normally oxidized with air to control the sulfide level and prevent the release of odorous compounds. This is done by countercurrently passing the black liquor through an air stream using a porous diffuser, sieve tray tower, packed tower or agitated air sparge. The oxidation reaction converts sodium sulfide ( $\text{Na}_2\text{S}$ ) to sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3$ ).



After NDCE or black liquor oxidation, the black liquor is then forced through spray nozzles into the recovery furnace, where it is burned providing heat to generate steam. This also conserves the inorganic chemicals, which create a molten smelt on the floor of the furnace.

The molten smelt, composed of sodium sulfide and sodium carbonate, is drained from the recovery furnace hearth through smelt spouts. In a smelt dissolving tank, the smelt is quenched with water, producing *green liquor*.

Sodium carbonate from the smelt is then converted to sodium hydroxide in the causticizer by adding calcium hydroxide. The calcium carbonate resulting from the reaction precipitates from the solution and is collected and sent to the lime kiln where it is converted to lime (calcium oxide). The calcium oxide is then slaked to produce calcium hydroxide for reuse in the causticizer.

## Methods of Determining Emissions

### 1. Digestion

Relief gases from the digestion process are usually treated by incineration. The emissions are affected by temperature, moisture content, flow rate and variability, sulfur gas and organic material concentrations, and flammability limits.

Gases from the blow tank are typically controlled using either a direct contact or surface condenser. Emissions are mainly affected by the frequency of blow. Batch digesters have higher emissions since the gases are released in surges rather than continuously, making the gas volume larger and harder to control. Major toxic emissions from blow tanks are methanol, acetone, and methyl mercaptan (*AP-42*<sup>4</sup>).

Tall oil recovery vents for continuous and batch systems are typically controlled by a white liquor scrubber.

Deknotter emissions are affected by residence time and the exposure of pulp to air. The major toxic emission from the deknotters is methanol. (*AP-42*).

Mill-specific source tests should be used where available, as there are no toxic emissions information available from *NCASI* and only hydrogen sulfide emission factors from *AP-42* for this source. *AP-42* provides information on particulate, sulfur dioxide, and carbon monoxide emissions.

### 2. Brownstock Washing

In the washing process, toxic emissions volatilize from the pulp and black liquor. Brownstock washers are typically controlled by incineration because the gas stream is small and incineration is most practical. Emissions mainly depend on the pulp production and type of digestion (batch or continuous). Different washer types will also affect the emissions depending on their contact with air, as enclosures vary. The largest toxic emissions from brownstock washers are from methanol, acetone, and acetaldehyde (*NCASI*).

Emissions from the decker hood vents and screens may be affected by residence time, air exposure, and equipment design and age. Fugitive toxic emissions from these sources include acetone, dimethyl disulfide, methyl mercaptan, methanol, ethanol, o-cresol and dimethyl sulfide (*AP-42* and *NCASI*).

Mill-specific source tests should be used where available. Toxic emission factors are available from *NCASI*<sup>i</sup> for these sources.

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<sup>4</sup> U.S. Environmental Protection Agency, *Compilation of Air Pollutant Emissions Factors Volume 1: Stationary Point and Area Sources*, Fifth Edition with Supplements, October 1997, Document No. AP-42.

## Chemical Recovery

DCE have higher emissions than NDCE due to direct contact of flue gases with liquor. Controls include condensation, liquid scrubbing, and thermal oxidation. Factors affecting the emissions are black liquor quality, chemicals used, evaporator design, temperature, moisture content, flow rate and variability, and flammability limits. Toxic emissions from an evaporator include methanol, acetone, dimethyl disulfide, dimethyl sulfide, and methyl mercaptan (*AP-42*).

Gaseous emissions from black liquor oxidation are controlled by incineration. Emissions are affected by liquor type (weak or strong), and oxidation contacting method and efficiency. Toxic emissions include methanol and acetone (*AP-42*).

Recovery furnaces are typically controlled by either wet bottom or dry bottom electrostatic precipitators, sometimes followed by a wet scrubber. Emissions are affected by precipitator design and combustion conditions. Trace metal emissions are dependent on the type of wood pulped and also the intensity of combustion (indirectly the temperature) and particulate collection efficiency. Toxic emissions from a recovery furnace include methanol, hydrochloric acid, dioxins and furans, metals, chloromethane, trichlorofluoromethane, acetaldehyde, and acetone (*AP-42* and *NCASI*).

Particulate control devices on smelt tanks are usually mist eliminators (demisters) that may be used in combination with a spray or packed tower scrubber. Alternate control devices include venturi scrubbers, cyclone spray scrubbers, or packed tower scrubbers. Smelt tank organic compound emissions are affected by the quality of the water used for dissolving the smelt, the quality of the vent gas scrubbing medium, and the residence time in the tank. Toxic emissions include methanol, formaldehyde, valeraldehyde, acetaldehyde, ammonia, dimethyl disulfide, dimethyl sulfide, and methyl mercaptan (*AP-42*). The largest toxic emissions from a smelt tank are methanol, formaldehyde, valeraldehyde, acetaldehyde, and methyl mercaptan (*NCASI*).

Lime kilns are most commonly controlled by wet scrubbers (venturi scrubbers) but can also be controlled by mist eliminators and/or electrostatic precipitators. Lime kiln emissions may be affected by concentration of organic constituents in the scrubbing medium is perhaps the most important factor. The level of organics in water or condensate used for lime mud washing, the fossil fuel combusted, and the efficiency of combustion also contribute to emission levels. The toxic emissions include naphthalene, methanol, formaldehyde, acetone, dimethyl disulfide, dimethyl sulfide, and methyl mercaptan (*NCASI*).

Mill-specific source tests should be used where available. Toxic emission factors are available from *NCASI*<sup>ii</sup> for these sources.

## Sulfite Pulping

The concept of sulfite pulping was created in the United States in 1867, however it was not used in a mill until 1874 by a Swedish chemist who was probably unaware of the U.S. Patent (MacDonald, 277). Sulfite pulping produces a lighter pulp than Kraft pulping. It can be used for newsprint, and when bleached can be used for writing papers and for the manufacture of viscose rayon, acetate filaments and films, and cellophane.

### Description of Process

Sulfite pulping follows many of the same steps as Kraft pulping. The major difference in sulfite pulping is that the digester “cooks” with a mixture of  $\text{H}_2\text{SO}_3$  (sulfurous acid) and  $\text{HSO}_3^-$  (bisulfite ion in the form of calcium, magnesium, sodium, or ammonium bisulfate). The pulp continues on through the same processes as in the Kraft pulping process.

However, the chemicals separated from the pulp in the washers may or may not go into a recovery process. Chemical recovery in sulfite pulping is practiced only if it is economical. If chemical recovery does occur the liquor goes through an evaporator and then to a recovery furnace. Here, smelt is not formed, but ash and  $\text{SO}_2$  are formed.

### Method of Determining Emissions

Sulfite mill emissions depend on the base used in the digestion ( $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{NH}_4\text{OH}$ ,  $\text{NaOH}$ ), the pH level, and the design of the digester. For calcium-based mills, particulate emissions are controlled by cyclone dust separation system and gaseous emissions are controlled by scrubbing with  $\text{CaO}$  or  $\text{CaCO}_3$  slurry. Magnesium-based mills are controlled by a chemical recovery system. Cyclones and scrubbers separate out  $\text{MgO}$  dust, then the  $\text{MgO}$  is hydrolyzed to a slurry which is used to scrub  $\text{SO}_2$  from the flue gas. For ammonium  $\text{SO}_2$  is scrubbed from the flue gas with fresh ammonia solution. Sodium-based mill particulate emissions are controlled by electrostatic precipitators. The largest emissions from a sulfite recovery furnace are methanol, ethanol, vinyl acetate, acetone, and acetaldehyde (*NCASI*).

Mill-specific source tests should be used where available. Toxic emission factors are available from *NCASI*<sup>iii</sup> for these sources.

## **Bleaching**

### **Description of Process**

The purpose of the bleaching process is to enhance the physical and optical qualities (whiteness and brightness) of the pulp by removing or decolorizing the lignin. Two approaches are used in the chemical bleaching of pulps. One approach called brightening, uses selective chemicals, such as hydrogen peroxide, that destroy chromographic groups but do not attack the lignin.

Brightening produces a product with a temporary brightness (such as newspaper) that discolors from exposure to sunlight or oxygen. The other approach (true bleaching) seeks to almost totally remove residual lignin by adding oxidizing chemicals to the pulp in varying combinations of sequences, depending on the end use of the product. This creates a longer lasting (sometimes permanent) whiteness, but it weakens the fibers and reduces sheet strength. The most common bleaching and brightening agents are chlorine, chlorine dioxide, hydrogen peroxide and sodium hydroxide.

Typically, the pulp is treated with each chemical in a separate stage. Each stage includes a tower, where the bleaching occurs; a washer, which removes bleaching chemicals and dissolved lignins from the pulp prior to entering the next stage; and a seal tank, which collects the washer effluent to be used as wash water in other stages or to be sewerred. Bleaching processes use various combinations of chemical stages called bleaching sequences.

The first stage in the bleaching process is the chlorination stage, whose primary function is to further delignify the pulp. Chlorine reacts with lignin to form compounds that are water-soluble or soluble in an alkaline medium, which aids in delignifying the pulp before it proceeds to the next bleaching stage.

The next stage after chlorination is typically the extraction stage. This stage and the remaining stages serve to bleach and whiten the delignified pulp. The extraction stage removes the chlorinated and oxidized lignin by solubilization in a caustic solution.

Chlorine dioxide is often used in bleaching, either in the chlorination stage (as a substitute for some of the chlorine usage - chlorine dioxide substitution) or as an additional chlorine dioxide stage. Chlorine dioxide has 2.63 times greater oxidizing power (on a pound per pound basis) than chlorine and is used for nearly all high brightness pulps.

The next stage is the actual bleaching stage. Hypochlorite is a true bleaching agent that destroys certain chromophobic groups of lignin. It also attacks the pulp so high cellulose degradation occurs in Kraft pulp. Application of hypochlorite to Kraft pulp is usually used only as an intermediate stage of the sequence or to produce semi-bleached pulps. In the bleach process, residual chlorine must be removed through washing in vacuum washers.

### **Methods of Determining Emissions**

During bleaching, side reactions produce chloroform, phenol, chlorinated phenolics and other chlorinated organics. The bleaching stage has been identified as one of the most significant

points of chloroform emissions. Studies conducted by NCASI show that bleaching sequences without hypochlorite have lower chloroform emissions. Chlorine emissions are controlled by scrubbing gaseous emissions with NaOH solution. ClO<sub>2</sub> emissions are controlled by scrubbing gases with alkaline hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>).

The foremost factor affecting emissions of organic compounds from bleach plants are the level and type of bleaching. Other factors are type of wood bleached, scrubber solutions, scrubber design, bleaching temperatures, and residence time. The toxic emissions from a bleach plant include carbon tetrachloride, chlorine, chloroform, benzene, methanol, methyl chloroform, chlorophenols, phenol, 2,3,7,8-TCDD, and 2,3,7,8-TCDF (*AP-42*).

There is also a new technology to reduce the amount of bleaching chemicals needed, therefore, reducing the amount of emissions. The technology is currently being developed by the Technological Institute in Iceland, Reykjavik, and involves using the enzymes produced by thermophilic organisms to dissolve the lignin in the pulp. The more lignin that can be removed, the fewer chemicals that will be needed in bleaching. (*Chemical Engineering Progress*)

Mill-specific source tests should be used where available. Toxic emission factors are available from *NCASI*<sup>v</sup> for these sources.

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## References

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<sup>i</sup> NCASI Technical Bulletin No. 701 is an update of NCASI Technical Bulletin No. 650 (1993), and compiles air toxic data from many different source tests and studies. The new document contains emissions factors for oxygen delignification systems, brownstock washers, deckers, thermal oxidizers, pulp and liquor storage tanks, kraft and sulfite recovery furnaces, lime kilns, smelt dissolving tanks, black liquor oxidation tanks, tall oil reactors, causticizing area vents, bleach plants, paper machines, and wood residue-fired boilers. Discussions of wood residue-fired boilers can be found in the Boiler chapter of this report. The NCASI document lists emissions for each source tested and also gives a median to represent the average emissions as long as at least 50% of the data was above the detection limit. If fewer than 50% of the data were above the detection limit, either the NOR-PLOT median or the SDIn median were used. For some processes or air toxics the number of sources tested is limited, therefore caution should be taken when using these data. Ecology does not endorse either of these methods and recommends that the user read the specific cautions listed in the report (NCASI, 26) as the ultimate use of the data will decide what numbers to use. NCASI recommends selecting a source from the list of sources and their

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operating parameters for each unit that most closely represents the emission source you are working with and use that source's emission factors.

<sup>ii</sup> Same as endnote 1.

<sup>iii</sup> Same as endnote 1.

<sup>iv</sup> Same as endnote 1.