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TECHNICAL INFORMATION *Bulletin*

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PULP AND PAPER INDUSTRY

INTRODUCTION

The bulk of wood tissue can be separated into fine fibers suitable for paper making. Cellulose, which is highly chemically resistant, is the main constituent of wood cell walls. Lignin serves as the adhesive material of wood, cementing the fibers and other cells together. Lignin is susceptible to degradation and dissolution by strong alkalis at elevated temperatures, by acids at elevated temperatures, and by oxidizing agents. Therefore, the lignin can be chemically removed from the wood, leaving the separated cellulosic fibers in the form of pulp which can be further processed into paper.

In addition to the cellulose and lignin, wood also contains several extraneous materials. These materials cover a wide range of chemically different substances, most of which can be separated and recovered as valuable by-products.

There are five basic operations necessary to economically convert wood to white paper.

1. Pulping
2. Chemical Recovery and By-Products
3. Power House
4. Bleach Plant
5. Paper Mill

PULPING

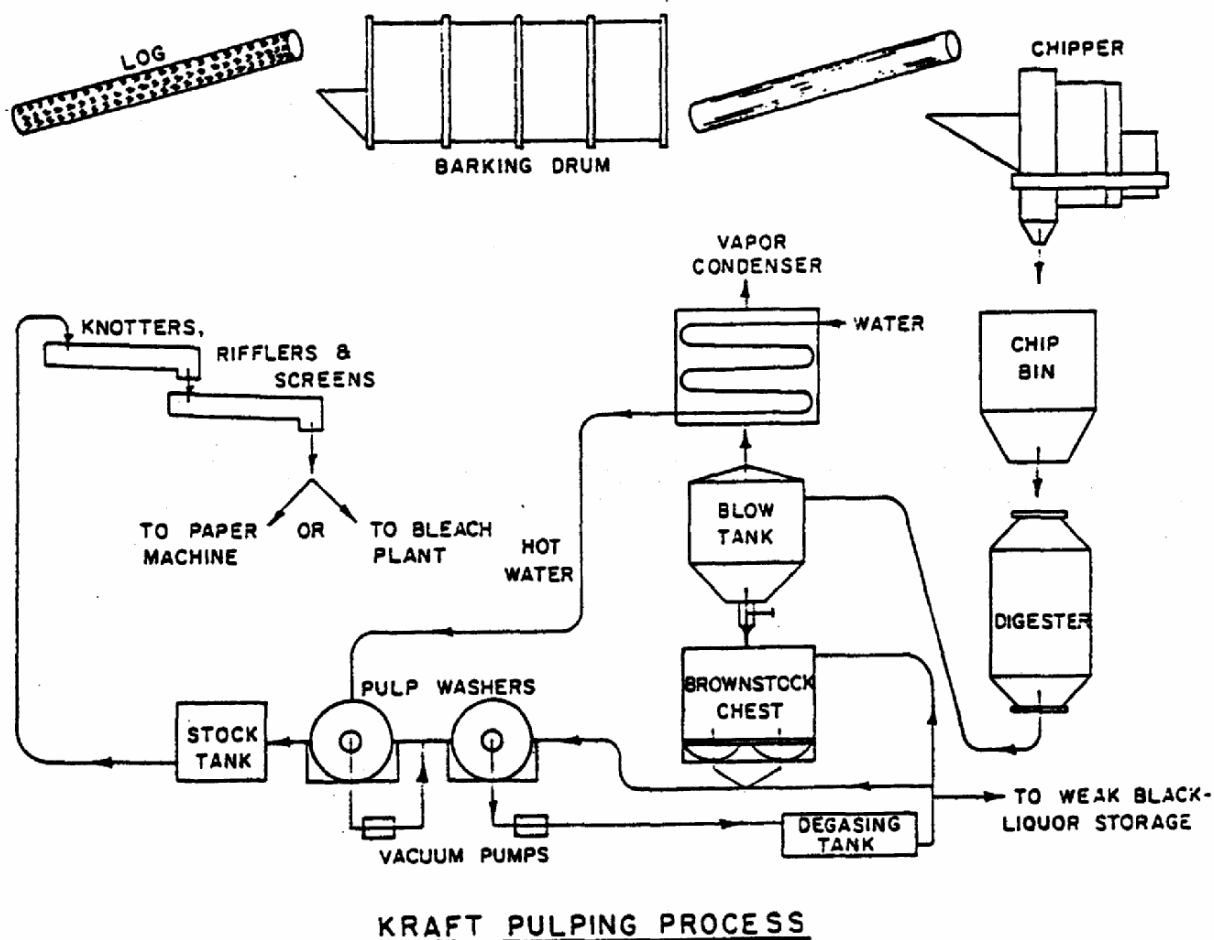
Wood is converted into pulp by mechanical, chemical, or semi-chemical processes. Sulfite,

sulfate (Kraft), and soda are the common chemical processes used while neutral sulfite is the principle semi-chemical process used.

Mechanical pulping does not involve a chemical process. Mechanical (or groundwood) pulp, used primarily for newsprint, is made by grinding the wood into pulp mechanically. Therefore, the liquids handled in mechanical pulping are simply water and pulps.

The purpose of chemical pulping is to solubilize and remove the lignin portion of wood, leaving the individual fibers free for processing into paper. Of the chemical pulping processes in use, the sulfate (Kraft) process accounts for over 90% of all chemical pulp produced. The Kraft process, Fig. 13, uses a mixture of sodium hydroxide (NaOH) and sodium sulfide (NaS) as the active chemical. Wood chips in a pressurized digester are subjected to a cooking liquor (white liquor) under elevated temperature and pressure. After sufficient time in the digester, the softened chips are "blown" into a large tank. From there the brown, pulpy mass is rinsed on large vacuum drum washers to remove residual cooking liquor.

In the sulfite process the cooking liquor can have one of four common bases: sodium, magnesium, calcium, and ammonium. The base is combined with a sulfur bearing compound to form the cooking liquor.



Semichemical (neutral sulfite) pulps are produced by cooking wood chips with sodium sulfite (Na_2SO_3) liquor which is maintained slightly alkaline.

CHEMICAL RECOVERY & BY-PRODUCTS **Sulfate (Kraft) Chemical Recovery**

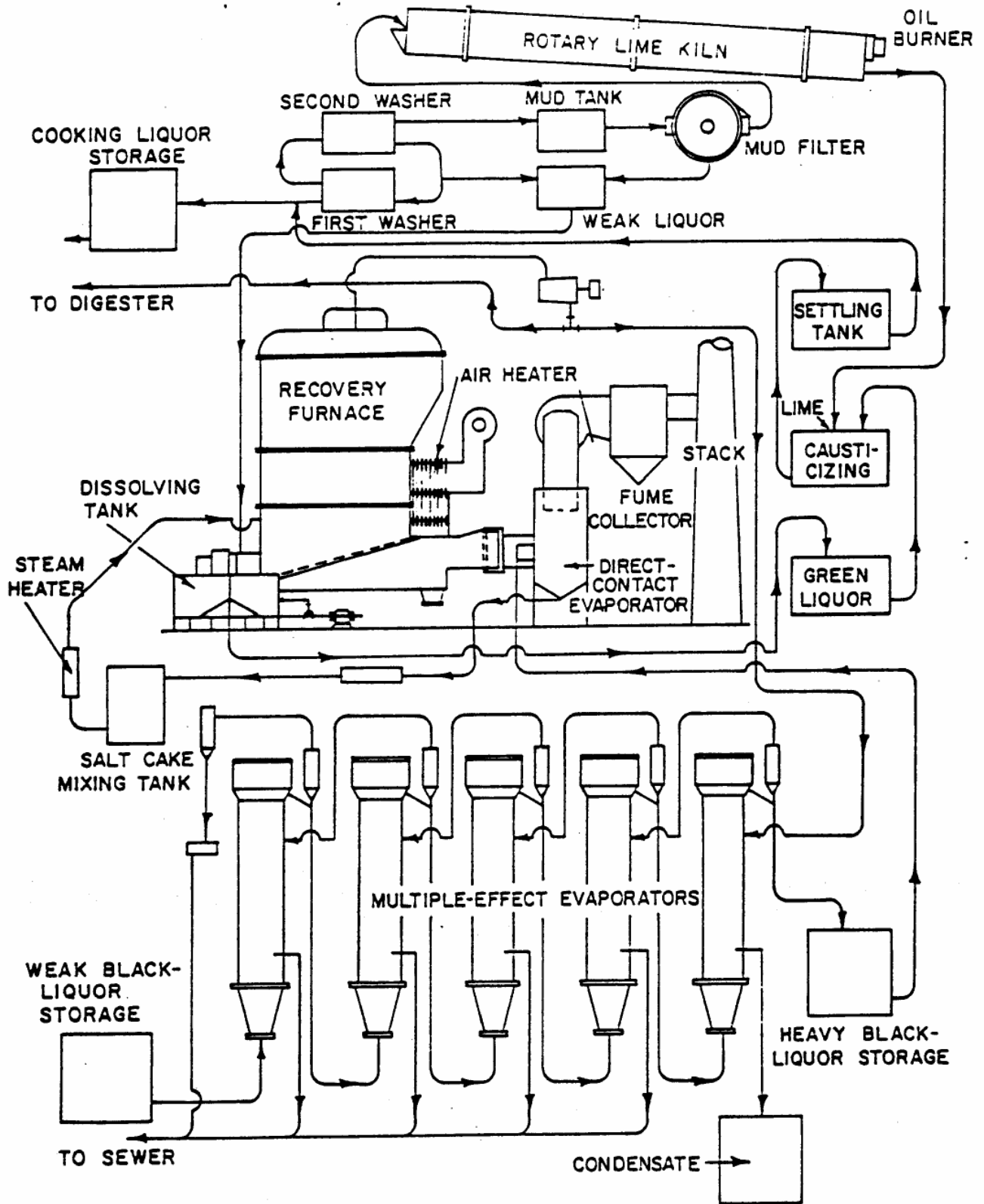
The chemical recovery process is utilized to recover valuable inorganic chemicals used in the cooking liquor and to provide power and steam for the mill. The cooking liquor extracted from the digester is very dark and is known as "black liquor." It is concentrated in multiple effect evaporators to 60-65% solids. At this concentration the quantity of dissolved organic compounds from the wood (lignin and others) is sufficient to allow the liquor to be burned in the recovery furnace. See Fig. 14.

By controlling the amount of excess air admitted to the furnace, and the temperature, the organics in the liquor can be burned. The inorganics collect on the bottom of the furnace as a molten salt or sodium carbonate (Na_2CO_3) and

sodium sulfide (Na_2S). Sodium sulfate (Na_2SO_4) is added to the liquor before burning as make-up and is reduced to Na_2S during burning. After dissolving in water, this mixture "green liquor" is reacted with milk of lime ($\text{Ca}(\text{OH})_2$) to form sodium hydroxide (NaOH) and calcium carbonate (CaCO_3). Since the Na_2S does not react with the lime, the resultant mixture of NaOH and Na_2S "white liquor" can be re-used to pulp more wood. The calcium carbonate (CaCO_3) lime mud is filtered off, burned in a lime kiln and re-used.

Sulfite Chemical Recovery

The sulfite process is broken down by degree of pH or acidity, ranging from the acid sulfite process. pH 1 to 2 to the alkaline sulfite process with a pH of 10 or higher. The most common sulfite system is the bisulfite process with a pH of 2 to 4. The recovery and fortification of spent sulfite liquor is complex and varied, with recovery of the base chemical and refortification of the sulfur ion being the common theme.



KRAFT PROCESS - CHEMICAL RECOVERY

By-Products

During the pulping and chemical recovery processes, many commercial by-products are produced. These by-products are produced either during digester relief (Kraft-turpentine or in the chemical recovery areas.

Economics in the sulfate (Kraft) chemical pulping process requires that the large amount of chemicals used in the cooking liquor be recovered and re-used.

The spent Kraft cooking liquor that is separated from the pulp at the brown stock washers is very dark and is known as "black liquor." This weak black liquor consists of 15 to 20% abrasive solids, fiber, and dissolved chemicals and has a pH of approximately 10. It is concentrated in multi-effect evaporators and eventually burned in a recovery furnace to produce power and steam for the mill. The chemicals that collect on the bottom of the furnace are, reprocessed to re-usable cooking liquor.

Weak Black Liquor (Up to 50% Solids)

As the weak black liquor is concentrated in the multi-effect evaporators, the higher solids content gives the liquor a higher viscosity. The liquor from the last stage will contain nearly 50% solids and the liquid viscosity will have increased to 80 - 150 SSU (15 - 37 CS). During evaporation, the process temperatures are increased from 200°F. (93°C.) to 220°F. (104°C.).

Heavy Black Liquor (Up to 70% Solids)

The black liquor from storage, containing 50% solids, is not concentrated enough to sustain combustion in the recovery furnace. Further evaporation is necessary and is accomplished in a direct contact or cascade type evaporator. The resultant "burning grade" black liquor contains up to 70% solids and the viscosity can be as high as 6300 SSU (1400 CS) after sodium sulfate make-up is added. The temperature must be maintained near 230°F. (110°C.) to insure flow and to maintain optimum firing in the recovery furnace. If allowed to cool, burning grade black liquor will solidify.

Power House

The liquids associated with power house applications, aside from water treatment chemicals, are condensate, boiler reed water, and fuel oil.

Bleach Plant

The color of unbleached chemical pulp ranges from the cream or tan of the sulfite process to the dark brown of the Kraft process. While most of the lignin has been removed by the pulping process, the remainder, along with other residuals, must be removed by bleaching.

While it is possible to improve the whiteness of the pulp in one stage, the use of several stages is more economical. Current practice uses combinations of chlorination with elemental chlorine (Cl₂), alkaline extraction with sodium hydroxide (NaOH), and various oxidative stages using sodium or calcium hypochlorite (NaOCl or Ca(OCl)₂), chlorine dioxide (ClO₂), or hydrogen peroxide (H₂O₂). The pulp is washed between stages to remove solubilized impurities. Many combinations of bleaching plant sequences are possible and each mill selects the one that best fits its requirements.

The most common bleaching sequence in Kraft pulping is a five-stage bleaching process "CEDED" shown in Fig. 15. The bleaching sequence used here is chlorination, alkaline extraction, chlorine dioxide bleaching, alkaline extraction 'again, and chlorine dioxide bleaching again.

PAPER MILL

The paper making process is essentially a system whereby the pulp is diluted to a very low consistency (about 1/2 percent) and continuously formed into a sheet of paper on a fast moving screen. The water is allowed to drain through the screen and the wet mass in continuous sheet form is press-rolled and dried.

Depending on the type of paper desired, many chemicals can be added to impart specific properties to the end product.