

EPA-450/3-77-005

**BACKGROUND DOCUMENT:
ACID SULFITE PULPING**

by

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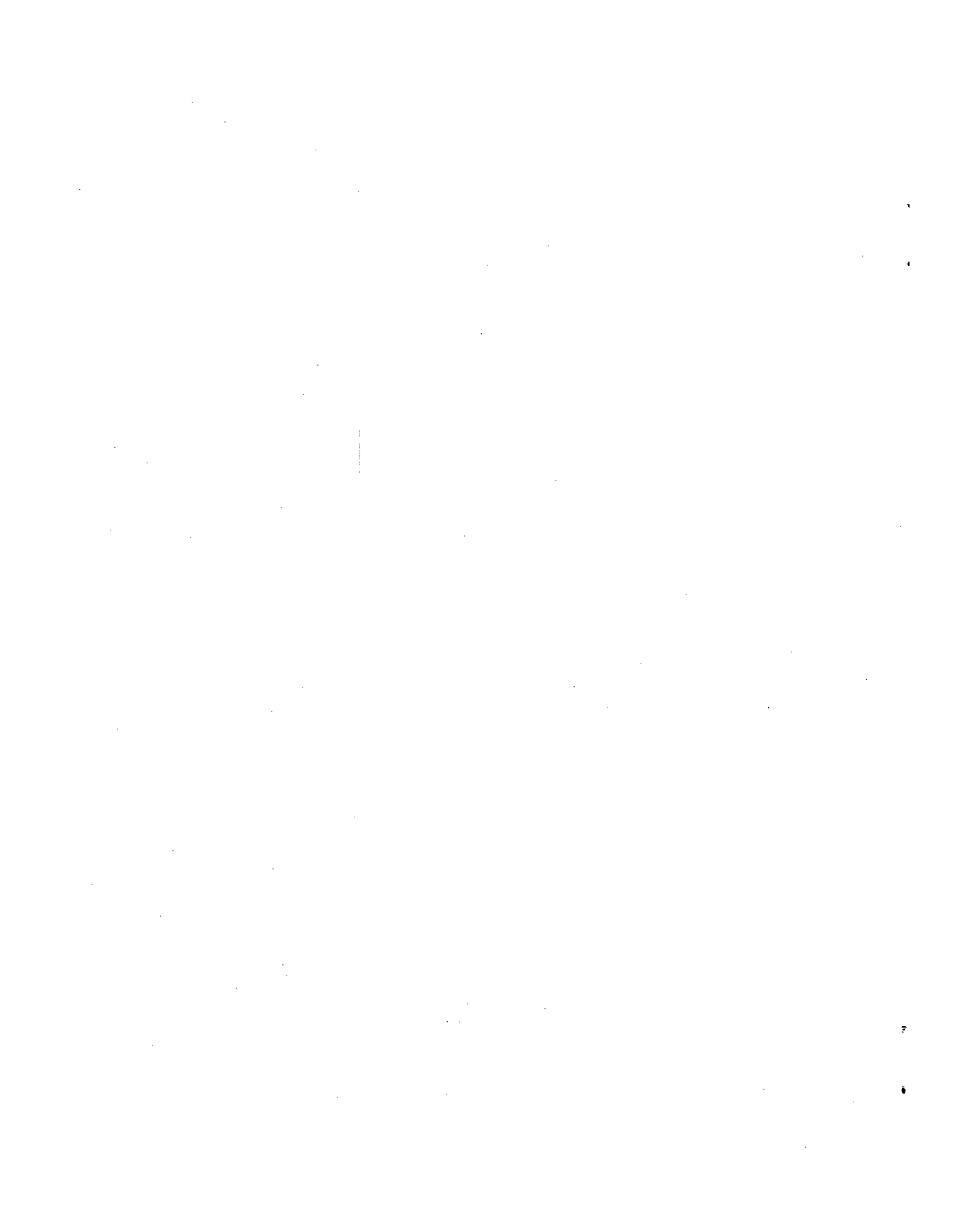
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1.0 GENERAL INFORMATION

The sulfite pulping industry primarily is characterized by the type of base chemical used in conjunction with sulfurous acid to effect delignification of gymnosperm woods. It further is characterized by the level of acidity during the digestion operation and by the extent of recovery of chemicals and waste heat.

During the first half of this century calcium was the base of choice used with sulfurous acid. Recently, however, the popularity of magnesium and ammonia as base chemicals has risen markedly with the result that they have become the dominant sulfiting agents. Among the reasons for the above trend is that chemical and heat recovery can be achieved more economically through use of magnesium and ammonia than through use of calcium. No small part is played by the restrictions placed upon plants in order to reduce effluents discharged into rivers and lakes.

Table 1¹ presents 1975 data on pulp and paper capacities of mills in the United States. In the United States, sulfite pulp comprises only a minor share (6.2%) of the total pulp produced. Sulfite operations primarily are centered in the states of Washington, Oregon, Wisconsin, and Maine. The outlook for sulfite pulping in the immediate future indicates slow growth.

From Table 2¹ it can be seen that at least one sulfite mill is being replaced by a kraft mill. This is in accordance with the recent trend towards the phasing out of calcium based sulfite mills.

Table 1. United States Mill Capacities¹ (tons/day)

| STATES | PAPER & BOARD | SULFITE PULP* | SULFATE PULP* | SODA PULP | SEMI- CHEMICAL | GROUND- WOOD | DEFI- BRATED WOOD PULP | SEC- ONDARY FIBER | OTHER PULPS |
|----------------------|------------------|------------------|------------------|--------------|-------------------|-----------------|---------------------------------|-------------------------|----------------|
| Alabama | 13,125 | | 8,745 | | 725 | 1,440 | 50 | 210 | |
| Alaska | | 640 | | | | | | | |
| Arizona | 850 | | 600 | | | 180 | | 100 | |
| Arkansas | 4,645 | | 4,559 | | | 400 | | 185 | |
| California | 5,254 | | 1,860 | | 240 | 65 | 55 | 1,427 | |
| Colorado | 110 | | | | | | | | |
| Connecticut | 1,798 | | | | | | | 457 | 50 |
| Delaware | 168 | | | | | | | | |
| District of Columbia | | | | | | | | | |
| Florida | 7,910 | 425 | 7,580 | | 340 | | 120 | 200 | 650 |
| Georgia | 13,765 | 450 | 13,025 | | 700 | | | 27 | |
| Idaho | 830 | | 917 | | | | | | |
| Illinois | 3,728 | | | | | 100 | 30 | 300 | 75 |
| Indiana | 1,470 | | | | 250 | | | 770 | 130 |
| Iowa | 250 | | | | 360 | | | | |
| Kansas | 340 | | | | | | | 155 | |
| Kentucky | 705 | | 600 | | 300 | | | 100 | 320 |
| Louisiana | 12,722 | | 10,135 | 115 | 1,083 | 635 | | 106 | |
| Maine | 7,812 | 1,450 | 3,505 | | | 2,820 | | 175 | |
| Maryland | 1,591 | | | | | 45 | | 170 | 665 |
| Massachusetts | 3,502 | | | | | | | 145 | |
| Michigan | 9,306 | | 825 | | 1,175 | 225 | | 1,095 | 485 |
| Minnesota | 4,078 | 120 | 750 | | 400 | 778 | | 100 | |
| Mississippi | 4,265 | | 4,570 | | 50 | 435 | 3,380 | 90 | |
| Missouri | 410 | | | | | 44 | | 16 | |
| Montana | 1,050 | | 1,200 | | | | | | |
| New Hampshire | 2,138 | | 700 | | 550 | | | 11 | |
| New Jersey | 5,393 | | | | | | 365 | 475 | |
| New York | 6,712 | 200 | 750 | 150 | 220 | 650 | | 1,390 | 70 |
| North Carolina | 5,743 | | 5,660 | | 520 | 350 | 100 | 235 | 245 |
| Ohio | 7,863 | 275 | 740 | | 800 | | | 699 | 16 |
| Oklahoma | 2,645 | | 1,300 | | 350 | | | | |
| Oregon | 8,694 | 805 | 5,431 | | 250 | 1,490 | | 53 | 200 |
| Pennsylvania | 7,455 | | 900 | | 240 | | 50 | 135 | 7 |
| Puerto Rico | 190 | | | | 125 | | | | |
| Rhode Island | 275 | | | | | | | | |
| South Carolina | 6,643 | | 4,454 | | 1,271 | 650 | | 493 | |
| Tennessee | 4,814 | 28 | 1,275 | 459 | 755 | 985 | | 525 | 534 |
| Texas | 5,988 | | 4,540 | | | 1,860 | | 375 | |
| Vermont | 530 | | | | | 50 | | 5 | |
| Virginia | 6,505 | | 4,550 | | 1,175 | 250 | | 725 | 375 |
| Washington | 7,066 | 3,880 | 5,411 | | 460 | 944 | | | 300 |
| West Virginia | 230 | | | | | | | | |
| Wisconsin | 9,300 | 1,478 | 1,305 | | 920 | 907 | 250 | 1,945 | |
| TOTALS | 185,333 | 9,751 | 96,887 | 724 | 13,259 | 15,253 | 4,400 | 12,888 | 4,122 |

*includes dissolved pulp

Table 2. New Pulp and Paper Mills Under Construction and Projected
for the United States¹

CRANE & CO., INC., DALTON, MASS.:
Under construction-new paper facility for the production of security papers, to replace the Government mill at the same location. Completion set for 1975.

FORT HOWARD PAPER CO., MISKOGEE, OKLA.:
Projected-tissue mill.

GREAT NORTHERN NEKOOSA, MAINE (No location specified):
Proposed-bleached hardwood kraft pulp mill, no date set.

HUDSON PULP & PAPER CO., PALATKA, FLORIDA:
Proposed-newsprint mill to produce 400 tpd from wastepaper, no date set.

INLAND CONTAINER CORP., INDIANAPOLIS, IND.:
Under construction-350 tpd corrugated medium mill to use 100% recycled fiber. Completion set for 1975.

MACMILLAN BLOEDEL, RICHMOND, CALIFORNIA:
Under construction-pulp mill to produce 100 tpd market pulp. Completion set for Spring, 1976. Projected-recycled newsprint mill at same location

OAK PULP & PAPER CO., POTEAU, OKLA.:
Proposed-300 tpd dissolving pulp mill, no date set.

ROBEL TISSUE MILLS, INC., PRYOR, OKLA.:
Under construction-tissue mill by Skybel Tissue Mills, Inc., of Holyoke, Mass. Completion set for 1975.

SCOTT PAPER CO., HINCKLEY, MAINE:
Under construction-750 tpd bleached kraft mill and sawmill to replace the 450 tpd sulfite mill at Winslow, Maine. Completion set for 1975.

VIRGINIA FIBRE CORP., RIVERVILLE, VA.:
Under construction-500 tpd corrugating medium mill. Completion set for 1976.

WEYERHAUSER CO., NORTH CAROLINA (No location specified):
Proposed-fiberboard mill. Completion set for 1975-1976.

2.0 PROCESS DESCRIPTION ^{2,3,4,5,6}

The sulfite pulping industry is characterized by several different processes, differing mainly in base chemical used and levels of chemical and heat recovery practiced. Different schemes exist for each process so that no one flow diagram can represent accurately the precise technique employed at more than one plant.

In general, basic operations can be identified which are common at most if not all plants. These are:

1. Digestion of chips;
2. Pulp washing; and
3. Chemical manufacture, recovery, and fortification.

Figure 1 illustrates the basic operations associated with magnesium-base pulping and recovery. This is only one of many schemes currently practiced. Pollution sources and their control from each process and operation are discussed in Section 3.0.

2.1 DIGESTION

Delignification of wood chips is performed in large cylindrical vessels of up to 6000 ft³ and capable of handling 20 tons of wood chips. In a batch-mode, the digesters are charged with chips, the cooking liquor containing essentially an acid bisulfite solution is added, and live steam is turned on. The pressure is raised to about 110 psi. The temperature increases until the desired value is reached; then the steam is shut off and the reaction mixture is held for a period of time sufficient to permit the principal chemical reactions to take place,

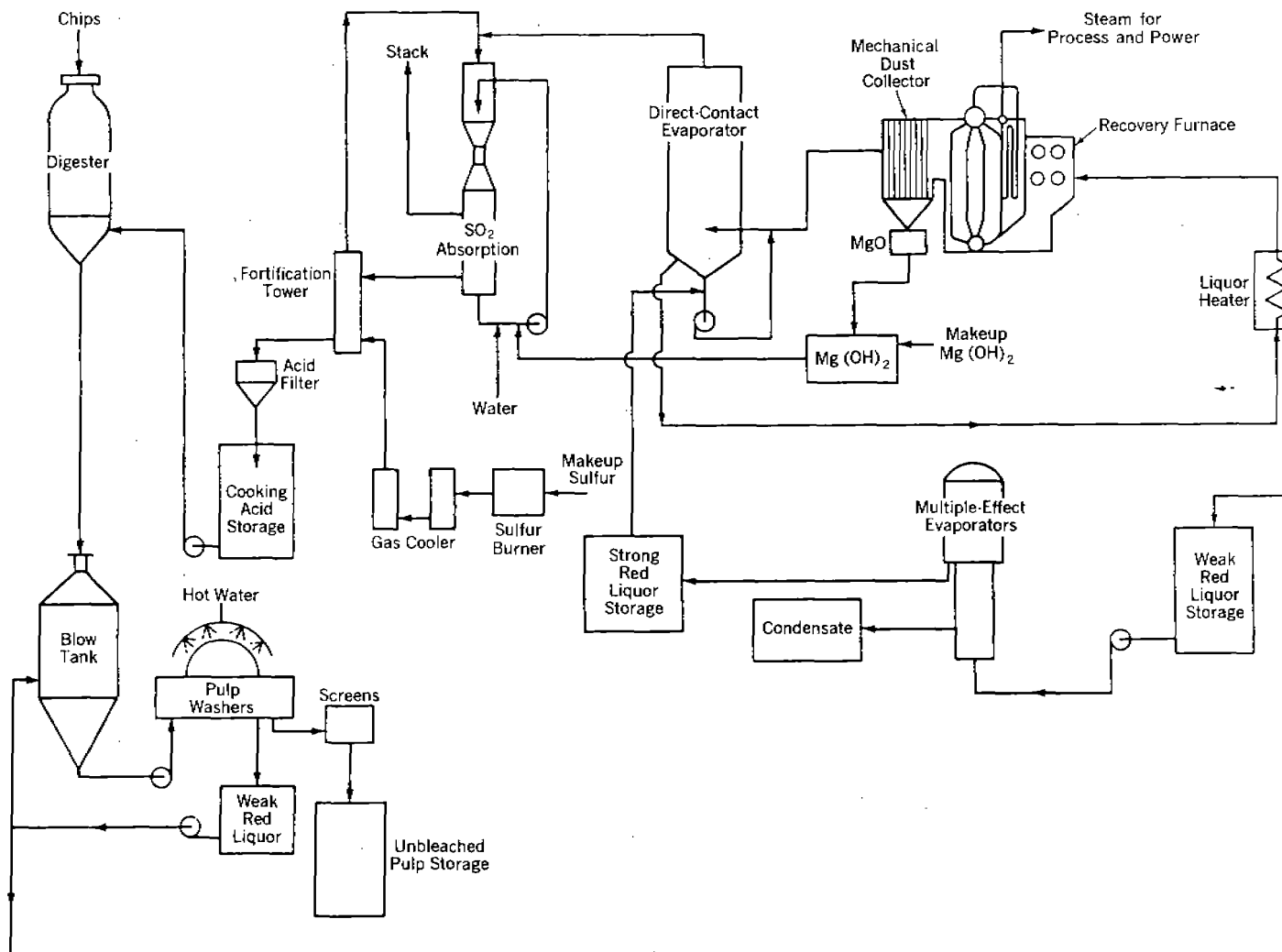


Figure 1. Simplified Process Flow Diagram of Magnesium-Base (Magnifite^R) Process Employing Chemical and Heat Recovery

these being the sulfonation and solubilizing of lignin with the bisulfite and the hydrolytic splitting of the cellulose-lignin complex. During the cooking cycle, constant pressure is maintained by drawing off amounts of liquid and gas through a relief system and returning these to a liquor storage tank or high pressure accumulator.

Toward the completion of the cooking cycle the pressure and temperature are lowered by removal of further amounts of liquor and gas from the digester to the high pressure accumulator by means of the relief system. The final pressure in the digester will be about 30-40 psi and the solution will contain primarily bisulfite with only a little sulfurous acid. The exact combination of pressure, temperature and cooking time will vary considerably from plant to plant.

The digester can be emptied by a variety of methods, the most common of which is blowing. In this case, a large valve situated near the base of the digester is opened and the material in the digester is blown under the remaining pressure in the vessel into a pit. Large amounts of steam containing significant amounts of sulfur dioxide are liberated. This can be a significant source of pollution if the blowpits are vented to the atmosphere. It is possible to recover the sulfur dioxide in scrubbers designed for this purpose.

In order to minimize potential pollution due to blowing, some plants employ a technique known as dumping. When this technique is utilized a more elaborate pressure relief system is required. The aim is to

relieve digester pressure to "near-atmospheric" by methods similar to those employed in blowing.

Thus, the SO₂ evolution potential is greatly diminished when the contents of the digester are removed. A common technique practiced with the dump system involves the removal of the pulp and spent liquor by use of recirculating liquor pumps. In this manner the emission of large quantities of sulfur dioxide-laden gas is abated. Water vapor and other gases which may flash off in the dump tank can be treated by the acid absorption system without the penalties of lower absorption efficiencies.

A variation of the above technique sometimes is used wherein a portion of the cooking liquor is withdrawn at the end of a cook and replaced with wash water. This lowers the pulp and liquor temperature below the boiling point and effectively keeps water and SO₂ from flashing off.

After the digestion operation and subsequent discharging, sulfite spent liquor drains through the bottom of the blowpit and either is treated and disposed, incinerated, or sent to a plant for recovery of heat and chemicals.

2.2 WASHING AND KNOTTING

The pulp, after separation from the spent liquor, is suspended in water and processed through screens and centrifugal cleaners for removal of knots, bundles of fibers, and other materials. Washing and knotting are considered to be very minor sources of sulfur dioxide emissions. If however, other sources are well controlled, washing and knotting can be a significant portion of the total plant emissions.

2.3 CHEMICAL MANUFACTURE, RECOVERY AND FORTIFICATION

The choice regarding whether chemical recovery is desirable is dictated by the following:

1. Costs of chemicals and their recovery;
2. Base Chemical (Calcium, Ammonia, Sodium, or Magnesium) used in conjunction with sulfurous acid; and
3. Regulations limiting plant effluents and emissions.

2.3.1 Calcium As Base

Calcium was the initial base-of-choice in the sulfiting industry while there was a good availability of low resin spruce, fir, and hemlock. It is gradually being replaced by ammonia, sodium, and magnesium bases.

When calcium is utilized, chemical and heat recovery usually are not practiced due to formation of scale in the evaporation steps preliminary to recovery, as well as formation of calcium sulfate ash in the furnace.

In lieu of the above, an acid plant of sufficient size to fulfill the total sulfite requirement for pulping is required. It is obtained by absorption of sulfur dioxide in water in a wide variety of packed towers. The sulfur dioxide is manufactured as follows:

Sulfur is burned at over 2000°F under conditions designed economically to maximize yield in a rotary sulfur burner or a spray sulfur burner. Gas thus formed is quickly cooled under conditions of low oxygen by surface heat exchangers. It also may be cooled directly by passage through a water spray.

Cooled gas is then absorbed in Jenssen towers which are acid resistant tile-lined and packed with limestone in accordance with the reaction $H_2O + SO_2 + CaCO_3 = Ca (HSO_3)_2 + H_2O + CO_2$. The resulting solution forms the bisulfite-sulfurous acid liquor required for pulping.

Although most of the sulfur dioxide is absorbed in the Jenssen towers, the acid plant can be a significant source of SO_2 emissions if secondary emission controls are not used following the Jenssen towers.

2.3.2 Ammonia As A Base

The use of ammonia as a sulfite pulping base has increased as calcium pulping has diminished. Increased production rates, better yield, applicability to a wider range of woods, and greater ease of processing and process control are given as reasons for the switch.

Aside from the above, ammonia based spent pulping liquor is ideal fuel for burning in recovery furnaces. It yields an ash-free combustion product. Ammonia generated in firing decomposes to nitrogen and hydrogen (which goes to water vapor). Heat is recovered by the burning of spent liquor in a furnace for steam production. Sulfur dioxide is recovered from the flue gas in an absorption system by use of anhydrous or aqueous ammonia to produce ammonium bisulfite used for pulping. It is necessary to burn some sulfur as described above to provide make-up sulfur dioxide. This sulfur dioxide is absorbed in the system serving the recovery furnace. Thus, acid plant emissions are accounted for by the recovery plant.

2.3.3 Magnesium As A Base

Along with ammonia, magnesium base pulping is one of the most commonly used sulfite pulping processes today. Advantages cited are:

1. Higher production rates can be attained using high reaction temperatures if proper pH control is maintained.
2. Wide variety of pulp can be made.
3. Pulping operations are simplified because the need for the relief step is lessened and consideration may be given to use of continuous digesters.
4. A simple system is available for recovery of heat and total chemical (magnesium and sulfur dioxide). The system is that shown in Figure 1.

In the magnesium based system (Magnefite^R process in this case), weak red liquor is concentrated in multiple-effect evaporators and a direct contact evaporator from 9 percent to 55 - 60 percent solids. Strong liquor is sprayed into the furnace (of which Figure 2 is typical) and burned, producing sufficient steam to run the evaporators as well as the cooking cycle. Flue gases are laden with magnesium oxide which is in the form of a fine white powder, removable by means of multiclone units. It is then steam slaked to produce magnesium hydroxide used in the sulfur dioxide absorption system.

After recovery of magnesium oxide, flue gas containing 1 percent sulfur dioxide is routed through a system of four venturi scrubbers, the first of which serves to cool the gas. The following three venturis (illustrated in Figure 3) continue the scrubbing action and achieve a high (98 percent) efficiency of sulfur dioxide removal. Slurry from the

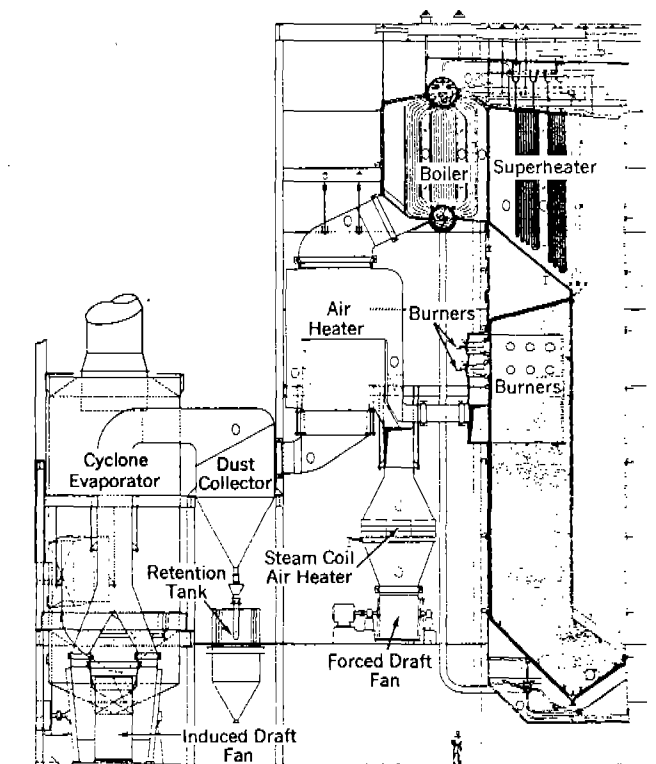


Figure 2. B&W Water-Cooled Furnace Magnesium Base Recovery Unit.

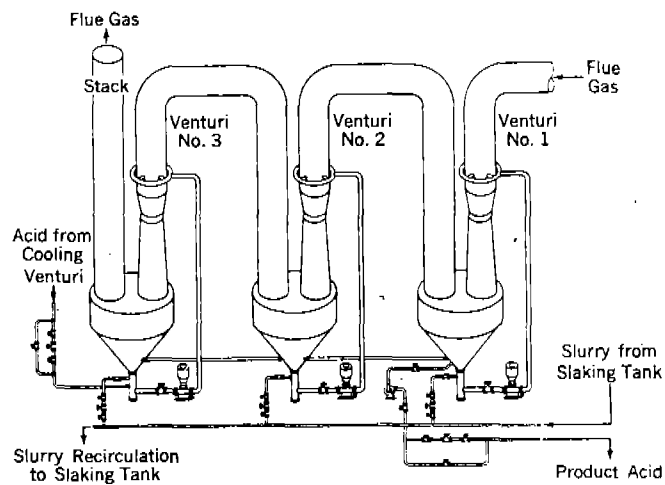


Figure 3. Sulfur Dioxide Absorption System.

slaking tank is the scrubbing medium. The pH of the scrubbing solution in each venturi is monitored and controlled by manipulating recycle rates and slurry flows. The resulting solution is passed through a fortification tower which provides make-up SO₂ and which ultimately is vented through the recovery system stack. A liquor of magnesium bisulfite resulting from the above treatment is then used in the cooking cycle.

2.3.4 Sodium As A Base

Sodium pulping yields a pulp which is considered to be of fine quality. It has the operating advantages mentioned for magnesium and ammonia and furthermore can be accomplished at a wide range of acidity. Due to high chemical cost, recovery is desirable.

Sodium based liquor may be concentrated and burned alone or in a recovery furnace associated with a kraft mill. The products of sodium based liquor burning are a smelt containing sodium sulfide with some sodium carbonate and a flue gas containing sulfur dioxide. The smelt may be used in a nearby kraft mill or it may be processed further to arrive at a sodium carbonate solution which then is used to absorb sulfur dioxide from flue gas. Make-up sulfur dioxide must also be added in order to arrive at sodium bisulfite liquor which is used in the cooking cycle.

3.0 FACTORS AFFECTING EMISSIONS^{2,3,4,5}

The acid sulfite pulping industry encompasses a broad spectrum of process, specific practices, and control methods. Emission potentials are dependent upon:

1. Base chemical utilized;
2. Level of acidity, or pH at which digestion is carried out, affects sulfur dioxide emissions from blow pits or dump tanks and any other vents associated with cooking or washing;
3. Technique utilized in pressure relief system and in emptying digester contents; and
4. Level of chemical and heat recovery practices.

Table 3 summarizes primary emissions sources and species.

3.1 BASE CHEMICAL UTILIZED

Base chemicals, namely sodium, ammonia, calcium and magnesium, affect emissions insofar as they dictate the various process routes followed which in turn do affect emissions. How the base chemicals are produced and brought together with sulfur dioxide often necessitates specific equipment such as absorbers designed for the special purpose of bringing the constituents together and at the same time control gaseous and particulate emissions. In the case of ammonium sulfiting, a potential for ammonia emission exists.

3.2 LEVEL OF ACIDITY OF DIGESTION PROCESS

The pH as well as digestion temperature and pressure surely affect the distribution of sulfur compounds in the gaseous, liquid, and solid phase. Acid sulfite pulping can take place at a wide range of pH levels. At very low pH sulfur dioxide can exist as sulfurous acid in which form it exerts considerable vapor pressure. At the intermediate pH ranges, sulfur

Table 3. Sources and Emissions in Sulfite Mills

| SOURCE | PRIMARY EMISSIONS |
|------------------------------------|--|
| Blow pit or dump tank and digester | Sulfur dioxide; water vapor; acid mist |
| Knotters, washers | Sulfur dioxide |
| Recovery furnace | Sulfur dioxide; particulate matter (depending on base); ammonia (if ammonium base) |
| Acid plant | Sulfur dioxide |

dioxide exists as bisulfite ion which exerts a much lower vapor pressure and presents less potential for sulfur dioxide emissions.

Table 4 indicates the predominant chemicals existing in various cooking liquors and relates these to the pH of the solution. At a pH below 6, it is proper to represent the sulfite in the cooking liquor as hydrosulfite ion (HSO_3^-) while above this pH it is represented as sulfite ion (SO_3^{--}). The calcium and sulfite combination is insoluble in aqueous solution of pH above 2. Hence, calcium sulfite cooking liquors are limited to the acid sulfite processes. Magnesium sulfite is soluble in solutions whose pH is below 7 (approximately), and it may be used in acid sulfite, bisulfite, and over the lower end of the neutral sulfite range of pH. Ammonium sulfite is soluble in solutions of a pH below 9 (approximately), while sodium sulfite is soluble over the entire range of pH. The desired range of pH for the cooking liquor will dictate the type of cooking chemicals which can be used.

3.3 DIGESTER RELIEF AND DISCHARGE TECHNIQUES

These affect emissions at least as much as pH. During the cooking operation, gas and liquid must be removed or recirculated in order to maintain proper digester operating parameters. A pressure relief system of varying elaborateness is employed which removes gas and liquid, returning these to accumulators which also serve as holding tanks for pulping liquor. The final temperature and pressure of the digested pulp are important keys in emission potential. If these are high, large volumes of gas containing sulfur dioxide will be released when the digester is discharged. From this point on, emissions potential is based upon level of control practiced. Scrubbing is the method

Table 4. Predominant Chemicals and pH of Sulfite Cooking Liquors

| Process | Predominant Chemical in Cooking Liquor | Approximate Initial pH @ 25°C |
|------------------|---|----------------------------------|
| Acid Sulfite | $H_2SO_3 + XHSO_3$ | 1-2 |
| Bisulfite | $XHSO_3$ | 2-6 |
| Neutral Sulfite | $XSO_3 + XCO_3$ | 6-9 ⁺ |
| Alkaline Sulfite | $XSO_3 + XOH$ | 10 ⁺ |

of choice, with any number of systems utilized for this purpose. They include:

1. Jenssen scrubbing with lime rock;
2. Caustic scrubbers; and
3. Multi-staged packed scrubbers.

When digester contents are blown under high pressure, it usually is not feasible to treat the vapors generated in the recovery plant or acid plant, due to intermittent lowering of scrubbing efficiency caused by the large volumes of gas.

Some plants have installed more elaborate pressure relief systems which are capable of lowering digester pressure to "near atmospheric". The digester contents then are pumped out into a tank with release of a volume of vapor which is lower than that released when blowing is employed.

In conjunction with the above, it is possible to remove a portion of the cooking liquor at the end of the digestion operation and replace it with wash water, thus lowering the temperature below the mixture boiling point. In this way, flashing of steam and sulfur dioxide is abated.

From this point on, emissions are dependent upon the control method utilized. Vent gases can be treated by:

1. Horizontal - packed-bed scrubber;
2. Venting to the acid plant absorption system;
3. Venting to recovery cycle absorption system; and
4. Numerous other scrubbing methods.

When blow pit or dump tank vapors are vented to the acid plant or recovery system, emissions will be accounted for by these systems.

3.4 LEVEL OF CHEMICAL AND HEAT RECOVERY

If chemicals are not recovered, disposal of waste liquor (more than half of the raw materials appears here as dissolved organic solids) presents serious pollution problems. For this reason, as well as for economic considerations, concerted attention has been focused upon the utilization of the spent cooking liquor. If chemicals are not recovered, an acid plant is necessary in order to produce the sulfurous acid required with the base chemical. Sulfur dioxide emission potential is highest in this operation since virtually all sulfur will exist in the form of SO_2 which must be absorbed. The sophistication of the absorption system will affect sulfur dioxide emissions emanating at this step.

If chemical and heat recovery is practiced, sulfur dioxide from the flue gas must be scrubbed out. Subsequent to this, a fortification step is required to provide make-up SO_2 into the sulfurous acid-bisulfite solution. Sulfur dioxide emission potential is similar to that of an acid plant although the absorption system will be arranged in quite a different manner as described in the process section.

If recovery of chemicals is practiced, particulate emissions occur but will be minimal in the case of ammonia based pulping. Magnesium oxide fume is the primary particulate matter from a magnesium based facility, although most of it can certainly be recovered by multiclone units. When calcium based liquor is burned, calcium is present as calcium oxide and sulfate

entrained in the flue gas as finely divided fly ash. Chemical recovery is infeasible when utilizing this process. Sodium based recovery presents some opportunity for particulate emissions of sodium carbonate and sodium sulfide. Usually, though, most of this material is recovered as a smelt to be processed further for reuse or sold to kraft mills.

4.0 DEVELOPMENT OF ACID SULFITE PULPING EMISSION FACTORS

From the preceding sections, the difficulties in categorizing the sulfite segment of the pulp industry readily can be appreciated. This is due to the wide spectrum of combinations of bases, pH ranges and recovery schemes in common practice. Thus typical emission factors applicable to all acid sulfite pulping mills are impossible to specify.

4.1 COMPILATION OF DATA

Table 5 presents a summary of basic data collected during the course of this study. The twelve plants from which data were collected comprise 55 percent of the nationwide capacity for sulfite pulp manufacturing.

Three major emission categories were determined. These are:

1. Digester relief and discharge system;
2. Recovery furnace; and
3. Acid plant.

The first category was broken down further according to type of control, base, and digester discharge techniques. No correlation was made with respect to pH since data were not available.

Table 5. Summary of Emissions Data and Recovery/Control Methods from Acid Sulfite Pulping^a

| Company | Location | Base | Capacity ADUT/day* | Acid Plant Emissions | |
|-------------------|------------------|-----------------|--------------------|---------------------------|--|
| | | | | 1b SO ₂ /ADUT* | Control Method |
| Publishers Paper | Newberg, OR | Mg | 220 | N.A. | N.A. |
| Publishers Paper | Oregon City, OR | Mg | 230 | N.A. | N.A. |
| Weyerhaeuser | Cosmopolis, WA | Mg | 535 | N.A. | N.A. |
| Weyerhaeuser | Longview, WA | Mg | 290 | N.A. | N.A. |
| Crown-Zellerbach | Camas, WA | Mg | 430 | N.A. | N.A. |
| 20 Great Northern | Millinocket, ME | Mg | 640 | N.A. | N.A. |
| Scott Paper Co. | Everett, WA | NH ₃ | 850 | 0.37 | Ammonia absorption followed by water and caustic scrubbing. |
| Scott Paper Co. | Anacortes, WA | NH ₃ | 140 | 0.22 | Ammonia absorption, water scrubbing, control of process variables. |
| ITT Rayonier | Port Angeles, WA | NH ₃ | 570 | 0.40 | Packed tower and Jenssen tower with limerock. |
| Boise Cascade | Salem, OR | NH ₃ | 250 | N.A. | N.A. |
| Georgia Pacific | Bellingham, WA | Ca | 590 | 0.60 | Not described. |
| ITT Rayonier | Hoquiem, WA | Na | 550 | 0.168 | Not described. |
| American Can Co. | Greenbay, WI | Ca | 150 | 7.7 | Jenssen tower scrubber |

^a All data on emissions is from the period 6/75 through 7/76

* ADUT - Air Dried Unbleached Tons

N.A. - Not applicable because this system is not used.

Table 5. Summary of Emissions Data and Recovery/Control Methods from Acid Sulfite Pulping^a (CONTINUED)

| | | Blow Pit/Dump Tank Emissions | | | |
|------------------|------------------|------------------------------|--|--|---|
| Company | | 1b SO ₂ / ADUT | 1b SO ₂ / ADUT/Min ^{**} | Control Method | Comments |
| Publishers Paper | Newberg, OR | 1.1 | Unknown | Multistaged-Packed Tower. | System installed in 9/73; SO ₂ reduced by 98%. |
| Publishers Paper | Oregon City, OR | 0.2 | Unknown | Horizontal Packed-Bed Scrubber and digester pump-out system. | System installed in 11/74; SO ₂ reduced by 99%. |
| Weyerhaeuser | Cosmopolis, WA | 0.0 | 0.0 | Pressure relief, dumping and venting to recovery-absorption system. | Dump tank emissions accounted for as part of recovery furnace emissions. |
| Weyerhaeuser | Longview, WA | 0.0 | 0.0 | Pressure relief, dumping and venting to recovery-absorption system. | Dump tank emissions accounted for as part of recovery furnace emissions. |
| Crown-Zellerbach | Camas, WA | 2.08 | 0.14 | Unknown | Magnefite process began in 1972. Lower free SO ₂ in cook liquor. |
| Great Northern | Millinocket, ME | 6.4 | | Cool water added at end of cycle. | |
| Scott Paper Co. | Everett, WA | 0.499 | 0.08 | Pressure Relief System vented to Acid Plant. Condensation system and scrubber. | About 54% of plant serviced by recovery system, 46% by acid plant. |
| Scott Paper Co. | Anacortes, WA | 25 | 33 | None, other than pressure relief system. | Qualifies for state small mill requirement of 50% reduction. |
| ITT Rayonier | Port Angeles, WA | 0.367 | 0.023 | Packed Tower followed by Jenssen lime rock scrubber. | |
| Boise Cascade | Salem, OR | 0.0 | 0.0 | Not described with regard to blow, dump or pump. Vented to recovery-absorption system. | Venting to recovery-absorption reduced emissions from 40lb/ADUT. |
| Georgia Pacific | Bellingham, WA | 0.029 ^b | 0.0006 ^b | Caustic scrubbing facility. | |
| ITT Rayonier | Hoquiem, WA | 1.99 ^b | 0.133 ^b | Chemical scrubber | Scrubber is insufficient in its capacity to handle volume of gas evolved. |
| American Can Co. | Greenbay, WI | 67 | 0.464 | Unknown | |

^a All data on emissions is from the period 6/75 through 7/76.

^b Unreliable data.

** 1b SO₂/ADUT/min - Air Dried Unbleached Tons per each minute digester is blown. This unit is indicative

Table 5. Summary of Emissions Data and Recovery/Control Methods from Acid Sulfite Pulping^a (CONTINUED)

| Company | Location | Recovery System Emissions | | |
|------------------|------------------|---------------------------|--------------|--|
| | | 1b SO ₂ /ADUT | 1b Part/ADUT | Recovery Control |
| Publishers Paper | Newberg, OR | 12.7 | 1.8 | Multiclones - MgO; 4 Venturi Scrubbers SO ₂ . |
| Publishers Paper | Oregon City, OR | 10 | 2.1 | Multiclones - MgO; 4 Venturi Scrubbers SO ₂ . |
| Weyerhaeuser | Cosmopolis, WA | 9.8 | 3.04 | Absorption System and Recovery not described. |
| Weyerhaeuser | Longview, WA | 8.18 | 4.85 | Absorption System and Recovery not described. |
| Crown-Zellerbach | Camas, WA | 5.85 | 2.76 | Multiclones - MgO; 4 Venturi Scrubbers-SO ₂ . |
| Great Northern | Millinocket, ME | 9.2 | 2.7 | Multiclones - MgO; 4 Venturi Scrubbers-SO ₂ . |
| Scott Paper Co. | Everett, WA | 4.54 | 0.765 | Ammonia scrubbing - SO ₂ followed by mist eliminator. |
| Scott Paper Co. | Anacortes, WA | N.A. | N.A. | _____ |
| ITT Rayonier | Port Angeles, WA | 8.48 | 0.871 | Ammonia scrubbing - SO ₂ followed by Brinks eliminator. |
| Boise Cascade | Salem, OR | 8.8 | 0.3 | SO ₂ scrubber (95%) followed by Brinks eliminator. |
| Georgia Pacific | Bellingham, WA | N.A. | N.A. | _____ |
| ITT Rayonier | Hoquiem, WA | 0.193 | 3.77 | Unknown |

^a All data on emissions is from the period 6/75 through 7/76.

N.A. - Not applicable because this system is not used.

Recovery furnace data are more generally applicable and classification of emission levels is limited to process. Acid plant data, where applicable, are also related only to process base.

While a sufficient amount of data were obtained from magnesium and ammonia-based mills, data from sodium and calcium mills were sparse and of doubtful value.

For each plant in Table 5, emissions data are presented for each of the previously mentioned categories. The control systems are mentioned briefly and commented upon. These are indicative of the diversity of practices throughout the industry. Emissions are tied to the production rates of unbleached pulp and presented as such.

4.2 TABULATION OF EMISSION FACTORS

Table 6 summarizes emission factors which are based upon Table 5. Values presented are derived from the latest data (6/75 - 7/76) submitted by plants in Oregon and Washington to their respective control agencies as well as tests performed by EPA at Great Northern, Millinocket, Maine and in house tests conducted by American Can Co., Greenbay, Wisconsin.

For the myriad of combinations of controls and recovery schemes, Table 6 should prove satisfactory if some specific plant data is available to the person making estimates.

Table 6. Emission Factors^a for Sulfite Pulping (Per Unit Weight of Air-Dried Unbleached Pulp)

EMISSION FACTOR RATING

| Source | Base | Type Control | RANKING OF EMISSION FACTOR | | | | | | | | |
|--|-----------------|--|-----------------------------------|------------|----------------|----------|------------------------|--------------|----------------------|-------|------|
| | | | PARTICULATE MATTER | | SULFUR DIOXIDE | | Measured Emission Data | Process Data | Engineering Analysis | TOTAL | Rank |
| | | | lb/ADUT* | kg/ADUMT** | lb/ADUT | kg/ADUMT | | | | | |
| Digester Relief and Discharge ^b | All | -Untreated | Neg | Neg | 10-70 | 5-35 | 15 | 5 | 5 | 25 | C |
| | MgO | -Multistaged-Packed Tower | Neg | Neg | 1.1 | 0.55 | 20 | 5 | 5 | 30 | B |
| | | -Horizontal-Packed Bed Scrubber & Pumpout | Neg | Neg | 0.2 | 0.1 | 20 | 5 | 5 | 30 | B |
| | | -Pressure relief, dumping, venting to recovery | Neg | Neg | 0.0 | 0.0 | | | | | |
| | | -Pressure relief blowing | Neg | Neg | 4.2 | 2.1 | 15 | 5 | 5 | 25 | C |
| | NH ₃ | -Pressure relief & scrubbing | Neg | Neg | 0.43 | 0.22 | 20 | 5 | 5 | 30 | B |
| | | -Pressure relief only | Neg | Neg | 25.0 | 12.5 | 5 | 5 | 5 | 15 | D |
| | Na | -Pressure relief & scrubbing | Neg | Neg | 2.0 | 1.0 | 10 | 5 | 5 | 20 | C |
| | Ca | -Unknown | Neg | Neg | 67.0 | 3.4 | 10 | 5 | 5 | 20 | C |
| | Recovery System | MgO | -Multiclone and venturi scrubbers | 2.9 | 1.5 | 9.3 | 4.7 | 20 | 8 | 8 | 36 |
| | NH ₃ | -Ammonia absorption & mist eliminator | 0.65 | 0.33 | 7.3 | 3.7 | 18 | 5 | 7 | 30 | B |

a
b

Table 6. Emission Factors for Sulfite Pulping (Per Unit Weight of Air-Dried Unbleached Pulp)...CONTINUED

EMISSION FACTOR RATING

| Source | Base | Type Control | RANKING OF EMISSION FACTOR | | | | | | | | |
|---|-----------------|--|----------------------------|------------|----------------|----------|------------------------|--------------|----------------------|-------|------|
| | | | PARTICULATE MATTER | | SULFUR DIOXIDE | | Measured Emission Data | Process Data | Engineering Analysis | TOTAL | Rank |
| | | | lb/ADUT* | kg/ADUMT** | lb/ADUT | kg/ADUMT | | | | | |
| Recovery System | Na | -Smelt Recovery Sodium Carbonate Scrubbing | 3.8 | 1.9 | 2.0 | 1.0 | 10 | 5 | 5 | 20 | C |
| Acid Plant | NH ₃ | -Ammonia absorption, water &/or caustic scrubbing, Jenssen scrubbing | Neg | Neg | 0.33 | 0.17 | 15 | 5 | 5 | 25 | C |
| | Na | -Unknown ^d | Neg | Neg | 0.17 | 0.09 | 5 | 5 | 5 | 15 | D |
| | Ca | Jenssen scrubbing | Neg | Neg | 7.7 | 3.9 | 10 | 5 | 5 | 20 | C |
| Other ^c Sources (Knotting, Washing, Filtering, etc.) | All | -Unknown | Neg | Neg | 11.6 | 5.8 | 5 | 0 | 5 | 10 | D |

* ADUT - Air Dried Unbleached Ton

** ADUMT - Air Dried Unbleached Metric Ton

^aEmissions are long-term averages. Recovery systems are purged periodically resulting in higher instantaneous emissions. Where blowing is practiced, emissions occur intermittently.

^bDuring cooking cycle digester relief system transfers sulfur dioxide-laden gases to pressure accumulators where they are reabsorbed for use in cooking liquor.

^cThough these sources are considered minor, there is evidence which indicates that they are significant when major sources are well controlled. Emission rates were derived from only one plant.

4.3 METHOD OF ESTIMATION OF EMISSION FACTORS

In order to estimate the emission factors, the following method was used.

1. Data for the latest possible one-year period (usually 8/75 - 7/76) was obtained from the responsible regulatory agency for each plant within its jurisdiction.
2. Emissions from each source were averaged and tabulated by month.
3. A one-year mean for each plant source was calculated.
4. One-year means (Table 5) for similar operations and control techniques between different plants were averaged to obtain the values in Table 6.
5. For uncontrolled digesters, old data (1972-1974) were used from several plants, and a range determined.
6. For "other sources", the percent obtained from all sources other than digesters and recovery operations during the 1975 EPA tests at Great Northern, Millinocket, Maine, was used and applied as a rough estimate across the board.

4.4 RANKING OF EMISSION FACTORS

The reliability of the estimates in Table 6 is based upon criteria in which each calculation is ranked according to the amount and type of information utilized. Categories and numerical values are based upon:

Measured emission data: 20 points; maximum

Process data: 10 points; maximum

Engineering analysis: 10 points; maximum

The contribution of each category to each factor was summed and ranking was assigned as follows:

| <u>Numerical Rank</u> | <u>Letter Rank</u> |
|-----------------------|--------------------|
| < 5 | E (poor) |
| 6-15 | D (fair) |
| 16-25 | C (average) |
| 26-35 | B (good) |
| 36-40 | A (excellent) |

For the purposes of this study, it is seen from Table 6, that most information was present as emission data. This information which generally was from the plants in question, was reconciled with the capabilities of the control technology utilized at each specific plant and the process data submitted. The qualitative engineering judgment of the contractor and his knowledge of the current state-of-the-art was put to use in accomplishing the above.

Since the information compiled was analyzed and related to three bases, two emission contaminants, and thirteen control strategies, the reliability is not as great as might have been expected if all sulfite plants used the same process and technology.

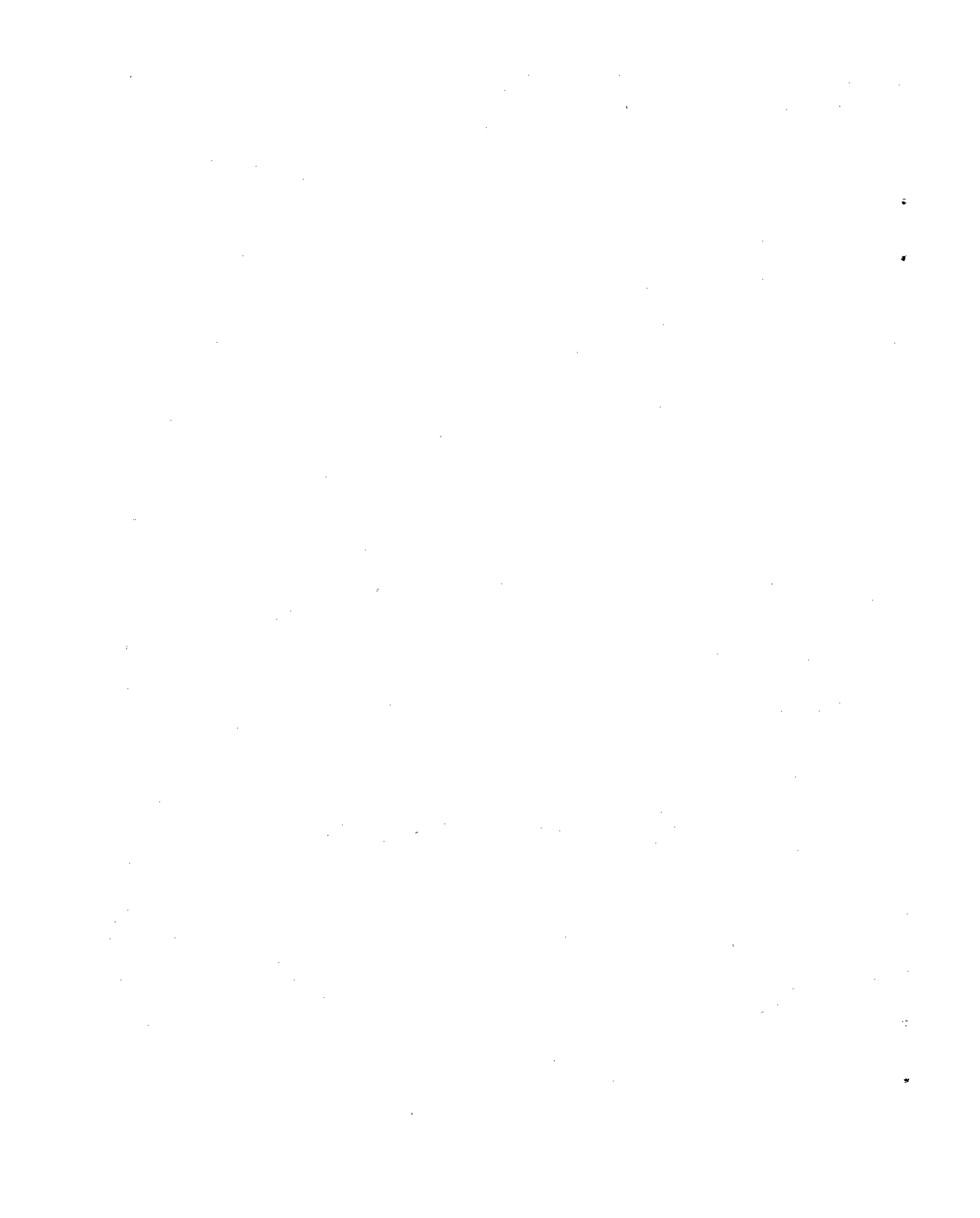
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APPENDIX

ADDRESS, PULP TYPES, AND
CAPACITIES OF ACID SULFITE MILLS
IN THE UNITED STATES

POST'S 1975 DIRECTORY



ALASKA

Ketchikan. Ketchikan Pulp Co., Box 1619 (99901)
Pulp Grades and Capacity: Dissolving magnesium
base sulfite 640 tpd, bleached pulp cap. 640 tpd.

Sitka. Alaska Lumber & Pulp Co., Inc., Box 1050 (99835)
Pulp Grades and Capacity: Alpha pulp, magnesium
base dissolving sulfite.

FLORIDA

Fernandina. ITT Rayonier, Inc., Zip (32034)
Pulp Grades and Capacity: Chemical cellulose 425 tpd,
(sulfite pulp) ammonia base.

MAINE

E. Mallinocket. Great Northern Paper Co., Zip (04430)
Pulp Grades and Capacity: Magnesium based sulfite,
groundwood 800 tpd (24 hr).

Winslow Scott Paper Co., Zip (04901)
Pulp Grades and Capacity: Calcium based sulfite
pulp and sulfite screenings 490 tpd.

NEW YORK

Glens Falls. Finch, Pruyn & Co., Inc., 1 Glen St. (12801)
Pulp Grades and Capacity: Ammonium base bisulfite
200 tpd.

OREGON

Newberg. Publishers Paper Co., Box 70 (97132)
Pulp Grades and Capacity: Magnesium based unbleached
sulfite 220 tpd; groundwood 420 tpd.

Oregon City. Publishers Paper Co., 419 Main St. (97045)
Pulp Grades and Capacity: Groundwood 400 tpd,
magnesium based sulfite 320 tpd, bleached pulp 100
tpd.

Salem. Boise Cascade Corp., 315 Commercial St. S. (97301)
Pulp Grades and Capacity: Ammonia base sulfite 250
tpd.

WASHINGTON

Anacortes. Scott Paper Co., 1709 R. Ave. (98221)
Pulp Grades and Capacity: Bleached, ammonia based
sulfite 140 tpd.

WASHINGTON (continued)

Bellingham. Georgia-Pacific Corp., Army & Chestnut Sts., Box 1236
(98225)
Pulp Grades and Capacity: Bleached, calcium based sulfite 500 tpd.

Camas. Crown Zellerbach. Zip (98607)
Pulp Grades and Capacity: Kraft 730 tpd, magnesium based sulfite 430 tpd, bleached pulp 980 tpd.

Cosmopolis. Weyerhaeuser Co., Zip (98537)
Pulp Grades and Capacity: Bleached sulfite 400 tpd.

Everett. Scott Paper Co., Zip (98201)
Pulp Grades and Capacity: Groundwood 30 tpd; ammonia based sulfite 850 tpd.

Hoquiam. ITT Rayonier, Inc., Box 299 (98550)
Pulp Grades and Capacity: Chemical cellulose and bleached sodium based sulfite paper-making pulps 475 tpd.

Longview. Weyerhaeuser Co., Zip (98632)
Pulp Grades and Capacity: Kraft 306 tpd; magnesium based sulfite 280 tpd; corrugating medium 240 tpd; bleached pulp 350 tpd.

Port Angeles. ITT Rayonier, Inc., Zip (98362)
Pulp Grades and Capacity: Chemical cellulose and bleached ammonia based sulfite paper-making pulps 475 tpd.

WISCONSIN

Appleton. Consolidated Papers, Inc., 1130 E. John (54911)
Pulp Grades and Capacity: Bleached calcium based sulfite 140 tpd.

Brokaw. Wausau Paper Mills Co., Zip (54417)
Pulp Grades and Capacity: Magnesium based sulfite 170 tpd.

Green Bay. American Can Co., Day St. (54305)
Pulp Grades and Capacity: Calcium based sulfite 150 tpd; groundwood 70 tpd.

Niagara. Niagara of Wisconsin Paper Corp., Zip (54151)
Pulp Grades and Capacity: Groundwood 150 tpd; bleached sulfite pulp 120 tpd.

WISCONSIN (continued)

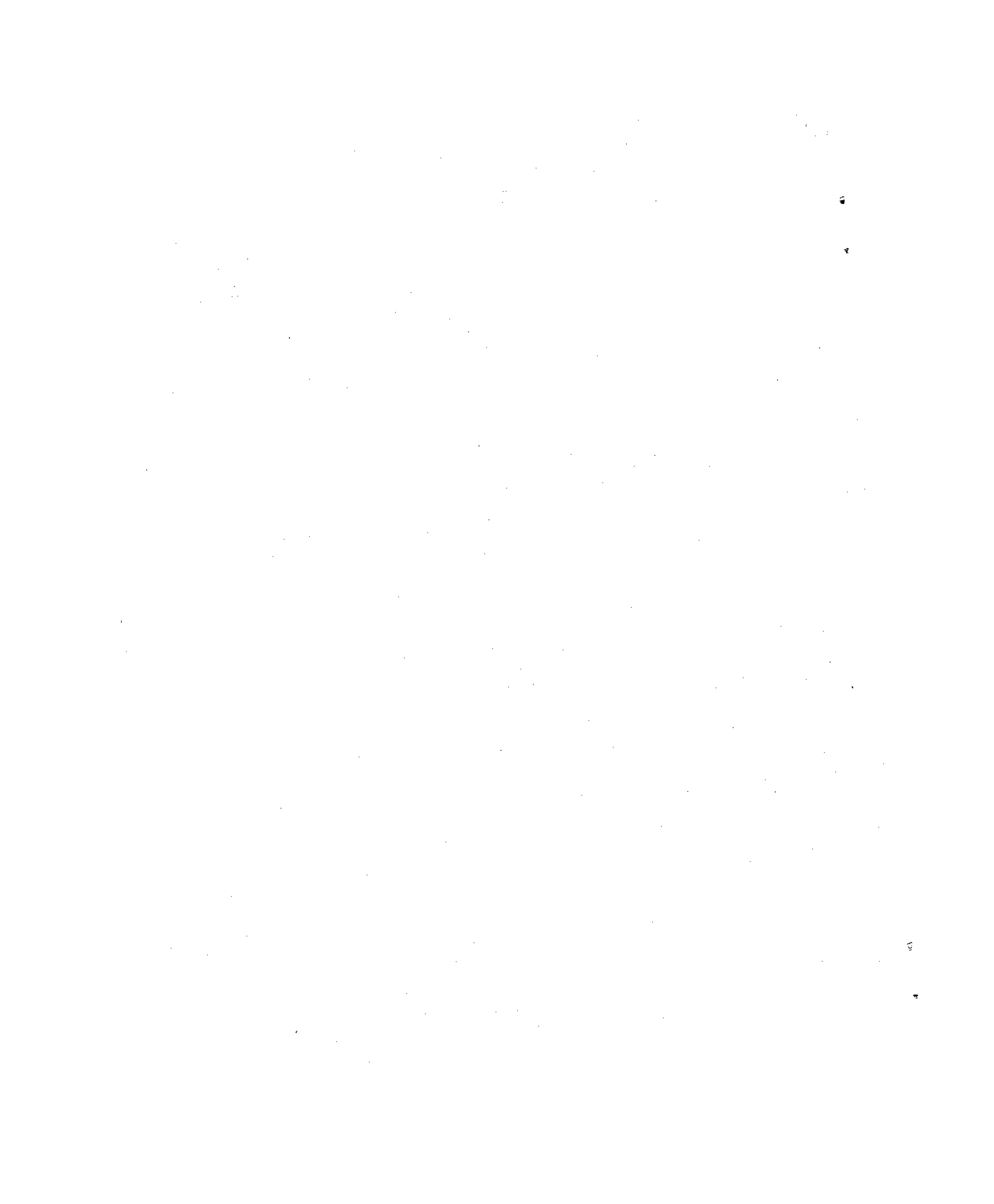
Oconto Falls. Scott Paper Co., Central Ave. (54154)
Pulp Grades and Capacity: Ammonia based sulfite
123 tpd; bleached pulp 123 tpd.

Park Falls. Flambeau Paper Co., 200 N. 1st Avenue (54552)
Pulp Grades and Capacity: Calcium based sulfite
120 tpd; bleached pulp 110 tpd.

Peshtigo. Badger Paper Mills, Inc., W. Front St., Box 149
(54157)
Pulp Grades and Capacity: Bleached, calcium based
sulfite 120 tpd.

Port Edwards. Nekoosa Edwards Paper Co., Inc., 100 Wisconsin River
Dr. (54469)
Pulp Grades and Capacity: Magnesium based sulfite
235 tpd.

Rothschild. Weyerhaeuser Co., Box 200 (54474)
Pulp Grades and Capacity: Bleached, calcium based
sulfite 200 tpd.



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| 16. ABSTRACT The sulfite pulping industry primarily is characterized by the type of base chemical used in conjunction with sulfurous acid to effect delignification of gymnosperm woods. It further is characterized by the level of acidity during the digestion operation and by the extent of recovery of chemicals and waste heat. This report describes the methodology used in obtaining emission factors for AP-42, Compilation of Air Pollutant Emission Factors on acid sulfite pulping. | | |
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