

## CHEMICAL RECOVERY COMBUSTION SOURCES AT U.S. SULFITE PULP MILLS

### 1.0 INTRODUCTION

This report summarizes information collected under EPA work assignment No. III-98 for chemical recovery combustion equipment at U.S. sulfite pulp mills that produce chemical pulp. The report:

1. Discusses the U.S. population of sulfite mills;
2. Provides a brief process description for the chemical recovery processes used at sulfite mills;
3. Discusses the types of chemical recovery combustion sources and process/air pollution control equipment used at sulfite mills;
4. Presents information on which mills have pulp mill source emission controls integrated with chemical recovery equipment; and
5. Presents hazardous air pollutant (HAP), particulate matter (PM), and sulfur dioxide (SO<sub>2</sub>) emission data for chemical recovery combustion sources.

### 2.0 U.S. POPULATION

There are currently 15 operating sulfite mills producing chemical pulp in 7 States.<sup>1</sup> (Note that those mills producing semichemical pulp using a neutral sulfite process [i.e., NSSC pulp] are not discussed in this report.) Over the years, the number of sulfite mills has steadily declined.<sup>2</sup> The majority of currently operating sulfite mills (i.e., 67 percent) are located in the States of Washington and Wisconsin, which have five mills each. Five States--Alaska, Florida, Maine, New York, and Pennsylvania--have one operating sulfite mill each. Company names and locations for the 15 sulfite mills are listed in Table 1.<sup>1</sup>

### 3.0 CHEMICAL RECOVERY PROCESS DESCRIPTION

The function of the chemical recovery process is to recover chemicals from spent sulfite cooking liquor (also called red liquor). At the currently operating sulfite chemical pulp mills,

TABLE 1. U. S. SULFITE PULP MILLS<sup>a, b</sup>

No.	Mill name	City	State
Magnesium base			
1	Weyerhaeuser Paper Company	Cosmopolis	WA
2	James River Corporation	Camas	WA
3	Wausau Paper Mills Company	Brokaw	WI
4	Georgia-Pacific Corporation-- Nekoosa Paper Company	Port Edwards	WI
5	Ketchikan Pulp Company	Ketchikan	AK
6	Great Northern Paper Company	Millinocket	ME
Ammonia base			
1	Scott Paper Company	Everett	WA
2	ITT Rayonier Inc.	Port Angeles	WA
3	Badger Paper Mills Inc.	Peshtigo	WI
4	ITT Rayonier Inc.	Fernandina Beach	FL
5	Finch, Pruyn, & Company, Inc.	Glens Falls	NY
6	Procter & Gamble	Mehoopany	PA
Calcium base <sup>c</sup>			
1	Georgia-Pacific Corporation	Bellingham	WA
2	Weyerhaeuser Paper Company	Rothschild	WI
3	Cross-Pointe Paper Company	Park Falls	WI

<sup>a</sup>Recent mill closings (1991-93):

1. Alaska Pulp Corporation in Sitka, AK (magnesium-based sulfite).
2. ITT Rayonier, Inc. in Hoquiam, WA closed sodium-based sulfite pulping operations; paper is now produced from purchased pulp.

<sup>b</sup>There are currently no operating sodium-based sulfite mills.

<sup>c</sup>Chemical recovery combustion units are not used at calcium-based sulfite mills.

an acid cooking liquor is used to cook the wood chips. Alkaline sulfite pulping is also possible but is largely experimental. The sulfite chemical pulping processes currently used at U.S. mills can be classified as either acid sulfite or bisulfite. In the acid sulfite process, the initial pH level of the cooking liquor is 1 to 2. In the bisulfite (also called Magnefite™ if a magnesium-base cooking liquor is used) process, the cooking liquor initial pH is 2 to 6. For comparison, cooking liquor used in the neutral sulfite semichemical process has an initial pH of 6 to 10, and kraft cooking liquor, which is an alkaline process, has an initial pH of about 13.5.<sup>3,4</sup> In addition to initial pH level, sulfite cooking liquors are also classified by the chemical base.

In preparing sulfite cooking liquors, cooled SO<sub>2</sub> gas is absorbed in water containing one of four chemical bases--magnesium (Mg), ammonia (NH<sub>3</sub>), sodium (Na), or calcium (Ca). Sulfur dioxide in spent cooking liquor can be recovered for all four liquor types. The bases Mg and Na can also be recovered. However, it is not practical to recover Ca, and NH<sub>3</sub> is destroyed when the spent liquor is combusted.

The remainder of this report discusses only Mg-based and NH<sub>3</sub>-based sulfite mills because existing mills that use combustion equipment to recover cooking liquor chemicals use one of these two processes. At Ca-based sulfite mills, by-products recovery (e.g., lignin chemicals and alcohol) is practiced but chemical recovery combustion equipment is not used.<sup>3</sup> Additionally, there are currently no Na-based sulfite mills operating in the United States.<sup>1</sup>

As indicated in Table 1, there are six Mg-based sulfite mills and six NH<sub>3</sub>-based sulfite mills. The system used to recover cooking chemicals is particular to the base. Brief process descriptions for Mg- and NH<sub>3</sub>-based sulfite mills are provided below, beginning with the point at which spent liquor enters the chemical recovery combustion unit.

### 3.1 MG-BASED SULFITE CHEMICAL RECOVERY PROCESS

A simplified process flow diagram for Mg-based sulfite mills is included as Figure 1. As shown in Figure 1, spent liquor is burned in a recovery furnace or fluidized bed reactor. Combustion of the spent liquor produces heat for steam generation and also exhaust gases that contain magnesium oxide (MgO) particulate and sulfur dioxide (SO<sub>2</sub>) gas. If a recovery furnace is used, the major portion of the MgO is recovered from the exhaust gases as a fine white powder using multiple cyclones. If a fluidized bed reactor is used, MgO is collected in a cyclone and as pulverized bed material.<sup>3</sup> The MgO is then slaked with water to form magnesium hydroxide (Mg(OH)<sub>2</sub>), which is used as circulating liquid in a series of absorption towers and/or venturi scrubbers designed to recover SO<sub>2</sub> from the recovery furnace exhaust gases. Prior to passing through the absorption towers/venturi scrubbers, exit gases from the MgO PM removal equipment enter a cooling tower. Cooling the gases increases SO<sub>2</sub> absorption. In the absorption towers/venturi scrubbers, SO<sub>2</sub> is recovered by reaction with Mg(OH)<sub>2</sub> to form a magnesium bisulfite solution. The magnesium bisulfite solution is then routed to a fortification tower where it is fortified with makeup SO<sub>2</sub> from a sulfur burner and subsequently used as cooking liquor in a digester. The fortification tower and sulfur burner area of the mill is typically referred to as the acid plant. However, the term acid plant is used loosely, and the acid plant may be defined to include the SO<sub>2</sub> absorption towers/venturi scrubbers. Some mills have installed equipment downstream of the SO<sub>2</sub> absorption equipment, such as a fiber-bed mist elimination system or an educted venturi scrubber, to further reduce PM and/or SO<sub>2</sub> prior to discharge to the atmosphere.

### 3.2 NH<sub>3</sub>-BASED SULFITE CHEMICAL RECOVERY PROCESS

A simplified process flow diagram for NH<sub>3</sub>-based sulfite mills is included as Figure 2. As shown in Figure 2, spent liquor is fired in a recovery furnace or combustor. Combustion of the spent liquor produces heat for steam generation and also combustion gases that contain recoverable SO<sub>2</sub>. The ammonia base

Figure 1. Mg-based sulfite chemical recovery process.

Figure 2.  $\text{NH}_3$ -based sulfite chemical recovery process.

is consumed during combustion, forming nitrogen and water. A small amount of ash is produced and periodically removed from the furnace bottom. Sulfur dioxide is recovered from cooled flue gas in an absorption tower/scrubbing system by reaction with fresh aqueous ammonia to form an ammonium bisulfite solution. The ammonium bisulfite solution is fortified with makeup SO<sub>2</sub> from a sulfur burner and used as cooking liquor in a digester. Exit gases from the absorption tower/scrubbing system are typically routed to a fiber-bed mist eliminator system for PM removal and mist elimination prior to being discharged to the atmosphere. Some mills have installed a scrubber or mesh-pad mist eliminator upstream of the fiber-bed mist eliminator system for additional emission control.

#### 4.0 CHEMICAL RECOVERY COMBUSTION SOURCES AND PROCESS/AIR POLLUTION CONTROL EQUIPMENT

Combustion sources and the process/air pollution control equipment that are located downstream of these combustion sources for each Mg- and NH<sub>3</sub>-based sulfite mill are listed in Table 2.<sup>5</sup> Note that some of the equipment operated downstream of the chemical recovery combustion device serves a dual role of process equipment and air pollution control (e.g., multiple cyclones used to collect MgO particulate and absorption towers used to recover SO<sub>2</sub>), whereas other equipment was installed for the sole purpose of reducing air emissions (e.g., an SO<sub>2</sub> scrubber or fiber-bed mist eliminator system installed downstream of an SO<sub>2</sub> absorption tower). More specific information on the chemical recovery equipment is presented by base chemical in the following subsections and in Appendices A and B.

##### 4.1 MG-BASED SULFITE MILLS

Mill-specific information, including schematics where available, for each Mg-based sulfite mill is presented in Appendix A. A summary of the chemical recovery combustion sources and process/air pollution control equipment operated at these mills follows.

TABLE 2. CHEMICAL RECOVERY COMBUSTION SOURCES AND  
 PROCESS/AIR POLLUTION CONTROL EQUIPMENT

Mill code	Combustion sources <sup>a</sup>	Process/air pollution control equipment
Magnesium base		
5	1 Copeland NDCE fluidized bed reactor	MgO PM removal equipment + 3-stage venturi scrubber
133	1 B&W NDCE fluidized bed reactor	Dust collector + cooling tower + 3-stage packed absorption tower
93	4 B&W NDCE recovery furnaces	Multiclone + cooling tower + 3-stage absorption tower + fiber-bed demister system (2 parallel sets)
80	2 B&W NDCE recovery furnaces & 1 B&W DCE recovery furnace	RF1 & RF2 (2 parallel sets): multiclones + cooling tower + 3 absorption towers + common educted venturi scrubber RF3: multiclone + cyclone evaporator + 3-stage venturi scrubber + 1 absorption tower + common educted venturi scrubber
12	1 B&W NDCE recovery furnaces	Multiclone + 4-stage venturi scrubber + packed-bed scrubber + mist eliminator
A	1 B&W recovery furnace	MgO recovery system (no additional information available)
Ammonia base		
52	1 B&W NDCE recovery furnace	Cooling tower + absorption tower + DynaWave® reverse jet scrubber + fiber-bed demister system
94	1 C-E NDCE recovery furnace	Absorption cooling tower + mesh pad demister + fiber-bed demister system
128	1 B&W NDCE recovery furnace	Absorption/cooling tower + fiber-bed demister system
121	2 NDCE recovery furnaces (1 B&W, 1 C-E)	Common absorption tower + mesh pads + fiber-bed demister system
41	4 NDCE recovery furnaces (2 are Loddby furnaces) <sup>b</sup>	SO <sub>2</sub> scrubber/absorber + fiber-bed demister system (number of parallel sets unknown)
B	1 Marathon Engineering DCE combustion unit (one-of-a-kind)	Venturi scrubbers + bubble tray absorption tower (incomplete information)

<sup>a</sup>Nondirect contact evaporator (NDCE) is used to indicate that there is no direct contact evaporator (DCE). The system may have multiple effect evaporators (MEE) and a concentrator or may have MEE only or MEE and vapor recompression evaporators.

<sup>b</sup>Information on the manufacturer of the other 2 recovery furnaces is not available.

#### 4.1.1 Chemical Recovery Combustion Sources

Four of the six Mg-based sulfite mills operate recovery furnaces to recover MgO and SO<sub>2</sub> from spent cooking liquor and produce steam. There are a total of nine recovery furnaces at these four mills--two mills operate one recovery furnace each, one mill operates three furnaces, and the fourth mill operates four furnaces. All nine recovery furnaces were manufactured by Babcock & Wilcox (B&W). A schematic of a B&W Mg-based sulfite recovery furnace is shown in Figure 3. As with kraft recovery furnaces, the furnaces may be a direct contact evaporator (DCE) furnace or a nondirect contact evaporator (NDCE) furnace, depending upon the final evaporation equipment following the multiple-effect evaporator (MEE). Alternatively, a mill may use neither a DCE nor NDCE. At these mills, the desired liquor solids content is achieved solely with the MEE. Information on the evaporator type is available for eight of the nine furnaces. Of these eight furnaces, one is a DCE recovery furnace and the others are either NDCE furnaces or use a MEE only. The magnesium-based sulfite recovery furnaces differ from kraft recovery furnaces in that there are no smelt beds. The red liquor solids firing rate for the magnesium-based sulfite recovery furnaces ranges from approximately 454,000 to 1.4 million pounds of red liquor solids per day (lb RLS/d). The average firing rate for the eight furnaces for which data are available is 627,000 lb RLS/d. In comparison, the average firing rate for kraft recovery furnaces is 2.3 million lb black liquor solids/d. Red liquor is fired at a solids content of between 52 and 60 percent.<sup>5</sup>

Two of the six Mg-based sulfite mills operate fluidized bed reactors. There is one reactor at each of the two mills. One reactor is a B&W reactor and the other is a Copeland reactor. The firing rate for the B&W reactor is approximately 535,400 lb RLS/d; the firing rate for the Copeland reactor is not available. Red liquor is fired at a solids content of 50 percent in the B&W reactor and 45 percent in the Copeland reactor.<sup>5</sup> Two schematics for the fluidized bed system are shown in Figure 4.

Figure 3. B&W Mg-based sulfite recovery furnace  
(Pulp and Paper Manufacturer, Volume 4, Sulfite Science and  
Technology, p. 271).

Figure 4a. General features of fluidized-bed incinerator.  
(Pulp and Paper Manufacturing, Volume 4, Sulfite Science  
and Technology, p. 276).

Figure 4b. Copeland fluidized-bed reactor system--  
Mg-based sulfite.  
(Pulp and Paper Manufacturing, Volume 4, Sulfite Science  
and Technology, p. 276).

shows the general features of a fluidized bed reactor and Figure 4b shows the Copeland reactor system. Spent liquor is fed through the top of the reactor chamber. Fluidizing gas at a carefully controlled flow rate passes up through the bed of solid particles setting the bed in fluid motion. The fluidized bed resembles a boiling liquid. An advantage of a fluidized bed reactor is that heat losses are minimal, which enables the temperature of a reaction to be easily controlled and maintained even with large variations in liquor supply or periods when there is no liquor supply. The organic matter in the spent liquor is converted to carbon dioxide and water and the magnesium complexes formed during pulping are decomposed to form MgO particulate and SO<sub>2</sub> gas. The MgO particulate is collected as pulverized bed material. Exhaust gases pass through a cyclone, which collects MgO entrained in the exhaust gases, and then through a waste heat boiler for steam production.<sup>3</sup>

#### 4.1.2 Chemical Recovery Process/Air Pollution Control Equipment

All of the Mg-based sulfite mills have MgO particulate removal equipment following the chemical recovery combustion device. With the recovery furnaces, multiple cyclones are used to remove the MgO particulate from the recovery furnace flue gas. With the fluidized bed reactors, MgO is collected in a cyclone and as pulverized bed material.

Information on the equipment installed downstream of the MgO recovery system is available for five of the six Mg-based sulfite mills. Each mill has SO<sub>2</sub> recovery equipment, which includes either absorption tower(s) and/or multiple-stage venturi scrubbers. The SO<sub>2</sub> recovery equipment uses Mg(OH)<sub>2</sub>, which is produced from the recovered MgO, as the SO<sub>2</sub> absorption fluid.

Of the five mills for which information is available, three have installed an air pollution control device downstream of the SO<sub>2</sub> absorption equipment. At one mill, fiber-bed mist eliminator systems (i.e., Brinks demister systems) are used for additional particulate control. There are two fiber-bed mist eliminator systems operated in parallel at this mill; each system controls emissions from two recovery furnaces. At the second mill, an

educted venturi scrubber provides additional control of air pollutants. Gas streams from all three recovery furnaces operated at the mill are routed to this scrubber. The third mill operates a packed bed scrubber and mist eliminator following the SO<sub>2</sub> absorption equipment. Neither of the two mills that have fluidized bed reactors have additional equipment downstream of the SO<sub>2</sub> recovery equipment.

#### 4.2 NH<sub>3</sub>-BASED SULFITE MILLS

Mill-specific information, including schematics where available, for each NH<sub>3</sub>-based sulfite mill is presented in Appendix B. A summary of the chemical recovery combustion sources and process/air pollution control equipment operated at these mills follows.

##### 4.2.1 Chemical Recovery Combustion Sources

Five of the six NH<sub>3</sub>-based sulfite mills operate recovery furnaces to recover SO<sub>2</sub> from spent cooking liquor and produce steam. The sixth mill has a Marathon Engineering combustion unit, which is a one-of-kind system. No process operating data are available for the Marathon Engineering combustor.

There are a total of nine NH<sub>3</sub>-based sulfite recovery furnaces--three mills operate one recovery furnace, one mill operates two furnaces, and one mill operates four furnaces. Manufacturers of these nine recovery furnaces include B&W, Combustion Engineering (C-E), and Loddby. Figure 5 is a schematic of a C-E recovery furnace. Spent red liquor is fired at solids concentrations ranging from 50 to 60 percent. Average solids firing rates for three of the five furnaces for which data are available are between 1.3 and 1.4 million lb RLS/day. Average firing rates for the other two furnaces for which data are available are 750,000 lb RLS/d/furnace.<sup>5</sup> The NH<sub>3</sub>-based sulfite recovery furnaces do not have smelt beds. However, a small amount of ash is produced and is periodically removed from the furnace bottom. Approximately 80 percent of the SO<sub>2</sub> in the spent liquor can be recovered.

Figure 5. C-E  $\text{NH}_3$ -based sulfite recovery furnace.  
(Pulp and Paper Manufacturer, Volume 4, Sulfite Science  
and Technology, p. 274).

#### 4.2.2 Chemical Recovery Process/Air Pollution Control Devices

All of the mills have some type of gas cooling system and SO<sub>2</sub> absorption system, typically a multi-sectioned tower with the lower sections for cooling and the upper sections for SO<sub>2</sub> absorption. Sufficient information on the equipment located downstream of the absorption/cooling system is available for five of the six mills. Each of these five mills has fiber-bed mist eliminator systems for controlling PM emissions. These systems consist of multiple tanks containing numerous filter elements (on the order of 20/tank). The filter elements, also called "candles," are densely packed with glass or polyester fibers. Liquid condensing from the stack gases continually removes some of the captured PM from the filter elements. In addition, the filter elements are periodically washed to remove PM. At one mill, a DynaWave® reverse jet scrubber precedes the fiber-bed mist eliminator system, serving as a precleaner. This scrubber removes particulate and absorbs SO<sub>2</sub>. Two other mills have mesh-pad mist eliminators preceding the fiber-bed mist eliminator system.

#### 5.0 INTEGRATION OF PULP MILL SOURCES WITH CHEMICAL RECOVERY EQUIPMENT

Available information on the integration of pulp mill and chemical recovery combustion source emissions for each Mg- and NH<sub>3</sub>-based sulfite mill is presented in Table 3. For the purposes of this discussion, MEE and vapor recompression (VRC) evaporators are included as "pulp mill sources." In Table 3, "yes" has been entered in the column labeled "common control device" if exit gases from at least one pulp mill source are routed to a piece of equipment located downstream of the chemical recovery combustion source. The next column indicates which pulp mill emission source(s) is tied into the chemical recovery loop. The table also lists the piece of equipment in the chemical recovery loop to which the pulp mill gases are routed.

Sufficient information is available to determine whether pulp mill and chemical recovery combustion sources have been integrated for 10 of the 12 Mg- and NH<sub>3</sub>-based sulfite mills. For

TABLE 3. INTEGRATION OF PULP MILL SOURCES WITH CHEMICAL RECOVERY EQUIPMENT

No.	Mill code	Common control device	Noncombustion pulp mill emission source integrated with chemical recovery equipment	Inlet location for integrated pulp mill gases	Reference
<b>Magnesium base</b>					
1	5	Yes	Blow gases, high-pressure accumulator and washer gases	Recovery gas system (3 venturi scrubbers)	Trip report
2	133	? <sup>a</sup>	?Digester relief & blow gases [Evaporator NCG's incinerated in fluidized bed reactor]	Sulfite acid making system; no information on exact location	Survey response
3	93	? <sup>a</sup>	?Digester relief & blow gases [Evaporator NCG's vented to atmosphere]	Sulfite acid making system; no information on exact location	Survey response
4	80	Yes	Evaporator NCG's	No. 1 and No. 2 cooling towers	Trip report
5	12	No	[Evaporator overhead, digester, and weak liquor storage tank vent gases incinerated in recovery furnace]	--	Trip reports
6	A	Yes	No information available	No information available	Mill contact
<b>Ammonia base</b>					
1	52	Yes	Washers, tanks, evaporator NCG's, dump chests, hot well, etc.	Absorption tower inlet	EPA/industry meeting (2/94)
2	94	Yes	MEE condenser, VRC evaporator, tanks (quench, stripper feed, ...)	Recovery furnace absorber	Trip report
3	128	Yes	Evaporator NCG's	Recovery furnace scrubber/absorber system	Test report
4	121	No	[Separate SO <sub>2</sub> scrubber for pulp mill emissions]	--	Mill contact
5	41	Yes	Evaporator overhead gases & strong liquor storage tank	Fortification tower (which is vented to furnace SO <sub>2</sub> scrubber/absorber)	Survey response
6	B	No	[Separate system for noncombustion sources; emission controls unknown]	--	Mill contact

<sup>a</sup>Survey response states that digester relief and blow gases are routed to the sulfite acid making system, which may or may not be a point located downstream of the chemical recovery combustion equipment.

7 of the 10 mills (70 percent), gases from at least one pulp mill source are integrated with the chemical recovery combustion flue gas process and air pollution control systems. Mills route pulp mill sources to the chemical recovery loop to recover SO<sub>2</sub> and reduce SO<sub>2</sub> emissions.

Of the three mills that have not integrated pulp mill sources with combustion source control systems, one mill incinerates evaporator overhead gases, digester gases, and weak liquor storage tank vent gases in the recovery furnace. The second mill has a separate SO<sub>2</sub> scrubber for pulp mill sources. Specifics of pulp mill source emission controls for the third mill are not available.

At the two mills for which sufficient information is unavailable, evaporator overhead gases are either incinerated in a fluidized bed reactor or vented directly to the atmosphere. Digester and relief gases are sent to the acid-making systems. The inlet location of the digester and relief gases to the acid making systems is unknown (i.e., whether these gases enter the system downstream of the fluidized bed reactor or at a point that is not tied into the chemical recovery equipment); therefore, a definite determination as to whether or not pulp mill sources are integrated with the chemical recovery equipment cannot be made.

One mill is currently evaluating the option of venting pulp mill gases to the recovery furnaces as combustion air for the purpose of odor control. To date, these tests have not been successful; boiler stability and corrosion are the main problems. ITT Rayonier has also explored this option but was not successful.<sup>7</sup>

#### 6.0 HAP, PM, AND SO<sub>2</sub> EMISSION DATA

The pollutant of concern at sulfite mills has traditionally been SO<sub>2</sub>, for both economic (i.e., recovered SO<sub>2</sub> is reused) and environmental reasons. Particulate matter emissions also have been controlled. At Mg-based sulfite mills, the recovery and reuse of the base chemical requires the use of PM emission control equipment. At some Mg-based sulfite mills, additional control devices have been installed for the sole purpose of

reducing SO<sub>2</sub> and PM stack emissions. At NH<sub>3</sub>-based sulfite mills, PM is controlled solely for environmental reasons. The equipment installed for chemical recovery or the reduction of SO<sub>2</sub> and PM emissions may provide incidental control of HAP's, such as the reduction of hydrogen chloride (HCl) emissions by a scrubber that was designed to reduce SO<sub>2</sub> emissions or the reduction of PM HAP emissions by a fiber-bed mist eliminator system that was designed to reduce total PM emissions. The following discussion presents available HAP, PM, and SO<sub>2</sub> emission test data for chemical recovery combustion sources at sulfite mills.

#### 6.1 HAP EMISSION DATA

The HAP emission data discussion is divided into two sections: (1) nonmetals and (2) metals.

##### 6.1.1 Nonmetals

Table 4 presents available sulfite recovery furnace data for those HAP's with a calculated annual emission rate greater than 1 ton per year (ton/yr) for a mill with a pulp production rate of 500 ton/d. Based on this data, which includes data from tests conducted at five mills, eight gaseous HAP would be emitted in quantities greater than 1 ton/yr at the emission and process rates measured during the tests. These eight HAP are methanol, acetaldehyde, formaldehyde, HCl, methyl ethyl ketone (MEK), tetrachloro-ethylene, chloromethane, and 1,2,4-trichlorobenzene. Test data are not available for the two fluidized bed reactors or the Marathon Engineering combustor.

Based on the limited data in Table 4, methanol is the predominant HAP. At Mill I, methanol accounted for 93 percent of total HAP emissions of 6.8 pounds per ton of red liquor solids (lb/T RLS). Acetaldehyde accounted for 3 percent of the total HAP emissions and formaldehyde accounted for 2 percent.<sup>6</sup> Factors that likely impacted HAP emission levels for the recovery furnaces at Mill I are (1) one of the recovery furnaces is a DCE furnace; (2) evaporator overhead gases are vented to the cooling towers, which are located downstream of the recovery furnaces; and (3) evaporator condensates, if available, are used in these cooling towers. At Mill P, methanol accounted for over

TABLE 4. SULFITE RECOVERY FURNACES: HAP DATA SUMMARY<sup>a</sup>

HAP	Emission factor, lb/ton red liquor solids	Annual emissions, ton/yr (mill pulp production rate = 200 ton/d) <sup>b</sup>	Annual emissions, ton/yr (mill pulp production rate = 500 ton/d) <sup>c</sup>	Reference <sup>d</sup>
methanol	6.30; 1.64; 0.511; 0.246	354; 92.1; 28.7; 13.8	884; 230; 71.7; 34.5	I; P; ITT; SFRB
acetaldehyde	0.195; 0.0354; 0.00166	11.0; 1.99; 0.0932	27.4; 4.97; 0.233	I; P; SFRB
formaldehyde	0.115; 1.74x10 <sup>-5</sup>	6.46; 9.77x10 <sup>-4</sup>	16.1; 0.00244	I; SFRB
HCl	0.0588	3.30	8.26	ITT
MEK	0.0137	0.769	1.92	P
tetrachloroethylene	0.0189	1.06	2.65	I
chloromethane	0.00934; 1.42x10 <sup>-5</sup>	0.524; 7.97x10 <sup>-4</sup>	1.31; 0.00199	SFRB; AK
1,2,4-trichlorobenzene	0.00983	0.552	1.38	P

<sup>a</sup>HAP with a calculated annual emission rate greater than 1 ton for a mill pulp production rate of 500 ton/d are listed. The emission rates are calculated from the average of the test runs.

<sup>b</sup>Based on a RLS feed rate of 640,000 lb/d, which was calculated using a conversion factor of 3,200 lb RLS/ton of pulp.<sup>5</sup>

<sup>c</sup>Based on a RLS feed rate of 1.6 MMlb/d, which was calculated using a conversion factor of 3,200 lb RLS/ton of pulp.<sup>5</sup>

<sup>d</sup>References

(I) A 1993 NCASI test conducted at Mill I, a Mg-based sulfite mill. The emission point tested was the final discharge point for flue gases from three recovery furnaces. The following equipment and practices may contribute to emissions: (1) one of the recovery furnaces is a DCE furnace; (2) evaporator overhead gases are vented to the cooling towers, which are located upstream of this discharge point; and (3) evaporator condensates, if available, are used in the cooling towers.

(P) A 1994 NCASI test conducted at Mill P, an NH<sub>3</sub>-based sulfite mill. The emission point tested was the final discharge point for flue gases from one recovery furnace. Evaporator overhead gases are vented to the recovery furnace scrubber/absorption system.

(ITT) A 1991 ITT Rayonier test conducted at the Port Angeles, Washington, mill. The emission point tested is the final discharge point for flue gases from one recovery furnace. The multiple effect evaporator condenser, VRC evaporator, and miscellaneous tanks are vented to the recovery furnace absorber.

(SRFB) A 1991 test at an NH<sub>3</sub>-based sulfite mill, for which test data are presented in the NCASI Technical Bulletin No. 650 (SRFB). The emission point tested was the final discharge point for one recovery furnace. Mill identification is unknown. Therefore, control device or side stream information cannot be determined.

(AK) A 1990 mill-sponsored test conducted at Alaska Pulp Corporation in Sitka, Alaska. The emission point tested is the final discharge point for recovery furnace No. 3. This mill has closed. Process and emission control equipment consisted of multiclones + cooling tower + absorption towers + chevron mist eliminator + 2 wet ESP's in parallel. Digester relief gases were vented to the acid making system.

89 percent of the total HAP emissions of 1.8 lb/T RLS and acetaldehyde accounted for 2 percent of the total.<sup>6</sup> Hazardous air pollutants were also measured at one inlet stream to the recovery furnace absorber at Mill P. The inlet stream analyzed was the exhaust stream from the recovery furnace. Evaporator overhead gases are also routed to the recovery furnace absorber but were not analyzed. Recovery furnace outlet and absorber outlet data are presented in Table 5. The major HAP constituents in the recovery furnace vent gases entering the absorber were formaldehyde (56 percent), methanol (19 percent), MEK (4 percent), and acetaldehyde (2 percent). The total HAP content at the furnace outlet, 0.37 lb/TRLS, was less than the total HAP emissions measured at the absorber outlet. The increase in HAP's across the absorber may be due to the evaporator overhead gases that are routed to the absorber. The evaporator overhead gases likely contain significant levels of methanol and other organic HAP's.<sup>6</sup>

The test data presented in Table 4 are from the following sources:

1. A 1993 test conducted at Mill I, a Mg-based sulfite mill, as part of an extensive National Council of the Paper Industry for Air and Stream Improvement, Inc. (NCASI) HAP emission test program;
2. A 1994 test conducted at Mill P, an NH<sub>3</sub>-based sulfite mill, which was also part of the NCASI HAP emission test program;
3. A 1991 test conducted at ITT Rayonier in Port Angeles, Washington, by ITT Rayonier Inc. as a screening test to increase their understanding of HAP's;
4. A 1991 test at an NH<sub>3</sub>-based sulfite mill, for which test data are presented in the NCASI Technical Bulletin No. 650 (SRFB); and
5. A 1990 mill-sponsored test conducted at Alaska Pulp Corporation in Sitka, Alaska.

Additional sulfite recovery furnace HAP data is available from a comprehensive air toxics test program conducted in late 1994 at Ketchikan Pulp Company in Ketchikan, Alaska. The tests

TABLE 5. SUMMARY OF EMISSION DATA FOR MILL P RECOVERY  
 FURNACE ABSORBER STACK

Analyte	No. of test runs		Emission factor, lb/ton RLS	Annual emissions, ton/yr <sup>b</sup>
	AQL <sup>a</sup>	Total		
FURNACE OUTLET				
formaldehyde	3	3	0.209	26.13
methanol	3	3	0.0721	9.01
terpenes	3	3	0.0471	5.89
methyl ethyl ketone	3	3	0.0158	1.98
acetone	3	3	0.0106	1.33
acetaldehyde	1	3	0.00849	1.06
trichloroethylene	1	3	0.00783	0.98
acrolein	1	3	0.00209	0.26
toluene	1	3	0.00145	0.18
SCRUBBER OUTLET				
methanol	3	3	1.64	205
terpenes	3	3	0.173	21.6
acetaldehyde	3	3	0.0354	4.43
acetone	3	3	0.0309	3.86
methyl ethyl ketone	3	3	0.0137	1.71
1,2,4-trichlorobenzene	3	3	0.00983	1.23
o-xylene	3	3	0.00544	0.68
styrene	1	3	0.00353	0.44
m,p-xylene	2	3	0.00321	0.40
toluene	3	3	0.00292	0.37
chlorobenzene	1	3	0.00165	0.21
methyl isobutyl ketone	1	3	0.00128	0.16
n-hexane	1	3	0.0011	0.14

<sup>a</sup>Above quantitation limit.

<sup>b</sup>Based on operation of 24 hr/d, 351 d/yr.

were conducted to support current permit negotiations with the State agency, which is requiring inclusion of as many Title III and Title V requirements as can be anticipated. There are currently no HAP permit limits; however, mill personnel anticipate that some HAP permit limits will be set during the first quarter of 1995. The test report may also include PM-10 data.<sup>7</sup>

#### 6.1.2 Metals

Emission data for HAP metals are available from one source, a 1990 mill-sponsored test conducted at Alaska Pulp Corporation in Sitka, Alaska. The quantity of HAP metals detected at the emission and process rates measured during the test was 45 lb/yr. The HAP metals detected were manganese compounds (33 lb/yr), lead compounds (5.4 lb/yr), chromium compounds (3.0 lb/yr), cadmium compounds (2.7 lb/yr), and arsenic compounds (1.1 lb/yr). These data are stack data for recovery furnace No. 3.<sup>8</sup> Flue gases from this furnace pass through multiclones, a cooling tower, absorption towers, a chevron mist eliminator, and two wet ESP's (in parallel) prior to discharge through the stack.<sup>9</sup> Total PM emissions for this recovery furnace were 0.030 gr/dscf at 8 percent O<sub>2</sub> based on data from the same December 1990 test.<sup>8</sup> June 1991 test results show PM emissions of 0.006 gr/dscf. For comparison, PM emissions for recovery furnaces Nos. 1 and 2 at this mill were 0.122 and 0.112 gr/dscf, respectively, based on June 1991 test results.<sup>9</sup> Note that this mill has recently closed.

#### 6.2 TOTAL PM EMISSION DATA

Available total PM emission data for the currently operating sulfite mills are presented in Table 6. Available PM permit limits also are included in this table. Data are available for six sulfite recovery furnaces. Test data are not available for the two fluidized bed reactors or the Marathon Engineering combustor. Total PM emissions range from 0.004 to 0.04 gr/dscf.<sup>5</sup> Percent oxygen data are not available for all of the data points.

TABLE 6. PM EMISSION DATA AND PERMIT LIMITS

Mill code	APCD downstream of SO <sub>2</sub> absorption equipment <sup>a</sup>	PM permit limit (gr/dscf) <sup>c</sup>	Outlet PM emissions (gr/dscf)	Notes
Mg-based				---
80	educted venturi scrubber	0.10	0.028	1990 average of monthly tests range: 0.011-0.05
12	packed-bed scrubber + mist eliminator	0.10 (total PM) 0.075 (PM-10 monthly average) 0.053 (12-month roll, PM-10)	0.030	outlet data are PM-10 emissions assumption: 75% of total PM is PM-10
NH <sub>3</sub> -based				---
52	DynaWave® reverse jet scrubber + fiber-bed mist eliminator	0.06 (2.5 lb/ADUTP) (opacity: 35%)	0.006-0.012 @ 8% O <sub>2</sub>	Range of 1994 monthly three-run averages (front-half Method 5) <sup>d</sup>
94	mesh-pad demister + fiber-bed mist eliminator	2.5 lb/ADUTP (opacity: 10%) <sup>b</sup>	0.004-0.0362 (0.2-1.62 lb/ADUTP)	1986-1990 data; quarterly tests required
128	fiber-bed mist eliminator	no information	0.03564	---
121	mesh-pad demister + fiber-bed mist eliminator	(based on recovery furnace firing rates)	~0.004	fiber-bed mist eliminator inlet concentration is ~0.201 gr/dscf
41	fiber-bed mist eliminator	no information	0.0055	

<sup>a</sup>All Mg-based mills have MgO particulate removal equipment (multiclones) upstream of the SO<sub>2</sub> absorption equipment.

<sup>b</sup>Actual opacity: 0-10% (monthly). An opacity CEM is not possible because of the wet furnace plume; the operational status of the mist eliminator is reported as an alternative to opacity monitoring.

<sup>c</sup>The State of Washington has the following PM standards for sulfite recovery furnaces: 0.06 gr/dscf for recovery furnaces built after 1/72 or 0.10 gr/dscf for recovery furnaces built before this date.

<sup>d</sup>For all monthly PM emission tests for 1988-93, PM emissions were at or below 0.017 gr/dscf.

A more detailed analysis of the data is needed if these data are used to set emission limits.

Although the lowest PM emission data are for NH<sub>3</sub>-based sulfite recovery furnaces, it cannot be concluded from this data set that Mg-based sulfite recovery furnaces are incapable of achieving similarly low emissions. The lower emission levels for NH<sub>3</sub>-based mills may be the result of more efficient PM control equipment. The lowest emission levels are achieved with a fiber-bed mist eliminator system. At least one Mg-based sulfite recovery furnace has a fiber-bed mist eliminator system; however, PM emission data are not available for this furnace. Emission stream characteristics for both Mg-based and NH<sub>3</sub>-based sulfite recovery furnaces are similar, i.e., saturated, low temperature exhaust streams. The Mg-base sulfite recovery furnaces discharge submicron particles; NH<sub>3</sub>-based sulfite recovery furnace particulate has been characterized as submicron fumes (generally known as "blue haze"). Because of the similar emission stream characteristics, the same PM emission control technologies are applicable to both Mg- and NH<sub>3</sub>-based sulfite recovery furnaces.<sup>9</sup>

### 6.3 SO<sub>2</sub> EMISSION DATA

Table 7 presents available SO<sub>2</sub> emission data. Available SO<sub>2</sub> permit limits are also included in this table. Table 7 includes data for six sulfite recovery furnaces and one fluidized bed reactor (mill code 133). Sulfur dioxide emissions vary widely from furnace to furnace, ranging from approximately 2.2 to 650 ppm.<sup>5</sup> The lowest emission level is for a Mg-based sulfite recovery furnace and is achieved with a 4-stage venturi scrubber followed by a packed-bed scrubber, which uses a caustic scrubbing medium, and a mist eliminator. This recovery furnace also has the lowest permit limit.

TABLE 7. SO<sub>2</sub> EMISSION DATA AND PERMIT LIMITS

Mill Code	SO <sub>2</sub> recovery and emission control equipment	SO <sub>2</sub> permit limit (ppm)	Outlet SO <sub>2</sub> emissions (ppm)	Notes
Mg-based				
133	3-stage packed absorption tower	no information	560	---
80	RF1&RF2 (2 parallel sets): 3 absrp. towers RF3: 3-stage v. scrubber + absrp. tower RF1-3: common ducted v. scrubber	360	110	1990 monthly CEM average range: 89.5-141.2
12	4-stage venturi scrubber + packed-bed scrubber + mist eliminator	10 (24-hr average)	2.23	---
NH <sub>3</sub> -based				
52	absorption tower + DynaWave® reverse jet scrubber + fiber-bed mist eliminator	300 (1-hr average) 20 lb/ADUTP (24-hr average)	51-99	range of 1994 monthly averages
94	absorption/cooling tower + mesh-pad demister + fiber-bed mist eliminator	300 (1-hr average)	10-190	1991 daily avg. (CEM); hourly avg. <300 ppm
128	absorption/cooling tower + fiber-bed mist eliminator	no information	150	---
121	absorption tower + mesh pads + fiber-bed mist eliminator	no information	~650	fiber-bed mist eliminator inlet concentration inlet is 666 ppm
41	scrubber/absorber + fiber-bed mist eliminator	no information	68	---

## 7.0 REFERENCES

1. Memorandum from V. Soltis, MRI, to project files. April 24, 1995. U.S. population of sulfite and stand-alone semichemical pulp mills.
2. Someshwar, A.V. and J.E. Pinkerton. Wood Processing Industry. In: Air Pollution Engineering Manual, Buonicore, A.J. and W.T. Davis (eds.). New York, Van Nostrand Reinhold. 1992. p. 844.
3. Ingruber, O.V., M.J. Kocurek, and A. Wong (eds.). Pulp and Paper Manufacturer, Volume 4, Sulfite Science and Technology. Joint Textbook Committee of the Paper Industry. 1985.
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6. Volatile Organic Emissions from Pulp and Paper Mill Sources. Part VIII-Sulfite Mills. NCASI. New York. Technical Bulletin No. 682. November 1994.
7. Memorandum from V. Soltis, MRI, to project files. January 18, 1995. Summary of telephone contacts with personnel at sulfite pulp mills.
8. Letter from A. Schuler, State of Alaska Department of Conservation, to D. Safriet, U. S. EPA/OAQPS. August 6, 1991. Source test data for Alaska Pulp Corporation in Sitka, Alaska.
9. Powers, W.E., M.W. Short, J.A. Evenson, and B.A. Dennison. "Retrofit Options for Controlling Particulate Emissions from a Magnesium Sulfite Recovery Furnace." TAPPI Journal. May 1992.

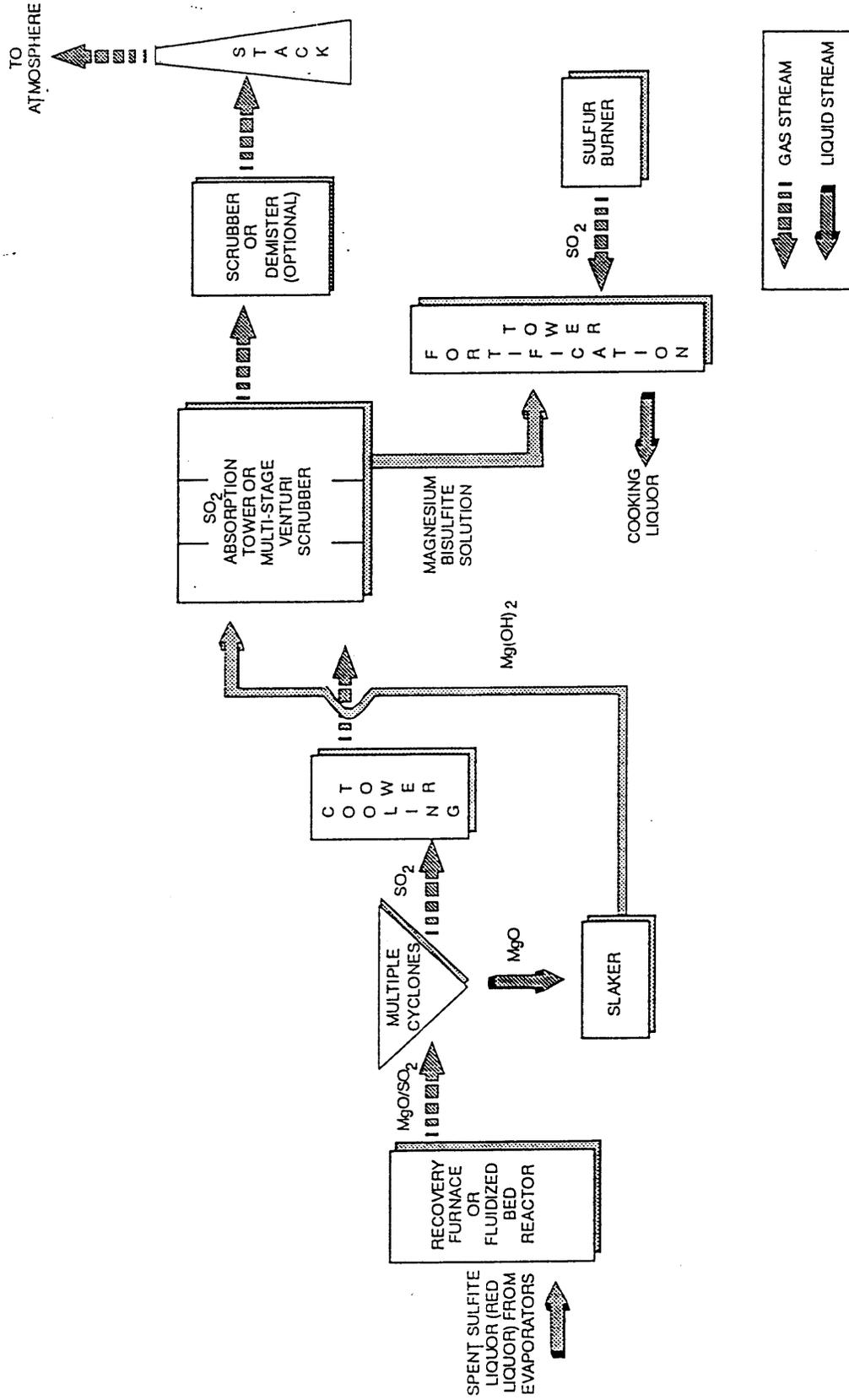


Figure 1. Mg-based sulfite chemical recovery process.

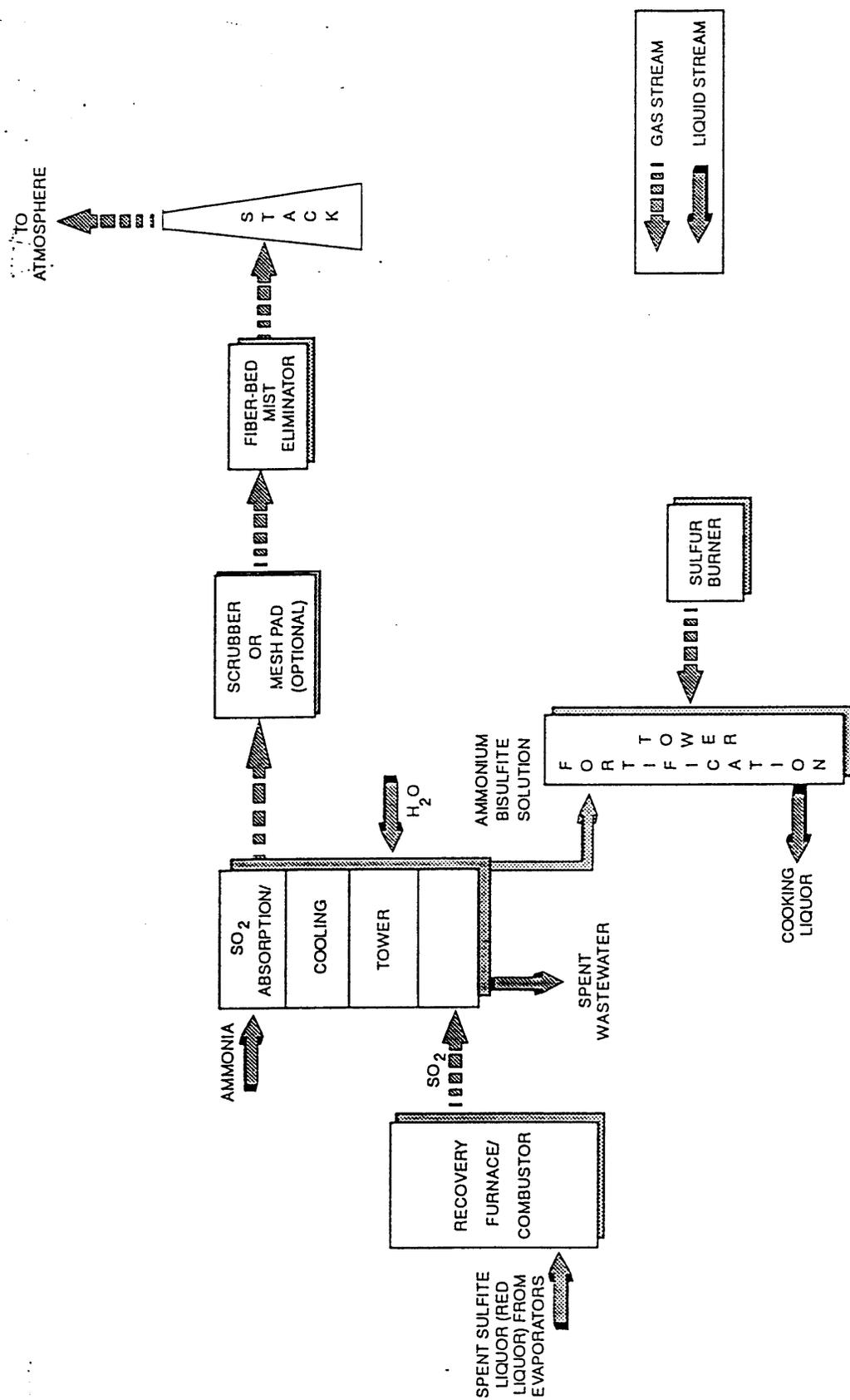


Figure 2. NH<sub>3</sub>-based sulfite chemical recovery process.

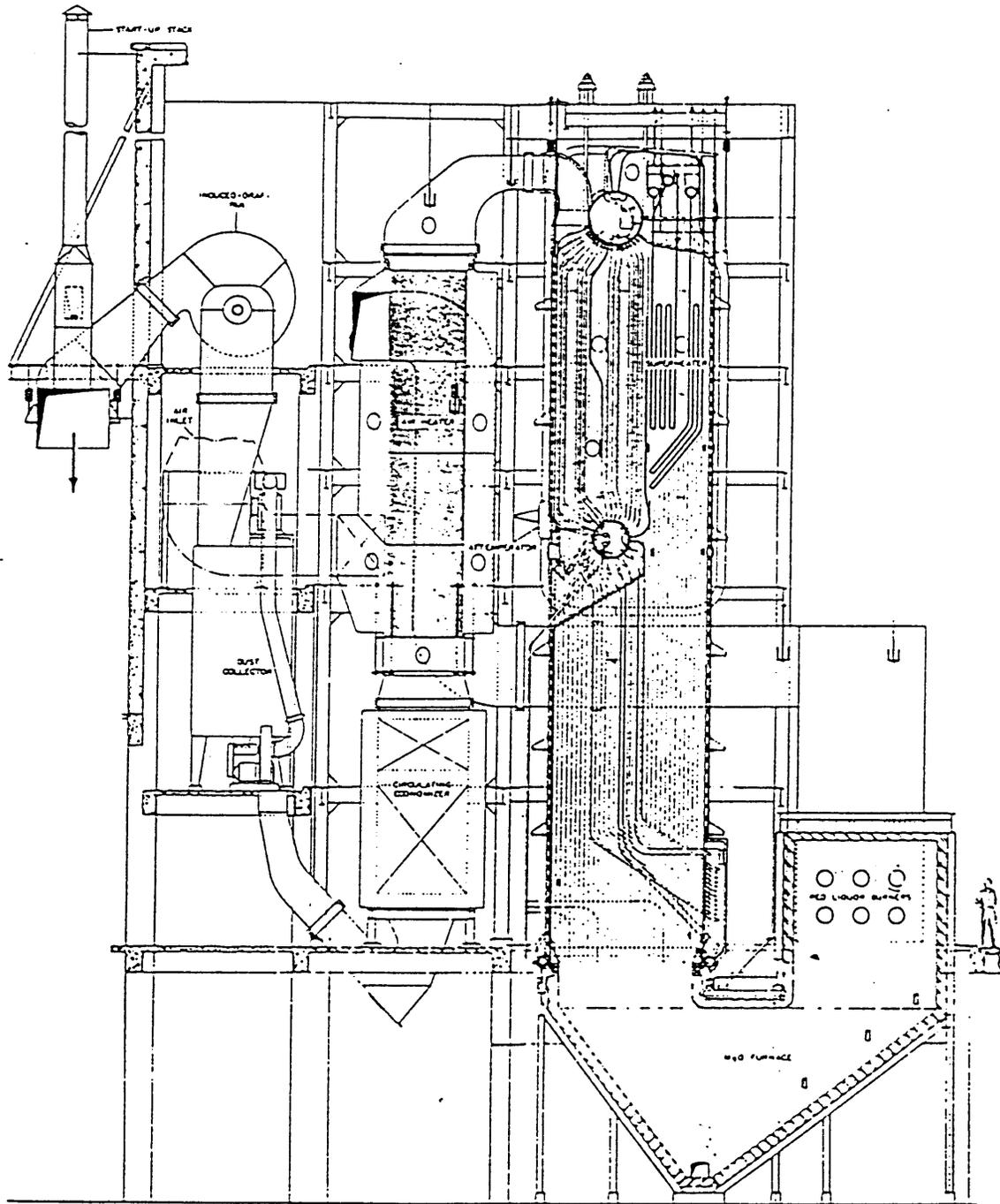


Figure 3. B&W Mg-based sulfite recovery furnace  
(Pulp and Paper Manufacturer, Volume 4, Sulfite Science and  
Technology, p. 271).

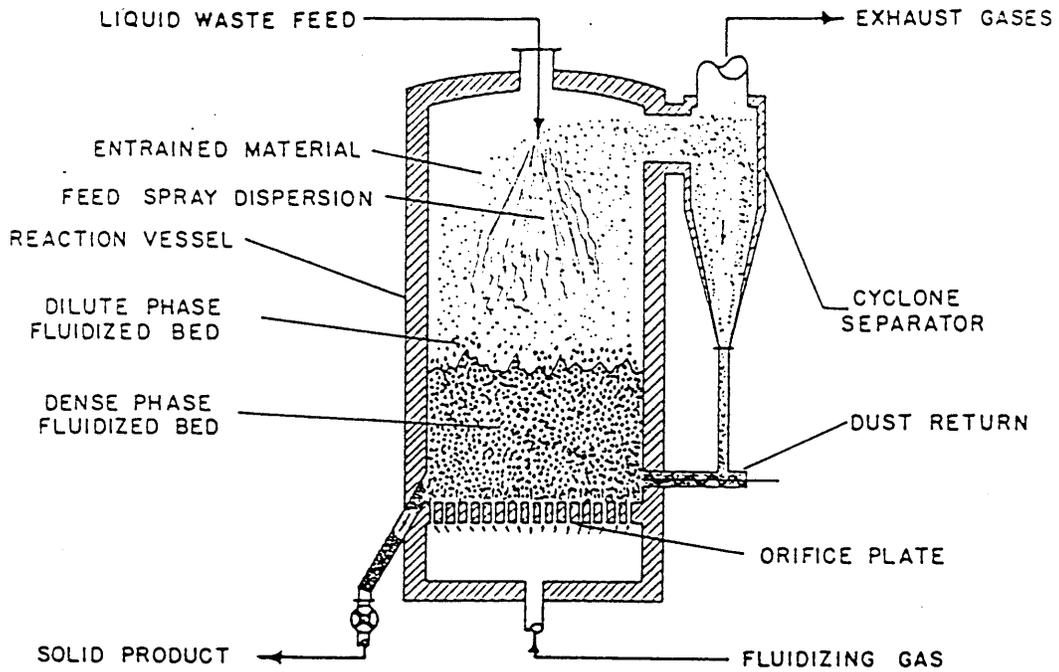


Figure 4a. General features of fluidized-bed incinerator. (Pulp and Paper Manufacturer, Volume 4, Sulfite Science and Technology, p. 276).

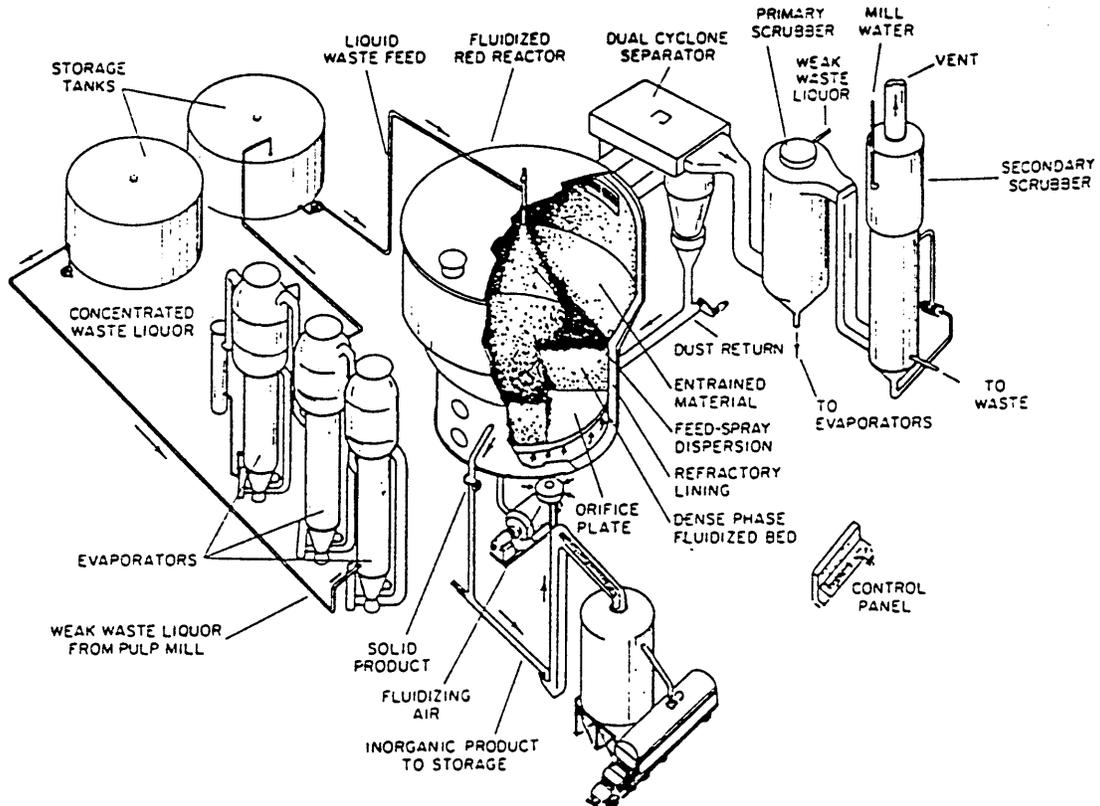


Figure 4b. Copeland fluidized-bed reactor system-- Mg-based sulfite. (Pulp and Paper Manufacturer, Volume 4, Sulfite Science and Technology, p. 276).

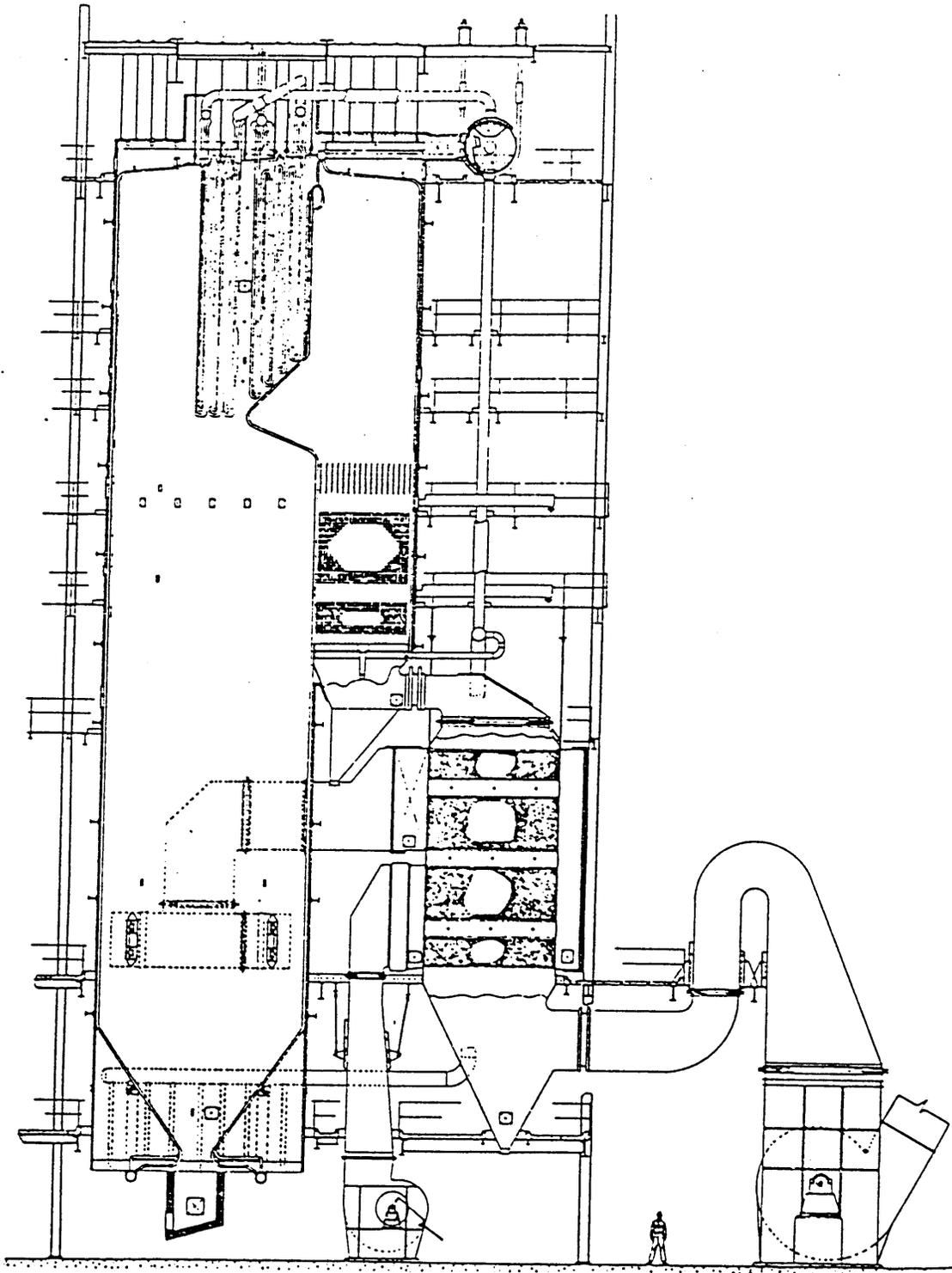


Figure 5. C-E  $\text{NH}_3$ -based sulfite recovery furnace.  
(Pulp and Paper Manufacturer, Volume 4, Sulfite Science  
and Technology, p. 274).

APPENDIX A

Mill Type: Mg-based sulfite

Mill Code: 5

Information available: NCASI 1991 MACT survey response (no information was provided for chemical recovery combustion equipment)  
Trip report

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Chemical recovery combustion equipment: 1 Copeland fluidized bed recovery reactor

Chemical recovery process/air pollution control equipment: MgO PM removal equipment + 3 venturi scrubbers

Chemical recovery process description: See Figure A-1. Weak red liquor from the 1st stage washer is concentrated in a 4-effect evaporator system to 45% solids. Evaporator overhead gases are vented directly to the atmosphere. Concentrated red liquor from the evaporators is sent to the recovery reactor. Magnesium oxide dust from the recovery reactor exit gases is collected and routed to the "mag system." The mag system consists of a washer and slaker, which are used to generate magnesium hydroxide ( $Mg(OH)_2$ ). The  $Mg(OH)_2$  is sent to one of three venturi scrubbers where it is used to scrub  $SO_2$  from the inlet gas streams; occasionally the  $Mg(OH)_2$  is sent directly to the acid plant. In addition to the recovery reactor exit gases after removal of MgO particulate, the following pulp mill sources are vented to the venturi scrubbers: (1) blow pit gases via the blow gas scrubber that uses fresh water as the scrubbing liquid, (2) high pressure accumulator gases, (3) acid plant fortification tower gases, (4) brown stock washer system vent gases, (5) vent gases from four storage tanks in the washing area, and (6) acid storage tank vent gases. Scrubbed gases from the venturi scrubbers are exhausted to the atmosphere through the main recovery stack. The magnesium bisulfite cooking acid formed in the venturi scrubbers is sent to the acid plant where make-up  $SO_2$  from the sulfur burner is added to compensate for losses in the cooking and liquor processing.

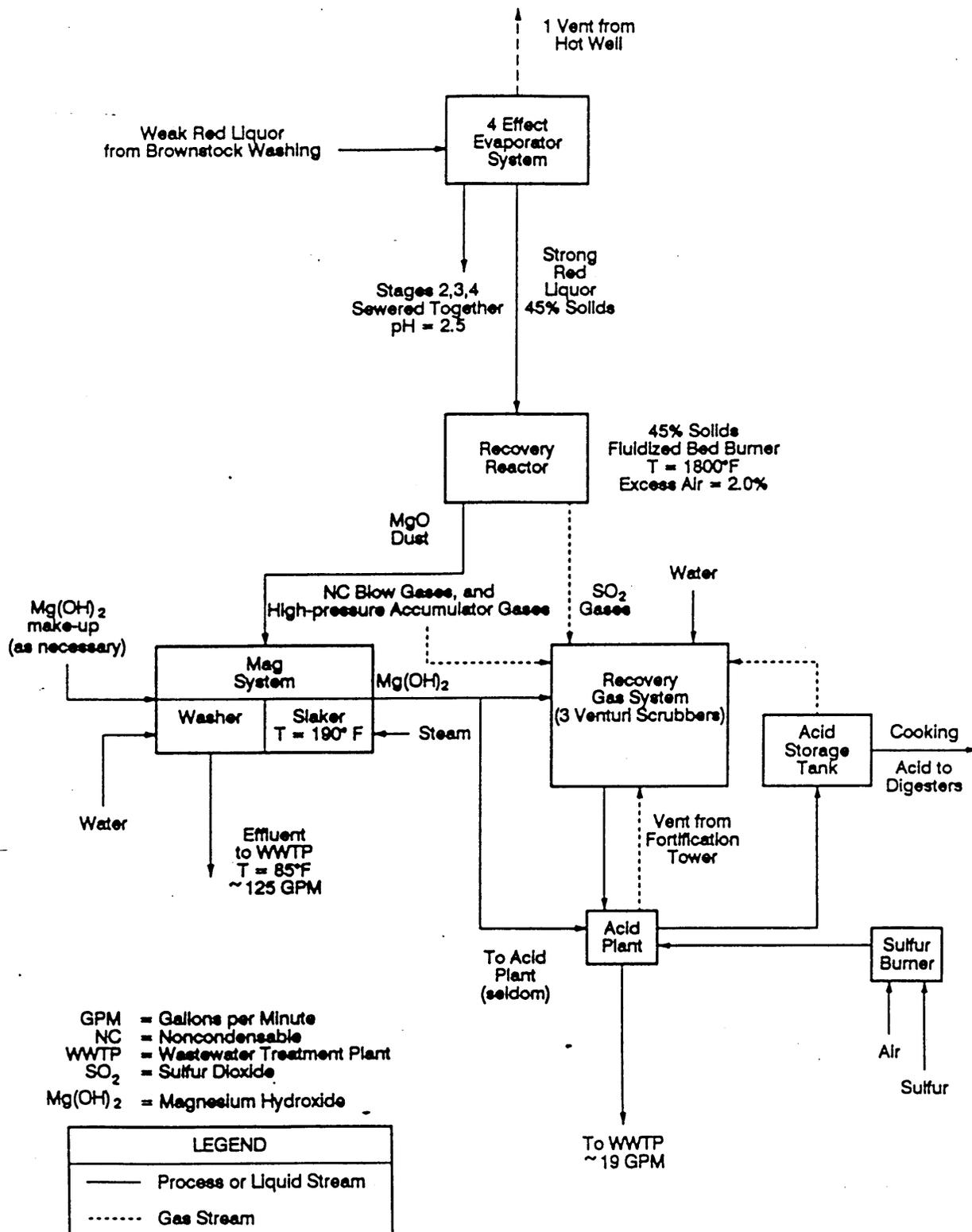


Figure A-1. Chemical recovery process at Mill 5.

Mill Type: Mg-based sulfite  
Mill Code: 133  
Information available: NCASI 1991 MACT survey response

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Chemical recovery combustion equipment: 1 1974 B&W fluidized bed reactor

Chemical recovery process/air pollution control equipment: 1974 dust collector + cooling tower + 1974 3-stage packed (absorption) tower

Chemical recovery process description: See Figure A-2. Concentrated red liquor from the 3-effect evaporator set is sent to the fluidized bed reactor. Evaporator overhead gases are also routed to the fluidized bed reactor for incineration. Exit gases from the fluidized bed reactor are routed at a flow rate of approximately 80,000 acfm at 440°F through a waste heat boiler to produce process steam and then through 144-tube Research Cottrell dust collector where magnesium oxide (MgO) particulate is removed. Pulverized bed particle material is also collected using a MgO bed grinder dust collector. The collected MgO particulate (8,839 tons/yr) is sent to a slurry tank, ash thickener tank, ash filter, and slaker tanks to produce magnesium hydroxide (Mg(OH)<sub>2</sub>). The Mg(OH)<sub>2</sub> slurry is the makeup scrubbing fluid in a 3-stage SO<sub>2</sub> absorption tower; a portion of the Mg(OH)<sub>2</sub> also is routed to the No. 3 evaporator. Exit gases from the dust collector are first routed to a gas cooling tower to improve SO<sub>2</sub> absorption and then to the 3-stage SO<sub>2</sub> absorption tower. The packing material in each stage of the absorption tower is 2 feet deep and the maximum liquid-to-gas ratio for each stage is 0.05 gal/acfm. The Mg(OH)<sub>2</sub> makeup rate for the 1st stage of the absorber is 191 gpm; the makeup rate for the 2nd and 3rd stages are 31 and 18 gpm, respectively. Purchased Mg(OH)<sub>2</sub> is also used in the absorber. The scrubbing fluid recirculation rate for the 1st stage of the absorption tower is 1,350 gpm; recirculation rates for the 2nd and 3rd stages are 1,575 and 2,350 gpm, respectively. The magnesium bisulfite solution formed in the absorption tower is sent to a fortification tower where makeup SO<sub>2</sub> from the sulfur burner is added. Exhaust gases from the fortification tower are routed to the absorption tower; there is also a vent from the tower to atmosphere. The flowrate of the gases entering the absorption tower is about 50,000 acfm at 140°F. Gases exit the absorption tower at approximately 130°F and are vented to the atmosphere.

Cost data: Capital and operating cost data for the dust collector and absorption tower are available in the NCASI 1991 MACT survey response.



Mill Type: Mg-based sulfite  
Mill Code: 93  
Information available: NCASI 1991 MACT survey response  
Telephone contact

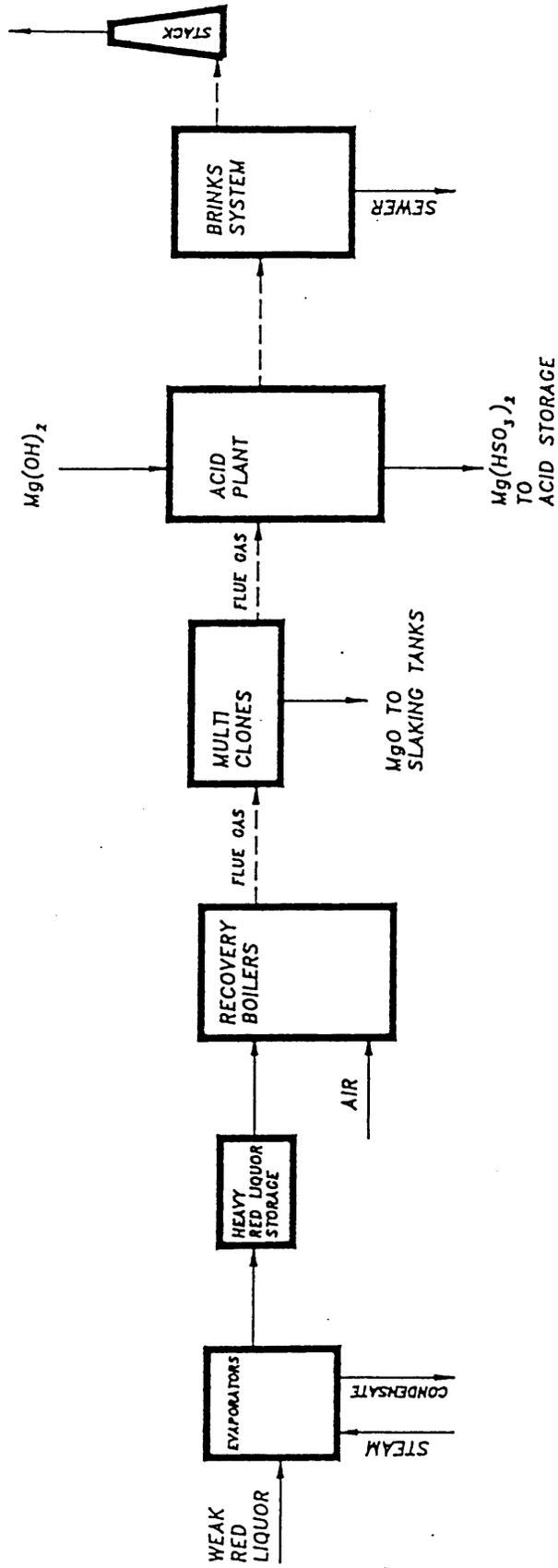
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Chemical recovery combustion sources: 4 B&W recovery furnaces (installation dates--Nos. 1 and 2, 1954; No. 3 1957; and No. 4 1966)

Chemical recovery process/air pollution control equipment: 2 parallel sets consisting of multiclones + 1 cooling tower + 3-stage countercurrent packed absorption tower + Brinks demister system

Chemical recovery process description: See Figure A-3. Heavy red liquor from the evaporator sets is fired in one of four recovery furnaces. The red liquor solids firing rate per furnace ranges from approximately 454,000 to 480,000 lb/d. Combustion gases from recovery furnace Nos. 1 and 2 are combined and routed to one set of process/air pollution control equipment, and gases from recovery furnaces Nos. 3 and 4 are combined and routed to a second set of process/air pollution control equipment. Each set of process/air pollution control equipment consists of multiclones, a cooling tower, a 3-stage countercurrent packed absorption tower, and a Brinks demister system that consists of 3 canisters. This system provides for MgO particulate recovery (multiclones), SO<sub>2</sub> recovery (cooling and absorption towers) and PM emission control (Brinks demister system). Slaked MgO (i.e., Mg(OH)<sub>2</sub>) is used as the scrubbing fluid in the SO<sub>2</sub> absorption tower. The magnesium bisulfite solution formed in the absorption tower is fortified with makeup SO<sub>2</sub> from the sulfur burner in a fortification tower, and the resulting product, Mg(HSO<sub>3</sub>)<sub>2</sub>, is sent to acid storage.

Cost data: Capital and annual costs for Brinks demister system included in NCASI 1991 MACT survey response.



## PARTIAL PROCESS DIAGRAM

Figure A-3. Chemical recovery process at Mill 93.

Mill Type: Mg-based sulfite  
Mill Code: 80  
Information Available: NCASI 1991 MACT survey response  
Trip reports  
NCASI test report (Mill I)

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Chemical recovery combustion equipment: 3 B&W recovery furnaces (installation dates--Nos. 1 and 2, 1957; No. 3, 1966)

Chemical recovery process/air pollution control equipment:

Recovery furnace No. 1--multiclones + cooling tower + 3 absorption towers + common educted venturi scrubber

Recovery furnace No. 2--multiclones + cooling tower + 3 absorption towers + common educted venturi scrubber

Recovery furnace No. 3--multiclones+ cyclone evaporator + 3-stage venturi scrubber + 1 absorption tower + common educted venturi scrubber

Chemical recovery process description: See Figure A-4. The solids content of the spent liquor is increased from approximately 25 percent to between 52 and 55 percent prior to firing in one of three recovery furnaces. The red liquor solids firing rate for recovery furnaces Nos. 1 and 2 is 562,400 lb/d/furnace; the firing rate for recovery furnace No. 3 is 588,000 lb/d. Exhaust gases from the furnaces contain MgO particulate and SO<sub>2</sub> gas. The MgO is recovered as a fine powder using multiclones. There are separate 4-chambered multiclones for each furnace. Following the multiclones, SO<sub>2</sub> is recovered in various absorption tower configurations. Exhaust gases from recovery furnace Nos. 1 and 2 are fed to separate cooling towers, then to separate SO<sub>2</sub> absorption towers. The exhaust stream from recovery furnace No. 3 is fed to a cyclone direct contact evaporator and then to a 3-stage venturi scrubber and absorption tower. From the SO<sub>2</sub> absorption towers, the exhaust streams from all three recovery furnaces are ducted to a common SO<sub>2</sub> scrubber and stack.

In collecting MgO, fresh water is sprayed from the sides of the hopper to wash the MgO particulate into a swirl chamber, forming an MgO slurry. The MgO slurry (magnesium hydroxide) is used as the scrubbing fluid in the venturi scrubbers and absorption towers. In addition, a portion of slurry is sewerred at a rate of 50 gpm. Fresh water and evaporator condensate, if available, is used as makeup to the cooling towers and the recirculated water from the cooling towers is used as makeup water for the absorption towers. The No. 1 and No. 2 recovery furnace absorption towers are essentially the same except for the packing material. The No. 1 recovery furnace absorption towers use saddle packing, and the No. 2 recovery furnace absorption towers use ceramic tile packing. The No. 3 absorption tower also uses saddle packing. In addition to cooling tower water, magnesium hydroxide from the MgO processing area is also added as makeup scrubbing fluid in the absorption towers. Recovered liquid from the absorption towers is sent to the acid processing plant for fortification with SO<sub>2</sub> formed from combustion of elemental sulfur in a sulfur burner. The final SO<sub>2</sub> scrubber to which gases from all three recovery furnaces are routed is a 1985 AirPol educted venturi scrubber. The scrubbing medium is fresh water; sodium hydroxide is added if the inlet SO<sub>2</sub> concentration is greater than 100 ppm. During SO<sub>2</sub> excursions the pH of the recirculating liquid drops to a level of approximately 2 to 3; caustic is then added to increase the pH to a range of 7 to 9. The scrubber pressure drop is achieved with the use of pumps.

The SO<sub>2</sub> concentration in the exit gases from the recovery furnaces is about 10,000 ppm. The exit gases from the cooling towers contain about 7,000 ppm SO<sub>2</sub>. The SO<sub>2</sub> concentration in the exit gases from the absorption towers is about 100 ppm, and stack gas SO<sub>2</sub> emissions range from approximately 90 to 140 ppm after the educted venturi scrubber.

Cost data: Capital and annual costs for the educted venturi scrubber are available in the NCASI 1991 MACT survey response.

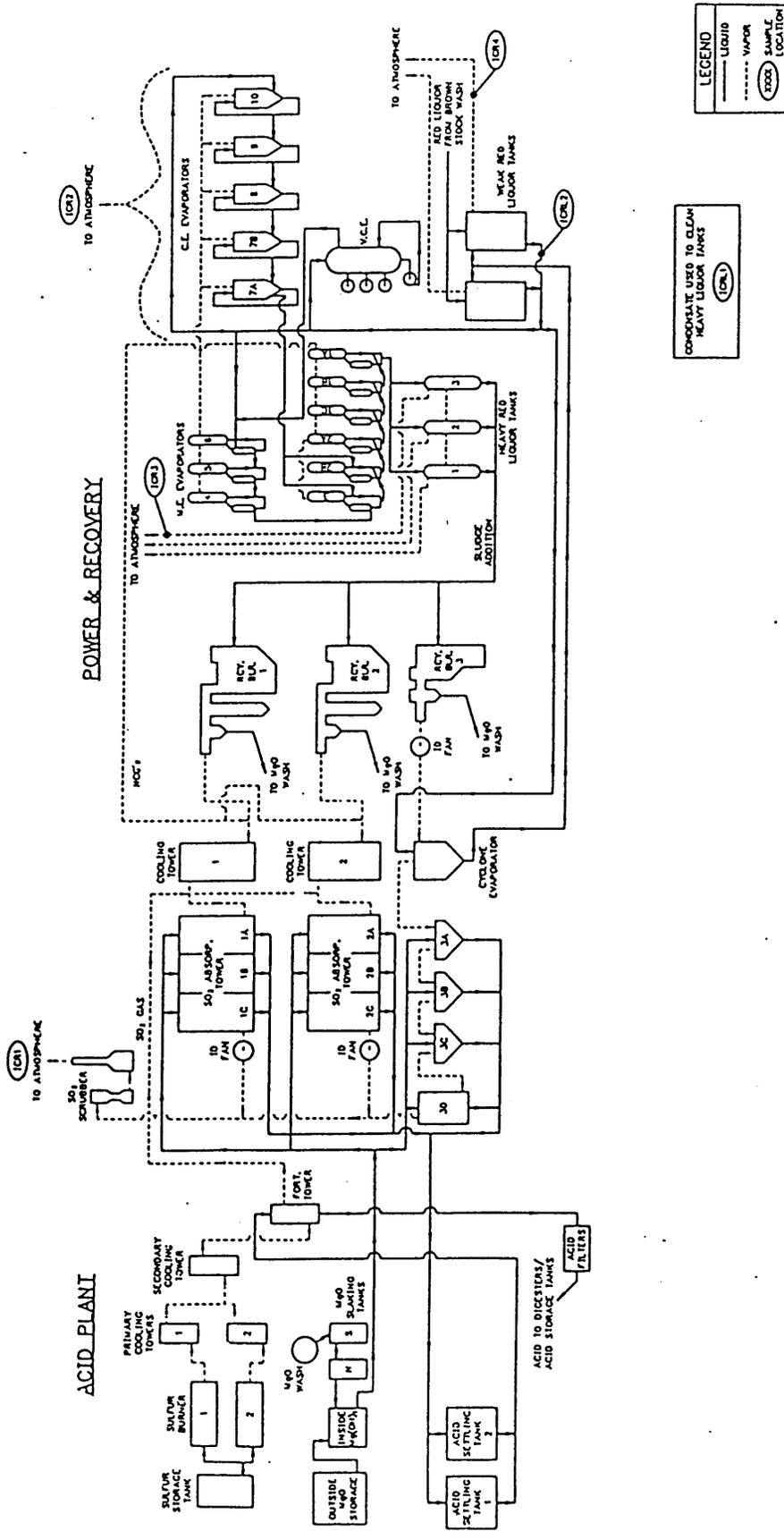


Figure A-4. Chemical recovery process at Mill 80.

Mill Type: Mg-based sulfite (+ kraft)  
Mill Code: 12  
Information Available: NCASI 1991 MACT survey response  
Trip report

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Chemical recovery combustion equipment: 1 1971 B&W recovery furnace

Chemical recovery process/air pollution control equipment: multiclone + 4-stage venturi scrubber + packed bed scrubber + mist eliminator.

Chemical recovery process description: See Figure A-5. Red liquor exits the multiple-effect evaporators (MEE) at a solids content of 55 to 60 percent and is fired in the recovery furnace at a design solids feed rate of 1.4 million lb/d. Noncondensable gases (~2,000 acfm) from the magnesite process digesters and MEE are routed to the recovery furnace for incineration. Recovery furnace flue gases consist primarily of SO<sub>2</sub> gas and MgO particulate. The flue gases first enter a multiclone where the MgO is recovered and then slaked to form Mg(OH)<sub>2</sub>. Following the multiclone, SO<sub>2</sub> is recovered from the flue gas in a 4-stage venturi scrubber, which uses the liquid from the MgO slaking tanks as scrubbing fluid. Exit gases from the venturi scrubber pass through a packed bed scrubber and mist eliminator for additional control of air pollutants. The packed bed scrubber is a 1990 Advanced Air Technology scrubber. The design inlet flowrate is 160,000 acfm at 165°F. The scrubbing medium is a caustic solution that contains fresh water. The recirculation rate is 2,200 gpm; 50-percent concentration by weight caustic solution is added at a rate of about 1 to 3 gpm. The packing material is rigid Munters packing at a depth of 6 feet.

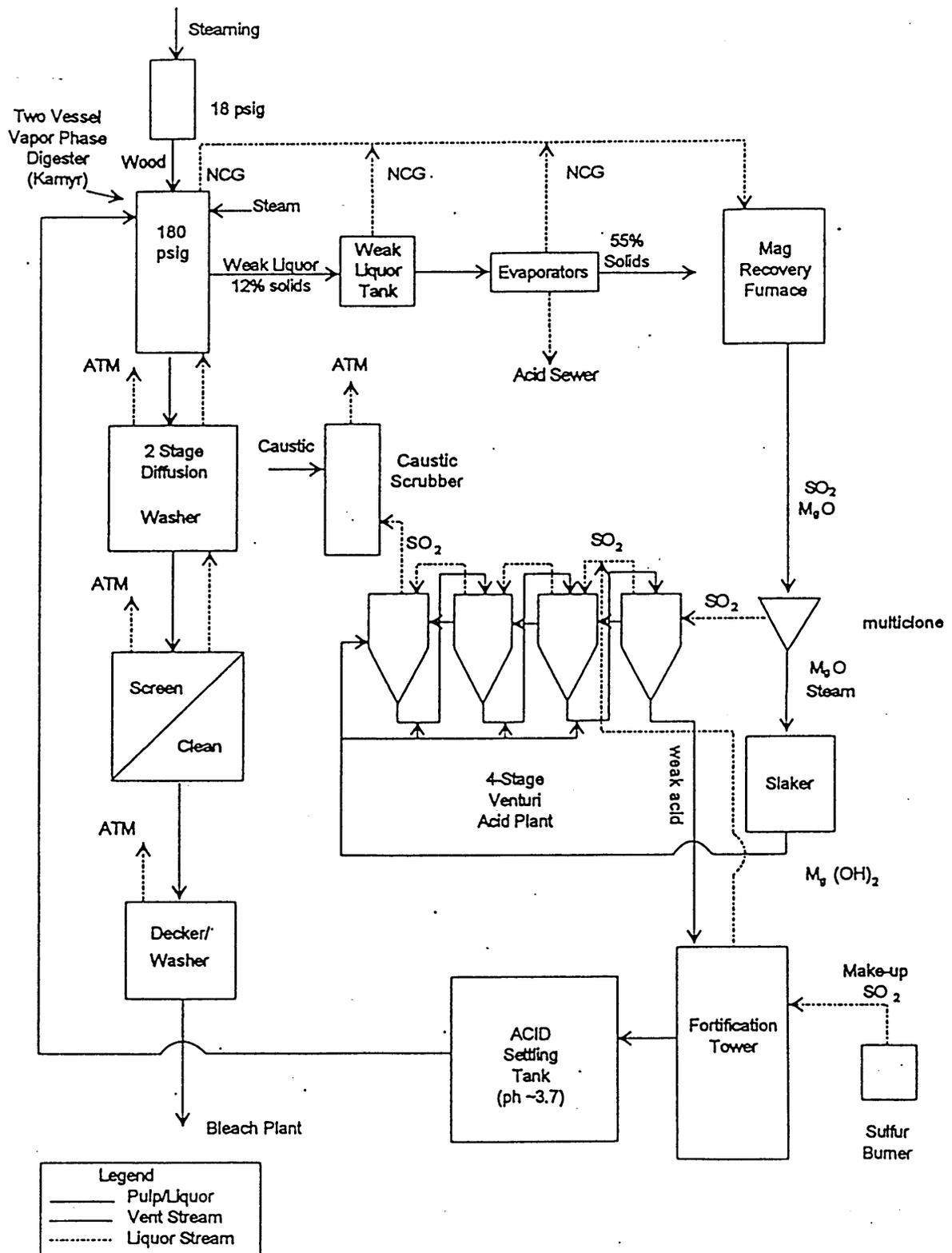


Figure A-5. Chemical recovery process at Mill 12.

Mill Type: Mg-based sulfite (+ groundwood)

Mill Code: A

Information Available: 1992 Lockwood-Post Directory  
Brief telephone contact

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Chemical recovery combustion equipment: 1 B&W recovery furnace (300,000 lbs steam/hr).

Chemical recovery process/air pollution control equipment: MgO recovery system. Information on additional equipment is not available.

APPENDIX B

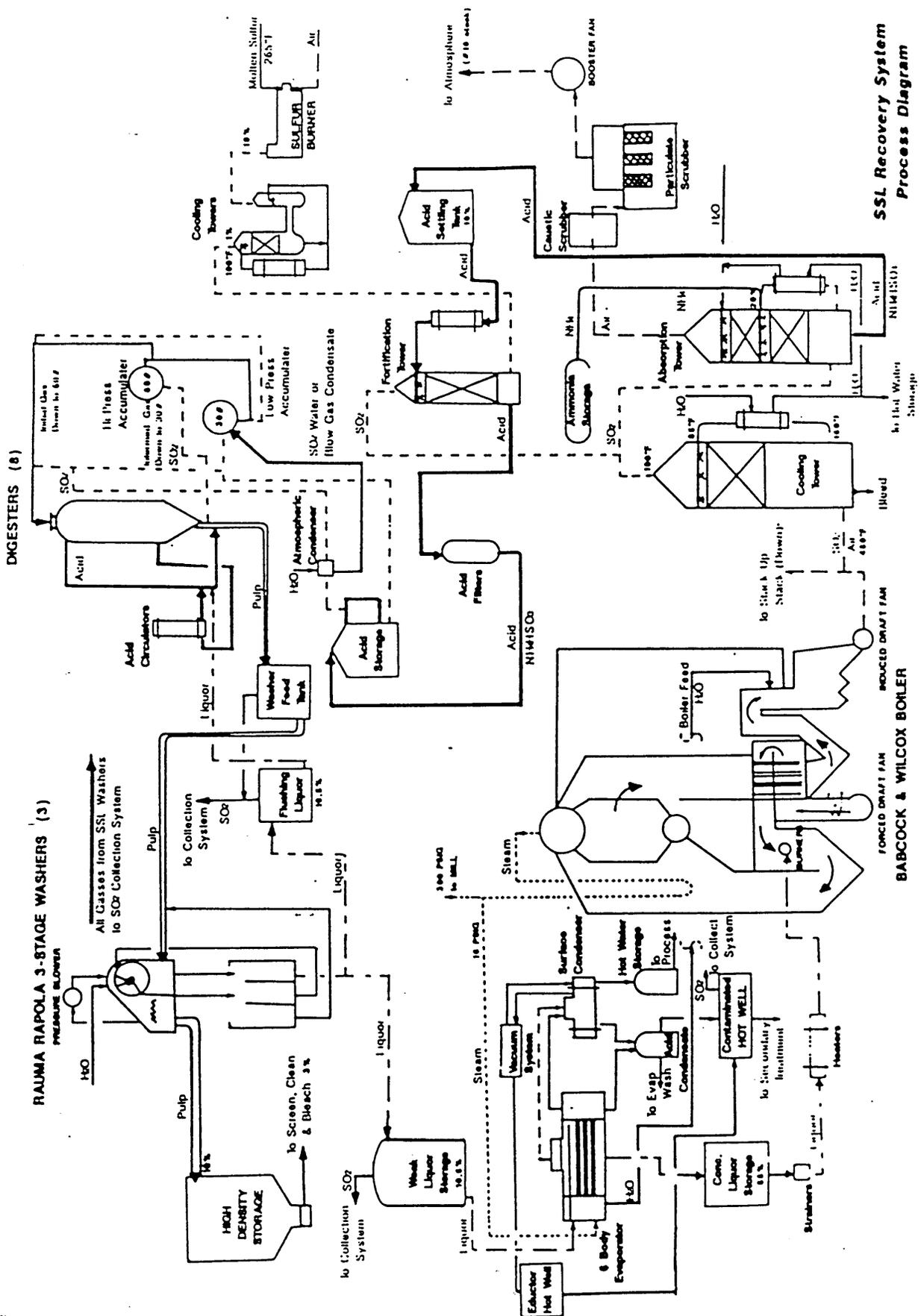
Mill Type: NH<sub>3</sub>-based sulfite  
Mill Code: 52  
Information Available: Mill-prepared process description  
NCASI 1991 MACT survey response (no information on recovery furnace was provided)

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Chemical recovery combustion equipment: 1 B&W recovery furnace

Chemical recovery process/air pollution control equipment: cooling tower + absorption tower + Dynawave reverse jet scrubber + Brinks demister system

Chemical recovery process description: See Figure B-1. Concentrated spent liquor at 53% solids from the MEE is fired in a recovery furnace at a rate of 1.375 MM lb/d. Ash from the burning of the liquor is removed manually daily. Combustion gases, which contain SO<sub>2</sub>, are routed to a cooling tower and then to an absorption tower to collect SO<sub>2</sub>. The absorption tower is a 17-foot diameter packed bed tower that consists of two beds, one of which is 10 feet deep and the other 5 feet deep. Ammonium hydroxide is used in the tower to absorb SO<sub>2</sub>, forming ammonium bisulfite. The ammonium bisulfite from the absorber is then fortified with SO<sub>2</sub> from a sulfur burner in a 4-foot diameter packed-bed fortification tower. In addition to recovery furnace flue gases, the following pulp mill sources are vented to the absorption tower: dump chests, washer feed chests, flushing liquor tanks, pressure washers, washer filtrate tanks, a filtered liquor tank, a liquor filter, acid storage tank, evaporator overhead gases, heavy liquor tanks, acid condensate tank, raw acid settling tank, weak liquor tank, contaminated hot well, condensate hot well, and fortification tower. Absorber exit gases are routed through a Dynawave reverse jet scrubber, which was installed in 1990 to control PM and SO<sub>2</sub> emissions. Makeup caustic (50 percent by weight) is added at a rate of 0 to 3 gpm to maintain a pH of 6.0. The SO<sub>2</sub> removal efficiency is approximately 80%. Final control of PM emissions is provided by a Brinks mist eliminator system. This system consists of 95 cylindrical filter elements (also called candles) in 6 tanks. Each candle is approximately 10-feet long with an outside diameter of 2 feet. Major modifications to the tank configurations were made in 1985 to improve washing efficiency and gas circulation through the candles. The modifications plus installation of the Dynawave scrubber improved the operation of the demister system by reducing plugging of the candles.



SSL Recovery System  
Process Diagram

Figure B-1. Chemical recovery process at Mill 52.

Mill Type: NH<sub>3</sub>-based sulfite  
Mill Code: 94  
Information Available: NCASI 1991 MACT survey response  
Trip report

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Chemical recovery combustion equipment: 1 1974 C-E recovery furnace (performance specs included with NCASI 1991 MACT survey response)

Chemical recovery process/air pollution control equipment: absorber-cooler tower + mesh pad demister + Brinks demister system

Chemical recovery process description: See Figures B-2 and B-3. Red liquor is concentrated to between 50 and 55 percent solids in vapor recompression (VRC) and multiple effect evaporators (MEE). Concentrated red liquor is then fired at a rate of 1.38 MM lb red liquor solids/d in a 1974 C-E recovery furnace to recover SO<sub>2</sub> and generate steam. The process does not require smelt dissolving tanks; ash produced during combustion is periodically removed from the furnace bottom. Combustion gases are routed to an absorber-cooler, where the gases are first cooled in the lower two zones to increase SO<sub>2</sub> recovery and then SO<sub>2</sub> is absorbed by aqueous ammonia in the upper two zones. The VRC evaporator, MEE condenser, and miscellaneous tanks are vented to the absorber-cooler. The ammonium bisulfite solution from the absorber-cooler is routed to the acid plant, where it is fortified with makeup SO<sub>2</sub> from a sulfur burner. The absorber-cooler also provides some PM emission control. Absorber-cooler exit gases are routed through a mesh pad located at the top of the absorber-cooler tower and a Brinks demister system to collect absorber-generated ammonia salts and recovery furnace PM. The Brinks demister system consists of 6 tanks with 21 fiberglass and polyester candles in each tank. The candle elements are 10 feet long with a diameter of 18 inches.

Limerock towers are used to collect SO<sub>2</sub> emissions from miscellaneous tank vents, acid plant overgases, and the blow tank recovery system.

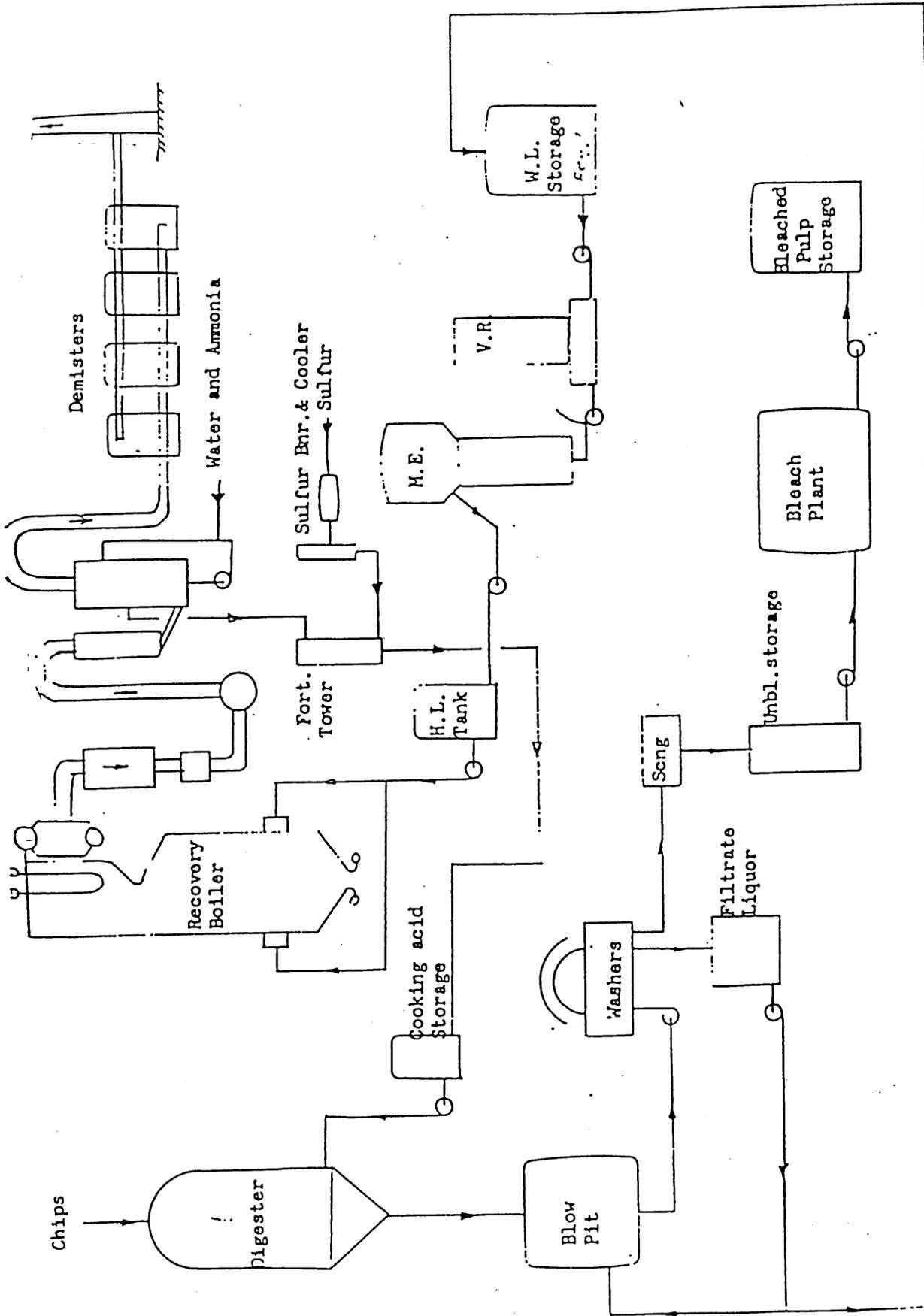


Figure B-2. Chemical recovery process at Mill 94.

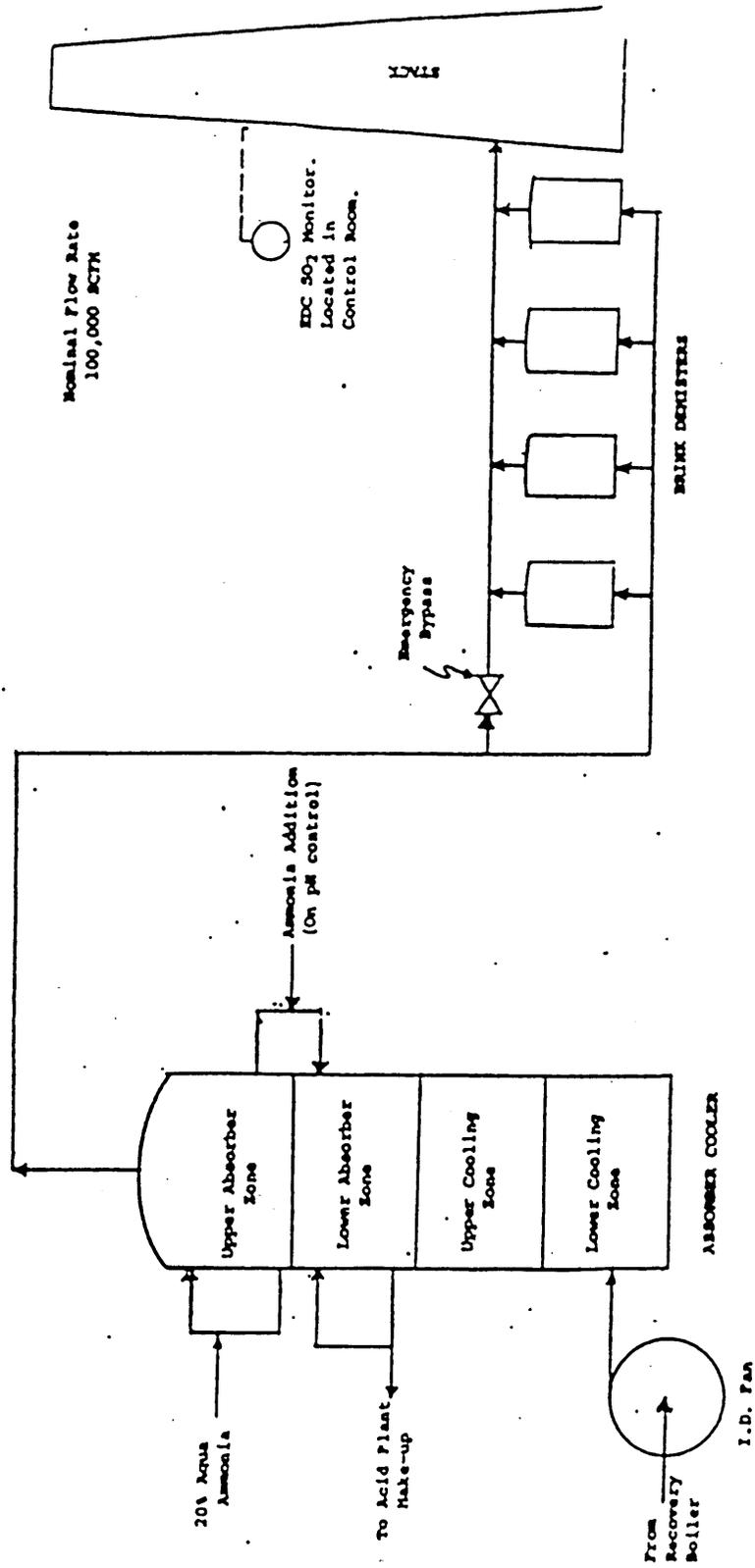


Figure B-3. Mill 94 recovery furnace air pollution controls.

Mill Type: NH<sub>3</sub>-based sulfite  
Mill Code: 128  
Information Available: NCASI 1991 MACT survey response  
NCASI test report (Mill P)

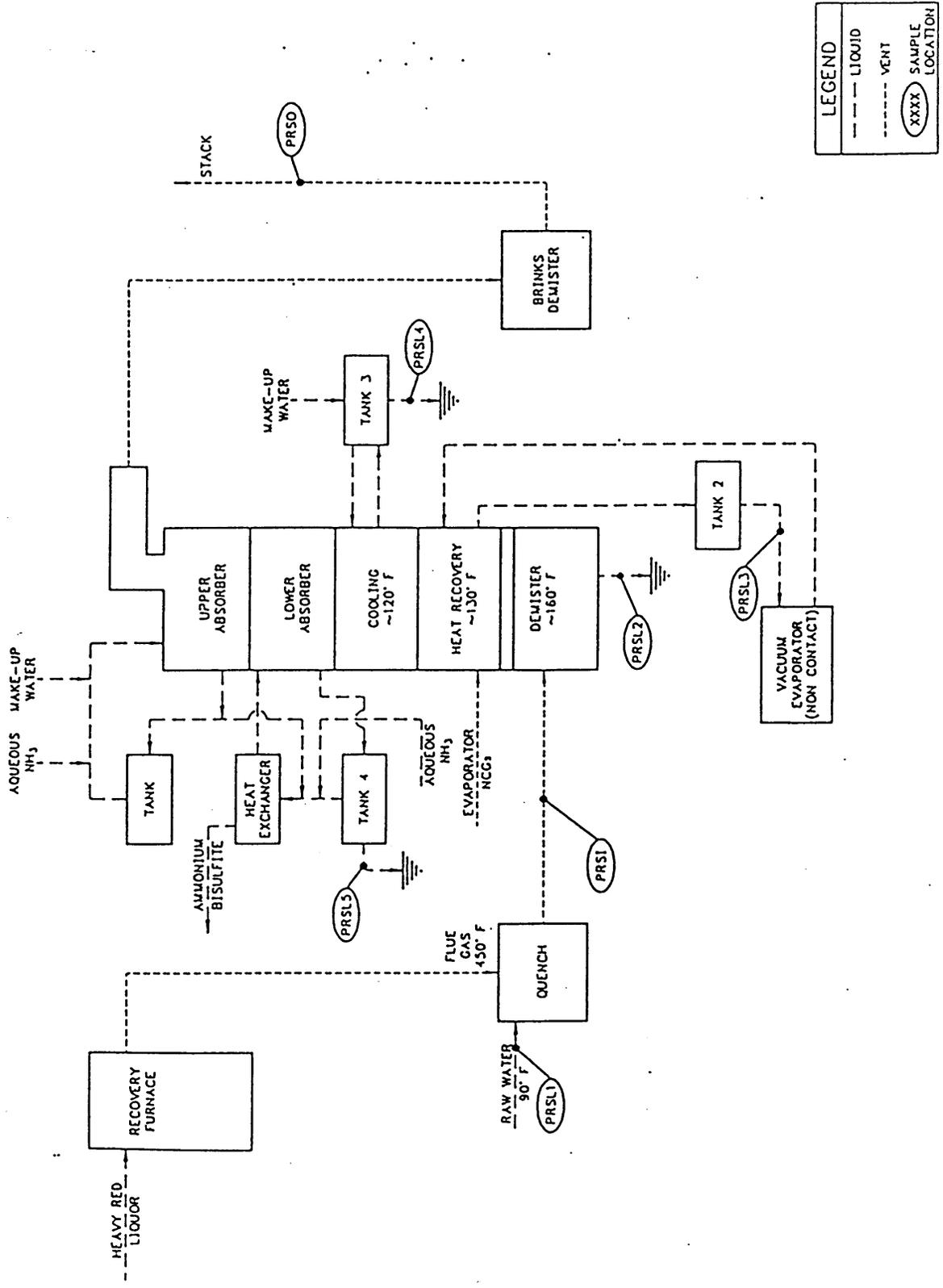
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Chemical recovery combustion equipment: 1 1975 B&W recovery furnace

Chemical recovery process/air pollution control equipment: Absorption/cooling tower + Brinks demister system

Chemical recovery process description: See Figure B-4. Spent sulfite liquor is concentrated in two parallel sets of falling film 6-effect MEE's to 54 percent solids. The concentrated liquor is fired in a 1975 B&W recovery furnace at an average solids firing rate of 1.3 MM lb/d. The recovery furnace produces heat for steam generation and oxidizes sulfur compounds to SO<sub>2</sub>. A five section absorption tower is used to recover SO<sub>2</sub> as bisulfite and capture additional heat. In the first section, flue gases at 450°F are quenched with a clean water spray to 160°F. In the next two sections, which are heat recovery zones, the flue gases are cooled to about 120°F. Most of the recovered heat drives the vacuum evaporator. Evaporator NCG's enter the tower in the heat recovery zone. The final two sections are SO<sub>2</sub> recovery zones where ammonia is used to absorb SO<sub>2</sub> as ammonium bisulfite. Ammonium bisulfite from the absorption tower is transferred to an ammonia tower, where additional ammonia, chilled water, and SO<sub>2</sub> are added. The solution is then transferred to a pressure absorption (fortification) tower where makeup SO<sub>2</sub> from the sulfur burners is added. Exit gases from the recovery furnace absorption tower are routed to a Brinks demister for removal of particulate ammonium salts.

"Nuisance gases" from pulping and acid production are routed to a wet scrubber that uses a make-up solution of either soda ash or caustic. Off gases from acid storage tanks and digester low pressure relief system are vented to the fortification tower.



LEGEND	
---	LIQUID
- - - -	VENT
XXXX	SAMPLE LOCATION

Figure B-4. Chemical recovery process at Mill 128.

Mill Type: NH<sub>3</sub>-based sulfite  
Mill Code: 121  
Information available: NCASI 1991 MACT survey response  
Telecon

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Chemical recovery combustion equipment: 2 recovery furnaces (1968 C-E and 1969 B&W)

Chemical recovery process/air pollution control equipment: SO<sub>2</sub> absorption tower + mesh pads + fume filters.

Chemical recovery process description: See Figure B-5. Spent liquor at 15% solids is concentrated to 50% solids in a Rosenblatt falling film evaporator. Concentrated liquor is fired into one of two recovery furnaces. Recovery furnace No. 2 is a 1968 C-E furnace and recovery furnace No. 4 is a 1969 B&W furnace. Combustion gases from the recovery furnaces are combined and then cooled with water and scrubbed with an aqueous ammonia solution in an SO<sub>2</sub> absorption tower. The water used in the absorption tower is fresh mill water. The absorption tower is a 1977 bubblecaps, tray tower manufactured by R. Katzen Associates. In the absorption tower, SO<sub>2</sub> reacts with the ammonium hydroxide solution to form an ammonium bisulfite solution. The ammonium bisulfite solution is returned to the sulfite pulping process. Gases exiting the SO<sub>2</sub> absorber pass through mesh pads and four fume filters to remove carryover liquid and PM prior to discharging to the atmosphere. These devices were also installed in 1977. The mesh pad, which is located at the top of the SO<sub>2</sub> absorption, was manufactured by Rust Engineering. The fume filters are Monsanto Brinks-type filters. These filters consist of four tanks containing 21 packed polyester candle elements each. One candle element is 10 feet high with a 2-foot diameter.

Emissions from pulp mill sources, such as the evaporator, are controlled with a separate SO<sub>2</sub> scrubber (referred to as the "pulp mill SO<sub>2</sub> scrubber"); pulp mill sources are not integrated with the chemical recovery sources.

Cost data: Capital and annual costs for SO<sub>2</sub> scrubber and PM fume filters available in NCASI 1991 MACT survey. response.

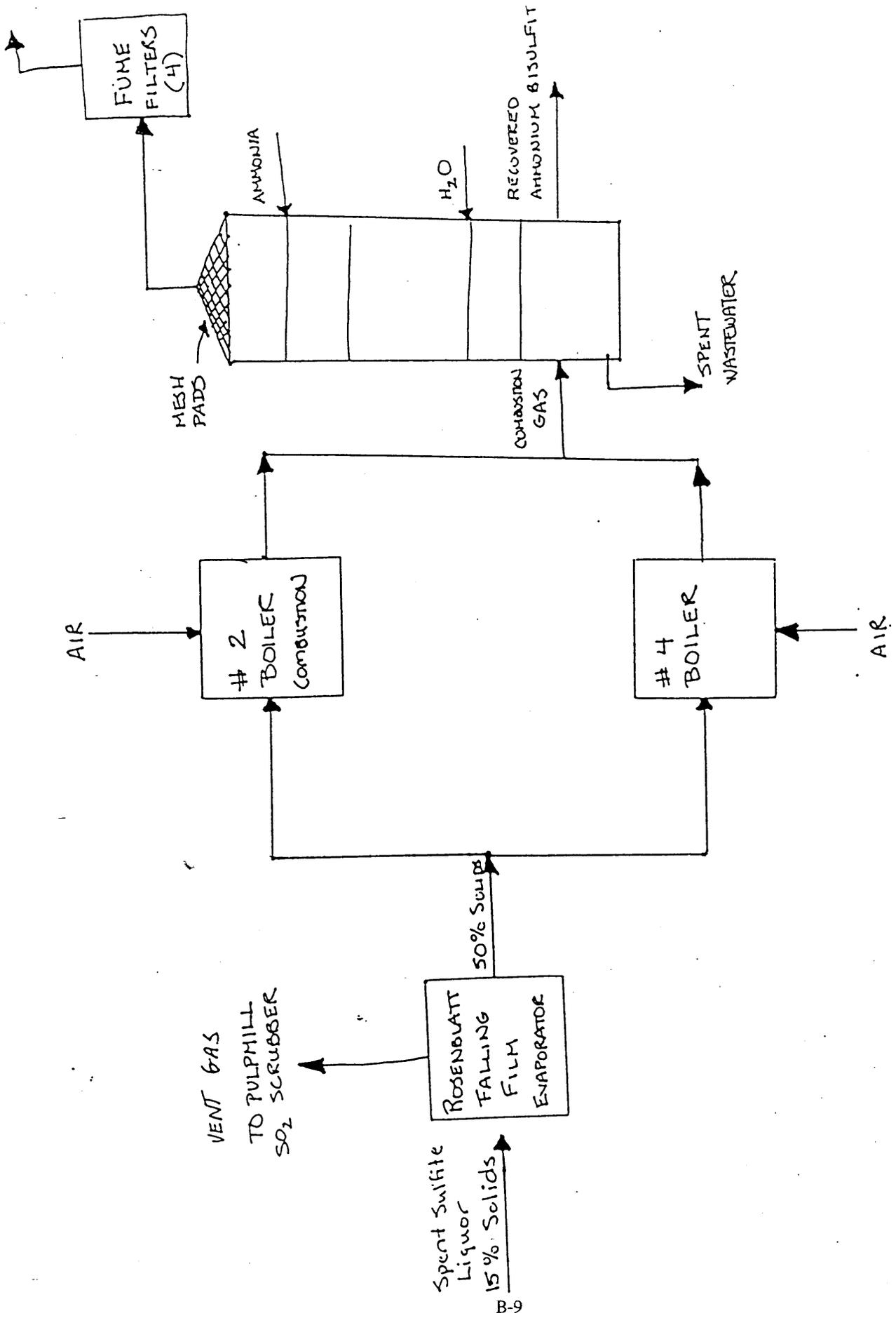


Figure B-5. Chemical recovery process at Mill 121.

Mill Type: NH<sub>3</sub>-based sulfite

Mill Code: 41

Information Available: NCASI 1991 MACT survey response (incomplete information was provided)

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Chemical recovery combustion equipment: 4 recovery furnaces (Nos. 8 and 10 are 1977 and 1987 Loddby furnaces; Nos. 6 and 7 were installed in 1974, information on the manufacturer is not available.)

Chemical recovery process/air pollution control equipment: SO<sub>2</sub> scrubber/absorber + Brinks demister system (possibly 2 parallel sets, although unclear from survey response.)

Chemical recovery process description: See Figure B-6. Spent liquor at 60% solids from the evaporators is fired in one of four recovery furnaces. Recovery furnaces Nos. 8 and 10 are Loddby furnaces with liquor solids feed rates of 750,000 lb/day each. Information on the firing rate or manufacturer for recovery furnaces Nos. 6 and 7 are not available. Combustion gases are routed to an SO<sub>2</sub> scrubber/absorber where SO<sub>2</sub> in the gases is absorbed using an ammonium solution. It is unclear from the survey response whether combustion gases from all 4 recovery furnaces are combined and routed to one scrubber/absorber or if there are two or more scrubber/absorbers. The resulting acid is then enriched with SO<sub>2</sub> in a fortification tower. Evaporator overhead gases are routed to the fortification tower, and the fortification tower is vented to the SO<sub>2</sub> scrubber. Exit gases from the SO<sub>2</sub> scrubber pass through fiber bed filters prior to discharge to the atmosphere. The fiber bed filters were manufactured by Monsanto. The fiber bed filter systems for the recovery furnaces Nos. 6 and 7 contain 40 elements each, and the fiber bed filter for recovery furnace No. 8 contains 81 elements. Information on the fiber bed filter system for the recovery furnace No. 10 is not available. Again, the number of separate demister systems is unclear based on survey response data. The elements are 12 feet long and 2 feet in diameter. The mill plans to replace the filter media with a denser media.

Cost data: Annual cost data are available for the Brinks demister system are available in the NCASI 1991 MACT survey response.

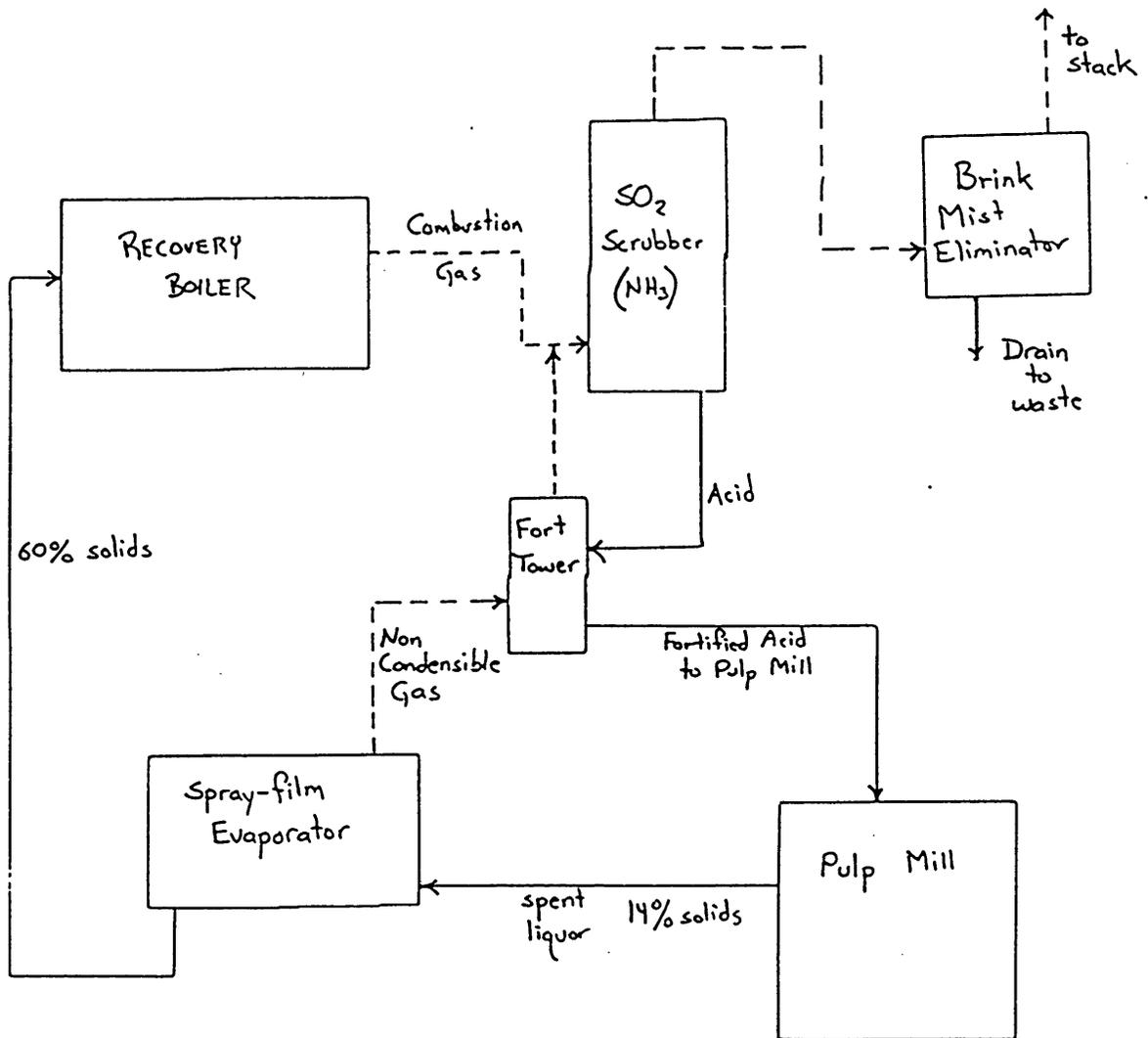


Figure B-6. Chemical recovery process at Mill 41.

Mill Type: NH<sub>3</sub>-based sulfite

Mill Code: B

Information Available: Brief mill contact

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Chemical recovery combustion equipment: Marathon Engineering combustion unit (one-of-a-kind)

Chemical recovery process/air pollution control equipment: venturi scrubbers (direct contact evaporators) + absorption tower (bubble trays) that includes a heat recovery stage. Additional information from the mill is needed.

Chemical recovery process description: Insufficient information available to describe process.