

## 8.10 Sulfuric Acid

### 8.10.1 General<sup>1-2</sup>

Sulfuric acid ( $\text{H}_2\text{SO}_4$ ) is a basic raw material used in a wide range of industrial processes and manufacturing operations. Almost 70 percent of sulfuric acid manufactured is used in the production of phosphate fertilizers. Other uses include copper leaching, inorganic pigment production, petroleum refining, paper production, and industrial organic chemical production.

Sulfuric acid may be manufactured commercially by either the lead chamber process or the contact process. Because of economics, all of the sulfuric acid produced in the U. S. is now produced by the contact process. U. S. facilities produce approximately 42 million megagrams (Mg) (46.2 million tons) of  $\text{H}_2\text{SO}_4$  annually. Growth in demand was about 1 percent per year from 1981 to 1991 and is projected to continue to increase at about 0.5 percent per year.

### 8.10.2 Process Description<sup>3-5</sup>

Since the contact process is the only process currently used, it will be the only one discussed in this section. Contact plants are classified according to the raw materials charged to them: elemental sulfur burning, spent sulfuric acid and hydrogen sulfide burning, and metal sulfide ores and smelter gas burning. The contributions from these plants to the total acid production are 81, 8, and 11 percent, respectively.

The contact process incorporates 3 basic operations, each of which corresponds to a distinct chemical reaction. First, the sulfur in the feedstock is oxidized (burned) to sulfur dioxide ( $\text{SO}_2$ ):



The resulting sulfur dioxide is fed to a process unit called a converter, where it is catalytically oxidized to sulfur trioxide ( $\text{SO}_3$ ):



Finally, the sulfur trioxide is absorbed in a strong 98 percent sulfuric acid solution:



#### 8.10.2.1 Elemental Sulfur Burning Plants -

Figure 8.10-1 is a schematic diagram of a dual absorption contact process sulfuric acid plant that burns elemental sulfur. In the Frasch process, elemental sulfur is melted, filtered to remove ash, and sprayed under pressure into a combustion chamber. The sulfur is burned in clean air that has been dried by scrubbing with 93 to 99 percent sulfuric acid. The gases from the combustion chamber cool by passing through a waste heat boiler and then enter the catalyst (vanadium pentoxide) converter. Usually, 95 to 98 percent of the sulfur dioxide from the combustion chamber is converted to sulfur trioxide, with an accompanying large evolution of heat. After being cooled, again by generating steam, the converter exit gas enters an absorption tower. The absorption tower is a packed column where acid is sprayed in the top and where the sulfur trioxide enters from the bottom. The

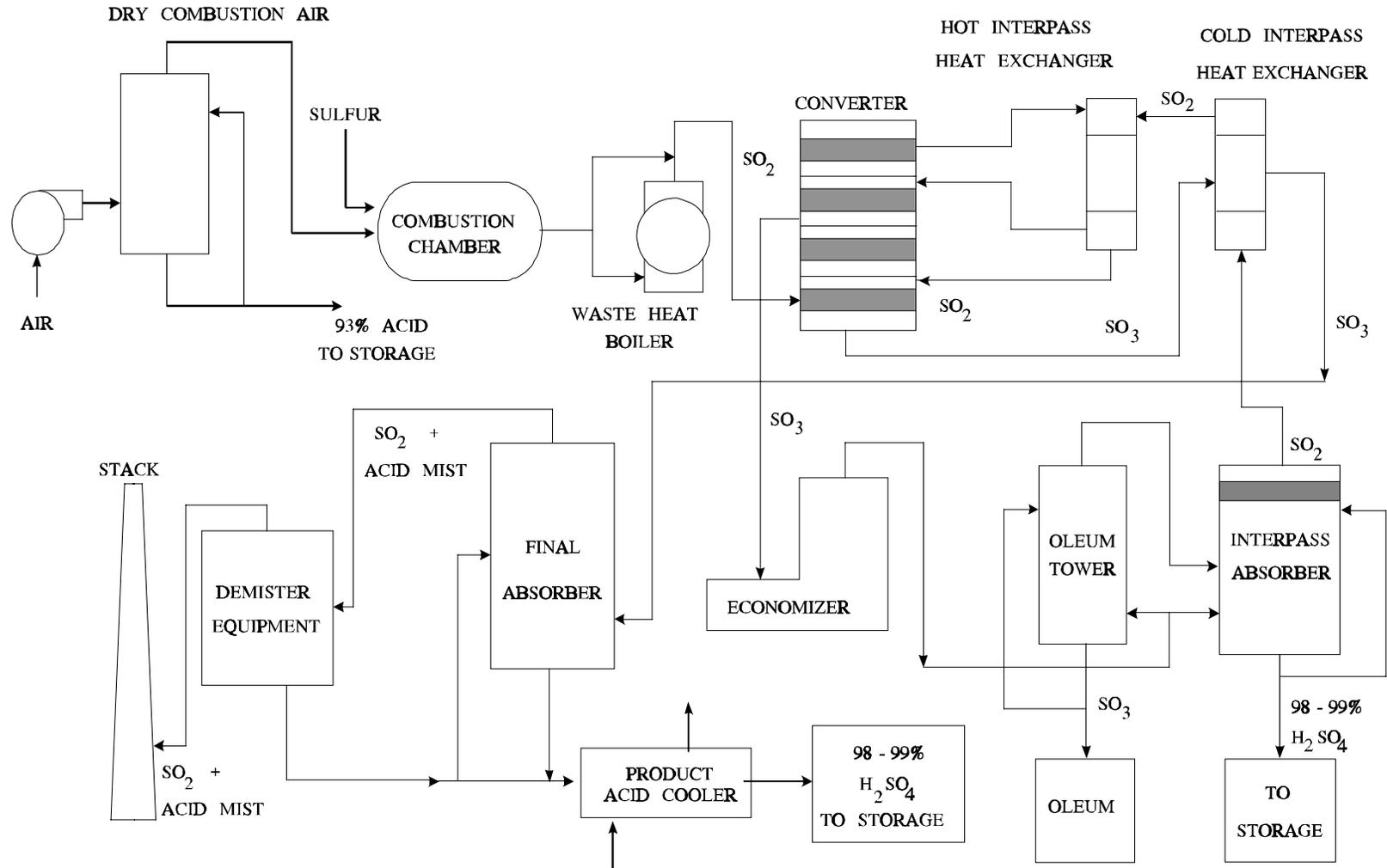


Figure 8.10-1. Typical contact process sulfuric acid plant burning elemental sulfur.

sulfur trioxide is absorbed in the 98 to 99 percent sulfuric acid. The sulfur trioxide combines with the water in the acid and forms more sulfuric acid.

If oleum (a solution of uncombined  $\text{SO}_3$  dissolved in  $\text{H}_2\text{SO}_4$ ) is produced,  $\text{SO}_3$  from the converter is first passed to an oleum tower that is fed with 98 percent acid from the absorption system. The gases from the oleum tower are then pumped to the absorption column where the residual sulfur trioxide is removed.

In the dual absorption process shown in Figure 8.10-1, the  $\text{SO}_3$  gas formed in the primary converter stages is sent to an interpass absorber where most of the  $\text{SO}_3$  is removed to form  $\text{H}_2\text{SO}_4$ . The remaining unconverted sulfur dioxide is forwarded to the final stages in the converter to remove much of the remaining  $\text{SO}_2$  by oxidation to  $\text{SO}_3$ , whence it is sent to the final absorber for removal of the remaining sulfur trioxide. The single absorption process uses only one absorber, as the name implies.

#### 8.10.2.2 Spent Acid And Hydrogen Sulfide Burning Plants -

A schematic diagram of a contact process sulfuric acid plant that burns spent acid is shown in Figure 8.10-2. Two types of plants are used to process this type of sulfuric acid. In one, the sulfur dioxide and other products from the combustion of spent acid and/or hydrogen sulfide with undried atmospheric air are passed through gas cleaning and mist removal equipment. The gas stream next passes through a drying tower. A blower draws the gas from the drying tower and discharges the sulfur dioxide gas to the sulfur trioxide converter, then to the oleum tower and/or absorber.

In a "wet gas plant", the wet gases from the combustion chamber are charged directly to the converter, with no intermediate treatment. The gas from the converter flows to the absorber, through which 93 to 98 percent sulfuric acid is circulated.

#### 8.10.2.3 Sulfide Ores And Smelter Gas Plants -

The configuration of this type of plant is essentially the same as that of a spent acid plant (Figure 8.10-2), with the primary exception that a roaster is used in place of the combustion furnace.

The feed used in these plants is smelter gas, available from such equipment as copper converters, reverberatory furnaces, roasters, and flash smelters. The sulfur dioxide in the gas is contaminated with dust, acid mist, and gaseous impurities. To remove the impurities, the gases must be cooled and passed through purification equipment consisting of cyclone dust collectors, electrostatic dust and mist precipitators, and scrubbing and gas cooling towers. After the gases are cleaned and the excess water vapor is removed, they are scrubbed with 98 percent acid in a drying tower. Beginning with the drying tower stage, these plants are nearly identical to the elemental sulfur plants shown in Figure 8.10-1.

### 8.10.3 Emissions<sup>4,6-7</sup>

#### 8.10.3.1 Sulfur Dioxide -

Nearly all sulfur dioxide emissions from sulfuric acid plants are found in the exit stack gases. Extensive testing has shown that the mass of these  $\text{SO}_2$  emissions is an inverse function of the sulfur conversion efficiency ( $\text{SO}_2$  oxidized to  $\text{SO}_3$ ). This conversion is always incomplete, and is affected by the number of stages in the catalytic converter, the amount of catalyst used, temperature and pressure, and the concentrations of the reactants (sulfur dioxide and oxygen). For example, if the inlet  $\text{SO}_2$  concentration to the converter were 9 percent by volume (a representative value), and the conversion temperature was  $430^\circ\text{C}$  ( $806^\circ\text{F}$ ), the conversion efficiency would be 98 percent. At this conversion, Table 8.10-1 shows that the uncontrolled emission factor for  $\text{SO}_2$  would be 13 kilograms

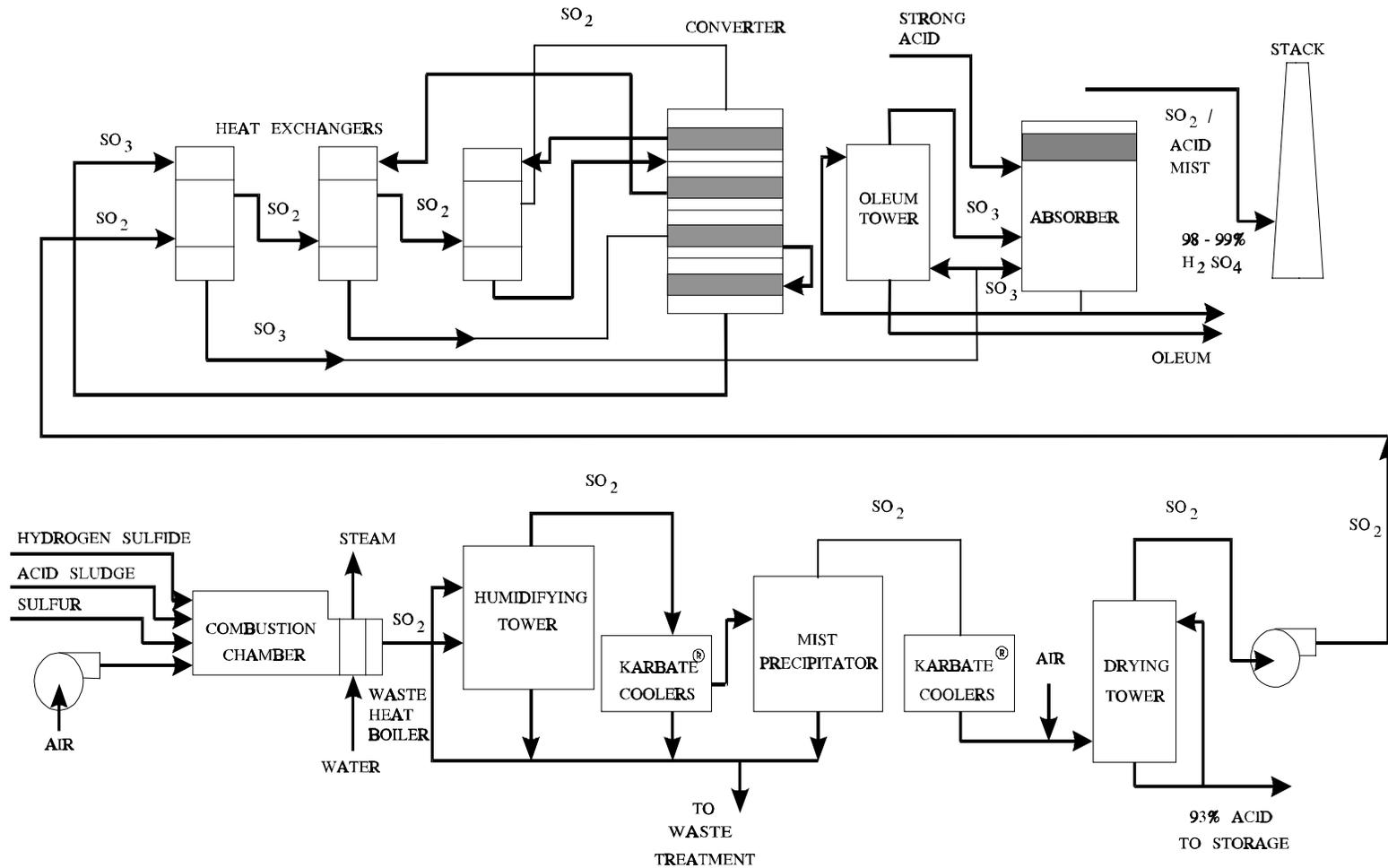


Figure 8.10-2. Basic flow diagram of contact process sulfuric acid plant burning spent acid.

per megagram (kg/Mg) (26 pounds per ton [lb/ton]) of 100 percent sulfuric acid produced. (For purposes of comparison, note that the Agency's new source performance standard [NSPS] for new and modified plants is 2 kg/Mg (4 lb/ton) of 100 percent acid produced, maximum 2 hour average.) As Table 8.10-1 and Figure 8.10-3 indicate, achieving this standard requires a conversion efficiency of 99.7 percent in an uncontrolled plant, or the equivalent SO<sub>2</sub> collection mechanism in a controlled facility.

Dual absorption, as discussed above, has generally been accepted as the best available control technology for meeting NSPS emission limits. There are no byproducts or waste scrubbing materials created, only additional sulfuric acid. Conversion efficiencies of 99.7 percent and higher are achievable, whereas most single absorption plants have SO<sub>2</sub> conversion efficiencies ranging only from 95 to 98 percent. Furthermore, dual absorption permits higher converter inlet sulfur dioxide concentrations than are used in single absorption plants, because the final conversion stages effectively remove any residual sulfur dioxide from the interpass absorber.

In addition to exit gases, small quantities of sulfur oxides are emitted from storage tank vents and tank car and tank truck vents during loading operations, from sulfuric acid concentrators, and through leaks in process equipment. Few data are available on the quantity of emissions from these sources.

Table 8.10-1 (Metric And English Units). SULFUR DIOXIDE EMISSION FACTORS FOR SULFURIC ACID PLANTS<sup>a</sup>

EMISSION FACTOR RATING: E

SO <sub>2</sub> To SO <sub>3</sub> Conversion Efficiency (%)	SO <sub>2</sub> Emissions <sup>b</sup>	
	kg/Mg Of Product	lb/ton Of Product
93 (SCC 3-01-023-18)	48.0	96
94 (SCC 3-01-023-16)	41.0	82
95 (SCC 3-01-023-14)	35.0	70
96 (SCC 3-01-023-12)	27.5	55
97 (SCC 3-01-023-10)	20.0	40
98 (SCC 3-01-023-08)	13.0	26
99 (SCC 3-01-023-06)	7.0	14
99.5 (SCC 3-01-023-04)	3.5	7
99.7 NA	2.0	4
100 (SCC 3-01-023-01)	0.0	0.0

<sup>a</sup> Reference 3. SCC = Source Classification Code. NA = not applicable.

<sup>b</sup> This linear interpolation formula can be used for calculating emission factors for conversion efficiencies between 93 and 100%: emission factor (kg/Mg of Product) = 682 - 6.82 (% conversion efficiency) (emission factor [lb/ton of Product] = 1365 - 13.65 [% conversion efficiency]).

### 8.10.3.2 Acid Mist -

Nearly all the acid mist emitted from sulfuric acid manufacturing can be traced to the absorber exit gases. Acid mist is created when sulfur trioxide combines with water vapor at a

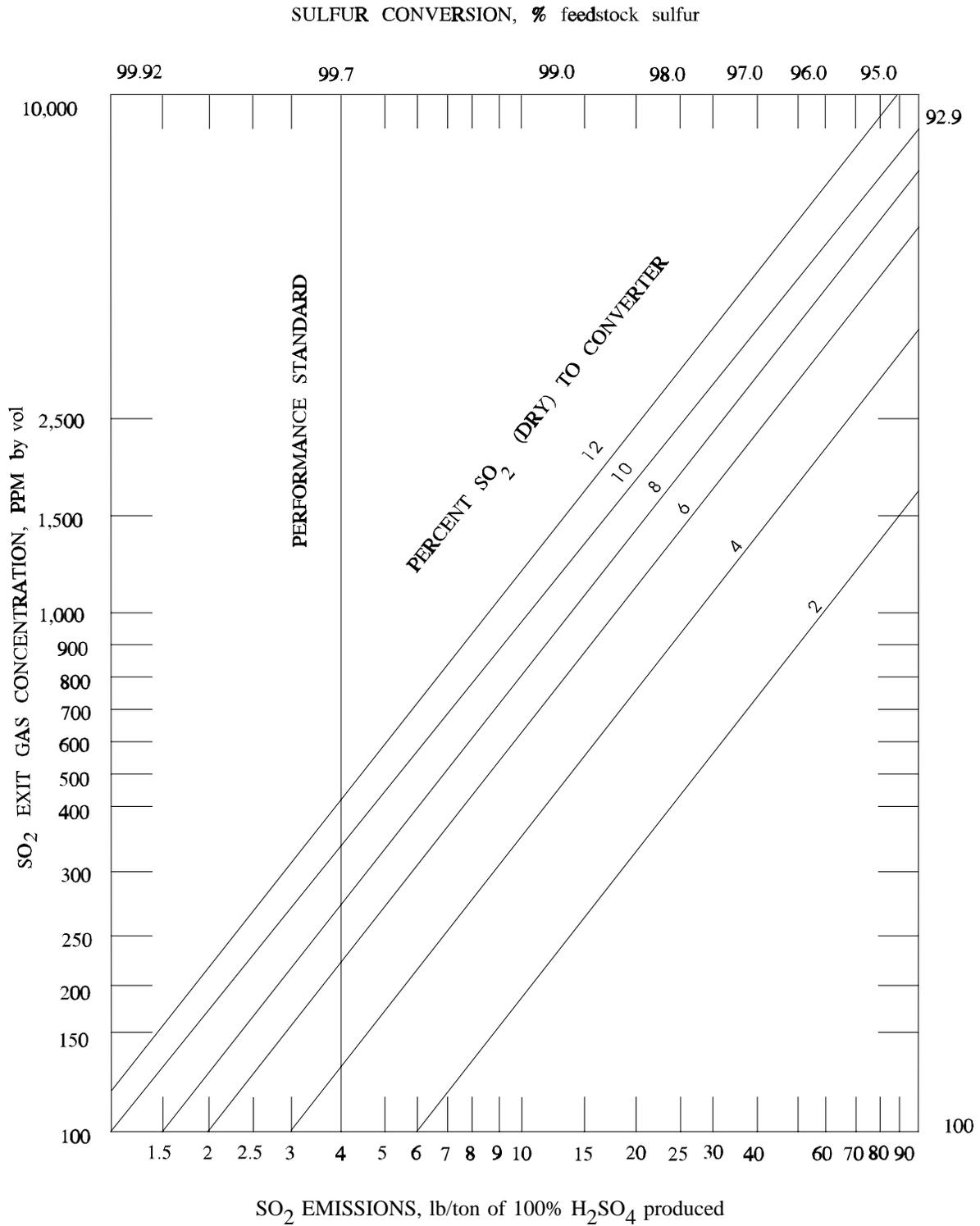


Figure 8.10-3. Sulfuric acid plant feedstock conversion versus volumetric and mass SO<sub>2</sub> emissions at various inlet SO<sub>2</sub> concentrations by volume.

temperature below the dew point of sulfur trioxide. Once formed within the process system, this mist is so stable that only a small quantity can be removed in the absorber.

In general, the quantity and particle size distribution of acid mist are dependent on the type of sulfur feedstock used, the strength of acid produced, and the conditions in the absorber. Because it contains virtually no water vapor, bright elemental sulfur produces little acid mist when burned. However, the hydrocarbon impurities in other feedstocks (i. e., dark sulfur, spent acid, and hydrogen sulfide) oxidize to water vapor during combustion. The water vapor, in turn, combines with sulfur trioxide as the gas cools in the system.

The strength of acid produced, whether oleum or 99 percent sulfuric acid, also affects mist emissions. Oleum plants produce greater quantities of finer, more stable mist. For example, an unpublished report found that uncontrolled mist emissions from oleum plants burning spent acid range from 0.5 to 5.0 kg/Mg (1.0 to 10.0 lb/ton), while those from 98 percent acid plants burning elemental sulfur range from 0.2 to 2.0 kg/Mg (0.4 to 4.0 lb/ton).<sup>4</sup> Furthermore, 85 to 95 weight percent of the mist particles from oleum plants are less than 2 micrometers ( $\mu\text{m}$ ) in diameter, compared with only 30 weight percent that are less than 2  $\mu\text{m}$  in diameter from 98 percent acid plants.

The operating temperature of the absorption column directly affects sulfur trioxide absorption and, accordingly, the quality of acid mist formed after exit gases leave the stack. The optimum absorber operating temperature depends on the strength of the acid produced, throughput rates, inlet sulfur trioxide concentrations, and other variables peculiar to each individual plant. Finally, it should be emphasized that the percentage conversion of sulfur trioxide has no direct effect on acid mist emissions.

Table 8.10-2 presents uncontrolled acid mist emission factors for various sulfuric acid plants. Table 8.10-3 shows emission factors for plants that use fiber mist eliminator control devices. The 3 most commonly used fiber mist eliminators are the vertical tube, vertical panel, and horizontal dual pad types. They differ from one another in the arrangement of the fiber elements, which are composed of either chemically resistant glass or fluorocarbon, and in the means employed to collect the trapped liquid. Data are available only with percent oleum ranges for 2 raw material categories.

#### 8.10.3.3 Carbon Dioxide -

The 9 source tests mentioned above were also used to determine the amount of carbon dioxide ( $\text{CO}_2$ ), a global warming gas, emitted by sulfuric acid production facilities. Based on the tests, a  $\text{CO}_2$  emission factor of 4.05 kg emitted per Mg produced (8.10 lb/ton) was developed, with an emission factor rating of C.

Table 8.10-2 (Metric And English Units). UNCONTROLLED ACID MIST EMISSION FACTORS FOR SULFURIC ACID PLANTS<sup>a</sup>

EMISSION FACTOR RATING: E

Raw Material	Oleum Produced, % Total Output	Emissions <sup>b</sup>	
		kg/Mg Of Product	lb/ton Of Product
Recovered sulfur (SCC 3-01-023-22)	0 - 43	0.174 - 0.4	0.348 - 0.8
Bright virgin sulfur (SCC 3-01-023-22)	0	0.85	1.7
Dark virgin sulfur (SCC 3-01-023-22)	0 - 100	0.16 - 3.14	0.32 - 6.28
Spent acid (SCC 3-01-023-22)	0 - 77	1.1 - 1.2	2.2 - 2.4

<sup>a</sup> Reference 3. SCC = Source Classification Code.

<sup>b</sup> Emissions are proportional to the percentage of oleum in the total product. Use low end of ranges for low oleum percentage and high end of ranges for high oleum percentage.

Table 8.10-3 (Metric And English Units). CONTROLLED ACID MIST EMISSION FACTORS FOR SULFURIC ACID PLANTS

EMISSION FACTOR RATING: E (except as noted)

Raw Material	Oleum Produced, % Total Output	Emissions	
		kg/Mg Of Product	lb/ton Of Product
Elemental sulfur <sup>a</sup> (SCC 3-01-023-22)	—	0.064	0.128
Dark virgin sulfur <sup>b</sup> (SCC 3-01-023-22)	0 - 13	0.26 - 1.8	0.52 - 3.6
Spent acid (SCC 3-01-023-22)	0 - 56	0.014 - 0.20	0.28 - 0.40

<sup>a</sup> References 8-13,15-17. EMISSION FACTOR RATING: C. SCC = Source Classification Code.

<sup>b</sup> Reference 3.

References For Section 8.10

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