



# EMERGENCY PLANNING AND COMMUNITY RIGHT-TO-KNOW ACT - SECTION 313

## Guidance for Reporting Sulfuric Acid (acid aerosols including mists, vapors, gas, fog, and other airborne forms of any particle size)

Section 313 of the Emergency Planning and Community Right-to-Know Act of 1986 (EPCRA) requires certain facilities manufacturing, processing, or otherwise using listed toxic chemicals to report their environmental releases of such chemicals annually. Beginning with the 1991 reporting year, such facilities also must report pollution prevention and recycling data for such chemicals, pursuant to section 6607 of the Pollution Prevention Act, 42 U.S.C. 13106. When enacted, EPCRA section 313 established an initial list of toxic chemicals that was comprised of more than 300 chemicals and 20 chemical categories. EPCRA section 313(d) authorizes EPA to add chemicals to or delete chemicals from the list, and sets forth criteria for these actions.

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## Section 1.0. Introduction

On June 30, 1995 (60 FR 34182), EPA modified the listing for sulfuric acid (Chemical Abstracts Service Number 7664-93-9) on the list of toxic chemicals subject to the reporting requirements under section 313 of the Emergency Planning and Community Right-to-Know Act of 1986 (EPCRA) (5). EPA modified the listing by deleting non-aerosol forms of sulfuric acid from the section 313 list based on the conclusion that they cannot reasonably be anticipated to cause adverse effects on human health or the environment. EPA added a modifier to the listing for sulfuric acid to exclude the non-aerosol forms. The listing now reads “Sulfuric acid (acid aerosols including mists, vapors, gas, fog, and other airborne forms of any particle size).” Therefore, beginning with the 1994 reporting year, facilities are no longer required to include non-aerosol forms of sulfuric acid in threshold and release determinations. In this document we will use the term “sulfuric acid aerosols” to indicate airborne forms of sulfuric acid as listed in section 313 of EPCRA.

The purpose of this document is to assist facilities in determining the sources and amounts of sulfuric acid aerosols that are to be included in threshold and release determinations under EPCRA section 313. This document is not meant to be exhaustive, but rather provide some guidance to help facilities in their determination of threshold and release quantities. Threshold and release determinations for sulfuric acid aerosols are highly dependent on site specific conditions and equipment. Therefore, this document can only provide general information concerning the possible formation and release of sulfuric acid aerosols.

### Section 1.1. Who Must Report

A plant, factory, or other facility is subject to the provisions of EPCRA section 313, if it meets all three of the following criteria:

- It is included in the primary Standard Industrial Classification (SIC) codes 20 through 39 and beginning January 1, 1998, it is in one of the following industries: Metal Mining, SIC code 10 (except SIC codes 1011, 1081, and 1094); Coal Mining, SIC code 12 (except SIC code 1241); Electric Utilities, SIC codes 4911, 4931, or 4939 (each limited to facilities that combust coal and/or oil for the purpose of generating power for distribution in commerce); Commercial Hazardous Waste Treatment, SIC code 4953 (limited to facilities regulated under the Resource Conservation and Recovery Act, subtitle C, 42 U.S.C. section 6921 *et seq.*); Chemicals and Allied Products-Wholesale, SIC code 5169; Petroleum Bulk Terminals and Plants, SIC code 5171; and, Solvent Recovery Services, SIC code 7389 (limited to facilities primarily engaged in solvent recovery services on a contract or fee basis); and
- It has 10 or more full-time employees (or the equivalent of 20,000 hours per year); and

- It manufactures (includes imports), processes or otherwise uses any of the toxic chemicals listed on the EPCRA section 313 list in amounts greater than the threshold quantities specified below.

In addition, pursuant to Executive Order 12856 entitled “Federal Compliance with Right-to-Know Laws and Pollutant Prevention Requirements,” federal facilities are required to comply with the reporting requirements of EPCRA Section 313 beginning with calendar year 1994. This requirement is mandated regardless of the facility’s SIC code.

## **Section 1.2. Thresholds**

Thresholds are specified amounts of toxic chemicals manufactured, processed, or otherwise used during the calendar year that trigger reporting requirements. Reporting is required for sulfuric acid aerosols if the following thresholds are exceeded.

- If a facility *manufactures* or *imports* 25,000 pounds of sulfuric acid aerosols over the calendar year.
- If a facility *processes* 25,000 pounds of sulfuric acid aerosols over the calendar year.
- If a facility *otherwise uses* 10,000 pounds of sulfuric acid aerosols over the calendar year.

The quantities of sulfuric acid aerosols included in threshold determinations are not limited to the amounts of sulfuric acid aerosols released to the environment. All sulfuric acid aerosols manufactured, processed, or otherwise used are to be counted toward threshold determinations. This includes any amount of sulfuric acid aerosols that may be generated in closed systems or that are generated in stacks prior to or after being treated by scrubbers.

## **Section 1.3. What Constitutes Aerosol Forms of Sulfuric Acid and Their Manufacture, Processing, or Otherwise Use**

For the purposes of the reporting requirements under EPCRA section 313, sulfuric acid aerosols include mists, vapors, gas, fog, and other airborne forms of any particle size. Note that there is no size limit for particles that must be included under the EPCRA section 313 sulfuric acid aerosols listing. Although the qualifier includes the terms mists, vapors, gas, and fog these terms are not specifically defined for EPCRA section 313 since the last part of the qualifier "other airborne forms of any particle size" makes it clear that any airborne form is covered by the listing. The specific terms mists, vapors, gas, and fog are included to make it clear that sulfuric acid that is identified as being in one of these forms would be covered by the sulfuric acid aerosols listing.

If sulfuric acid is present in the form of a gas, fog, vapor, or mist or any other airborne form then sulfuric acid is considered to be in the aerosol form and is covered by the EPCRA section 313

sulfuric acid aerosols listing. Solutions of sulfuric acid which do not become airborne are not covered by the EPCRA section 313 sulfuric acid aerosols listing but such solutions may generate sulfuric acid aerosols during their manufacture, processing or otherwise use. In general, sulfuric acid aerosols are manufactured any time a solution of sulfuric acid is made to become airborne such as when it is sprayed or distilled. If the generation of sulfuric acid aerosols through spraying or other means is intentional (i.e., it is intended that the sulfuric acid aerosol be generated for a particular use activity) then, in addition to manufacturing the sulfuric acid aerosol, such aerosols are also being otherwise used. Thus, spraying of sulfuric acid aerosols on to an item for cleaning, etching, or other purposes constitutes the manufacture and otherwise use of sulfuric acid aerosols. If sulfuric acid aerosols are used in a process in which any part of the sulfuric acid becomes incorporated into a product which is then distributed in commerce then, under EPCRA section 313, the sulfuric acid aerosols are considered to have been processed.

## **Section 2.0. Guidance On Sulfuric Acid Aerosols For Certain Specific Activities That Generate Aerosols Forms**

EPA has provided the following guidance for specific activities that generated sulfuric acid aerosols. The guidance in sections 2.1, 2.2, and 2.3 is intended to apply only to the specific situations discussed in these sections. If you are not sure whether this guidance applies to the situation at your facility, then EPA should be consulted before using this guidance.

### **Section 2.1. Sulfuric Acid Aerosols Generated In Acid Reuse Systems**

When solutions of sulfuric acid are aerosolized the “manufacture” of a listed chemical (sulfuric acid aerosols) has occurred. This is a result of the qualifier to the sulfuric acid listing, which excludes non-aerosol forms and limits the reporting to aerosol forms only. The addition of the acid aerosol qualifier has an impact on certain processes that, prior to the addition of the qualifier, would not have been considered to be “manufacturing” a listed chemical. Acid reuse systems that use aqueous solutions of sulfuric acid to generate acid aerosols, use the acid aerosols, condense them back into solution, and then reuse the acid solution again and again are impacted by the addition of the acid aerosol qualifier. In such processes, the continuous reuse of the acid solutions generates very large quantities of acid aerosols that technically should be counted towards the “manufacture” [the generation of the acid aerosol is the “manufacture” of sulfuric acid (acid aerosol)] and “otherwise use” thresholds. This may result in many facilities greatly exceeding the “manufacture” and “otherwise use” reporting thresholds that, prior to the addition of the qualifier, would not have exceeded thresholds.

While it is technically correct to apply all of the quantities of acid aerosols generated in such systems towards the “manufacture” and “otherwise use” reporting thresholds, EPA did not intend to increase the reporting burden as a result of addition of the sulfuric acid aerosol qualifier. In addition, under EPA’s general approach to reuse systems, a toxic chemical is not counted toward thresholds each time it is reused but only once per reporting period, and that approach would apply to

sulfuric acid reuse systems were it not for the aerosol qualifier. Therefore, EPA is providing the following guidance to reduce the reporting burden for facilities that operate such processes and to bring the treatment of such systems into alignment with EPA's general approach to reuse.

Rather than having facilities count all quantities of acid aerosol generated in such systems towards the "manufacture" and "otherwise use" thresholds, EPA will allow facilities to apply the total volume of acid in these systems only once to these thresholds. For example, if an acid reuse system starts the year with 2000 pounds of acid and 500 pounds is added during the year then the total amount applied towards acid aerosol thresholds would be 2500 pounds. This reflects a one time per year counting of all of the acid molecules as being in the acid aerosol form rather than counting them over and over again each time the acid aerosol form is generated and subsequently used. Since in these acid reuse systems the acid aerosols are "manufactured" and then "**otherwise used**" the 10,000 pound "otherwise use" threshold would be the threshold that would first trigger reporting from such systems.

This guidance applies only to acid reuse systems and the reporting of sulfuric acid aerosols under EPCRA section 313. This guidance does not apply to any other types of processes or to any other listed chemical.

## **2.2. Sulfuric Acid Aerosols Removed By Scrubbers**

When a scrubber is used to remove sulfuric acid aerosols prior to or in a stack, the acid aerosols are usually converted to the non-aerosol form. The non-aerosol forms of sulfuric acid are not reportable under EPCRA section 313 because the qualifier to the sulfuric acid listing includes only acid aerosol forms. Sulfuric acid as a discrete chemical has not actually been destroyed by the scrubber, but the form of sulfuric acid reportable under EPCRA section 313 has been destroyed. Therefore, since sulfuric acid aerosols removed by scrubbers are converted to a non-reportable form, the quantity removed by the scrubber can be reported as having been treated for destruction.

## **2.3. Sulfuric Acid Aerosols Generated In Storage Tanks**

Sulfuric acid aerosols are generated in the empty space (head space) above sulfuric acid solutions contained in storage tanks. The amounts of acid aerosols generated in such storage tanks are to be applied towards the "manufacture" threshold for sulfuric acid aerosols. In such storage tanks the sulfuric acid molecules are constantly moving between the atmosphere and the solution. EPA does not intend for facilities to count such movement of the acid molecules in and out of the stored acid solution as continuous "manufacture" of sulfuric acid aerosols. For such storage tanks the amount of acid aerosol to be applied towards the "manufacture" threshold is the average amount that existed in the atmosphere above the acid solution during the year.

Each facility should determine the average conditions for their specific storage tank (i.e., the capacity of the tank, the average amount in the tank, the average head space in the tank, the

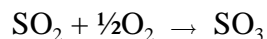
concentration of the acid solution stored, the temperature, and other information that may have an impact on aerosol calculations) and make the appropriate calculation of the amount of acid aerosol to apply towards the “manufacture” threshold. Any amounts of sulfuric acid aerosols that may be released from the storage tank through venting or fugitive releases must also be included in the threshold determination. If the storage tank is refilled and drawn down several times during the year then the calculations should be based on all of the acid that was stored in the tank. For example, if a 10,000 pound capacity tank is refilled and drawn down 6 times during the year (such that 60,000 pounds of acid were stored in the tank during the year) then the tank calculations, based on the average condition for one 10,000 pound tank of acid, should be multiplied by 6.

### Section 3.0. Sulfuric Acid And Its Formation In Air

Sulfuric acid ( $\text{H}_2\text{SO}_4$ ) is miscible in water in all proportions and has a strong attraction for water. The anhydrous chemical boils at  $279.6^\circ\text{C}$  (1). Commercial sulfuric acid normally contains 93 to 98% sulfuric acid with the remainder being water. A boiling point-composition diagram (Figure 1, Appendix 1) for aqueous sulfuric acid, indicates that below 75%  $\text{H}_2\text{SO}_4$ , the vapor evaporating from a solution of the acid is essentially water. This fact is illustrated in Table 1a of Appendix 1, which contains the partial pressure of sulfuric acid and total vapor pressure of the solution over aqueous sulfuric acid solutions at various concentrations (1). Since the partial pressure of concentrated sulfuric acid is very low, little sulfuric acid is expected to volatilize from sulfuric acid solutions such as may be present in storage tanks. However, as discussed above, the amount of acid aerosols generated is dependent on the quantity of acid in the tank(s) during the year, the concentration, temperature, and other factors. The information in Appendix 1 and the guidance in section 2.3 can be used to assist in determining if significant amounts of sulfuric acid aerosols are present in storage tanks.

Sulfuric acid containing dissolved sulfur trioxide ( $\text{SO}_3$ ) is known as oleum, fuming sulfuric acid or disulfuric acid. The vapor pressure of sulfuric acid over oleum containing 10% to 30% of free  $\text{SO}_3$  by weight is shown in Table 2a of Appendix 1 (2). Since the vapor pressure of sulfur trioxide over oleum is high, sulfuric acid aerosols also form when oleum is exposed to air containing moisture.

Sulfuric acid is generally formed by the oxidation of sulfur dioxide ( $\text{SO}_2$ ) and the reaction of the resulting sulfur trioxide ( $\text{SO}_3$ ) with water.



While thermodynamically,  $\text{SO}_2$  has a strong tendency to react with oxygen to form  $\text{SO}_3$ ; under normal tropospheric (lower atmosphere) conditions the reaction rate is very slow in the gas phase (3, 17, 18, 19). Other than within a reaction chamber,  $\text{SO}_2$  is unlikely to generate  $\text{SO}_3$  and then sulfuric acid. However, once  $\text{SO}_3$  is formed, it is converted to  $\text{H}_2\text{SO}_4$  so rapidly (within milliseconds) at normal

humidities, that any reaction in which SO<sub>3</sub> is formed in moist air is equivalent to forming H<sub>2</sub>SO<sub>4</sub> (3,18). In stacks from combustion processes, moisture in the **stack** would be expected to convert any SO<sub>3</sub> present into sulfuric acid aerosols. This being the case, the quantity of SO<sub>3</sub> generated in such stacks (multiplied by 98.08/80.07, the molecular weight of sulfuric acid divided by the molecular weight of sulfur trioxide) should be included with those of H<sub>2</sub>SO<sub>4</sub>. If SO<sub>3</sub> is produced within a stack or unit of the plant without moisture present, sulfuric acid aerosols would not be produced. Although the SO<sub>3</sub> releases may be converted to H<sub>2</sub>SO<sub>4</sub> in the environment, facilities are not responsible for conversions that may take place in the environment after a chemical that is not listed under EPCRA section 313, such as SO<sub>3</sub>, has been released. Therefore, if SO<sub>3</sub> is the chemical that is released from the facility, the facility is not required to include it, or any H<sub>2</sub>SO<sub>4</sub> produced in the environment from the released SO<sub>3</sub>, in any EPCRA section 313 calculations of thresholds or releases.

### Section 3.1. Industrial Sources Of Sulfuric Acid Aerosols

It is clear that industries required to report *sulfuric acid aerosol* releases will be among those that had previously reported *sulfuric acid* releases to air under EPCRA section 313. Facilities that previously reported over 25,000 pounds of sulfuric acid releases to air have exceeded the manufacturing threshold quantity of sulfuric acid aerosols necessary for reporting under the new listing. Additional facilities may be required to report because releases of sulfuric acid to air would not have included, for example, amounts of sulfuric acid aerosols that were produced in the stack and subsequently removed by scrubbers or produced internally during sulfuric acid manufacturing, processing, or use and that were removed by scrubbers prior to the stack. Since these amounts of sulfuric acid aerosols do count towards the EPCRA section 313 threshold determinations, facilities with less than 25,000 pounds of air releases are not excluded from reporting. In addition, some facilities may be using sulfuric acid aerosols in excess of 10,000 pounds and would also be required to report. According to the 1993 Toxics Release Inventory (TRI), there were 191 facilities reporting releases of 25,000 pounds or more of sulfuric acid to air. The number of these facilities in each of 2-digit standard industrial categories (SIC) is shown in Table 1, as well as the prominent types of industries within the category that have reported sulfuric acid emissions to air. The industries shown in italics include 34 facilities that are in the 80th percentile (over 178,000 pounds per year) for sulfuric acid releases to air. These 34 facilities' air emissions are almost entirely from point sources, suggesting that either sulfuric acid is formed in the stack from sulfur trioxide or sulfuric acid is aerosolized in a process that leads to its release in the stack. Thirty two of these sites reported producing the sulfuric acid; the copper smelters and phosphate fertilizer plants produced sulfuric acid for sale or distribution.

**Table 1. Industrial Categories of Facilities Emitting over 25,000 lbs/yr of Sulfuric Acid Aerosols in 1993**

Category (SIC Code)	No. Sites*	Major Industries**
Paper and Allied Products (26)	185	<i>Pulp, paper and paperboard mills.</i>
Chemicals and Allied Products (28)	53	<i>Phosphate fertilizers; Industrial inorganic chemicals.</i>



Category (SIC Code)	No. Sites*	Major Industries**
Primary metal industries (33)	23	<i>Copper smelting; Blast furnaces and steel mills</i>
Food and Kindred Products (20)	11	<i>Wet corn milling; fats and oils; liquors; malt beverages.</i>
Lumber, Wood Products (24)	8	Sawmills; Reconstituted wood products
Stone, clay, glass, concrete (32)	6	<i>Glass</i>
Petroleum refining (29)	4	<i>Petroleum refining</i>
Metal Products, except machinery (34)	4	Metal coatings
Tobacco Manufacturers (21)	1	Tobacco stemming and redrying

\*A site may list more than one SIC code.

\*\*The industries shown in italics include facilities that are in the 80th percentile for sulfuric acid releases to air.

The industrial breakdown does not necessarily indicate that emissions result from processes unique to the industry. For example, phosphate fertilizer manufacturers, which use sulfuric acid to make phosphoric acid and normal superphosphate, may produce their own sulfuric acid from elemental sulfur and may also use it captively. Sulfuric acid emissions from phosphate fertilizer manufacturing may therefore be primarily from sulfuric acid manufacturing. Similarly, sulfuric acid is a known component in flue gas from fossil fuel combustion and waste incineration. The  $\text{SO}_3/\text{H}_2\text{SO}_4$  ( $\text{SO}_3$ , as stated previously is immediately transformed into sulfuric acid in the presence of water) produced from combustion sources is between 1 and 3% of the  $\text{SO}_x$  emitted by these sources (the rest being  $\text{SO}_2$ ). It is not clear why sulfuric acid is emitted from combustion sources. A possible explanation is that there are substances in the flue gas or on the stack walls that catalyze the oxidation of sulfur dioxide to sulfur trioxide, similar to the heterogeneous reactions that can occur in the atmosphere (17-19). Sulfuric acid is also formed in some flue desulfurization processes (7).

### Section 3.1.1 Pulp and Paper Mills

The kraft pulping process involves the digesting of wood chips at elevated temperature in “white liquor”, an aqueous solution of sodium sulfide and sodium hydroxide, to dissolve the lignin that binds the cellulose fibers of the wood together. The spent liquor used to digest wood chips, called “black liquor”, is combusted in recovery furnaces to recover heat and cooking chemicals. Sulfuric acid is present in flue gas from kraft recovery furnaces and has been cited as being one of the five most prevalent air toxics released from recovery furnaces of the direct contact evaporator (DCE) and non-direct contact evaporator (NDCE) types (21). In a DCE, the flue gas comes in contact with the black liquor, whereas in a NDCE, it does not. Field tests on five Kraft recovery furnaces showed  $\text{SO}_3/\text{H}_2\text{SO}_4$  levels ranging from 0 to 3 ppm in the flue gas, with an average level of 0.81 ppm, or about 10% of that found in fossil fuel plants burning fuel containing 1-3% sulfur (4). In these tests, no correlation was found between  $\text{SO}_2$  and  $\text{SO}_3/\text{H}_2\text{SO}_4$  levels. Therefore, one cannot estimate emission factors for  $\text{SO}_3/\text{H}_2\text{SO}_4$  based on those for  $\text{SO}_2$ . While EPA has compiled emission factors for pollutants from

kraft, acid sulfite, and neutral sulfite semichemical (NSSC) pulping (9), no emissions factors have been presented for SO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub>. However, industry tests of Kraft recovery furnaces have been performed between 1989 and 1993 and the results are presented in Table 2 (20).

**Table 2. Emission Factors from Kraft Recovery Furnaces\***

Mill Code (date built/rebuilt)**: Control device/ Type evaporator	Type	BLS MPPD	H <sub>2</sub> SO <sub>4</sub> Emissions in lb/ton BLS	
			Range	Average
A: WB, Cascade	DCE	3.12	ND to 4.7E-02	1.6E-02
B: ESP	DCE	16.56	ND to 1.5E-02	8.4E-03
RFI (1973): WB ESP, Cascade	DCE	4.60	ND to 2.5E-02	1.4E-02
RFRIG1 (1991):WB ESP, Cyclone	DCE	0.85		ND(2.0E-02)
RFRIG2 (1991): WB ESP, Cyclone	DCE	2.63	ND to 1.9E-02	8.2E-03
<i>SUMMARY</i>	<i>DCE</i>		<i>ND to 1.9E-02</i>	<i>8.4E-03 (Median)</i>
C: DB	NDCE	9.84	0.21 to 0.91 ppm	3.3E-02
D: DB ESP	NDCE	18.60	0.17 to 2.98 ppm	7.1E-02
E: ESP	NDCE	12.00	0.49 to 1.71 ppm	5.1E-02
RFO (1986): DB ESP	NDCE	1.90		ND(1.3E-02)
<i>SUMMARY</i>	<i>NDCE</i>		<i>ND to 1.6E-01</i>	<i>4.2E-02 (Median)</i>

\* Abbreviations: BLS = black liquor solids; ND = not detected; DCE = direct contact evaporator; NDCE = non-direct contact evaporator; ESP = electrostatic precipitator; WB = wet bottom; DB = dry bottom; MPPD = million pounds per day. Type evaporator given for DCE types only.

\*\*Mills with codes not preceded by "RF" are from a 1980 study (4). Dates when these mills were built or rebuilt are not available.

The median sulfuric acid emissions from the direct contact (DCE) and non-direct contact (NDCE) evaporator recovery furnaces, 8.4E-03 pounds per ton black liquor solids (BLS) and 4.2E-02 pounds per ton BLS, respectively, can be used to estimate sulfuric acid emissions. For example, if a kraft mill using 1100 air dry tons of unbleached pulp per day (ADTUBPD) generates 3300 pounds BLS per ADTUBPD operates two DCE furnaces 365 days per year, the pounds of H<sub>2</sub>SO<sub>4</sub>, H, emitted during the year will be:

$$H = 1100 \text{ ADTUBPD} \times 365 \text{ days/year} \times (3300 \text{ lbs. BLS/ADTUBPD} \times \text{ton BLS}/2000 \text{ lbs BLS} \times 8.4 \times 10^{-3} \text{ lbs. H}_2\text{SO}_4/\text{ton BLS}) = 5,565 \text{ lbs. of H}_2\text{SO}_4$$

The pounds of sulfuric acid aerosols produced in recovery furnaces on site should be combined with that produced from fuel oil and coal combustion. Should the total equal or exceed 25,000 pounds per year, reporting would be required under EPCRA Section 313. It should be noted that sulfuric acid used at the site for such purposes as ClO<sub>2</sub> generation, pH control, and ion exchange generation no longer must be reported since aerosol forms of H<sub>2</sub>SO<sub>4</sub> are not involved.

### Section 3.1.2 Acid Aerosols from Sulfuric Acid Manufacture

Sulfuric acid may be manufactured commercially by either the lead chamber process or the contact process. However, sulfuric acid is usually produced by the contact process (1, 2, 10, 22). In the contact process, sulfur is oxidized to  $\text{SO}_2$ , which is subsequently fed into a converter where it is catalytically oxidized to  $\text{SO}_3$ . Finally, the sulfur trioxide is absorbed in a strong sulfuric acid solution or oleum. Sulfuric acid plants are further classified by feedstock: elemental sulfur burning, spent sulfuric acid and hydrogen sulfide burning, and metal sulfide ores and smelter gas burning. Contact sulfuric acid plants vary in design depending on the raw material used to produce  $\text{SO}_2$ . Oleum is also produced in contact plants, where  $\text{SO}_3$ -containing gases are passed through a special oleum tower. Regeneration of spent sulfuric acid is another form of sulfuric acid manufacture, often performed in order to comply with antipollution regulations (1).

#### Sulfuric Acid Manufacture

The amount of sulfuric acid aerosols produced in sulfuric acid manufacture is a function of the type of sulfur feedstock, the concentration of the absorbing acid, and the conditions in the absorber (1, 2, 22). Elemental sulfur produces little acid mist when burned because there is little water present. However the hydrocarbons in other feedstock (such as spent acid) produce water vapor during combustion. The affect of acid strength on mist production is illustrated by results showing 0.5 to 5.0 kilograms (kg) of uncontrolled acid aerosol emissions per Megagram (Mg) of acid produced (1.0 to 10.0 pounds (lb) of acid emissions per ton of acid produced) from oleum plants burning spent acid compared with 0.2 to 2.0 kg/Mg (0.4 to 4.0 lb/ton) of emissions from 98% sulfuric acid plants burning elemental sulfur. In addition, the aerosol particle size from oleum plants is finer than that from the 98% sulfuric acid plants. The operating temperature of the absorption tower affects  $\text{SO}_3$  absorption and, accordingly, acid mist formed in the exit gas.

In an elemental sulfur burning plant, after the sulfur is burned to  $\text{SO}_2$  and catalytically converted to  $\text{SO}_3$ , the gas enters one or multiple absorption towers (packed columns), usually operated in countercurrent, in which the sulfur trioxide is absorbed in sulfuric acid of 98-99% concentration to form more sulfuric acid (1, 2, 22). The optimal operating temperature of the absorption tower depends on the strength of the acid produced, throughput rate, inlet sulfur trioxide concentrations and other factors peculiar to a particular plant. The optimal concentration of the absorbing acid is the azeotrope (see Appendix 1), 98.3%, where the combined vapor pressures of  $\text{H}_2\text{SO}_4$ ,  $\text{SO}_3$ , and water are at a minimum. At lower concentrations, the water vapor partial pressure is higher and there is a greater risk of sulfuric acid mist formation. At higher concentrations the tail gas will contain increased amounts of  $\text{H}_2\text{SO}_4$  and  $\text{SO}_3$  because of their higher partial pressures. Both sulfuric acid mist formed within the system and gaseous sulfuric acid vaporized from the concentrated acid in the absorption towers and carried along with the predominant sulfur trioxide gas, constitute sulfuric acid aerosols that are being manufactured and therefore contributing to the manufacturing threshold of sulfuric acid aerosols for reporting under section 313 of EPCRA. Sulfuric acid mists entrained in tail

gas are separated by special filters and determined by measurement of the acid content.

### Regeneration of Spent Sulfuric Acid

The regeneration of spent sulfuric acid normally comprises two major steps, concentration to the highest feasible level and decomposition of the spent acid (1). Water is essentially the only substance evaporated (other than volatile organic impurities) in concentrating the acid to <75% H<sub>2</sub>SO<sub>4</sub>. Vapors evolved during the concentration of spent sulfuric acid to a more highly concentrated state (93-98% H<sub>2</sub>SO<sub>4</sub>) contain significant quantities of gaseous sulfuric acid (1). The formation of this gaseous sulfuric acid contributes to the manufacturing threshold of sulfuric acid aerosols for reporting under section 313 of EPCRA. Spent sulfuric acid may be concentrated in either vacuum or drum concentrators. While vacuum concentrators yield negligible emissions, those from drum concentrators contain acid mist. Exit gas is passed through scrubbers before being vented to the atmosphere. Emissions from acid drum concentrators operating at 55, 73, and 100% of capacity are reported to be 7034, 2401, and 2334 metric ton/day (12).

### Acid Aerosol Emissions

Nearly all the sulfuric acid aerosols emitted from sulfuric acid manufacturing plants come from the absorber exit gases. The exit gas contains small amounts of SO<sub>2</sub>, even smaller amounts of SO<sub>3</sub>, and sulfuric acid vapor and mist. Even with efficient gas drying, mist formation is impossible to eliminate completely. Once formed, these aerosols are of such a fine particle size and so stable that only a small amount can be removed in the absorber. Sulfuric acid is normally combined with SO<sub>3</sub> in determining an emission factor because SO<sub>3</sub> reacts so rapidly with water vapor. The emission factor for SO<sub>3</sub> is calculated as 100% H<sub>2</sub>SO<sub>4</sub> and added to the H<sub>2</sub>SO<sub>4</sub> value.

Sulfuric acid mists are always formed when sulfur trioxide combines with water vapor at temperatures below the dew point of sulfur trioxide. The dew point is a function of gas composition and pressure and is generally around 140-170°C. Equations are available that predict the dewpoint for different concentrations of H<sub>2</sub>O and H<sub>2</sub>SO<sub>4</sub> (4). Examples are given in Section 3.1.5 in Tables 6 and 8 for coal and fuel oil combustion.

### Use of Sulfuric Acid Emission Monitoring Data

Some sulfuric acid manufacturing facilities may have sulfuric acid emission monitoring data available that can be used to estimate emissions for sulfuric acid mist under the Clean Air Act New Source Performance Standards (NSPS). Sulfuric acid plants constructed or modified after August 17, 1971, are subject to a sulfuric acid mist emissions limit of 0.15 pounds of sulfuric acid per ton of 100% sulfuric acid produced (see Part 60 Subpart H of Title 40 of the Code of Federal Regulations). If such information is available, it is preferable to use such data for estimating uncontrolled emissions of sulfuric acid, rather than published emission factors since monitoring data should be the best available data. If the measured data available is for controlled emissions, then the amount of sulfuric acid generated prior to emission controls should be calculated based on the average actual

control efficiency for the acid mist.

$$\text{Uncontrolled H}_2\text{SO}_4 \text{ emissions} = \text{actual emissions to air}/(1-\text{efficiency})$$

(Efficiency expressed as a fraction)

Emission factors for sulfuric acid plants have been compiled by EPA (10). Uncontrolled emission factors for various sulfuric acid plants are shown in Table 3. Table 4 contains emission factors for plants using three of the most commonly used fiber mist eliminator control devices, vertical tube, vertical panel, and horizontal duel pad types.

**Table 3. Uncontrolled Emission Factors for Sulfuric Acid Plants**

Raw material	Oleum* produced % Total output	Emissions of H <sub>2</sub> SO <sub>4</sub> aerosol per unit product	
		kg/Mg	lb/ton
Recovered sulfur	0-43	0.174-0.4	0.348-0.8
Bright virgin sulfur	0	0.85	1.7
Dark virgin sulfur	0-100	0.16-3.14	0.32-6.28
Spent acid	0-77	1.1-1.2	2.2-2.4

\*Sulfuric acid containing dissolved sulfur trioxide. Also known as fuming sulfuric acid or disulfuric acid.

**Table 4. Controlled Emission Factors for Sulfuric Acid Plants**

Raw material	Oleum* produced % Total output	Emissions of H <sub>2</sub> SO <sub>4</sub> aerosol per unit product	
		kg/Mg	lb/ton
Elemental sulfur	---	0.064	0.128
Dark virgin sulfur	0-13	0.26-1.8	0.52-3.6
Spent acid	0-56	0.014-0.20	0.28-0.40

\*Sulfuric acid containing dissolved sulfur trioxide. Also known as fuming sulfuric acid or disulfuric acid.

### Section 3.1.3. Smelters

Sulfuric acid is a byproduct of metals production, notably copper, and is accordingly sometimes referred to as smelter acid. Smelters produce sulfuric acid by the contact process with the raw material being classified as ‘metal sulfide ores and smelter gas burning’ (see Section 3.1.2). The smelter gas (SO<sub>2</sub> from the smelter furnace) is passed through cyclone dust collectors, electrostatic dust and mist precipitators, and scrubbing and gas cooling towers to remove dust, acid, mist and other impurities. The gas is then converted to SO<sub>3</sub> and then H<sub>2</sub>SO<sub>4</sub> in processes similar to those used in sulfuric acid plants using elemental sulfur as a raw material (Section 3.1.2). Therefore, the potential for sulfuric acid aerosols formation is similar to the described above in the third paragraph of Section 3.1.2.

### **Section 3.1.4. Petroleum Refining**

Crude oil contains a small amount of sulfur as an impurity. As a result, sulfur oxides are emitted from petroleum refineries. EPA has compiled emission factors of sulfur oxides,  $\text{SO}_x$ , for petroleum refining, but factors for sulfuric acid are not provided (11). However, according to information provided by the American Petroleum Institute (API), the staff in API's Health and Environmental Sciences Department uses the following EPA reference for sulfuric acid emission factors: EPA. 1995. *Compilation of Air Pollutant Emission Factors*. Vol. 1: Stationary Point and Area Sources. Section 8.10, AP-42, 5th ed. (January 1995). Research Triangle Park, NC: U.S. EPA, OAQPS.

### **Section 3.1.5. Sulfuric Acid Aerosol Formation In Stacks From Combustion Processes**

Sulfuric acid aerosols are often formed in flue gas in a stack during combustion of fuel oil, coal, or other sulfur-containing fuels. Both water and sulfur trioxide are combustion products and they have great affinity for each other; as discussed they react quickly to form sulfuric acid. When flue gas is cooled to temperatures at or below the dew point, a sulfuric acid mist will form from any sulfuric acid gas present (16). The dew point is the temperature at which the air becomes saturated and produces dew; sulfuric acid mists are always formed when sulfur trioxide combines with water vapor at temperatures below the dew point of sulfur trioxide. Because of the enormous attraction between sulfur trioxide and water "only a very small amount of sulfur trioxide in combustion gas is required to draw water from the gas and form a fairly concentrated acid" (16). In fact, flue gas containing 1% sulfuric acid has the corrosive properties of 85% sulfuric acid solution. All sulfuric acid produced within the stack, including the gas not just the mist, falls under the EPCRA section 313 definition of a sulfuric acid aerosol. The information on dew points can be used to determine if any of the sulfuric acid present as gas will form a mist that could potentially condense inside the stack.

Tables 5 and 7 below contain expected sulfur trioxide levels in flue gas resulting from the combustion of fuel oil and coal, respectively, as a function of the sulfur content of the fuel and the percent of excess air available (16). If water is present in the stack, Tables 5 and 7 can be used to estimate the amount of sulfuric acid gas that can be formed. Tables 6 and 8 contain empirically-derived dew points of  $\text{SO}_3$  for different concentrations of  $\text{SO}_3$  in stack gas of oil- and coal-fired units, respectively. These tables can be used to determine whether the stack temperature is below the dew point of  $\text{SO}_3$  and sulfuric acid mists are being formed in the stack in flue gas. Examples of how to use these tables to determine the dew point of  $\text{SO}_3$  are given below.

Assume a typical oil-fired unit is burning fuel oil containing 2% sulfur and that 17% excess air is present. From Table 5, we see that 15 ppm of  $\text{SO}_3$  will be present in the flue gas and available to form sulfuric acid gas. From Table 6, we find that the dew point of  $\text{SO}_3$  should be  $139^\circ\text{C}$ . Therefore, if the temperature in the stack is at or below  $139^\circ\text{C}$ , sulfuric acid mists will very likely form in the stack.

As an example dealing with coal combustion, assume a typical unit is burning coal containing 3% sulfur in the presence of 25% excess air. From Table 7, we see that between 20 and 40 ppm of SO<sub>3</sub> will be present in the flue gas and available to form sulfuric acid gas. From Table 8, we find that the dew point should be between 136°C and 143°C. Therefore, if the temperature in the stack is at or below 136°C to 143°C, sulfuric acid mists will very likely form in the stack.

**Table 5. SO<sub>3</sub> Production in Oil Fired Units**

Excess air (%)	SO <sub>3</sub> Concentration in Flue Gas (ppm)					
Sulfur in fuel (%)	0.5	1.0	2.0	3.0	4.0	5.0
5	2	3	3	4	5	6
11	6	7	8	10	12	14
17	10	13	15	19	22	25
25	12	15	18	22	26	30

**Table 6. Dew Point of SO<sub>3</sub> in Stacks of Oil Fired Units\***

SO <sub>3</sub> in gas (ppm)	5	10	15	20	25	30	35	40	45	50	55	60	65	70
Dew point (°C)	130	135	139	141	143	145	147	148	149	150	151	152	153	154

\*Using typical value of 10% water in oil

**Table 7. SO<sub>3</sub> Production in Coal Fired Units**

Excess air (%)	SO <sub>3</sub> Concentration in Flue Gas (ppm)					
Sulfur in fuel (%)	0.5	1.0	2.0	3.0	4.0	5.0
25	3 - 7	7 - 14	14 - 28	20 - 40	27 - 54	33 - 66

**Table 8. Dew Point of SO<sub>3</sub> in Stacks of Coal Fired Units\***

SO <sub>3</sub> in gas (ppm)	5	10	15	20	25	30	35	40	45	50	55	60	65	70
Dew point (°C)	125	130	134	136	138	140	142	143	144	145	146	147	148	149

\*Using typical value of 6% water in coal

Steel stacks are generally designed and operated so that a temperature between 135°C (275°F) and 149°C (300°F) is maintained throughout the stack (16). These stack temperatures are such that they may be below the dew point for SO<sub>3</sub> in the flue gas, leading to the formation of sulfuric acid mists in the stacks.

### Section 3.1.6. Coal Combustion

Sulfuric acid aerosols are produced as a byproduct from boilers during coal combustion. U.S. coals contain from 0.2% to 7% sulfur by weight (13). On average, about 95% of sulfur present in bituminous coal will be emitted as gaseous sulfur oxides ( $\text{SO}_x$ ) when burned, whereas somewhat less will be emitted when subbituminous coal is burned (15). In general, boiler size, firing configuration, and boiler operations have little effect on the percent conversion of sulfur in fuel to sulfur oxides. About 0.7% of fuel sulfur is emitted as  $\text{SO}_3/\text{H}_2\text{SO}_4$  (15). This information can be expressed as an uncontrolled emission factor (EF) of  $0.43 \times S$  pounds  $\text{H}_2\text{SO}_4$  per ton of coal burned, where S is the weight percent sulfur in coal. The uncontrolled emission factor also represents the amount of sulfuric acid *produced* in the stack, as well as that released to the atmosphere in the absence of scrubbers or other emission control devices. The emission factor for sulfur oxides ( $\text{SO}_x$ ) for bituminous coal combustion *should not be used* to estimate sulfuric acid emissions since the factor includes sulfur dioxide. If C is the tons of coal burned, the pounds of  $\text{H}_2\text{SO}_4$  generated (H), would be:

$$H = 0.43 \times S \times C$$

For example, if 9,000 tons of coal were burned and the coal contained 3% sulfur, then:

$$H = 0.43 \times 3 \times 9,000 = 11,610 \text{ pounds of } \text{H}_2\text{SO}_4$$

Note that the values for the variables C and S have been chosen as an illustration. Values must be chosen that are appropriate for the particular operations at each facility.

### Section 3.1.7. Fuel Oil Combustion

Sulfuric acid aerosols are produced during fuel oil combustion from the oxidation of sulfur contained in the fuel. There are various types of fuel oil combustion operations; the type of operation depends on the type of fuel oil burned. There are mainly five types of fuel oil used for commercial, industrial, and residential use in the U.S. The No. 1 and No. 2 fuel oils are known as distillate oils. They have high volatility, low viscosity, and <0.3% sulfur by weight. They are primarily used in domestic and small commercial operations. The No. 5 (also called low sulfur No. 6) and No. 6 fuel oils are known as residual oils. They have low volatility, high viscosity, and high sulfur content. They are mainly used in industrial operations. The No. 4 fuel oil is a mixture of distillate and residual oils and can be used for both types of operations. Typical sulfur contents of fuel oil are (13):

Fuel Oil Grade	Sulfur Content (wt %)
No. 1	0.09
No. 2	0.22
No. 4	1.35
No. 5	0.84
No. 6	3.97



Uncontrolled SO<sub>x</sub> emissions are almost entirely dependent on the sulfur content of the fuel and are not affected by boiler size and design or the grade of fuel being burned. On the average, over 95% of the sulfur in fuel oil is converted to SO<sub>2</sub> on combustion; about 1 to 5 percent is further oxidized to sulfur trioxide where it readily reacts with water vapor in flue gas to form sulfuric acid aerosols. The emission factor (EF) for uncontrolled fuel oil combustion from industrial boilers is 0.002 x S pounds SO<sub>3</sub> per gallon of fuel oil burned (14) or 0.00245 x S pounds H<sub>2</sub>SO<sub>4</sub> per gallon of fuel oil burned, where S is the weight percent sulfur in the fuel oil. The uncontrolled emission factor also represents the amount of sulfuric acid *produced* in the stack, as well as that released to the atmosphere in the absence of scrubbers or other emission control devices. An example of the use of the emission factor (EF) to calculate the pounds of sulfuric acid generated is shown below. If F is the number of gallons of fuel oil burned, the pounds of H<sub>2</sub>SO<sub>4</sub> generated (H), would be:

$$H = 0.00245 \times S \times F$$

For example, if 4,500,000 gallons of fuel oil were burned and the fuel oil contained 3.97% sulfur, then:

$$H = 0.00245 \times 3.97 \times 4,500,000 = 43,769 \text{ pounds of H}_2\text{SO}_4$$

Note that the values for the variables F and S have been chosen as an illustration. Values must be chosen that are appropriate for the particular operations at each facility.

#### **Section. 4.0. Measurement Methods**

For source sampling, EPA has specified extractive sampling trains and analytical procedures for SO<sub>3</sub> and sulfuric acid aerosols (7, 8). Separation of particles containing Na<sub>2</sub>SO<sub>4</sub> may present problems in cases such as Kraft paper mills (4). If sodium sulfate is present, analytical results for sulfuric acid would be high.

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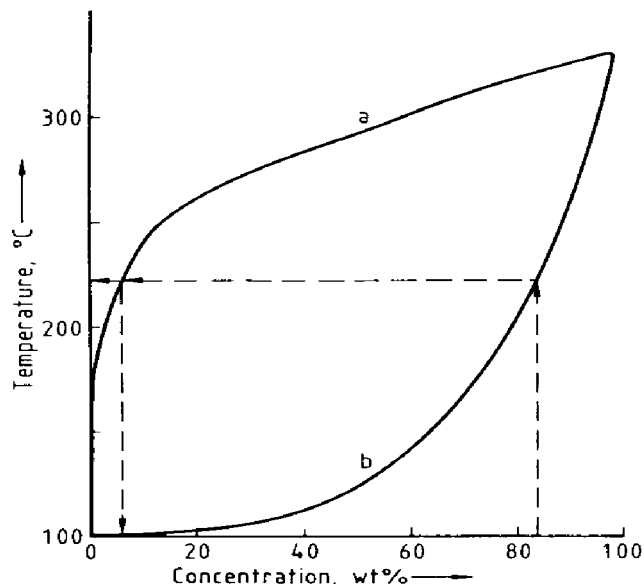
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## APPENDIX 1



**Figure 1a.** Boiling curves for sulfuric acid at 1013 mbar a) Vapor; b) Liquid (reference 1).

Information in the above figure shows that if the vapor above a solution of 85% sulfuric acid, boiling at 223 °C, were to be completely condensed it would contain approximately 7 percent H<sub>2</sub>SO<sub>4</sub>. At concentrations below approximately 75% H<sub>2</sub>SO<sub>4</sub>, the vapor that evaporates from the solution is essentially water.

**Table 1a. Sulfuric Acid Partial Pressure and Total Vapor Pressure (bar) over Aqueous Sulfuric Acid\***

°F	Weight Percent Sulfuric Acid					
	20.0	40.0	60.0	80.0	98.0	100.0
32	.843E-20 (.534E-02)	.344E-17 (.326E-02)	.438E-14 (.836E-03)	.161E-10 (.197E-04)	.187E-08 (.117E-07)	.228E-08 (.323E-08)
68	.769E-18 (.205E-01)	.193E-15 (.130E-01)	.149E-12 (.367E-02)	.305E-09 (.115E-03)	.224E-07 (.121E-06)	.273E-07 (.435E-07)
104	.389E-16 (.649E-01)	.649E-14 (.427E-01)	.317E-11 (.131E-01)	.379E-08 (.531E-03)	.191E-06 (.914E-06)	.230E-06 (.425E-06)
140	.121E-14 (.175)	.144E-12 (.119)	.462E-10 (.395E-01)	.334E-07 (.204E-02)	.122E-05 (.538E-05)	.147E-05 (.319E-05)
176	.254E-13 (.417)	.225E-11 (.290)	.492E-09 (.104)	.222E-06 (.668E-02)	.622E-05 (.257E-04)	.743E-05 (.193E-04)
212	.381E-12 (.891)	.264E-10 (.634)	.402E-08 (.244)	.117E-05 (.192E-01)	.261E-04 (.103E-03)	.310E-04 (.966E-04)
302	.106E-09 (4.132)	.460E-08 (3.090)	.316E-06 (1.392)	.343E-04 (.170)	.493E-03 (.180E-02)	.574E-03 (.287E-02)
392	.883E-08 (13.107)	.278E-06 (10.245)	.975E-05 (5.312)	.457E-03 (.913)	.470E-02 (.166E-01)	.538E-02 (.427E-01)
482	.312E-06 (31.939)	.793E-05 (26.056)	.156E-03 (15.351)	.358E-02 (3.439)	.278E-01 (.985E-01)	.314E-01 (.389)
572	.591E-05 (64.407)	.130E-03 (54.869)	.156E-02 (36.361)	.266E-01 (9.916)	.117E-00 (.425)	.130E-00 (.2476)

\* Total pressure is in parentheses. Conversion Factors: 1 bar = 0.98677 atmospheres = 14.7 psia = 760 mm Hg = 0.1 MPa

The above table contains the partial pressure of sulfuric acid and total vapor pressure of the solution (in parentheses) over aqueous sulfuric acid solutions in the concentration range of 20 to 100 weight percent sulfuric acid (1). From Table 1a we see that the partial pressure of sulfuric acid above a sulfuric acid solution is very low compared to the total vapor pressure for sulfuric acid solutions below 80% sulfuric acid; the bulk of the vapor being composed of water. Consequently when a solution of sulfuric acid boils, more water than sulfuric acid is volatilized, so that the concentration of the remaining acid increases and the boiling point of the solution rises. This process continues until the acid concentration reaches 98.3 weight %  $H_2SO_4$ , when an azeotrope (a mixture of two liquids that boils at constant composition; i.e., the composition of the vapor is the same as that of the liquid) is formed and the concentration of sulfuric acid in the vapor is the same as that of the solution. The vapor above sulfuric acid solutions containing more than 98.3 weight %  $H_2SO_4$  also includes considerable amounts of  $SO_3$ , thus the difference between the partial pressure and total pressure of 100% sulfuric acid is the partial pressure of sulfur trioxide. Since the partial pressure of concentrated sulfuric acid is very low, little sulfuric acid is expected to volatilize from sulfuric acid solutions such as may be present in storage tanks. No experimental data are available on sulfuric acid aerosol emissions from storage tanks.

Above  $340^\circ C$ ,  $H_2SO_4$  decomposes into sulfur trioxide and water. The vapor-phase reaction of sulfur trioxide and water results in aerosols of sulfuric acid. The  $H_2SO_4/H_2O/SO_3$  system is important in the production of sulfuric acid by the contact process as well as in the prevention of corrosion from condensing sulfuric acid in stack emissions from the combustion of sulfur-containing fuels. Sulfuric acid containing dissolved sulfur trioxide is known as oleum, fuming sulfuric acid or disulfuric acid. The vapor pressure of sulfuric acid over oleum containing 10% to 30% of free  $SO_3$  by weight is shown in Table 2a (2). Since the vapor pressure of sulfur trioxide over oleum is high, sulfuric acid aerosols also form when oleum is exposed to air containing moisture.

**Table 2a. Sulfuric Acid Partial Pressure (bar) over Oleum\***

°C	Free $SO_3$ in oleum, %		
	10	20	30
20	.227 E-08	.120 E-08	.40 E-09
40	.1467 E-07	.667 E-08	.267 E-08
60	.7333 E-07	.400 E-07	.1333 E-07
80	.3066 E-06	.1600 E-06	.600 E-07
100	.1067 E-05	.5333 E-06	.2133 E-06

Conversion Factors: 1 bar = 0.98677 atmospheres = 14.7 psia = 760 mm Hg = 0.1 Mpa;  
 $^\circ F = 1.8 (^\circ C) + 32$ .