TOXICS RELEASE INVENTORY
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 the annual quantity of such chemicals entering each environmental medium. Such facilities must also report pollution prevention and recycling data for such chemicals, pursuant to section 6607 of the Pollution Prevention Act, 42 U.S.C. 13106. EPCRA section 313 is also known as the Toxics Release Inventory (TRI).

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DISCLAIMER

This guidance document is intended to assist industry with EPCRA section 313 reporting for sulfuric acid (acid aerosols including mists, vapors, gas, fog, and other airborne forms of any particle size). In addition to providing an overview of aspects of the statutory and regulatory requirements of the EPCRA section 313 program, this document also provides recommendations and emissions factors to assist industry with EPCRA reporting. These recommendations do not supersede any statutory or regulatory requirements, are subject to change, and are not independently binding on either EPA or covered facilities. Additionally, if a conflict exists between guidance on this site and the statutory or regulatory requirements, the conflict must be resolved in favor of the statute or regulation.

Although EPA encourages industry to consider these recommendations and emissions factors, in reviewing this document, industry should be aware that these recommendations and emissions factors were developed to address common circumstances at typical facilities. The circumstances at a specific facility may significantly differ from those contemplated in the development of this document. Thus, individual facilities may find that the recommendations and emissions factors provided in this document are inapplicable to their processes or circumstances, and that alternative approaches or information are more accurate and/or more appropriate for meeting the statutory and regulatory requirements of EPCRA section 313. To that end, industry should use facility specific information and process knowledge, where available, to meet the requirements of EPCRA section 313. EPCRA section 313 also provides that, in the absence of such readily available data, a reporting facility may make reasonable estimates to meet those EPCRA section 313 requirements. Facilities are encouraged to contact the Agency with any additional or clarifying questions about the recommendations and emissions factors in this document, or if the facility believes that EPA has incorrectly characterized a particular process or recommendation.

Additional guidance documents, including industry specific and chemical specific guidance documents, are also available on TRI's GuideME website:
https://ofmpub.epa.gov/apex/guideme_ext/f?p=guideme:gd-list

SECTION 1.0 INTRODUCTION

This document contains guidance information specific to reporting sulfuric acid to the Toxics Release Inventory (TRI). For background on the TRI program, resources for determining whether a facility must report, and reporting requirements, please refer to the current TRI Reporting Forms and Instructions, also available on GuideME.

On June 30, 1995 (60 FR 34182), EPA modified the listing for sulfuric acid (Chemical Abstracts Service Registry Number 7664-93-9) (H_2SO_4) 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) (1). 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 reporting year 1994, 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 may be included in threshold and release determinations under EPCRA section 313. This document is not meant to be exhaustive, but rather provides 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 Thresholds

Thresholds are specified amounts of toxic chemicals manufactured, processed, or otherwise used during the calendar year that trigger reporting requirements. Reporting for sulfuric acid is required if any of 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 1.2 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 Section 2.1, Section 2.2, and Section 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 Closed Loop Acid Reuse Systems

When solutions of sulfuric acid are aerosolized the "manufacture" of a listed chemical (sulfuric acid aerosols) has occurred. 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. Closed loop 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 closed loop 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 closed loop acid reuse systems.

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 2,000 pounds of acid and 500 pounds is added during the year then the total amount applied towards acid aerosol thresholds would be 2,500 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 closed loop acid reuse systems and the reporting of sulfuric acid aerosols and hydrochloric acid aerosols under EPCRA section 313. This guidance does not apply to any other types of processes or to any other listed chemical.

Section 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. The quantity of all sulfuric acid aerosols manufactured must be counted towards the "manufacture" threshold regardless of whether it is subsequently treated for destruction.

Section 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 drawn down and refilled several times during the year, then the calculations should be based on the cumulative amount of acid stored in the tank. For example, if a 10,000 pound capacity tank is drawn down and refilled six 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 conditions for one 10,000 pound tank of acid, should be multiplied by 6. (See Appendix A and the next section for more information.)

SECTION 3.0 SULFURIC ACID AND ITS FORMATION IN AIR

Sulfuric acid is miscible in water in all proportions and has a strong attraction for water. The anhydrous chemical boils at 279.6°C (2). Commercial sulfuric acid normally contains 93 to 98% sulfuric acid with the remainder being water. A boiling point-composition diagram (Figure A-1, Appendix A) for aqueous sulfuric acid, indicates that below 75% H_2SO_4, the vapor evaporating from a solution of the acid is essentially water. This fact is illustrated in Table A-1 of Appendix A which contains the partial pressure of sulfuric acid and total vapor pressure of the solution over aqueous sulfuric acid solutions at various concentrations and temperatures (2). 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 A 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 (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 SO_3 by weight is shown in Table A-2 of Appendix A (3). 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 (SO_2) and the reaction of the resulting sulfur trioxide (SO_3) with water.

Equation 1

$$SO_2 + \tfrac{1}{2} O_2 \rightarrow SO_3$$

Equation 2

$$SO_3 + H_2O \leftrightarrow H_2SO_4$$
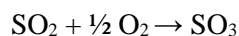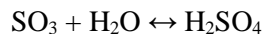
While SO_2 has a strong tendency to react with oxygen to form SO_3, the reaction rate is very slow in the gas phase under normal tropospheric (lower atmosphere) conditions (4 - 7). Therefore, a reaction chamber is typically required to generate the SO_3 needed for sulfuric acid production. The reaction of SO_3 and H_2O to form H_2SO_4 is reversible and the extent of conversion or the equilibrium between reactants and products is dependent on the concentration of H_2O and temperature. In any combustion processes, moisture in the stack would be expected to convert any SO_3 present into sulfuric acid aerosols and sulfuric acid aerosols would also be expected to undergo dissociation forming SO_3 and H_2O depending on percent moisture content and temperature (8). If there is no moisture present within a stack where SO_3 is produced, sulfuric acid aerosols would not be manufactured. Releases of SO_3 may be converted to H_2SO_4 in the environment; however, facilities are not responsible for chemicals that manufacture in the environment. Therefore, if SO_3 is released from the facility and H_2SO_4 is manufactured in the environment from the released SO_3, the facility is not required to include these amounts in EPCRA 313 threshold calculations for sulfuric acid aerosols.

Section 3.1 Industrial Sources of Sulfuric Acid Aerosols

There are certain types of facilities that will likely need to report sulfuric acid aerosols. This section provides information on these types of facilities.

For example, facilities that release over 25,000 pounds of sulfuric acid to air are required to report since they exceed the reporting threshold for sulfuric acid manufacture. Additional facilities may need to report even though they have no air releases of sulfuric acid. For example, the facility needs to consider the amounts of sulfuric acid aerosols that were manufactured in the stack and subsequently removed by

scrubbers or produced internally during sulfuric acid manufacturing, processing, or otherwise use and that were removed by scrubbers prior to the stack. In addition, some facilities may be using sulfuric acid aerosols in excess of the 10,000 pound threshold that triggers the reporting requirement.

According to the 2016 Toxics Release Inventory (TRI), there were 706 facilities that reported sulfuric acid. The number of these facilities by industry is shown in Table 3-1. 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 (9). The SO_3/H_2SO_4 (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 SO_x emitted by these sources (the rest being SO_2 (10)). 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 (5 - 7). Sulfuric acid is also formed in some flue desulfurization processes (11).

Table 3-1: Count of Facilities Reporting Sulfuric Acid and Total Air Releases by Industry for Reporting Year 2016

NAICS Industry Code	Industry Description	Count of Facilities	Total Air Releases
2121	Coal Mining	4	485,401
2122	Metal Mining	17	1,395,096
2211	Electric Utilities	251	59,558,781
311	Food	19	849,189
3121	Beverages	1	4,102
3122	Tobacco	1	—
321	Wood Products	1	35,000
322	Paper	40	3,106,285
324	Petroleum	73	5,519,906
325	Chemicals	116	4,453,419
326	Plastics And Rubber	1	35
327	Nonmetallic Mineral Product	18	976,856
331	Primary Metals	45	2,453,978
332	Fabricated Metals	38	78,758
333	Machinery	4	27
334	Computers And Electronic Products	42	39,791
335	Electrical Equipment	3	635
336	Transportation Equipment	2	3,935
4246	Chemical Wholesalers	5	313

NAICS Industry Code	Industry Description	Count of Facilities	Total Air Releases
4247	Petroleum Bulk Terminals	7	313,130
562	Hazardous Waste	5	6,196
	Other	13	538,088
	Total	**706**	**79,818,920**

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 direct contact evaporator (DCE) and non-direct contact evaporator (NDCE) recovery furnaces (12). 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 SO_3/H_2SO_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 (13). In these tests, no correlation was found between SO_2 and SO_3/H_2SO_4 levels. Therefore, one cannot estimate emissions factors for SO_3/H_2SO_4 based on those for SO_2. While EPA has compiled emissions factors for pollutants from kraft, acid sulfite, and neutral sulfite semichemical (NSSC) pulping (14), no emissions factors have been presented for SO_3/H_2SO_4. However, industry tests of kraft recovery furnaces were performed between 1989 and 1993 and the results are presented in Table 3-2 (15).

Table 3-2: **Emissions Factors from Kraft Recovery Furnaces**

Mill Code (date built/rebuilt)[*]: Control device / Type evaporator	Type	BLS MPPD	H₂SO₄ 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
SUMMARY	*DCE*		*ND to 1.9E-02*	*8.4E-03 (Median)*
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)
SUMMARY	*NDCE*		*ND to 1.6E-01*	*4.2E-02 (Median)*

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

1,100 air dry tons of unbleached pulp per day (ADTUBPD) generates 3,300 pounds BLS per ADTUBPD and operates two DCE furnaces 365 days per year, the pounds of H_2SO_4, denoted as H below, emitted during the year will be:

H = 1100 ADTUBPD $\times$ 365 days/year $\times$ (3300 lb BLS/ADTUBPD $\times$ ton BLS/2000 lb BLS) $\times$ 8.4E-03 lb H_2SO_4/ton BLS = 5,565 lb of H_2SO_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_2 generation, pH control, and ion exchange generation no longer must be reported since aerosol forms of H_2SO_4 are not involved.

3.1.2 Acid Aerosols from Sulfuric Acid Manufacture

Either the lead chamber process or the contact process may be used to manufacture sulfuric acid commercially; however, the contact process is usually used (2, 3, 16, 17). In the contact process, sulfur is oxidized to SO_2, which is subsequently fed into a converter where it is catalytically oxidized to 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 SO_2. Oleum is also produced in contact plants, where 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 (2).

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 (2, 3, 17). 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 effect of acid strength on mist production is illustrated by comparing oleum plants to sulfuric acid plants. In oleum plants burning spent acid, there are 0.5 to 5.0 kilograms (kg) of uncontrolled acid aerosol emissions per Megagram (Mg) of acid produced (1.0 to 10.0 lb of acid emissions per ton of acid produced). This compares to 0.2 to 2.0 kg/Mg (0.4 to 4.0 lb/ton) of emissions from 98% sulfuric acid plants burning elemental sulfur (10). 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 SO_3 absorption and, accordingly, acid mist formed in the exit gas.

In an elemental sulfur burning plant, after the sulfur is burned to SO_2 and catalytically converted to 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 (2, 3, 17). 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 specific to a particular plant. The optimal concentration of the absorbing acid is the azeotrope (see Appendix A), 98.3%, where the combined vapor pressures of H_2SO_4, 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 H_2SO_4 and 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 (2). Water is essentially the only substance evaporated (other than volatile organic impurities) in concentrating the acid to >75% H_2SO_4. Vapors evolved during the concentration of spent sulfuric acid to a more highly concentrated state (93-98% H_2SO_4) contain significant quantities of gaseous sulfuric acid (2). 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 (18).

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_2, even smaller amounts of SO_3, 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_3 in determining an emissions factor because SO_3 reacts so rapidly with water vapor. The emissions factor for SO_3 is calculated as 100% H_2SO_4 and added to the H_2SO_4 value (10).

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 dew point for different concentrations of H_2O and H_2SO_4 (13). Examples are given in Section 3.1.5 in Table 3-6 and Table 3-7 for fuel oil and coal 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 emissions factors since monitoring data are usually the best available data. If the measured data available are 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.

Equation 3

Uncontrolled H_2SO_4 emissions = actual emissions to air/(1-efficiency)

Efficiency expressed as a fraction

EPA has compiled emissions factors for sulfuric acid plants (16). Uncontrolled emissions factors for various sulfuric acid plants are shown in Table 3-3. Table 3-4 contains emissions factors for plants using three of the most common fiber mist eliminator control devices: vertical tube, vertical panel, and horizontal duel pad types.

Table 3-3: Uncontrolled Emissions Factors for Sulfuric Acid Plants

Raw material	Oleum* produced % Total output	Emissions of H₂SO₄ 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 3-4: Controlled Emissions Factors for Sulfuric Acid Plants

Raw Material	Oleum* Produced % Total Output	Emissions of H₂SO₄ 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.

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_2 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_3 and then H_2SO_4 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 aerosol formation is similar to that described above in the third paragraph of Section 3.1.2.

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 emissions factors of sulfur oxides, SO_x, for petroleum refining, but factors for sulfuric acid are not provided (19). 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 emissions 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.

3.1.5 Sulfuric Acid Aerosol Formation in Stacks from Combustion Processes

Sulfuric acid aerosols are often formed in flue gas in the stack during combustion of fuel oil, coal, or other sulfur-containing fuels. Both water and sulfur trioxide are combustion products with high affinity for each other; as discussed they react quickly to form sulfuric acid. All sulfuric acid produced within the stack, including both the gas and the mist, falls under the EPCRA section 313 definition of a sulfuric acid aerosol. Refer to Equation 2 above.

Table 3-5: Percent Conversion of SO₃ to H₂SO₄ as a function of temperature and percent water

ºF	1%	2%	3%	4%	5%	6%	7%	8%	9%	10%	20%	40%
	Water (%); Conversion of SO3 to H2SO4 (%)											
350	98.5	99.3	99.5	99.6	99.7	99.7	99.8	99.8	99.8	99.8	99.9	100.
400	93.1	96.4	97.6	98.2	98.5	98.8	98.9	99.1	99.2	99.3	99.6	99.8
500	48.7	65.5	74.0	79.2	82.6	85.1	86.9	88.4	89.5	90.5	95.0	97.4
550	23.1	37.6	47.5	54.5	60.2	64.4	67.8	70.7	73.0	75.1	85.8	92.3
600	9.58	17.6	24.2	29.9	34.7	39.0	42.7	46.0	48.9	51.5	68.1	81.1
700	1.72	3.47	5.09	6.70	8.24	9.75	11.2	12.6	13.9	21.2	26.4	41.8
800	0.40	0.78	1.16	1.54	2.67	2.30	2.67	3.04	3.40	4.06	7.25	13.5

Note: Data calculations are sensitive to the number of significant figures especially at the lower conversions.

The values in Table 3-5 were calculated by EPA using JANAF free energy data (20) and equilibrium constant values at various temperatures. (See Appendix B for details.) Formation of sulfuric acid from sulfur trioxide and water increased at lower temperatures and higher moisture content, but dissociation of sulfuric acid to sulfur trioxide and water increased at higher temperatures and lower moisture content. For EPCRA section 313 reporting purposes, EPA recommends that facilities use the lowest temperature from boiler to stack exit to calculate the percent conversion of SO₃ to H₂SO₄. For a complete calculation, please refer to Appendix A.

Table 3-6 and Table 3-7 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 (21). 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 3-7, between 20 and 40 ppm of SO₃ will be present in the flue gas and available to form sulfuric acid (acid aerosols).

Table 3-6: SO₃ Concentration in Flue Gas for Oil Fired Units

Excess air (%)	0.5	1.0	2.0	3.0	4.0	5.0
	Sulfur in fuel (%); SO3 Concentration (ppm)					
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 3-7: SO₃ Concentration in Flue Gas for Coal Fired Units

Excess air (%)	0.5	1.0	2.0	3.0	4.0	5.0
	Sulfur in fuel (%); SO3 Concentration (ppm)					
25	3 - 7	7 - 14	14 - 28	20 - 40	27 - 54	33 - 66

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 (22). On average, about 95% of sulfur present in bituminous coal will be emitted as gaseous sulfur oxides (SO_x) when burned, whereas somewhat less will be emitted when subbituminous coal is burned (23). In general, boiler size, firing configuration, and boiler operations have little effect on the percent conversion of sulfur in fuel to sulfur oxides (23). About 0.7% of fuel sulfur is emitted as SO_3/H_2SO_4 (23). Another 0.7% of fuel sulfur is released as particulate sulfate (23).

Example 1: Reporting sulfuric acid (acid aerosols) for coal combustion

Forty thousand tons of a bituminous coal containing 3 percent by weight of sulfur were burned during one year at a coal-fired electricity generating plant. Analyses showed that the average stack temperature was 400 degrees Fahrenheit and the water content was 8 percent. Assume that 90 percent of the sulfuric acid (acid aerosols) formed was captured by the scrubber and the remainder was released to the atmosphere. Has the facility exceeded the reporting threshold for sulfuric acid (acid aerosols) manufacture? If so, how should the facility report the data?

1) Threshold Determination:

In this example, 40,000 tons of coal were burned and the coal contained 3% sulfur. The facility can estimate the quantity of SO_3 produced, using the atomic mass unit ratio SO_3 amu/S amu = 80.06/32.06 = 2.497, and the AP-42 emissions factor for SO_3/H_2SO_4:

0.7% of fuel sulfur is emitted as SO_3 and an equal 0.7 percent of fuel sulfur is released as particulate sulfate (SO_4^{2-}) (23).

(i) Quantity of SO_3 produced = 0.03 * 40,000 tons * 2,000 lb/ton* 0.007 * 2.497 = 41,950 lb.

Using Equation 6 (see Appendix B) and converting temperature in degrees Fahrenheit to temperature in Kelvin with T = [(400 º F – 32) * 5/9] + 273.15 = 477.5 º K and using pH_2O = 0.08 atmospheres, the facility can obtain the result that 98.9 percent of the SO_3 is converted to H_2SO_4 (acid aerosols) at that temperature and water content in the stack. [N.B.: In lieu of calculating the percent conversion, one can use Table 3-5, with double interpolation of temperature and % H_2O if necessary, or use Table B-2 and interpolate % H_2O if necessary.]

Thus, using the factor for H_2SO_4 amu/SO_3 amu = 98.076/80.06 = 1.225, the quantity of H_2SO_4 (acid aerosols) manufactured = 41,950 lb * 0.989 * 1.225 = 50,823 lb.

(ii) Since another 0.7% of fuel sulfur is released as particulate sulfate (SO_4^{2-}), the quantity of H_2SO_4 (acid aerosols) manufactured = 0.03 * 40,000 lb* 2,000 lb/ton* 0.007 * 1.225 = 51,394 lb.

Total quantity of H_2SO_4 (acid aerosols) manufactured = (50,823 lb + 51,394 lb) = 102,217 lb.

The facility exceeded the 25,000 pound manufacturing threshold for H_2SO_4 (acid aerosols) and the facility must file Form R for H_2SO_4 (acid aerosols) under section 313 of EPCRA.

2) Release and Other Waste Management Calculations:

50,823 lb (from 1 (i)) of this example) of H_2SO_4 (acid aerosols) goes through the scrubber, which captures 90% H_2SO_4 (acid aerosols) or 50,823 lb * 0.9 = 45,741 lb, and the remaining 5,082 lb (50,823 lb - 45,741 lb) H_2SO_4 (acid aerosols) is released to the atmosphere via the stack. 5,082 lb should be reported in Section 5.2 (stack or point emissions) of Form R, and repeated in Section 8.1 (quantity released) of Form R.

For EPCRA section 313 reporting purposes, the quantities of H_2SO_4 (acid aerosols) captured by the scrubber and the particulate are considered as treated for destruction. Therefore, 97,135 lb (102,217 lb - 5,082 lb) of H_2SO_4 (acid aerosols) should be reported in Section 8.6 (quantity treated on site) of Form R.

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 for different fuel oil grades are provided in Table 3-8 below (22):

Table 3-8: Fuel Oil Sulfur Content by Grade

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_x 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 average, over 95% of the sulfur in fuel oil is converted to SO_2 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 (9). The emissions factor (EF) for uncontrolled fuel oil combustion from industrial boilers is $0.002 \times S$ pounds SO_3 per gallon of fuel oil burned (9) or $0.00245 \times S$ pounds H_2SO_4 per gallon of fuel oil burned, where S is the weight percent sulfur in the fuel oil. The uncontrolled emissions 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 emissions factor (EF) to calculate the pounds of sulfuric acid manufactured is shown below. If F is the number of gallons of fuel oil burned, the pounds of H_2SO_4 manufactured (H), would be:

Equation 4

$H = 0.00245 \times S \times EF$

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

Equation 5

$H = 0.00245 \times 3.97 \times 4,500,000 = 43,769$ pounds of H_2SO_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.

Example 2: Reporting sulfuric acid (acid aerosols) for fuel oil combustion

Annually, a facility burns three million gallons of No. 6 fuel oil in a tangentially fired boiler exceeding 100 million Btu per hour. On average, the oil contains a sulfur content of 3.6 percent and the stack is maintained at a temperature of 500 degrees Fahrenheit with a 6 percent water content.

1) Threshold Determinations:

The emissions factor from Table 3-5 for SO_3 in this example is $5.7 \times S$ or $5.7 \times 3.6 = 20.5$ lb/10^3 gal. The total SO_3 formed was 20.5 lb/10^3 gal $\times$ 3,000,000 gal = 61,500 lb.

Using Equation 6Equation 6 (see Appendix B) and converting temperature in degrees Fahrenheit to temperature in Kelvin with $T = [(500\ °F - 32) \times 5/9] + 273.15 = 533\ °K$ and using $pH_2O = 0.06$ atmospheres, one obtains the result that 84 percent of the SO_3 is converted to H_2SO_4 at that temperature and water content in the stack. Therefore, the quantity of H_2SO_4 (acid aerosols) formed was 61,500 lb $\times$ 0.84 = 51,700 lb, which exceeds the threshold for reporting.

2) Release and Other Waste Management Calculations:

Assuming that half of the H_2SO_4 (acid aerosols) is converted to particulate sulfate (51,700 lb/2 = 25,850 lb) and the scrubber removes 90 percent of the other half of the H_2SO_4 (acid aerosols) or 25,850 lb $\times$ 0.90 = 23,270 lb then 25,850 lb minus 23,270 lb = 2,580 lb is released to the atmosphere. Note that this conversion is assumed but the actual conversion number may vary according to the type of control equipment and operating conditions at the facility.)

The facility should report these results in Form R as 2,580 pounds/year in Section 5.2 (stack or point emissions) and repeated in Section 8.1 (quantity released) and 49,100 pounds/year in Section 8.6 (quantity treated on site). The latter figure is the 23,270 pounds treated in the scrubber plus the 25,850 pounds of particulate sulfate formed.

SECTION 4.0 MEASUREMENT METHODS

For source sampling, EPA has specified extractive sampling trains and analytical procedures for SO_3 and sulfuric acid aerosols (11, 24). Separation of particles containing Na_2SO_4 may present problems in cases such as kraft paper mills (13). If sodium sulfate were present, analytical results for sulfuric acid would be high.

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APPENDIX A. Sulfuric Acid Vapor Pressure
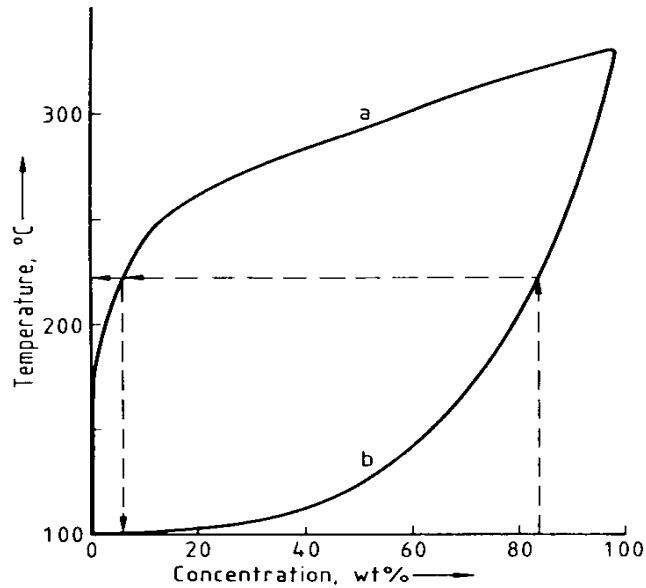
Figure A-1: Boiling curves for sulfuric acid at atmospheric pressure

The graph above shows sulfuric acid partial pressure (a) as a function of aqueous sulfuric acid concentration (b) and temperature (1). For example, the figure shows that if the vapor above a solution of 85% sulfuric acid boiling at 223°C were completely condensed, it would contain approximately 7 percent H_2SO_4. At concentrations below approximately 75% H_2SO_4, the vapor that evaporates from the solution is essentially water.

Table A-1: Sulfuric Acid Partial Pressure and Total Vapor Pressure over Aqueous Sulfuric Acid

°F	Weight Percent Sulfuric Acid; Sulfuric Acid Partial Pressure (bar); (Total pressure in parentheses) (bar)					
	20.0	**40.0**	**60.0**	**80.0**	**98.0**	**100.0**
32	0.843E-20 (0.534E-02)	0.344E-17 (0.326E-02)	0.438E-14 (0.836E-03)	0.161E-10 (0.197E-04)	0.187E-08 (0.117E-07)	0.228E-08 (0.323E-08)
68	0.769E-18 (0.205E-01)	0.193E-15 (0.130E-01)	0.149E-12 (0.367E-02)	0.305E-09 (0.115E-03)	0.224E-07 (0.121E-06)	0.273E-07 (0.435E-07)
104	0.389E-16 (0.649E-01)	0.649E-14 (0.427E-01)	0.317E-11 (0.131E-01)	0.379E-08 (0.531E-03)	0.191E-06 (0.914E-06)	0.230E-06 (0.425E-06)
140	0.121E-14 (0.175)	0.144E-12 (0.119)	0.462E-10 (0.395E-01)	0.334E-07 (0.204E-02)	0.122E-05 (0.538E-05)	0.147E-05 (0.319E-05)
176	0.254E-13 (0.417)	0.225E-11 (0.290)	0.492E-09 (0.104)	0.222E-06 (0.668E-02)	0.622E-05 (0.257E-04)	0.743E-05 (0.193E-04)
212	0.381E-12 (0.891)	0.264E-10 (0.634)	0.402E-08 (0.244)	0.117E-05 (0.192E-01)	0.261E-04 (0.103E-03)	0.310E-04 (0.966E-04)

°F	Weight Percent Sulfuric Acid; Sulfuric Acid Partial Pressure (bar); (Total pressure in parentheses) (bar)					
	20.0	40.0	60.0	80.0	98.0	100.0
302	0.106E-09 (4.132)	0.460E-08 (3.090)	0.316E-06 (1.392)	0.343E-04 (0.170)	0.493E-03 (0.180E-02)	0.574E-03 (0.287E-02)
392	0.883E-08 (13.107)	0.278E-06 (10.245)	0.975E-05 (5.312)	0.457E-03 (0.913)	0.470E-02 (0.166E-01)	0.538E-02 (0.427E-01)
482	0.312E-06 (31.939)	0.793E-05 (26.056)	0.156E-03 (15.351)	0.358E-02 (3.439)	0.278E-01 (0.985E-01)	0.314E-01 (0.389)
572	0.591E-05 (64.407)	0.130E-03 (54.869)	0.156E-02 (36.361)	0.266E-01 (9.916)	0.117E-00 (0.425)	0.130E-00 (2.476)

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 A-1 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°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 A-2 (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 A-2: Sulfuric Acid Partial Pressure over Oleum

°C	Free SO$_3$ in oleum, %; Sulfuric Acid Partial Pressure (bar)		
	10	20	30
20	0.227 E-08	0.120 E-08	0.40 E-09
40	0.1467 E-07	0.667 E-08	0.267 E-08
60	0.7333 E-07	0.400 E-07	0.1333 E-07
80	0.3066 E-06	0.1600 E-06	0.600 E-07
100	0.1067 E-05	0.5333 E-06	0.2133 E-06

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

APPENDIX B. Manufacture of Sulfuric Acid (acid aerosols) by Coal or Oil Combustion

SO₃ to H₂SO₄ Conversions:

Hardman et al.(3) used a classical physical chemistry methodology for calculating the formation constant, K_p, of H_2SO_4 from SO_3 in the presence of H_2O. The method consists of using the standard free energies of formation of the reactants and products to obtain the change in free energy (ΔF) for the reaction. ΔF is related to K_p by $\Delta F = -RT \ln K_p$ where R is the gas constant (1.9873 cal/mole/degree) and T is the absolute temperature in Kelvin. (See Table B-1.) A linear plot of log K_p versus the reciprocal of the temperature T in Kelvin yields,)H, the heat of reaction from the slope. (See Figure B-1.)

The reverse of the formation reaction is the dissociation of H_2SO_4 to SO_3 and H_2O. The equilibrium constant for the reverse reaction is the reciprocal of the aforementioned K_p. The extent of the conversion or the equilibrium between reaction and product species is dependent on the concentration of H_2O and the temperature.

To calculate the conversion of SO_3 to H_2SO_4 in the presence of water, it is assumed that at the elevated temperatures in fuel oil- and coal burning facilities, the water is completely vaporized as is the H_2SO_4 formed from gaseous SO_3 and, therefore, the H_2SO_4 is considered to be a sulfuric acid (acid aerosols). Thus, if the facility is at atmospheric pressure then the partial pressure of water in the vapor mixture of combustion products can be equated to one-atmosphere pressure times the percent water divided by 100. This figure is used in the equilibrium expression for the conversion of SO_3 to H_2SO_4 according to the following chemical reaction and its equilibrium expression:

$$SO_3 + H_2O \leftrightarrow H_2SO_4$$

$$K_p = \frac{[H_2SO_4]}{[SO_3]\,[H_2O]}$$

Concentrations as pressures in atmospheres, temperature in Kelvin, and K_p is the equilibrium constant for the formation of H_2SO_4 from SO_3 in the presence of H_2O

The value for the equilibrium constant K_p is determined from free energy data obtained from JANAF Thermochemical Tables (4). The results are shown in Table B-1.

Table B-1: Free Energy and Equilibrium Constant Values for SO₃-H₂SO₄ Equilibrium

Temp, T (Kelvin)	SO3 (kcal/mole)	H2O (kcal/mole)	H2SO4 (kcal/mole)	ΔF (kcal/mole)	Kp	ln Kp
300	-88,652	-54,617	-156,685	-13,416	5.946E+09	22.506
400	-86,597	-53,519	-149,796	-9,680	1.947E+05	12.179
500	-84,310	-52,361	-142,636	-5,965	4.051E+02	6.004
600	-81,919	-51,156	-135,364	-2,289	6.821	1.92
700	-79,441	-49,915	-128,014	1,342	0.381	-0.965
800	-78,213	-48,646	-121,928	4,931	0.045	-3.102
900	-74,230	-47,352	-113,105	8,477	0.0087	-4.7

The regression equation can be determined from a plot of ln K_p versus $1/T$ (See Figure B-1):

ln K_p = 12,274.4/T – 8.022 or

log K_p = log ([H_2SO_4] / [SO_3][H_2O] = 5330/T – 8.022

[H_2SO_4] / [SO_3][H_2O] = exp (5330/T – 8.022)

[H_2SO_4] / [SO_3] = exp (5330/T – 8.022) × pH_2O = S

Where pH_2O = % H_2O / 100

$\qquad$ % Conversion = 100 × [H_2SO_4] /([SO_3] + [H_2SO_4])

$\qquad$ = 100 / ([SO_3] / [H_2SO_4]) + 1) = 100 / [(1 / S) + 1]

Finally, on rearranging one gets:

Equation 6
% Conversion = 100 S / (1 + S)

Equation 6 was used to calculate the conversion of SO_3 to H_2SO_4 at various temperatures and water contents and the results are compiled in Table 3-1.

The results for 8 percent water are summarized in Table B-2. A typical calculation is illustrated as follows:

$\qquad$ Data set: $\qquad$ 8 % H_2O (pH_2O = 0.08 atmospheres); $\quad$ Temperature = 500 ºF

$\qquad$ T = [(500 ºF – 32) × 5/9] + 273.15 = 533 K

$\qquad$ S = $10^{(5330/533 – 8.022)}$ × 0.08 = (100 × $10^{(1.978)}$) × 0.08 = 7.60

$\qquad$ % Conversion = 100 × 7.60 / (1 + 7.60) = 88.4% (from Equation 6)

Table B-2: Percent Conversion of SO₃ to H₂SO₄ in the Presence of 8% H₂O

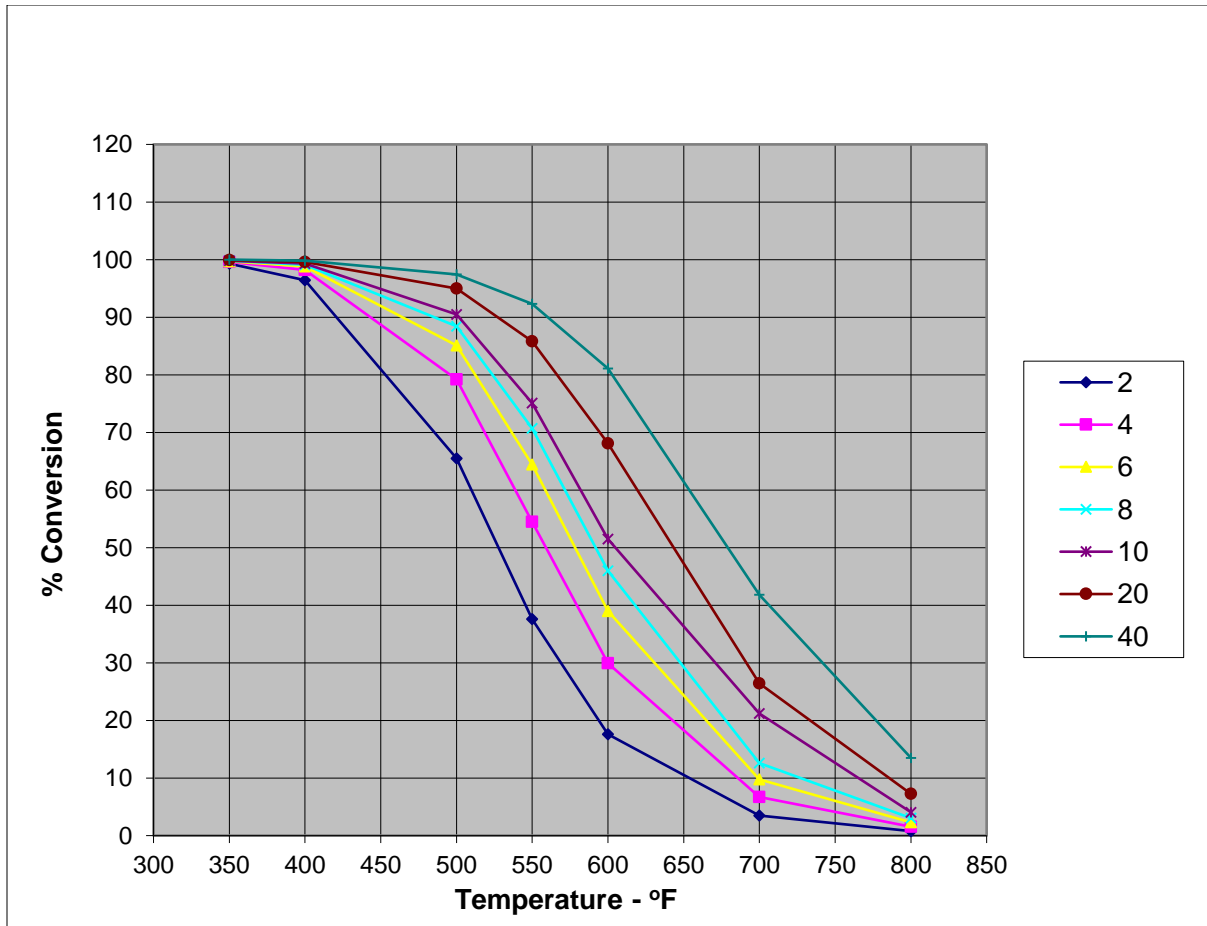| Temperature (ºF)	Percent Conversion
350	99.8
400	99.1
500	88.4
550	70.7
600	46.0
700	12.6
800	3.04

The full table of results at various water concentrations and temperatures is displayed in Table 3-5 in the main body of this paper. Although stacks in electricity generating facilities that combust coal and oil are not expected to have water contents as high as 20 or 40 percent, those calculations are added to the chart to display the trends as water content increases.

The results are plotted in the graphs of ln K_p versus the reciprocal of the temperature in Kelvin (Figure B-1) and the percent conversion of SO_3 to H_2SO_4 versus temperature at various water contents (isolines) (Figure B-2).
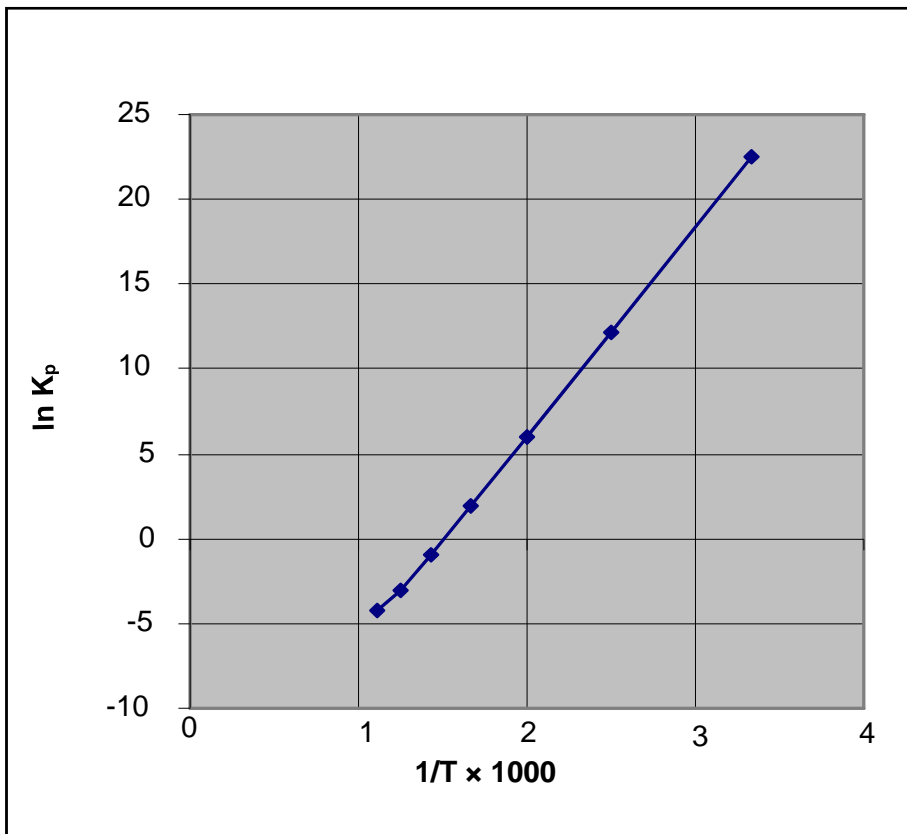
Figure B-1: ln K_p vs Reciprocal of Temperature in Kelvin

Figure B-2: Percent conversion of sulfur trioxide to sulfuric acid versus temperature at various water contents

Discussion:

U.S. coals contain from 0.2% to 7% sulfur by weight (4). Some facilities employ fluidized bed procedures for removing some of the sulfur from the coal prior to using it as a fuel. On average, about 95% of sulfur present in bituminous coal will be emitted as gaseous sulfur oxides (SO$_x$) when burned, whereas somewhat less will be emitted when sub-bituminous coal is burned. In general, boiler size, firing configuration, and boiler operations have little effect on the percent conversion of sulfur in fuel to sulfur oxides (5). Sulfuric acid (acid aerosols) condenses and/or reacts with particulate matter to form particulate sulfate. About 0.7% of fuel sulfur is emitted as SO$_3$/ H$_2$SO$_4$ and an equal 0.7 percent as particulate sulfate (SO$_4^{2-}$) (6). For EPCRA section 313 reporting purposes, the equivalent amount of acid aerosols that corresponds to the amount of particulate sulfate should be included for threshold determination and this amount should be considered treated on-site and reported in sections 7A and 8.6, Part II of Form R.

Similarly, burning fuel oil leads to uncontrolled sulfur emissions that are almost entirely dependent on sulfur content of the fuel and are not affected by boiler size, burner design, or grade of fuel being fired (7). As stated previously, on average, 95 percent of the fuel sulfur is converted to SO$_2$, about 1 to 5 percent is further oxidized to SO$_3$, and 1 to 3 percent is emitted as particulate sulfate (7).

When a scrubber is used to remove sulfuric acid (acid aerosols) prior to or in a stack, the acid aerosols are usually converted to the non-aerosol form. The scrubber has not actually destroyed sulfuric acid as a

discrete chemical, but the aerosol form of sulfuric acid reportable under EPCRA section 313 has been treated. Since the treatment procedure is on site, the quantities of aerosol form of sulfuric acid that were converted to the non-aerosol form of the sulfuric acid should be reported. That is, since sulfuric acid (acid aerosols) removed by scrubbers is converted to a non-reportable form of H_2SO_4, the quantity removed by the scrubber can be reported as having been treated for destruction. This is illustrated in the example in Section 3.1.6 in the main body of this paper. Note that the non-aerosol forms of sulfuric acid released or emitted are not reportable under EPCRA section 313 because the qualifier to the sulfuric acid listing includes only acid aerosol forms.

B.1   References

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