

SNAP CODE: 040401

SOURCE ACTIVITY TITLE: PROCESSES IN INORGANIC CHEMICAL INDUSTRIES
Sulphuric Acid

NOSE CODE: 105.09.10

NFR CODE: 2 B 5

1 ACTIVITIES INCLUDED

This sector covers emissions released from sulphuric acid production plants. Emissions released from all process steps are taken into account.

2 CONTRIBUTION TO TOTAL EMISSIONS

The contribution of emissions released from sulphuric acid production plants to the total emissions in the countries of the CORINAIR90 inventory are given as follows:

Table 1: Contribution to total emissions of the CORINAIR90 inventory (28 countries)

Source-activity	SNAP-code	Contribution to total emissions [%]							
		SO ₂	NO _x	NMVOC	CH ₄	CO	CO ₂	N ₂ O	NH ₃
Sulphuric Acid	040401	0.7	0	0	-	0	0	-	-

0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)

- = no emissions are reported

3 GENERAL

3.1 Description

This chapter covers all production steps within the plant and hence include the production of sulphur dioxide, sulphur trioxide, sulphuric acid and "oleum". The following figure provides an example of a flow sheet of a double contact sulphuric acid plant:

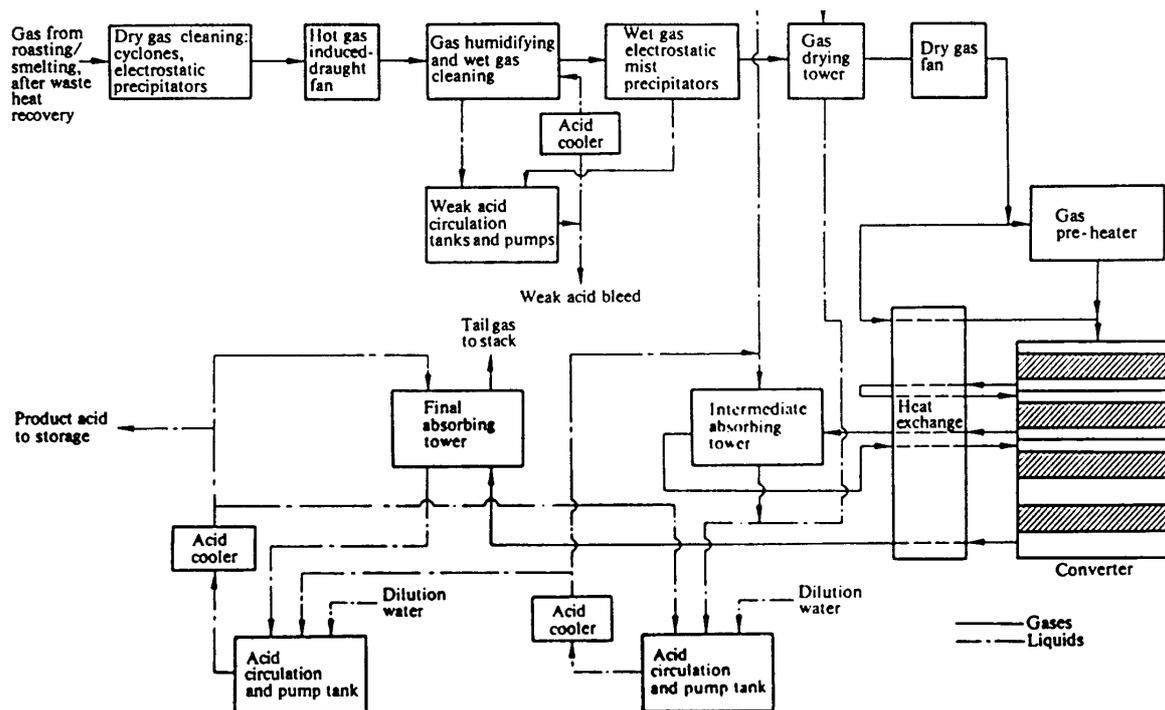


Figure 1: Double contact sulphuric acid plant (schematic, based on /7/)

For SO₂ emissions the relevant process units are the cleaning of SO₂-containing raw gas, the converter, the final absorbing tower, and scrubbers (see also section 3.4). Scrubbers may be installed for the cleaning of raw gas and behind the tail gas cleaning (see also section 3.3).

3.2 Definitions

Oleum highly concentrated sulphuric acid (a solution of uncombined SO₃ dissolved in H₂SO₄).

3.3 Techniques

In principle the commercial production of sulphuric acid includes the following steps:

- Production of gases containing SO₂ and cleaning of the gases obtained if necessary,
- Oxidation of SO₂ to SO₃ and absorption of the SO₃ obtained.

3.3.1 Production of gases containing SO₂ /cf. 3/

Sulphur dioxide is produced by the oxidation of elemental sulphur with air, by the roasting of sulphidic ores with the addition of air, or by the decomposition of sulphates and spent sulphuric acids etc. in air. Elemental sulphur, which is obtained either from natural deposits (e.g. Frasch-process sulphur) or from the desulphurisation of natural gas or crude oil (recovered sulphur), is burned at temperatures between 900 °C and 1,800 °C; the SO₂ content of the combustion gases is generally up to 18 vol.-%. The sulphur content of sulphidic ores is

converted into SO₂ by roasting it with air at more than 600 °C; the SO₂ content of the roaster gases is normally between 3 and 15 vol.-%. The usual types of furnaces are multiple-hearth furnaces, rotary kilns, fluid bed roasters, pyrite fines furnaces, sinter roasters and flash smelters, depending on the roasting material.

Roaster gases containing dust are fed to a gas cleaning system: wet separators and electrostatic precipitators, either single or in combination.

100 % sulphur dioxide is obtained

- by scrubbing the gases containing SO₂ with appropriate solvents (e.g. alkaline absorbents) and subsequently driving out the dissolved SO₂ by heating it (it is then dried, compressed and liquefied by refrigeration),
- by means of combined compression and separation of the gas containing SO₂,
- by conversion of 100 % SO₃ or oleum with elemental sulphur or hydrogen sulphide.

The waste gas containing SO₂ from the production of 100 % sulphur dioxide is generally fed to a sulphuric acid plant or cleaned by scrubbing at a pH value of between 5 and 6. The by-product is a sodium sulphite/sodium bisulphite solution, which may be added to the scrubber liquid.

The waste gas coming from the liquefaction process of sulphur containing gases is in general fed to a sulphuric acid plant.

3.3.2 Oxidation of SO₂ to SO₃ and absorption of the SO₃ obtained /cf. 3/

A distinction is made between plants for the production of sulphuric acid and plants for the processing of products containing sulphur. The end product is always sulphuric acid.

The contact process without intermediate absorption, the single contact process, is used to process SO₂ gases with low and widely varying SO₂ contents. The gases containing SO₂ are oxidised to SO₃ in the presence of catalysts containing alkali and vanadium oxides. The SO₃ is absorbed (by oleum and water) and converted to sulphuric acid.¹ The contact process with intermediate absorption, the double contact process, is widely used and has a primary conversion efficiency of 85 to 93 %. After cooling the gases, the SO₃ obtained is absorbed in the intermediate absorber by means of sulphuric acid with a concentration of 98 to 99 wt.-%. The SO₃ formed in the second stage is absorbed in a final absorber. In general, SO₂ gases containing 8 to 10.5 vol.-% SO₂ are used for this process.

1 Older process types also exist which today are of lower relevance. These older process types can be summarised as "nitrogen oxide processes": The production and the cleaning of the SO₂ gases are comparable to the contact process. However, for the conversion of the SO₂, nitrogen oxide is used as a catalyst which operates as an oxygen carrier. Depending on the lining of the reaction chamber, two processes are known: the lead chamber process (which is no longer in operation) and the tower process (brick lined chamber, advanced "lead chamber"-process).

The wet contact process is mainly used to process gases containing hydrogen sulphide from coke ovens, gasworks or oil refineries. The gases containing 15 to 100 vol.-% sulphides (e.g. hydrogen sulphide) etc. are burned autothermally with excess air in a combustion furnace. After cooling the SO_2 is oxidised to SO_3 in a converter (with alkali/vanadium oxide). After condensation or absorption, sulphuric acid with a concentration of 78 wt.-%, is generally obtained. A modified wet contact process is used for the direct processing of hot gases with low SO_2 contents (< 1.0 vol.-%) and high water contents e.g. from Claus plants. Sulphuric acid is obtained with concentrations of 78 to 93 wt.-%. The wet/dry contact process with intermediate condensation is based on sulphur combustion and is used in the processing of waste air contaminated with sulphur compounds (e.g. hydrogen sulphide). The SO_2 gases are converted in wet contact stages and then absorbed. The sulphuric acid obtained is cleaned in different steps. For processing oxygen-free gases to sulphuric acid, the lowest possible content per unit volume varies between 40 to 120 g sulphur per m^3 , depending on the components in the input gas.

The waste gas containing SO_2 from the contact process can be fed into an intermediate absorption process, which reduces SO_2 emissions by approximately 80 %. Further reduction can be achieved by lowering the gas velocity in the contact process or by installing a fifth contact bed. SO_2 emissions from the double contact process can be reduced by up to 30 %, if a 5-bed system is installed instead of a normal 4-bed system.

The reduction of sulphuric acid aerosols can be achieved with for example candle filters, electrostatic precipitators or venturi scrubbers.

By applying an oxidising gas scrubbing process (e.g. Peracidox) for the waste gas cleaning downstream of a double contact process, SO_2 emissions can be reduced by up to 90 % and SO_3 emissions by up to 50 %. The oxidising agent is either peroxosulphuric acid or hydrogen peroxide. No waste products are obtained.

To reduce emissions of SO_2 and SO_3 from the contact process without intermediate absorption, a NH_3 tail gas scrubbing can be installed; the reduction efficiency for SO_2 emissions is up to 75 % and for SO_3 emissions up to 50 %. The products of this process are ammonium sulphite or ammonium bisulphite (for SO_2) and ammonium sulphate (for SO_3).

3.4 Emissions

The main relevant pollutants are sulphuric oxides (SO_x), which include sulphur dioxide (SO_2) and sulphur trioxide (SO_3). For CORINAIR, SO_2 and SO_3 should be reported together expressed as SO_2 . Relevant process steps are listed below in Figure 1. Emissions of nitrogen oxides (NO_x), non-methane volatile organic compounds (NMVOC)², carbon monoxide (CO)

2 The production of organic compounds gives rise to spent sulphuric acid which may contain organic compounds, salts etc. Depending on the type and degree of contamination, spent sulphuric acid is decomposed and processed to sulphuric acid in a contact plant. Slightly contaminated dilute acids can be concentrated to between 65 and 75 wt.-% and then subsequently evaporated to a concentration of ca. 96 wt.-%. /3/

and ammonia (NH₃) are negligible^{3,4}. Emissions of heavy metals (e.g. from roasting sulphur in the smelter gas) are not relevant due to the fact that most of them are particle bound and separated by the wet gas cleaning (e.g. electrostatic precipitation). Heavy metals remaining in the flue gas are mostly absorbed by the sulphuric acid formed in the converter.

SO₂ emissions are released from the production of gases containing SO₂ (raw gas preparation)⁵, the oxidation of SO₂ to SO₃ (converter) and the absorption of SO₃ obtained (H₂SO₄ production).

Nearly all sulphur dioxide emissions from sulphuric acid plants are found in the exit stack gases. In addition to these, small quantities of sulphur oxides are emitted from storage tank vents as well as from tank truck vents during loading operations, from sulphuric acid concentrators, and through leaks in process equipment. Few data are available on the quantity of emissions from these non-stack sources /1/.

3.4.1 Production of gases containing SO₂ (raw gas) /cf. 3/⁵

Extensive analysing of sulphur dioxide emissions released by the stacks of sulphuric acid plants shows that the major part of the SO₂ emissions is an inverse function of the sulphur conversion efficiency (SO₂ oxidised to SO₃). This conversion is affected by the number of stages in the catalytic converter, the amount of catalyst used, temperature and pressure, and the concentration of the reactants (sulphur dioxide and oxygen). /1/ The efficiency of converting sulphur dioxide to trioxide is for the single contact process about 97 to 98 % and for the double contact process usually 99.5 % /cf. 7/. Depending on the raw material and the process, the waste gases contain up to 0.12 g SO₃ per m³ before scrubber /3/.

Exhaust gases from the absorption process have an SO₂ concentration of 2,500 to 3,000 mg/m³. The residual gas from the separation of the liquefaction process has an SO₂ concentration of up to 300 g/m³. No exhaust gases occur when reducing SO₃ with sulphur or H₂S. Emissions from raw gas cleaning may occur.

3.4.2 Oxidation of SO₂ to SO₃ and absorption of the SO₃ obtained (H₂SO₄ production)

SO₂ emissions are relevant for the process steps: converter, final absorption tower and scrubbers (if installed). The emissions are released through the stack.

Large quantities of sulphuric acid mist may be formed by the combustion of hydrogen sulphide (e.g. from coke ovens) and during decomposition processes, due to the oxidation of nitrogen compounds /3/. Concerning mist emissions an unpublished report by the US-EPA found that uncontrolled mist emissions from oleum plants burning spent acid range from 0.5

3 Oleum plants also produce mist emissions of sulphuric acid.

4 For sulphuric acid production only SO₂ is relevant. Other pollutants may be released from the preparation of SO₂ feed gas (roasting, smelting etc.), which are not covered here.

5 Emissions from the production of raw gases containing SO₂ are not considered here.

to 5.0 kg/Mg. 85 to 95 wt.-% of the mist particles from oleum plants are less than two microns in diameter, compared to only 30 wt.-%. /1/

3.5 Controls

Control measures are an integral part of the production process (see sections 3.3.1 and 3.3.2 and figure 1). Control measures include the oxidising gas scrubbing process and the tail gas scrubbing with NH₃.

4 SIMPLER METHODOLOGY

For the production of sulphuric acid only a simpler methodology is provided; a detailed methodology is not proposed (see section 5). Here "simpler methodology" refers to the calculation of emissions based on emission factors and activities. The simpler methodology covers the pollutant SO_x.

The annual emission is determined by an activity and an emission factor:

$$E_i = EF_i \cdot A \quad (1)$$

E_i annual emission of pollutant i

EF_i emission factor of pollutant i

A activity rate

The activity rate A and the emission factor EF_i have to be determined on the same level of aggregation by using available data (e.g. production of sulphuric acid, see also Section 6).

Emission factors for emissions of SO₂ and SO₃ are given in Table 2 based on literature data. The required unit of the emission factors according to CORINAIR90 is mass pollutant/mass product [g/Mg].

5 DETAILED METHODOLOGY

A detailed methodology is not proposed, due to the low emission relevance of the production of sulphuric acid compared to the total anthropogenic emissions (see Section 2). Emission measurements appear to be not necessary for inventory purposes.

6 RELEVANT ACTIVITY STATISTICS

The activity according to CORINAIR90 should be reported in mass product/year [Mg/a]. The total production of sulphuric acid can be derived directly from statistics available on an European level. For individual point sources, data from national sources (e.g. associations of chemical industries) should be used.

The following statistics contain data concerning the production of sulphuric acid:

- United Nations (ed.): Industrial Statistics Yearbook 1991; Vol. I, Commodity Production Statistics, New York 1993; ISIC 3511-47 (production of sulphuric acid)

The following statistics on a European level contain only economic variables, such as number of enterprises, number of employees, turnover for the "Manufacture of basic industrial chemicals and manufacture followed by further processing of such products".

- Office for Official Publication of the European Communities (ed.): Annual Statistics 1990; Luxembourg; 1992
- Statistical Office of the European Communities (EUROSTAT) (ed.): CRONOS Databank; 1994

7 POINT SOURCE CRITERIA

According to the CORINAIR90 methodology, sulphuric acid plants should be considered as point sources.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

The following Table 2 contains emission factors for the relevant pollutants SO₂ and SO₃ based on literature data. Emissions are expressed with reference to different compounds. Emission factor are given in relation to SO₂, SO₃, SO_x, and SO₄²⁻.

Table 2: Emission factors for the production of sulphuric acid (expressed as 100 % acid)

Process	Emission factors in terms of production of 100 % H ₂ SO ₄ [g/Mg]							
	SO ₂		SO ₃		SO _x ⁸⁾		SO ₄ ²⁻	
	range	value	range	value	range	value	range	value
Contact process without intermediate absorption (single absorption)	10,000 - 25,000 ²⁾	17,000 ⁷⁾ 14,000 ²⁾ 17,500 ²⁾⁵⁾	400 - 600 ⁷⁾		1,100 - 17,000 ³⁾	9,050 ³⁾		
Contact process with intermediate absorption (double absorption)	1,500 - 4,000 ²⁾⁶⁾	<1,000 ⁴⁾⁷⁾ 2,700 ²⁾⁶⁾ 2,600 ⁷⁾	100 - 150 ⁷⁾		1,000 - 5,000 ²⁾ 1,900 - 7,200 ³⁾	3,000 ²⁾ 4,550 ³⁾	100 - 300 ²⁾⁶⁾	200 ²⁾⁶⁾
- with constant gas conditions								
- with fluctuating gas conditions	3,300 - 6,600 ⁷⁾		300 - 400 ⁷⁾					
- Decomposition plants (spent sulphuric acid)		6,600 ⁷⁾		400 ⁷⁾				
Wet contact process								
- 78 % sulphuric acid		17,000 ⁷⁾		350 ⁷⁾				
- 98 % sulphuric acid		17,000 ⁷⁾		400 ⁷⁾				
Wet/dry contact process with intermediate condensation/absorption		3,300 ⁷⁾	100 - 150 ⁷⁾					

¹⁾ AIRS, EPA /6/;

⁵⁾ old contact process, average conversion of 97.3 %

⁸⁾ SO_x: mixture of SO₂ and SO₃; proportions are not specified

²⁾ CORINAIR /2/;

Contact process

absorber conversion 97 %

³⁾ RIVM /4/;

⁶⁾ for Germany and the

absorber conversion 99.9 % 2,000¹⁾

20,000¹⁾

4) Swedish plants (in general) /5/;	Netherlands;	absorber conversion 99.5 %	3,500 ¹⁾	absorber conversion 96 %
	7) based on /3/;	absorber conversion 99 %	7,000 ¹⁾	27,500 ¹⁾
		absorber conversion 98 %	13,500 ¹⁾	absorber conversion 95 % 35,000 ¹⁾
				absorber conversion 94 % 41,000 ¹⁾
				absorber conversion 93 % 48,000 ¹⁾

9 SPECIES PROFILES

The emissions contain sulphur dioxide (SO₂) and sulphur trioxide (SO₃) depending on the efficiency of converting sulphur dioxide to sulphur trioxide (see also Section 3.4).

10 UNCERTAINTY ESTIMATES

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

Weakest aspects discussed here are related to emission factors. Technique specific emission factors are provided in table 2. CORINAIR90 data can only be used in order to give a range of emission factors with respect to point and area sources. Further work should be invested in the analysis of measured data in order to decrease the range of emission factors given or to provide a further split of emission factors taking into account further technical specifications.

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

13 TEMPORAL DISAGGREGATION CRITERIA

Temporal disaggregation of annual emission data (top-down approach) should provide a split into monthly, weekly, daily and/or hourly emission data. Temporal disaggregation of annual emissions released from sulphuric acid plants can be obtained by taking into account the time of operation.

However, data for the annual time of operation should take into account, that sulphuric acid plants produce during the whole year, and the production of sulphuric acid is a continuous process.

14 ADDITIONAL COMMENTS

15 SUPPLEMENTARY DOCUMENTS

16 VERIFICATION PROCEDURES

As outlined in the chapter on "Concepts for Emission Inventory Verification" different verification procedures can be recommended. Verification procedures considered here are principally based on the verification of emission data on a national level and on a plant level. Verification on a plant level takes into account, e.g. the number of sulphuric acid plants considered, and relies on comparisons between calculated emissions/emission factors and those derived from emission measurements.

Emission data for sulphuric acid production can be verified on national level by comparing annual emissions related to the territorial unit to independently derived emission estimates (e.g. obtained by using population equivalents).

17 REFERENCES

- /1/ US-EPA (ed.): Compilation of Air Pollutant Emission Factors, Vol. 1: Stationary Point and Area Sources, 1986, AIR CHIEF Version 2.0 Beta, April 1992
- /2/ CITEPA (ed.): CORINAIR - Emission Factor Handbook, part 1: Default Emission Factors from stationary sources; 1992
- /3/ Verein Deutscher Ingenieure (ed.): Emission Control Sulphuric Acid Plants; Nr. 2298; Düsseldorf (Germany); 1984
- /4/ Bol, B; Kohnen, E. A. E. M.: Produktie van Zwavelzuur; RIVM-report 736301143; RIZA-report 92.003/43; Maart; 1993
- /5/ Ms. Froste; Mr. Kvist; Ms. Haclund; personal communication; February 1995 (Swedish EPA)
- /6/ EPA (ed.): AIRS Facility System; EPA-Document 450/4-90-003, Research Triangle Park; March 1990
- /7/ Parker, Albert: Industrial Air Pollution Handbook; London; 1978

18 BIBLIOGRAPHY

19 RELEASE VERSION, DATE AND SOURCE

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20 POINT OF ENQUIRY

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