

SULPHURIC ACID PRODUCTION FROM COKE OVEN GAS

1 GENERAL INFORMATION

Sulphuric acid is an important basic inorganic chemical, due to its various industrial applications. Most of the sulphuric acid is consumed by the fertiliser industry. Other important applications are the oil refining industry, the production of pigments, and the steel industry and extraction processes of the non-ferrous metal industry. Sulphuric acid is used for the production of explosives, synthetics, viscose and washing agents and for special applications in the chemical industry.

The reference installation for the production of sulphuric acid is located at a steel works. The installation uses hydrogen sulphide containing gases from purifying coke oven gas. About 20 tons sulphuric acid per day of are produced in a dry single contact process.

2 INDUSTRIAL PROCESSES USED

In addition to H₂S coke oven gas consists of several other gases like CO, CO₂, CH₄, H₂, C_nH_m, Benzene, Naphthalene, NH₃ und HCN and has to be purified. A detailed process schema is presented in Figure 1.

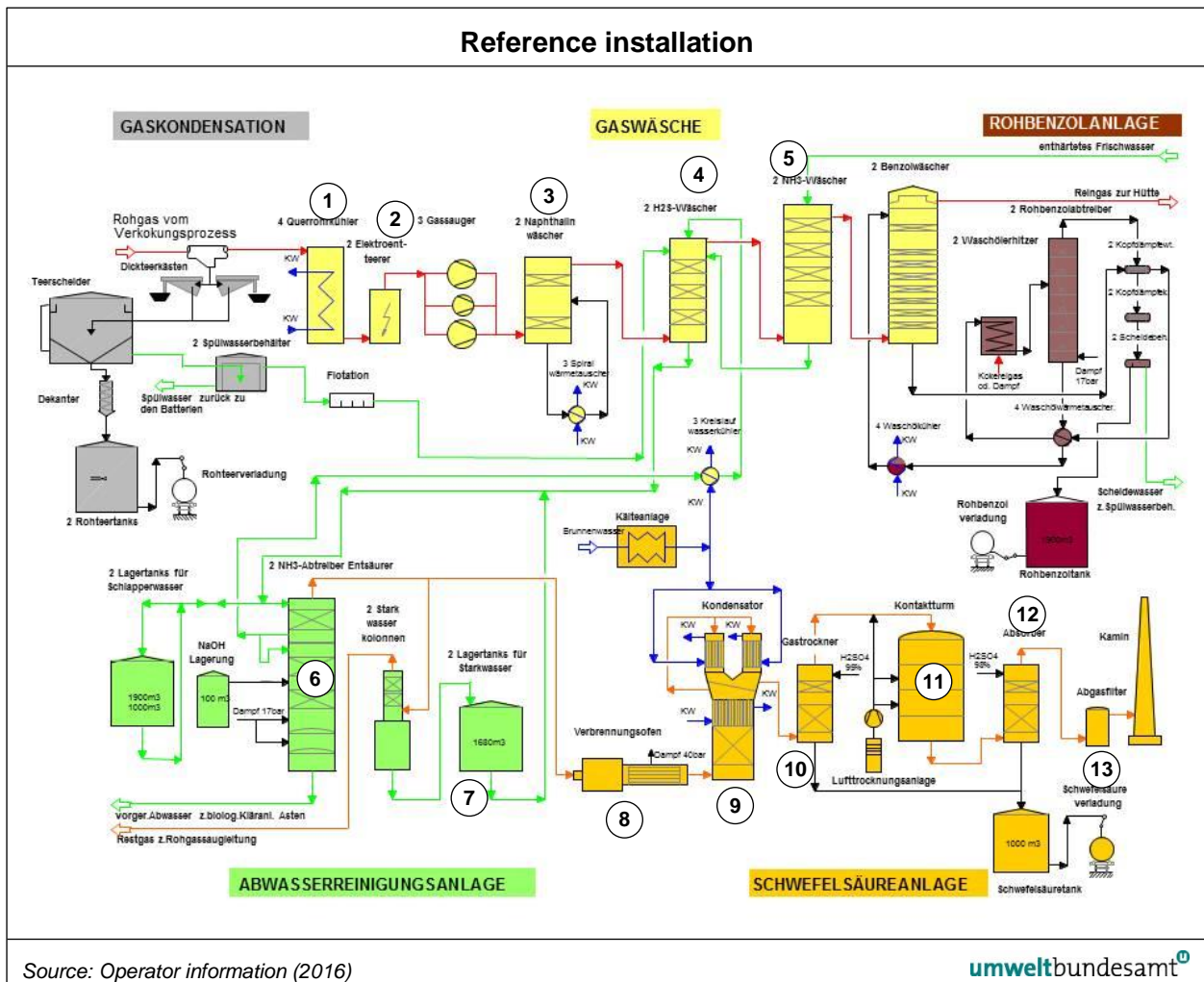
After cooling to condense water (1) and electrical tar removal (2) the gas pass through different scrubbers: a naphthalene scrubber (3), a H₂S scrubber (4) and a NH₃ scrubber (5). Loaded water from the NH₃ scrubber is used in the H₂S scrubber. Washer fluid from the H₂S scrubber, which is loaded with ammonium sulphide, is stripped in a two stage stripper (6) with steam. In the first stage H₂S is stripped, in the second stage NH₃ is stripped. Part of the deacidified alkaline water after the stripper is recirculated as washing fluid into the H₂S scrubber. During shut down of the following sulphuric acid plant, the ammonium sulphide solution is stored (7) and processed later.

The H₂S and NH₃ containing gas is incinerated in a horizontal furnace (8) at 1,000 – 1,500 °C. The temperature is reduced to approx. 300 °C and about 5 – 6 tons of steam (45 bar, 250 °C) per hour is produced in the boiler. In the condenser (9) the temperature is further reduced to about 15 °C to condense water and dry the gas stream. Cooling water that is further cooled down by a chiller is used as cooling water. Sinter candle filters are used to remove aerosols. Before entering the contact tower, the gas stream is dried with concentrated sulphuric acid (10) and heated to 400 °C.

The contact tower (11) consists of four catalyst layers; the first three are V₂O₅ based, the last is based on V₂O₅ doped with caesium. After the conversion in each of the first three layers the temperature is between 400 and 450 °C, after

the caesium doped layer the temperature is between 370 and 380 °C. Heat exchangers between the layers reduce the temperature and the waste heat is used to heat a partial flow before entering the contact tower.

In the absorber (12) the SO₃ is absorbed in concentrated sulphuric acid and cooled in a shower cooler with water from a nearby river. Before leaving through the stack aerosols in the waste gas are removed by candle filters (13). The conversion rate is between 99.0 and 99.5 %.



Source: Operator information (2016)

Figure 1: Process schema of the reference installation.

3 CURRENT EMISSION AND CONSUMPTION LEVELS

3.1 Air

SO₂ and SO₃ (H₂SO₄ aerosols) are the major air emissions of the contact process. NO_x arise from residual ammonia in the sulphide containing gas or burning at high temperatures.

3.1.1 Sulphur dioxide (SO₂)

The formation of SO₂ emissions is due to an incomplete reaction of SO₂ into SO₃ on the catalyst. SO₂, which is not converted into SO₃, is hardly absorbed in water. SO₂ emissions are dependent on SO₂ content of the raw gases and on the conversion rate of the contact process (UMWELTBUNDESAMT 2001).

Emission limit values for SO₂ of 1,000 mg/Nm³ as half hourly averages and 150 kg/d are prescribed by permit. Approx. 20 tons of SO₂ (i.e. ca. 55 kg/d) are discharged yearly. The distribution of half hour average values and daily average values of SO₂ emissions are presented in Table 1.

In the year 2015 more than 98% of the half hourly averages (HHA) and more than 99% of the daily averages (DA) were within the range of 200 – 500 mg/Nm³. Over a period of 6 years (2010 – 2015) 98.6% of the HHA were also within the above mentioned range.

Emissions of SO ₂ [mg/Nm ³]	Half hourly averages (2010 – 2015)		Half hourly averages (2015)		Daily averages (2015)	
0.1 – 100	11	(0.0%)	3	(0.0%)	0	(0.0%)
>100 – 200	21	(0.0%)	1	(0.0%)	0	(0.0%)
>200 – 300	9,430	(9.8%)	1,060	(6.6%)	17	(5.0%)
>300 – 400	38,964	(40.5%)	9,092	(57.0%)	201	(58.9%)
>400 – 500	46,436	(48.3%)	5,506	(34.5%)	120	(35.2%)
>500 – 600	1,133	(1.2%)	212	(1.3%)	3	(0.9%)
>600 – 700	122	(0.1%)	64	(0.4%)	0	(0.0%)
>700 – 800	17	(0.0%)	2	(0.0%)	0	(0.0%)
>800 – 900	13	(0.0%)	1	(0.0%)	0	(0.0%)
>900 – 1,000	15	(0.0%)	1	(0.0%)	0	(0.0%)
>1,000.0	74	(0.1%)	3	(0.0%)	0	(0.0%)
Total	96,236	(100.0%)	15,945	(100.0%)	341	(100.0%)

Table 1:
SO₂ emissions to air from steel mill H₂SO₄ plant. (Source: Operator information 2016).

Chronological sequences of half hourly averages and daily averages of SO₂ emissions are presented in Figure 2 and Figure 3.

Figure 2:
Half hourly averages of
SO₂ emissions to air
from steel mill H₂SO₄
plant.

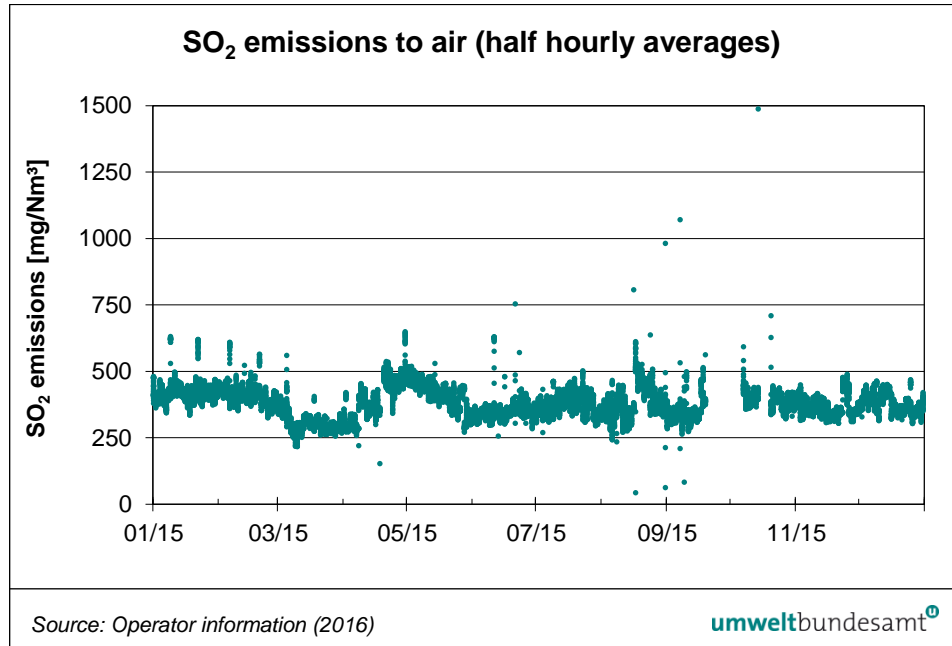
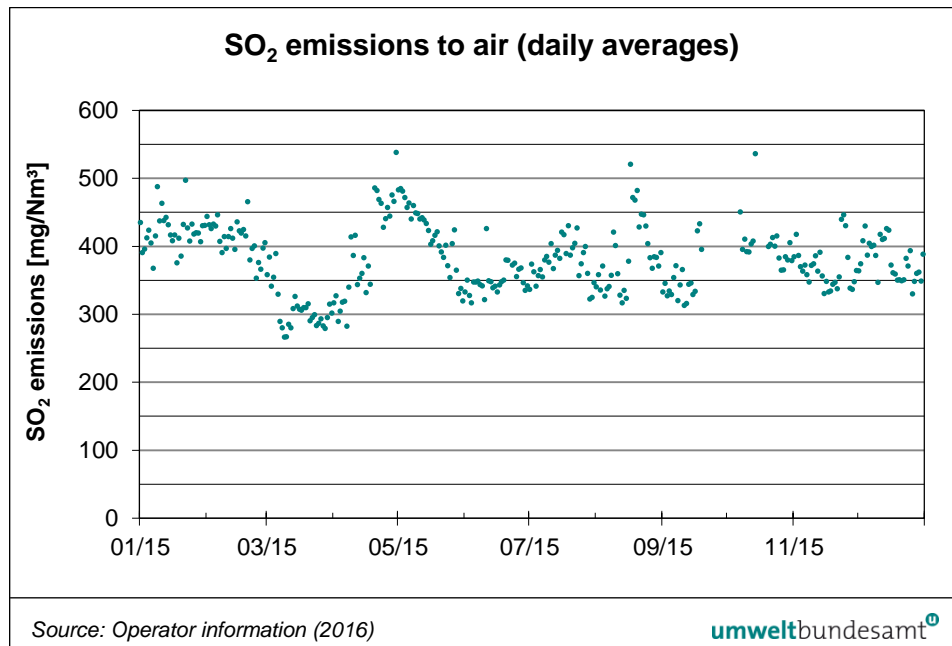


Figure 3:
Daily averages of SO₂
emissions to air from
steel mill H₂SO₄ plant.



3.1.2 Sulphur trioxide (SO₃)

The formation of SO₃ emissions takes place due to an incomplete absorption. SO₃ emissions have to be measured every two weeks and must not exceed 60 mg/Nm³.

The distribution of SO₃ emissions over a period of 6 years (2010 – 2015) are presented in Table 2. All values are under 50 mg/Nm³ and therefore below the emission limit value. Over 90% of the periodically measured data is within the range of 10 – 40 mg/Nm³.

Emissions of SO ₃ [mg/Nm ³]	averages* (2010 – 2015)	
0 – 5	0	(0.0%)
6 – 10	0	(0.0%)
11 – 15	6	(8.6%)
16 – 20	8	(11.4%)
21 – 25	29	(41.4%)
26 – 30	9	(12.9%)
31 – 35	9	(12.9%)
36 – 40	4	(5.7%)
41 – 45	3	(4.3%)
46 – 50	2	(2.9%)
>50	0	(0.0%)
Total	70	(100.0%)

Table 2: SO₃ emissions to air in the years 2010 to 2015. (Source: Operator information)

*) averages are calculated per month from two sets of three half hour measurements each.

Chronological sequences of SO₃ emissions over six years (2010 – 2015) are presented in Figure 4 according to Table 2.

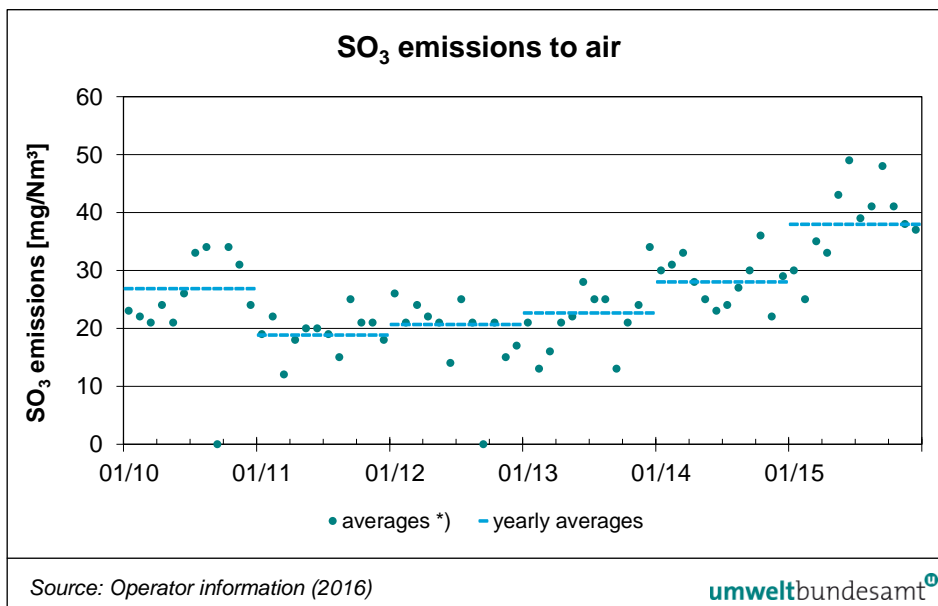


Figure 4: SO₃ emissions to air in the years 2010 to 2015. (Source: Operator information 2016; *) averages are calculated per month from two sets of three half hour measurements each.)

3.1.3 Nitrogen oxides (NO_x)

NO_x emissions are measured yearly. Since there is no regulation in the permit, there is no emission limit value. Table 3 presents the results for the years 2010 to 2015.

The emission values range from 31 – 131 mg/Nm³ with oxygen contents between approx. 7.5 – 9.5%.

Table 3:
*NO_x emissions to air
 from steel mill H₂SO₄
 plant. (Source: Operator
 information 2016).*

Year	NO _x [mg/Nm ³]	Oxygen content [vol.%]
2010	104	8.3
2011	131	7.9
2012	103	9.4
2013	66	8.6
2014	72	8.4
2015	31	7.6

The values are the average of three half hourly average samples referring to standard conditions and dry air.

3.2 Water

Waste water arises from drying the gas after the incinerator in the condensing unit and in the stripping process, which is not part of sulphuric acid reference plant. The waste water is treated together with other waste water streams from the coking plant at the municipal waste water treatment plant. The collective waste water from the coking plant and the affiliated plants is monitored together.

Due to the local conditions (e.g. availability of sufficient cooling water; cold climatic European region) and in accordance with the permit and the horizontal BREF Industrial Cooling Systems, “once through cooling systems” without cooling towers are installed to avoid e.g. the formation of “industrial snow and ice” resulting from condensing steam emissions from cooling towers during winter.

3.3 Waste

Approximately every four years broken catalyst beads and dust are removed from the catalyst layers and fresh catalyst is added. No other wastes arise from the production process.

3.4 Energy

The sulphuric acid production is an exothermic process. Heat from burning the H₂S/NH₃-vapor from the stripping process is used to produce 5 – 6 t/h steam with 45 bar and 250 °C. This steam is used for the stripping process. With the excess heat from the catalytic oxidation of SO₂ to SO₃ a partial flow before entering the contact tower is heated. The residual flow is heated with burners using coke oven gas as fuel. Overall more heat is needed than excess heat is produced.

4 REFERENCES

UMWELTBUNDESAMT (2001): Wiesenberger, H.; Kircher, J.: Stand der Technik in der Schwefelsäureerzeugung im Hinblick auf die IPPC-Richtlinie. Monographien, Bd. M-137. Umweltbundesamt, Wien.