

SULPHURIC ACID PRODUCTION

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 furthermore used for the production of explosives, synthetics, viscose and washing agents and for special applications in the chemical industry.

The sulphuric acid production plant the reference installation is located at a local industrial park. The location is connected to the railway network and has a shipment point for loading and unloading of ships.

The two production lines use purified liquid sulphur from oil refineries as raw material. After combustion, SO₂ is subsequently oxidised and absorbed in a Double Contact Double Absorption process resulting in sulphuric acid. Waste heat is utilized in waste heat boilers and the steam is converted in a steam turbine.

Both production lines have a combined capacity of approx. 240,000 t/a. Sulphuric acid is produced with a concentration of 96 – 98%. Concentrations between 30 % and 80 % are produced in smaller batches.

2 INDUSTRIAL PROCESSES USED

Starting point for the production of sulphuric acid at the reference installation utilizing a double contact double absorption process is purified liquid sulphur. The liquid sulphur is delivered at 140 – 150 °C. The double contact process can be utilized when an autothermic operation is possible. Therefore, the SO₂ concentration has to be at least 4% in the reaction gases.



In the first step the sulphur is combusted in rotary burners with an excess of dry air (dried with sulphuric acid). The oxygen level is adjusted to the subsequent step to ensure a complete oxidation to SO₃. A waste heat boiler is used to reduce the gas temperature to 450 °C and to produce steam with 400 °C and 40 bars. The gas stream containing SO₂ from reaction (1) is subsequently fed into the catalytic converter without further purification.

In the second step the gas containing sulphur dioxide reacts in the contact tower with excess oxygen to sulphur trioxide (2). The contact tower consists of four catalyst layers, each with a size of approx. 20 m³ of V₂O₅ based catalyst. Since

the conversion is an exothermic process, the gas temperature rises from approx. 400 – 450 °C to 600 – 650 °C. Heat exchangers between the catalyst layers reduce the gas temperature to approx. 400 – 450 °C.

With double contact processes SO₃ is absorbed in an intermediate absorber installed after the second catalyst layer. Gases supplied to the intermediate absorber are cooled in counter current to the gases leaving the intermediate absorber, thereby SO₂ gases leaving the intermediate absorber being heated. The gases are conducted to the final catalyst layer for the conversion of the residual SO₂ to SO₃. The reaction product is absorbed in a final absorber resulting in sulphuric acid (3) with a concentration of 96 – 98%.

With the intermediate absorber after the third catalyst layer the reaction equilibrium can be shifted towards SO₃ by removing the product. Thus higher conversion rates can be achieved resulting in lower SO₂-emissions. The intermediate absorber can be placed after the second or third catalyst bed.

The gas leaving the stack has a SO₂ concentration of approx. 300 – 700 mg/Nm³. The conversion rate is between 99.82 and 99.85% (source: operator information). Sulfuric acid aerosols in the waste gas stream of line one are removed by Kimre B-Gon Filters, aerosols in the stream of line 2 are removed by use of cartridge filters.

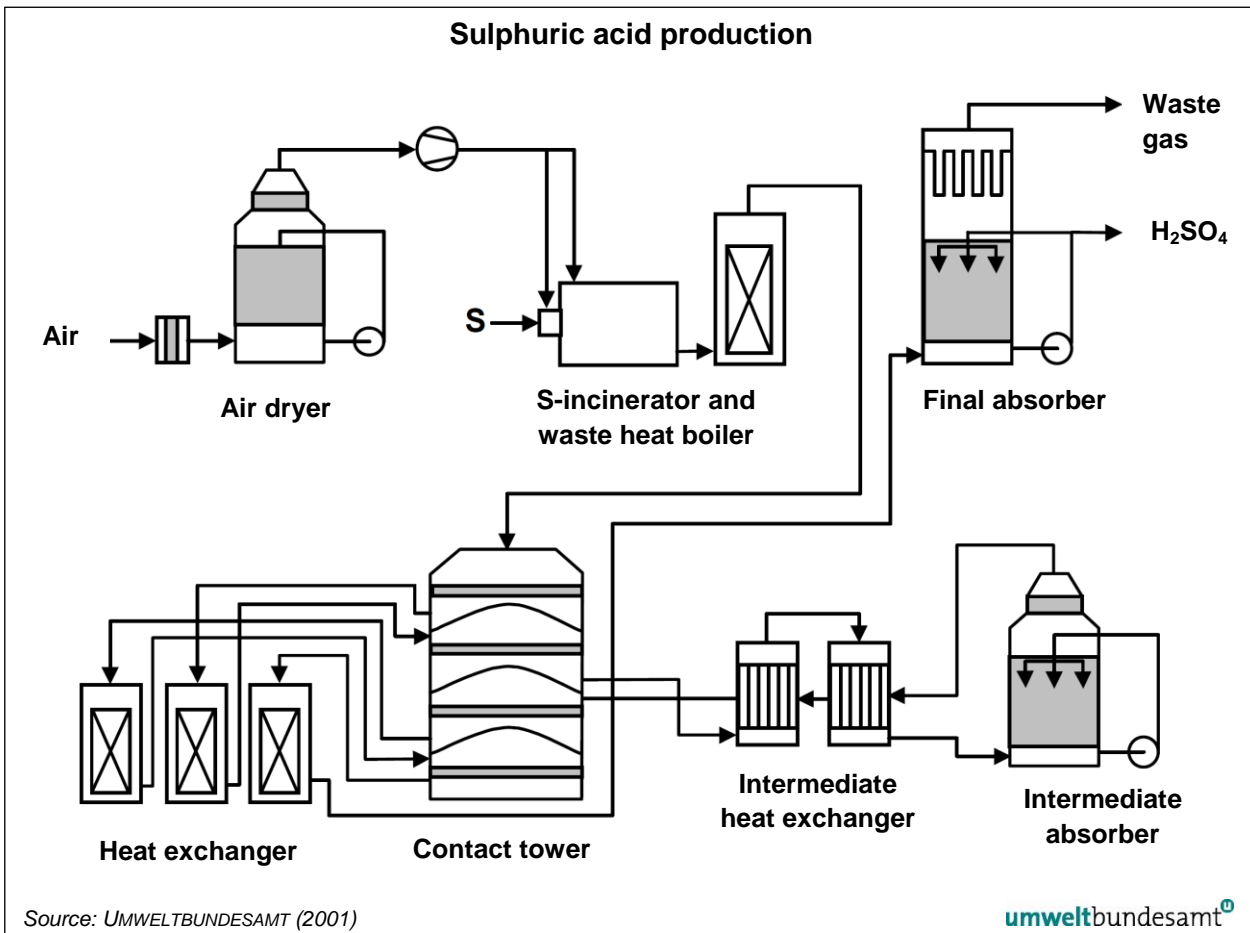


Figure 1: Schematic diagram of the sulphuric acid production.

3 CURRENT EMISSION AND CONSUMPTION LEVELS

3.1 Air

SO₂ and SO₃ (H₂SO₄ aerosols) are the major air emissions of the contact process.

The formation of SO₂ emissions is due to an incomplete reaction of SO₂ into SO₃ in the catalyst beds. 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. The conversion rate is highly dependent on operating characteristics such as working temperature, O₂/SO₂ ratio, and time rate of change of the SO₂ content in the reaction gas.

Therefore, the optimisation of the O₂/SO₂-ratio and lowering the entrance temperature in the single catalyst beds is shifting the thermodynamic equilibrium to the product side. Additionally, activity losses of the catalyst can be avoided.

The two sulphuric acid production lines have waste gas streams of 40,000 Nm³/h and 25,000 Nm³/h, respectively.

The requirements of the local permitting authority dated Feb. 2nd, 1981 do include an emission limit value of 1,030 mg/Nm³ for line 2.

The SO₂ emissions are monitored continuously for both lines. The distribution of two hours average values and daily average values of SO₂ emissions over 6 months (November 2015 until April 2015) for both lines are presented in Table 1.

Table 1: SO₂ emissions to air for line 1 and 2. (Source: Operator information)

Emissions of SO ₂ [mg/Nm ³]	2-hours averages				daily averages			
	Line 1		Line 2		Line 1		Line 2	
0 – 300	0	(0.0%)	13	(0.6%)	0	(0.0%)	0	(0.0%)
301 – 400	195	(9.1%)	284	(13.5%)	15	(8.2%)	24	(13.2%)
401 – 500	1,380	(64.1%)	946	(44.8%)	120	(65.9%)	87	(47.8%)
501 – 600	576	(26.7%)	712	(33.7%)	47	(25.8%)	57	(31.3%)
601 – 700	1	(0.0%)	86	(4.1%)	0	(0.0%)	9	(4.9%)
701 – 800	1	(0.0%)	69	(3.3%)	0	(0.0%)	5	(2.7%)
>800	1	(0.0%)	1	(0.0%)	0	(0.0%)	0	(0.0%)
Total	2,154	(100.0%)	2,111	(100.0%)	182	(100.0%)	182	(100.0%)

The emission values refer to dry gas and standard conditions (0°C and 1,013 mbar). The oxygen content of the waste gas stream is approximately 7 – 8% O₂.

The emission values (two hours average values and the daily averages) for line 1 are almost uniformly within 300 – 600 mg SO₂/Nm³ 99.9%. Approximately a quarter of the detected values are upper range of 500 – 600 mg SO₂/Nm³. The majority of the two hours average values (64.1%) and the daily averages (65.9%) were detected between 400 – 500 mg SO₂/Nm³. The emission values for line 2 were in the range of 300 – 800 mg SO₂/Nm³, whereas only 3.3% of the two hours averages and 2.7% of the daily averages were detected between

700 – 800 mg SO₂/Nm³. The majority of the emission values (92% of the two hours averages and 92.3% of the daily averages) were between 300 – 600 mg SO₂/Nm³.

The SO₂ emissions correspond to the amount of sulphur combusted in stage 1 one of the process. Higher amounts of sulphur input lead to higher SO₂ emissions. The sulphur input ranges are 2.5 – 4.0 t/h for line 1 and 3.5 – 6.5 t/h for line 2.

Chronological sequences of two hour average values of SO₂ emissions for line 1 are presented in Figure 2 and for line 2 in Figure 3.

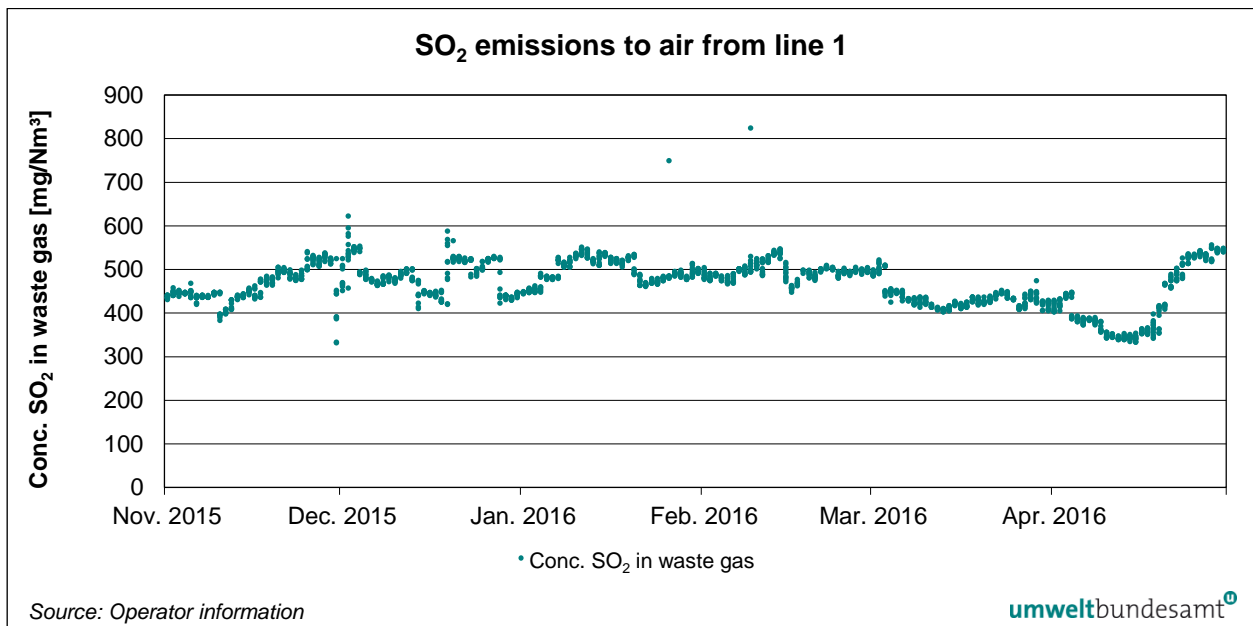


Figure 2: SO₂ emissions to air from line 2 in relation to oxidised sulphur (2h-averages).

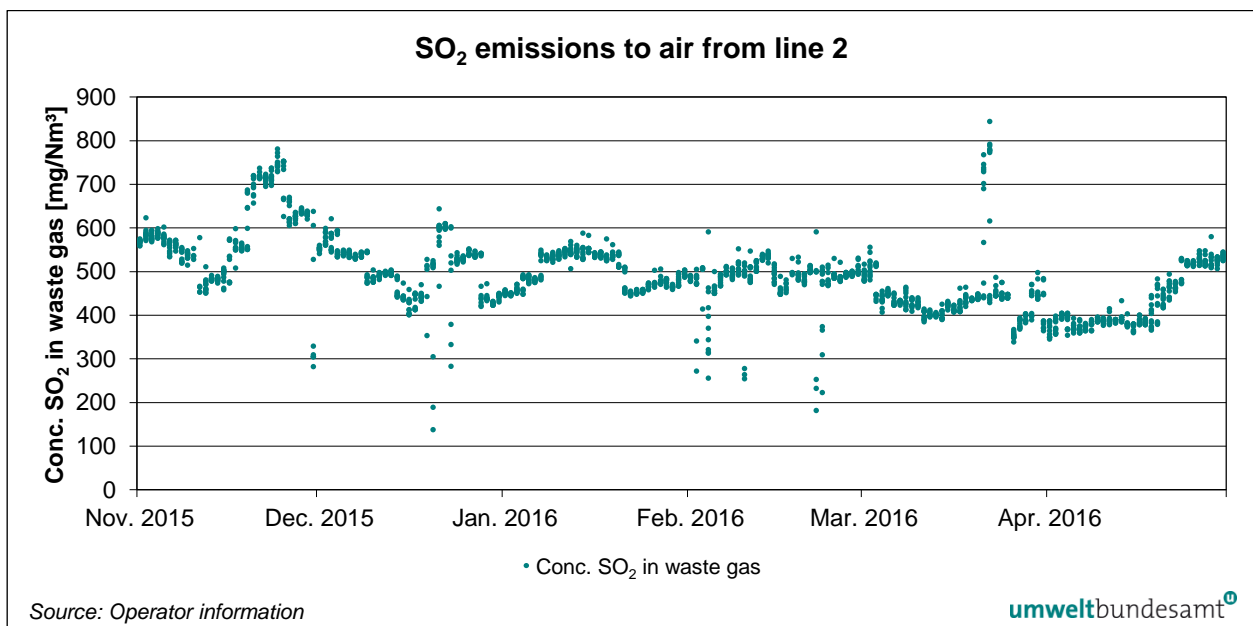


Figure 3: SO₂ emissions to air from line 2 in relation to oxidised sulphur (2h-averages).

The formation of SO_3 emissions and H_2SO_4 mists takes place due to an incomplete absorption. There are no measures to reduce SO_3 emissions to air. No emission limit values are specified for SO_3 in line one. The emission limit in the official notification document for line 2 was specified to be below $0.4 \text{ kg SO}_3/\text{t H}_2\text{SO}_4$.

3.2 Water

The reference installation has several wells next to a river to provide water in drink water and process water quality. No waste water arises from the sulphuric acid production.

3.3 Waste

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

3.4 Energy

Excess heat is used at the reference installation to produce 30 t/h steam with 40 bar and 400 °C. The steam is converted into electricity by an on-site steam turbine which is cooled by air coolers.

The sulphuric acid production is in general an exothermic process. Figure 4 shows a literature known energy scheme of a double contact double absorption process with a SO_2 concentration of 11% in the gas stream and a capacity of 1.000 t/d H_2SO_4 (MÜLLER 1994).

Energy input into the system comes from the chemical energy of the sulphur and the electrical energy from the ID fans (a).

Superheated steam is produced to recover process heat:

- from the combustion gases after the incinerator (b),
- in the boiler (c),
- in the steam superheater (e) after catalyst layers (d), (f) and (k),
- in a heat exchanger (g)
- and an economizer (l).

Some heat recovered in the third catalyst layer (h) is used to reheat the reaction gas after the intermediate absorber (j) in the intermediate heat exchanger (i)

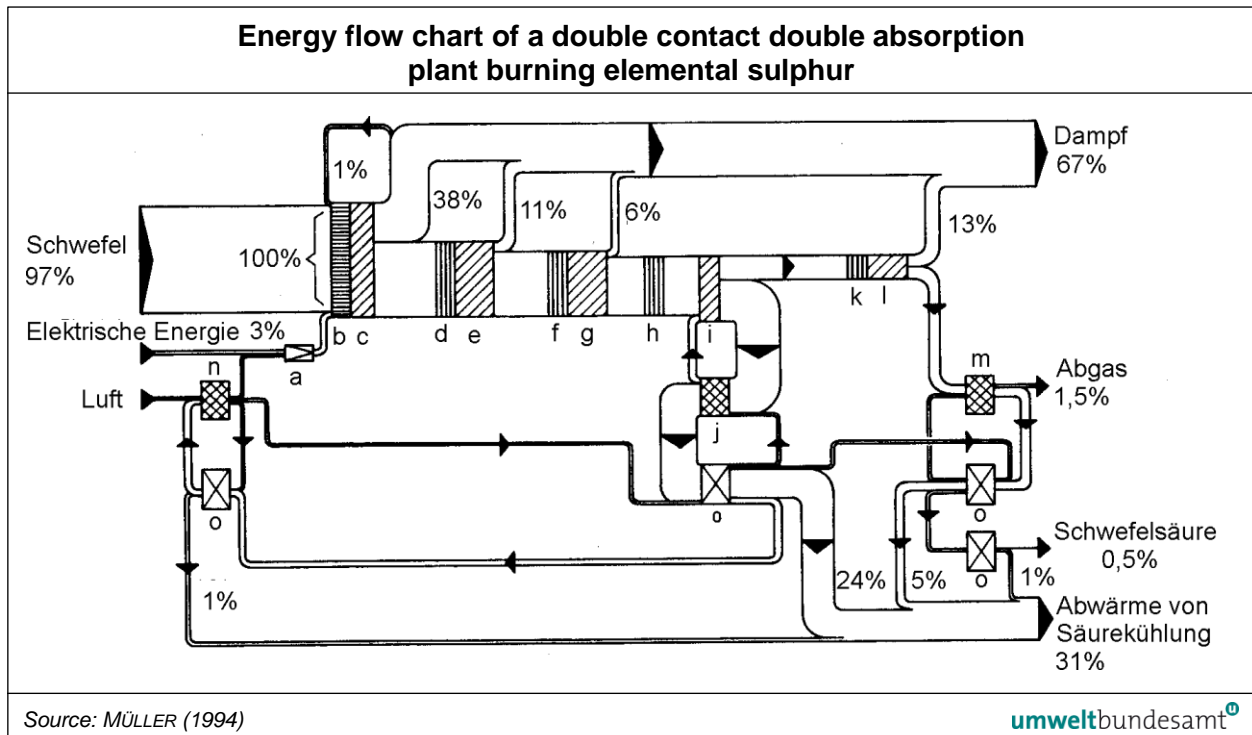


Figure 4: Energy flow chart of a double contact double absorption plant burning elemental sulphur (1,000 t/d H_2SO_4 , 11% SO_2) (source: MÜLLER 1994)

Up to approx. 67% of process waste heat can be converted to superheated steam. Approx. 30 – 40% of waste heat, which is released in the intermediate absorber (n), the final absorber (o) and the gas drying (m), is available at a temperature level between 85 and 120 °C. It is possible to use this energy; the rest is lost as thermal loss, in the waste gas and the product.

By using the waste heat a thermal efficiency of 85 – 90% is possible. State of the art sulphuric acid plants generate approx. 6 GJ/t H_2SO_4 (KONGSHAUG 1998).

In addition to the thermal energy, which comes from the sulphur's chemical energy, energy is needed for the gas transport and added by the electric ID fans. The energy needed for the ID fans, which is the greatest part of the plant's electricity demand, ranges from 35 to 50 kWh/t H_2SO_4 – depending on the SO_2 concentration in the raw gas – and increases with decreasing SO_2 concentrations.

4 REFERENCES

KONGSHAUG (1998): Energy consumption and greenhouse gas emissions in fertilizer production; In: IFA technical conference papers – Marrakech (Marocco) 28 September - 1 October 1998

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