

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 by the reference installation for the production of viscose fibre.

The reference installation is operating three sulphuric acid production lines using different technologies for the production. All three production plants work after the principle that sulphur or sulphur containing waste gases are burned.

Sulphur-containing gases generated during the spinning process are collected and recovered as the chemicals carbon disulphide and sulphuric acid. The co-product sodium sulphate is produced from the input chemicals sulfuric acid and sodium hydroxide solution. (Source: Operator information 2016).

2 INDUSTRIAL PROCESSES USED

The production of viscose fibres includes the treatment of pulp in several process steps with carbon sulphide and a subsequent spinning step in sulphuric acid baths. The waste gases contain CS₂ and H₂S (strong odorous gases and weak odorous gases) and are combusted to avoid odour emissions. The thereof obtained H₂SO₄ is reused in the production process.

Table 1: Information of the three sulphuric acid production lines 2015. (Source: Operator information 2016)

	Technology	Output H ₂ SO ₄ t/d	Output steam GJ/d	Input	Input	Input	Conversion %
				Liquid sulphur t/h	Strong gas m ³ /h	Weak gas m ³ /h	
Sulphuric acid production line 1	dry contact process	300	964 (45 bar)	4.1	-	-	99.9
Sulphuric acid production line 2	wet/dry contact process	72	203 (45 bar)	0.68	80	6,560	99.8
Sulphuric acid production line 3	TOPSOE	151	924 (45 bar)	0.69	850	24,600	99.9

Another process used to produce sulphuric acid is the combustion of elemental sulphur. The resulting sulphur dioxide is converted in sulphur trioxide in a double contact process and finally absorbed in water for the formation of H_2SO_4 . Elemental sulphur is also added to strong odour gases if the sulphur concentration is not high enough.

The reference installation operates three sulphuric acid production lines as shown in Table 1.

Description sulphuric acid production line 1 – dry contact process

In production line 1 elemental sulphur is combusted for the formation of SO_2 , which is subsequently oxidised to SO_3 in a 4 layer double contact process with intermediate absorption after layer 3.

Sulphur handling systems

Liquid sulphur is pumped to the burner of the furnace from the sulphur storage tank. All pipes and filters are double-walled and heated in order to avoid the solidification of liquid sulphur before it is burned.

Sulphur furnace

The liquid sulphur (ca. 4,000 kg/h) is injected into the sulphur furnace with a pressurised atomiser burner. The combustion air is dried in a drying tower with concentrated H_2SO_4 in counter-flow.

The gas after the furnace contains approx. 10 – 11 vol% SO_2 , the temperature in the furnace is approx. 1,070 °C. After the furnace the gas is cooled to approx. 460 °C in the waste heat boiler.

Contact tower – dry contact process

The conversion of SO_2 to SO_3 is carried out in the contact tower in 4 layers applying a vanadium pentoxide catalyst.

Since the conversion is an exothermic process, the gas temperature rises from approx. 460 °C to 600 °C (layer 1). For shifting the process to the product side, the temperature is lowered after each layer by a heat exchanger to approx. 460 °C.

Acid unit

After layer 3, the gas is cooled with boiler feed water to 225 °C and enters the intermediate absorber. SO_3 is removed from the gas stream resulting in concentrated sulphuric acid.

The gas which does not contain SO_3 anymore is heated to 420 °C with steam and conducted to the fourth layer. The remaining SO_2 is oxidised to SO_3 and, after heat exchange, conducted to the final absorber. In the final absorber, SO_3 is removed via concentrated, trickled H_2SO_4 in counter flow. The resulting sulphuric acid is stored in a 2,000 t tank or is pumped to the viscose production unit.

The exhaust gas is cleaned by cartridge filters to avoid sulphuric acid mist. The waste gas stream is 22,500 Nm^3/h (source: operator information 2015).

Description sulphuric acid production line 2 – LURA 1

This H_2SO_4 production unit was built in order to eliminate H_2S and CS_2 from the strong odour gases which occur during the production of viscose. The strong gases contain 40 – 45 Vol% H_2S and 15 – 25 Vol% CS_2 . Dependent on the

availability of strong gases from the production process elemental sulphur is fed into the line to ensure a steady SO_2 concentration in the combustion gas. The conversion to sulphuric acid is carried out in a combined wet/dry contact process (Source: Operator information 2016).

Before entering the furnace, condensate in strong odour gases is separated. The strong gases and liquid sulphur are combusted at $1,100\text{ }^\circ\text{C}$ to ensure a steady SO_2 concentration of 7 – 8 Vol%. After passing the heat recovery boiler the gas is fed into the contact tower.

Sulphur furnace

The conversion of SO_2 to SO_3 is carried out in a 4 layer contact tower applying a vanadium pentoxide catalyst.

Contact tower

Excess heat due to the chemical reaction is discharged after each layer with a heat exchanger.

The wet contact process is necessary as the gases contain water (if H_2S is burned H_2O is generated) and so H_2SO_4 is formed during the catalytic oxidation of SO_2 to SO_3 . Therefore, the gas enters the intermediate absorber after layer 3 with approx. $360\text{ }^\circ\text{C}$ to avoid corrosion due to condensation of H_2SO_4 .

H_2SO_4 mist formed in the intermediate absorber is separated by mist filter.

The remaining SO_2 is oxidised to SO_3 in layer 4 by a dry contact process and removed as H_2SO_4 in the final absorber.

Both absorption towers (intermediate absorber after level 3 and final absorber after level 4) are filled with packing material. The gas stream is channelled in counter current to H_2SO_4 .

Absorption towers

The formed H_2SO_4 is conducted continuously to tanks. It is reused in the spinning process.

H_2SO_4 mist in the exhaust gas ($6,500\text{ Nm}^3/\text{h}$) is abated by cartridge filters (Source: Operator information 2016).

Description sulphuric acid production line 3 – TOPSOE

The production line 3 is utilized, as production line 2, to abate H_2S and CS_2 generated in the production of viscose.

Therefore, strong odour gases from the spinning process and weak odour gases from the spinning vats (serves also as combustion air supply) are combusted in a furnace for the formation of SO_2 . Before the weak gas enters the furnace, it is cleaned via a gas scrubber to remove remaining substances and solids from the spinning baths.

Sulphur furnace

To ensure constant operating conditions (SO_2 and temperature), liquid sulphur is dosed. If necessary to reach the required reaction temperature, fuel oil extra light is co-combusted. The ignition burner uses natural gas.

The combustion gas is cooled in the waste heat boiler and the energy is used for the steam production.

The gas is conducted with $400\text{ }^\circ\text{C}$ in the converter, which has 2 catalyst layers for oxidising SO_2 to SO_3 . After layer 1, the gas is cooled down by an intermediate cooler. Both layers are filled with TOPSOE- H_2SO_4 -catalyst.

SO₂-converter

Subsequently the gas is cooled to approx. 290 °C in a process gas cooler. Water is dosed adequately for the formation of acid in terms of steam after the cooler. Condensation nuclei are added and the gas is conducted to the WSA-condenser.

WSA condenser The WSA condenser is a vertical tube falling film condenser/concentrator with tubes made of borosilicate, acid and shock resistant glass. The process gas flows up the tubes and is cooled by ambient air circulating on the outside of the tubes. Sulphuric acid condenses in the tubes and flows downward counter-current to the process gas. This contact with the hot process gas concentrates the acid to the desired concentration. The acid is collected (260 °C) cooled by adding already cooled down acid and delivered to the storage tanks with 35 °C. (<http://www.sulphuric-acid.com/techmanual/Technology/wsa.htm>)

The condenser is cooled with air. The generated hot air (230 °C) is used to pre-heat the boiler feed water.

To reduce the remaining SO₂ contamination in the exhaust air, a peroxide scrubber is installed. The total efficiency is about 99.9%. The exhaust gas volume is 21,000 Nm³/h.

3 CURRENT EMISSION AND CONSUMPTION LEVELS

3.1 Air

SO₂ and SO₃ (H₂SO₄ aerosols) are the major air emissions in the production of sulphuric acid.

SO₂ emissions are emitted 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, the oxygen concentration, the reaction parameters (temperature) and the resulting conversion rate of the contact process.

In Table 2 emission limit values (ELV) are presented. Line 1 and line 2 have similar ELVS of 700 mg/Nm³ and 625 mg/Nm³ respectively. Line 3 has an emission limit value of 200 mg/Nm³.

The emissions have to be monitored continuously according to the figures presented in Table 2.

Table 2:
Emission limit values for
SO₂ of sulphuric acid
production lines 1-3.
(Source: Operator
information 2016)

	Emission limit values ^{1), 2), 3)}	monitoring
line 1 dry contact process	700 mg/Nm ³	continuous recorded as daily average
line 2 wet/dry contact process	625 mg/Nm ³	continuous recorded as daily average
line 3 TOPSOE	200 mg/Nm ³	continuous, recorded as daily average

¹⁾ Ge20-13-01-310-2010, Ge20-13-01-372-2010

²⁾ Ge20-13-01-158-2010, Ge20-13-01-372-2010

³⁾ Ge20-13-01-315-2003

The distributions of the daily average values of SO₂ emissions for the 3 lines are presented in Table 3 and Figure 2. The daily averages were recorded during April and July 2016. According to the emission limit values the lowest emissions were obtained for line 3 (TOPSOE process with subsequent H₂O₂ scrubber) were the values were in the range of 120 – 160 mg/Nm³. For line 1 and 2 the majority of daily averages in the reference period were between 500 – 700 mg/Nm³.

Some measured values are higher than the emission limit values because the plant is operated at the upper capacity limit. For the emission limit value compliance, validated values (measured values minus the measurement uncertainty) are used. All validated values are below the emission limit value.

[mg/Nm ³]	Line 1		[mg/Nm ³]	Line 2		[mg/Nm ³]	Line 3	
	No. of values			No. of values			No. of values	
500 – 600	18	16%	400 – 500	3	2%	75 – 100	0	0%
600 – 700	60	52%	500 – 600	8	7%	100 – 125	2	2%
700 – 800	37	32%	600 – 625	8	7%	125 – 150	119	98%
Total	115	100%	625 – 650	38	31%	150 – 175	0	0%
			650 – 700	64	53%	175 – 200	0	0%
			Total	121	100%	Total	121	100%

Table 3:
Daily averages of SO₂ emissions to air.
(Source: Operator information 2016)

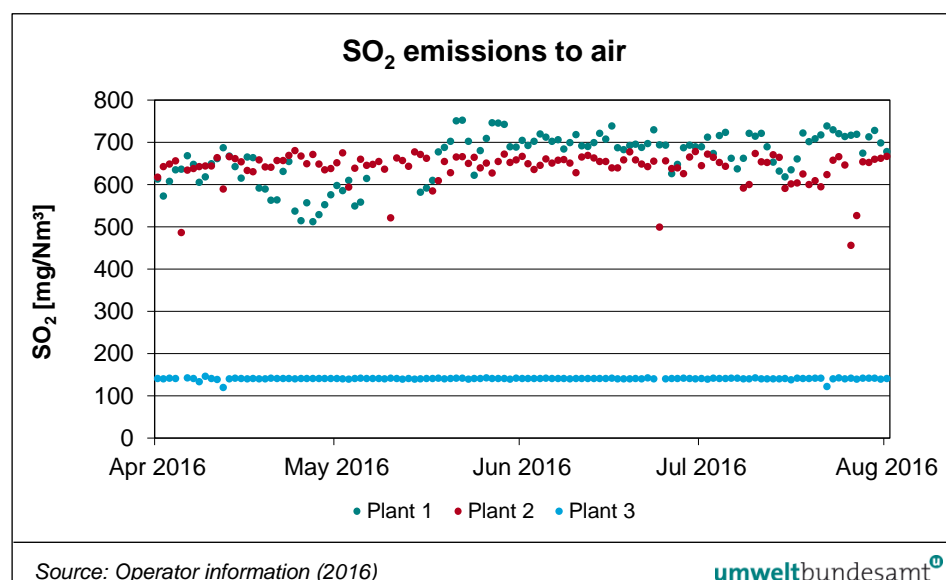


Figure 1:
Daily averages of SO₂ emissions to air.

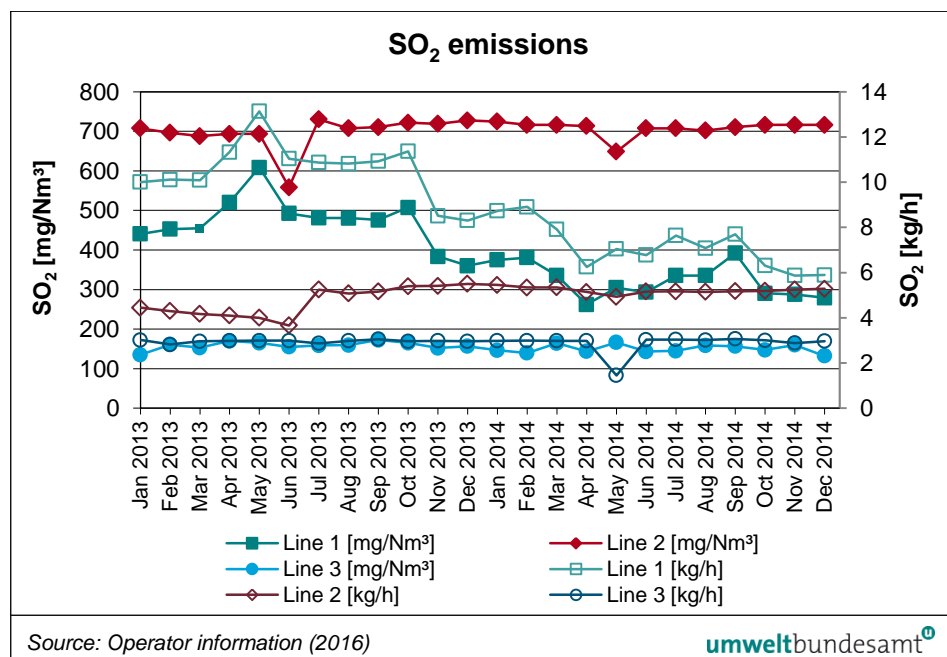
Month	line 1	line 2	line 3	line 1	line 2	line 3
	[mg/Nm ³]			[kg/h]		
Jan 2013	441	708	135	10.01	4.45	3.02
Feb 2013	453	697	161	10.11	4.30	2.82
Mar 2013	455	688	153	10.09	4.17	2.96
Apr 2013	520	694	170	11.33	4.10	2.98
May 2013	609	694	165	13.14	4.00	2.99
Jun 2013	492	558	155	11.04	3.66	2.99
Jul 2013	481	730	158	10.87	5.25	2.87

Table 4:
Monthly averages of SO₂ emissions to air 2013 and 2014. (Source: Operator information 2016)

Month	line 1	line 2	line 3	line 1	line 2	line 3
	[mg/Nm ³]			[kg/h]		
Aug 2013	481	708	159	10.82	5.08	2.98
Sep 2013	476	711	173	10.93	5.16	3.05
Oct 2013	508	722	165	11.37	5.40	2.96
Nov 2013	384	719	152	8.51	5.41	2.98
Dec 2013	360	728	157	8.31	5.50	2.96
Jan 2014	375	725	147	8.73	5.45	2.98
Feb 2014	381	716	140	8.91	5.34	2.99
Mar 2014	336	716	164	7.91	5.35	2.98
Apr 2014	262	713	144	6.25	5.14	2.98
May 2014	305	649	166	7.05	4.93	1.45
Jun 2014	293	708	143	6.78	5.16	3.03
Jul 2014	336	708	145	7.64	5.17	3.04
Aug 2014	336	702	159	7.08	5.15	3.02
Sep 2014	392	711	157	7.70	5.18	3.07
Oct 2014	290	716	147	6.31	5.19	3.00
Nov 2014	288	716	160	5.87	5.25	2.88
Dec 2014	279	716	132	5.89	5.28	2.97

In Table 4 and Figure 2 monthly averages of SO₂ emissions for the three production lines over a period of two years (January 2013 – December 2014) are displayed. The monthly averages (MA) of line 1 (double contact dry process) are mostly in the range of 200 – 500 mg/Nm³ with only one value above 500 mg/Nm³. The range of monthly averages for line 2 (wet/dry contact process) for the two year period (2013 – 2014) is 600 – 700 mg/Nm³. The lowest monthly averages within the range of 100 – 200 mg/Nm³ were obtained for line 3 (TOPSOE process with subsequent H₂O₂ scrubber).

Figure 2:
Monthly averages of
SO₂ emissions to air.



The formation of SO₃ emissions takes place due to incomplete absorption. SO₃ emissions are monitored periodically 4 times a year for line 1 as well as line 2 and monthly for line 3. No measures are taken to reduce SO₃ emissions to air and no emission limit value is permitted.

SO ₃ [mg/Nm ³]	Minimum	Yearly Average	Maximum
Line 1	9.1	16.5	22.4
Line 2	12.2	21.2	26.3
Line 3	7.6	20.3	50.6

Table 5:
SO₃ emissions to air for
production lines 1,2
and 3. (Source:
Operator information
2016)

Minimum and Maximum emission values represent averages over four hours. All emission values were obtained during 1 year (June 2015 – July 2016) and refer to standard conditions (0°C and 1,013 mbar) and dry gas.

Emission values for SO₃ are presented in Table 5 and range from 9.1 – 22.4 mg/Nm³ for line 1. Line 2 has a similar range from 12.2 – 26.3 mg/Nm³. Minimum values and yearly average for line 3 are also similar compared to the other production lines. The maximum value is 50.6 mg/Nm³ and therefore higher in relation to line 1 and 2.

Including the maximum averages, all SO₃ emission values are within the range of ≤50 mg/Nm³.

The sulphuric acid production lines are fully enclosed, therefore no fugitive emissions SO₂ and SO₃ occur.

Fugitive emissions

3.2 Water

No waste water arises from the sulphuric acid production.

3.3 Waste

The first catalyst layers are exchanged every 5 to 10 years, the other layers every 10 to 15 years. The decision to exchange the catalyst is made depending on the catalysts reaction rate. In between the catalyst exchanges the catalyst beads are sieved to remove dust.

Used catalyst material is recycled in the metal industry.

3.4 Energy

The sulphuric acid production is an exothermic process. Excess heat is used to produce steam.

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.

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