

Sulfur Dioxide

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Survey Table

The corrosion behavior of the individual materials was evaluated on the basis of experience gained in practice and the conditions described in the following text.

Material Type No.*	Behavior**	Material Type No.*	Behavior**	
A	Metallic materials	A 35	Platinum metals (Ir, Os, Pd, Ru) and their alloys + to –	
A 1	Silver and silver alloys	+ to –	A 36	Tin and tin alloys + to –
A 2	Aluminium	+ to –	A 37	Tantalum, niobium, and their alloys +
A 3	Aluminium alloys	+ to –	A 38	Titanium and titanium alloys +
A 4	Gold and gold alloys	+	A 39	Zinc, cadmium and their alloys + to –
A 5	Cobalt and cobalt alloys	+ to –	A 40	Zirconium and zirconium alloys +
A 6	Chromium and chromium alloys	+ to –	A 41	Other metals and alloys +
A 7	Copper	+ to –	B	Non-metallic inorganic materials
A 8	Copper-aluminium alloys	+ to –	B 1	Asbestos +
A 9	Copper-nickel alloys	+ to –	B 2	Natural stones + to –
A 10	Copper-tin alloys (bronze)	+ to ⊕	B 3	Carbon and graphite +
A 11	Copper-tin-zinc alloys (red brass)	+ to –	B 4	Binders for building materials (e.g. mortar and concrete) + to –
A 12	Copper-zinc alloys (brass)	+ to –	B 5	Acid-resistant building materials and binders (putties) +
A 13	Other copper alloys	+ to –	B 6	Glass + to ⊕
A 14	Unalloyed steels and cast steel	+ to –	B 7	Quartz ware and quartz glass +
A 15	Unalloyed cast iron	+ to –	B 8	Enamel +
A 16	High-alloy cast iron, high-silicon cast iron	+ to ⊕	B 9	Porcelain +
A 17	Structural steels with up to 12 % chromium	+ to –	B 10	Stoneware +
A 18	Ferritic chromium steels with more than 12 % chromium	+ to –	B 11	Refractory materials +
A 19	Ferritic-austenitic steels with more than 12 % chromium	+ to –	B 12	Oxide ceramic materials + to –
A 20	Austenitic chromium-nickel steels	+ to –	B 13	Metallo-ceramic materials (carbides, nitrides) +
A 21	Austenitic chromium-nickel-molybdenum steels	+ to ⊕	B 14	Other inorganic materials + to –
A 22	Austenitic chromium-nickel steels with special alloying additions	+ to ⊕	C	Organic materials
A 23	Special iron-based alloys	+ to –	C 1	Natural fibers (wool, cotton, silk + etc.)
A 24	Magnesium and magnesium alloys	+ to –	C 2	Bituminous compositions (bitumen, asphalt, pitch) ⊕
A 25	Molybdenum and molybdenum alloys	+ to ⊕	C 3	Fats, oils, waxes + to ⊕
A 26	Nickel	+ to –	C 4	Wood + to –
A 27	Nickel-chromium alloys	+ to –	C 5	Modified cellulose + to –
A 28	Nickel-chromium-iron alloys	+ to –	C 6	Furan resins + to ⊕
A 29	Nickel-chromium-molybdenum alloys	+ to ⊕	C 7	Polyolefins and their copolymers + to ⊕
A 30	Nickel-copper alloys	+ to –	C 8	Polyvinyl chloride and its copolymers + to ⊕
A 31	Nickel-molybdenum alloys	+ to –	C 9	Polyvinyl esters and their copolymers +
A 32	Other nickel alloys	+ to ⊕	C 10	Phenolic resins +
A 33	Lead and lead alloys	+ to ⊕	C 11	Acrylic resins + to ⊕
A 34	Platinum and platinum alloys	+ to –	C 12	Polyamides + to –
			C 13	Polyacetals ⊕ to –

Material Type No.*	Behavior**	Material Type No.*	Behavior**
C 14	Polyesters	+	
C 15	Polycarbonates	+ to -	
C 16	Polyurethanes	+ to -	
C 17	Alkyd resins	+ to -	
C 18	Epoxy resins	+ to ⊕	
C 19	Fluorocarbon resins	+	
C 20	Polyvinylidene chloride	+	
C 21	Amino resins	⊕	
C 22	Silicones	+	
C 23	Other synthetic materials	+ to ⊕	
D	Materials with special properties		
D 1	Coatings and linings	+	
D 2	Seals and packings	+	
D 3	Composite materials	+	
D 4	Heat-resistant and scaling-resistant alloys	+	
D 5	Natural and synthetic elastomers	+ to -	
D 6	Powder metallurgical materials	+ to -	

* Any notes in the text are entered under the same number as the materials, (for example A1, B5, C7)

** + resistant/⊕ fairly resistant/- unsuitable. Where no indication of corrosion resistance is made, experimental data is not available.

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Introduction

– Physical properties –

Sulfur dioxide (SO₂) is a colorless, non-combustible, toxic gas. Its most important physical properties are summarized in Table 1. Since the critical temperature is very high, sulfur dioxide can easily be condensed by compression to give a colorless, readily mobile liquid [1, 2].

Properties	Value
Melting point (101.3 kPa)	197.5 K (−75.65 °C)
Heat of fusion (melting point)	115.6 J/g
Dynamic viscosity at 273 K (0 °C)	368 Pa s
Density at 263 K (−10 °C)	1.46 g/cm ³
Critical density	0.525 g/cm ³
Critical pressure	7.88 MPa
Critical temperature	430.5 K (157.35 °C)
Boiling point under 101.3 kPa	263 K (−10 °C)
Heat of vaporization (boiling point)	402 J/g
Normal density at 273 K (0 °C) (101.3 kPa)	2.93 kg/m ³
Relative density based on air = 1 (273 K (0 °C), 101.3 kPa)	2.263
Molar volume (273 K (0 °C), 101.3 kPa)	21.9 l/mol
Standard enthalpy of formation	−297.2 kJ/mol
	−4,636 J/g
Specific heat c_p (101.3 kPa) at 273 K (0 °C)	586 J/(kg K)
Specific heat c_p (101.3 kPa) at 373 K (100 °C)	662 J/(kg K)
Specific heat c_p (101.3 kPa) at 573 K (300 °C)	754 J/(kg K)
Specific heat c_p (101.3 kPa) at 773 K (500 °C)	816 J/(kg K)

Table 1: Physical properties of sulfur dioxide [1]

Figure 1 shows the vapor pressure curves of liquid sulfur dioxide as a function of temperature and the dew points of gases with various sulfur dioxide contents under various pressures [1]. Liquid sulfur dioxide boils under normal pressure at 263 K (-10°C) and solidifies at 197.5 K (-75.65°C). Liquefied, pure sulfur dioxide does not conduct electricity; however, it becomes a good electrical conductor as a result of impurities, such as inorganic salts, and especially iodides, thiocyanates, bromides and chlorides [1, 2].

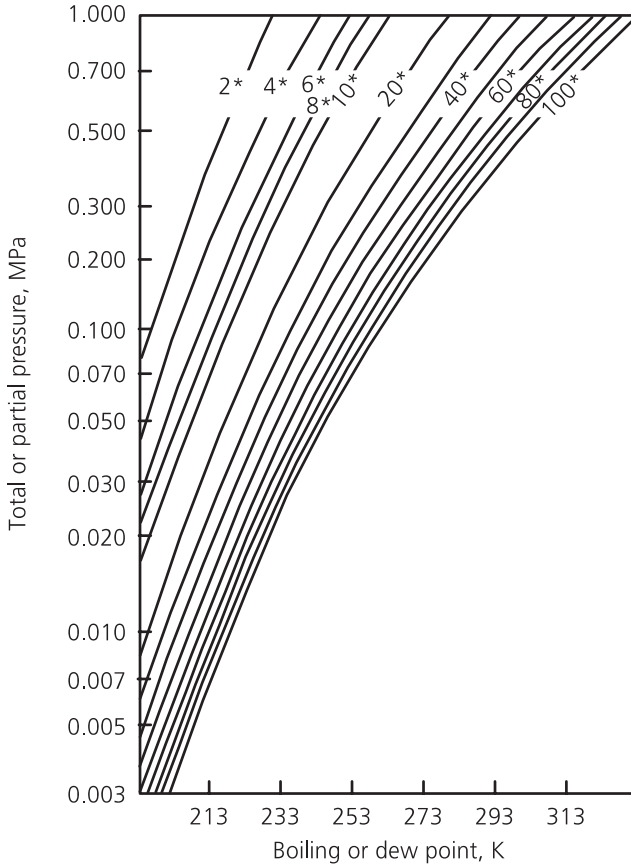


Figure 1: Equilibrium vapor pressure of pure SO_2 and dew points of SO_2 -containing gases of various concentrations as a function of the pressure [1]
* SO_2 concentrations in percent by volume

Gaseous sulfur dioxide is readily soluble in water. Its solubility increases as the partial pressure increases and the temperature drops. Figure 2 shows the relationship.

Only a small proportion of sulfur dioxide reacts with water to give H_2SO_3 , “sulfurous acid” [2, 3]. This is a weak acid which cannot be prepared in the pure state, since it dissociates completely on evaporation. One liter of water at 293 K (20°C) dissolves

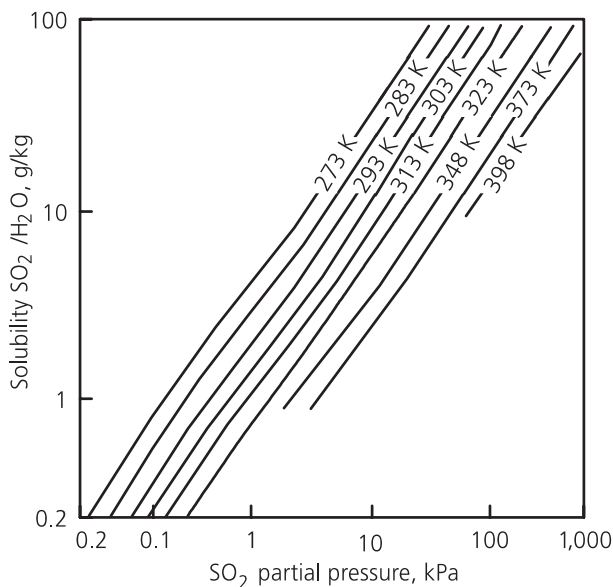
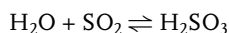
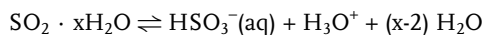


Figure 2: Solubility of sulfur dioxide in water as a function of the temperature and SO₂ partial pressure [1]

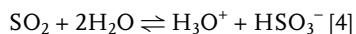
40 l sulfur dioxide. The opinion was held for a long time that such a solution contained, as just mentioned “sulfurous acid” in equilibrium with physically dissolved sulfur dioxide which would be formed by a Lewis acid/base reaction of SO₂ with H₂O according to the equation:



More recent studies have led to the conclusion that there is no indication that a compound of the formula H₂SO₃ in fact exists. Rather, it must be assumed that the hydrated SO₂ molecules form HSO₃⁻ ions directly:



or stated more simply:



Regardless of this knowledge, the term “sulfurous acid” is still used below as a synonym for the acid aqueous solution of sulfur dioxide, since there are differences in the corrosion behavior of the materials in sulfuric acid solution. Aqueous solutions of alkali metal compounds absorb considerably more sulfur dioxide than pure water because of the formation of bisulfite and sulfite ions. Because of its industrial importance, the solubility of sulfur dioxide in sulfuric acid is shown in Figure 3.

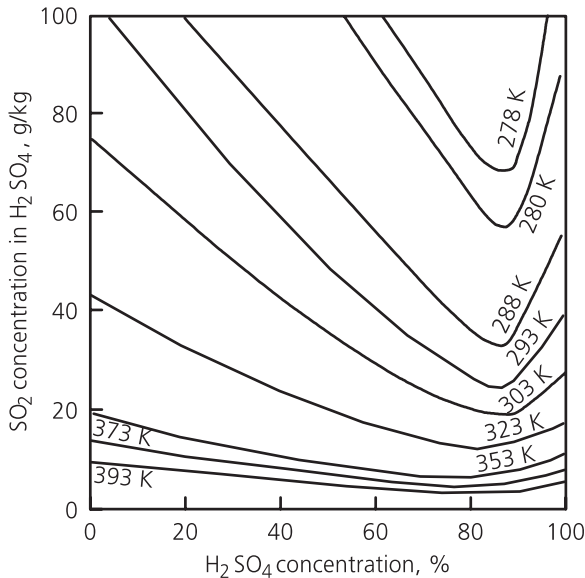


Figure 3: Solubility of SO_2 in sulfuric acid under an SO_2 partial pressure of 101.3 kPa [1]

– *Chemical properties* –

Sulfur dioxide is very stable chemically and undergoes more severe thermal dissociation only above 2,273 K (2,000 °C). It may be split by shockwaves, UV rays, X-rays or electrical discharges [1].

The chemical reaction of SO_2 with oxygen to give SO_3 is of particular interest for the production of sulfuric acid. This reaction is the most important industrial reaction of sulfur dioxide. It takes place in the gas phase only at higher temperatures, and gives a relatively high yield only with a catalyst.

In aqueous solution in the presence of activated coke or nitrous fumes, sulfur dioxide can also be oxidized to sulfuric acid by air or by an oxidizing agent (e.g. hydrogen peroxide) at low temperatures.

The reactions with hydrogen, methane, carbon monoxide and carbon require high temperatures and/or catalysts. Mixtures of elemental sulfur and hydrogen sulfide as well as carbon oxysulfide and carbon disulfide are formed with carbon compounds.

Sulfur dioxide reacts with hydrogen sulfide (Claus reaction). Sulfur is produced on a large industrial scale by this route. The reaction proceeds at a high rate above 573 K (300 °C) in the gas phase, whereas catalysts are necessary at lower temperatures.

In aqueous solutions, sulfur dioxide and hydrogen sulfide react even at normal temperatures to give elemental sulfur.

Metals are oxidized simultaneously to metal oxides and metal sulfides by sulfur dioxide at higher temperatures. Liquid sulfur dioxide is a good solvent with partly

water-like properties. It is miscible with liquid sulfur trioxide in all proportions. The fact that aromatic hydrocarbons dissolve more readily in liquid sulfur dioxide than aliphatic hydrocarbons is utilized industrially for the extraction of aromatics from crude oil by the Edeleanu process [1].

– Occurrence –

Volcanic gases contain sulfur dioxide, as well as other components. The annual amount of sulfur dioxide from all the volcanoes still active on earth is about 10^7 t. The amount of sulfur dioxide introduced into the environment by volcanoes is estimated as being lower than that from air pollution. Sulfur dioxide is released into the atmosphere in motor vehicle exhaust gases (from all combustion engines), by burning fossil fuels, by smelting and roasting ores, by refining crude oil, by bleaching processes (foodstuffs, sugar, textiles etc.), during papermaking and glass production, by fumigation of vessels with sulfur, during extermination of insects and by many other processes [2].

Table 2 summarizes the average amount of pollutant based on the amount of fuel for diesel and petrol engines. The contamination of the starting substances, in this case the sulfur content of the fuels, should be taken into account with these values, which correspond to the “end product” of exhaust gas.

<i>Engine type</i>	<i>Exhaust components</i>		<i>Fuel g/l</i>
Internal combustion engine			
Cars	carbon monoxide	CO	249.00
	hydrocarbons	CH	9.62
	nitrogen oxides	NO _x	9.85
	sulfur dioxide	SO ₂	0.37
	lead	Pb	0.37
Diesel engine			
Trucks	carbon monoxide	CO	29.50
	hydrocarbons	CH	1.80
	nitrogen oxides	NO _x	7.20
	sulfur dioxide	SO ₂	4.15
	soot		1.90

Table 2: Average emissions, based on the fuel consumption of petrol and diesel engines [6]

The sulfur content in petrol of less than 0.1 % is very low. In diesel fuel it may be up to 0.5 %. Thus 0.37 g/l sulfur dioxide is released by combustion in petrol engines (cars) and 4.15 g/l from diesel engines (trucks) [6].

Sulfur dioxide is the toxic constituent of "London smog". It is partly oxidized in the air to sulfuric acid and is therefore the main cause of "acid rain", the pH of which can sometimes be below 3. The reduction in pH in lakes can mean that aluminium salts which are toxic to fish are dissolved out of the mud on the bottom. Sulfur dioxide present in the atmosphere and the sulfuric acid formed pass inside the leaves of plants through the stomata. Here they destroy the chlorophyll, the cell plasma and the cell nucleus and inactivate enzymes. Because the cells which open and close the stomata are diseased, the plants lose water and finally dry up [4].

Soils with a sufficiently high lime content can largely neutralize the acid rain, whereas those low in lime content succumb to overacidification. As a consequence, the fine roots of trees and the Mycorrhiza fungi living in symbiosis with them die off, another cause of damage to forests by sulfur dioxide. It has also been found that mixtures of pollutants are, in many cases, considerably more toxic than the individual noxious gases (synergism). For example, the toxic effect of sulfur dioxide is increased considerably by nitrogen oxides or ozone [4]. As well as this harmful effect on the flora, and subsequently fauna, sulfur dioxide is also responsible for corrosion of all types of buildings. This has resulted in the demand for restricted sulfur dioxide emission, or its removal altogether, e.g. by flue gas desulfurization.

– Toxicology –

The effect of sulfur dioxide on humans and animals comprises essentially irritation and damage to the mucosa due to formation of "sulfurous acid" [4].

The olfactory threshold of SO₂ is 0.3–2.5 ppm. In most people, SO₂ concentrations of 5–10 ppm cause irritation of the respiratory tract. Higher concentrations cause a severe, dry cough, and sulfur dioxide contents above 400–500 ppm can be potentially fatal if inhaled for a period of minutes [1].

The maximum concentration at work (MAC value) is 2 ppm [7, 9, 15]. The consequences of long-term action of sulfur dioxide are described in [7]. Corneal clouding in the eyes and frostbites may occur in contact with liquid sulfur dioxide [4, 7].

– SO₂ production –

The production of sulfur dioxide is of major economic importance, since about 98 % is used for sulfuric acid production [1].

The most important raw materials for the production of gases containing SO₂ are elemental sulfur and pyrites (FeS₂). Naturally occurring pyrite contains 42–48 % sulfur, as well as various other components, such as copper, zinc, lead, arsenic and cobalt. Small amounts of bismuth, antimony, tellurium, mercury, thallium, calcium, indium, silver and gold are also present. Other sulfidic ores, such as copper pyrite, zinc blende and galena, are processed to produce metals. The sulfur dioxide inevita-

bly obtained during roasting of these sulfides is used mainly for sulfuric acid production. Table 3 summarizes the composition of important pyrites.

Name	Chemical composition, %					
	S	Fe	Cu	Zn	As	Pb
Meggen	47	41	0.02	1.0	0.1	0.4
Rio Tinto	48.5	42.5	1.0	2.0	0.50	1.1
Sulitjelma	48	44	0.1	0.6	0.1	0.02
Cyprus	48.5	42.4	0.6	0.1	0.02	traces

Table 3: Composition of important pyrites [8]

The pyrite roasting reaction 5 can be broken down into the four reaction steps 1–4. The enthalpy values quoted are based on 298 K (25 °C).

1. $2 \text{FeS}_2 \rightarrow 2 \text{FeS} + \text{S}_2$ (gaseous)
 $\Delta H = +293 \text{ kJ/mol}$
 2. S_2 (gaseous) + $2 \text{O}_2 \rightarrow 2 \text{SO}_2$
 $\Delta H = -723 \text{ kJ/mol}$
 3. $2 \text{FeS} + 3 \text{O}_2 \rightarrow 2 \text{FeO} + 2 \text{SO}_2$
 $\Delta H = -948 \text{ kJ/mol}$
 4. $2 \text{FeO} + 0.5 \text{O}_2 \rightarrow \text{Fe}_2\text{O}_3$
 $\Delta H = -282 \text{ kJ/mol}$
-
5. $2 \text{FeS}_2 + 5.5 \text{O}_2 \rightarrow \text{Fe}_2\text{O}_3 + 4 \text{SO}_2$
 $\Delta H = -1,660 \text{ kJ/mol}$

The precise explanation of the reaction steps can be found in [1, 8].

The maximum SO_2 content reached in the roasting gases, if burning is carried out in air, is about 16 % by volume, depending on the pyrite composition. If a slight excess of air is present, SO_2 contents of 13–14 % by volume are obtained in general. Pure oxygen increases the concentration, but is used only rarely because of the high costs. The fluidized bed furnace is currently preferred for pyrite roasting, which was previously carried out in shaft furnaces, double-deck furnaces, rotary kilns or powder roasting furnaces [1, 8].

Combustion of sulfur with air is the easiest means of sulfur dioxide production. Sulfur combustion is, therefore, used exclusively for production of 100 % SO_2 . If air containing 20.95 % O_2 is used, SO_2 concentrations of 20.5 % by volume can theoretically be achieved.

Liquid sulfur is currently used almost exclusively for sulfur combustion, its low viscosity at 413–423 K (140–150 °C) enabling it to be sprayed through nozzles. This is an essential prerequisite if sulfur combustion is to be as complete as possible. The upper concentration limit for industrial production of SO_2 gases is about 18 % by volume SO_2 [1, 8].

The theoretical combustion temperature for production of SO_2 gas using dried air at 333–353 K (60–80 °C) and liquid sulfur at 413 K (140 °C) is about 1,273 K (1,000 °C), and increases as the sulfur dioxide concentration increases (Figure 4) [1, 8].

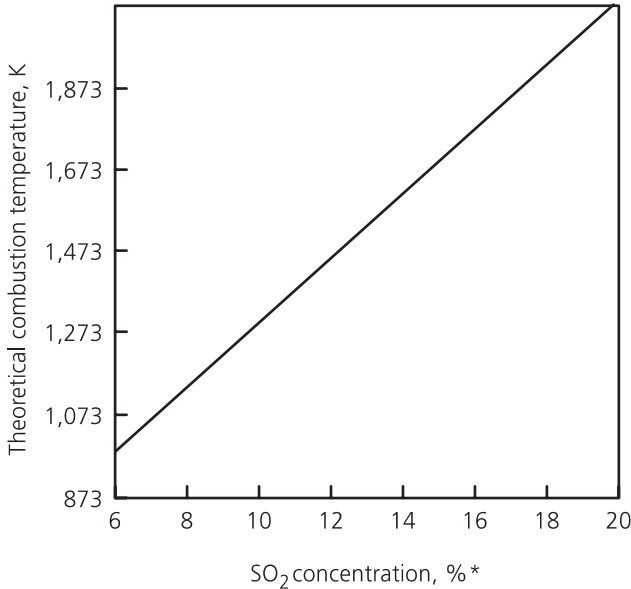


Figure 4: Theoretical sulfur combustion temperature, using dried air at 353 K (80 °C) and liquid sulfur at 413 K (140 °C), as a function of the SO_2 concentration of the combustion gases [1, 8]
* percent by volume

Sulfur combustion furnaces with atomizing burners for liquid sulfur are used almost exclusively in industry today. The structure of a sulfur combustion furnace according to a design by Lurgi is described in [1, 8]. The steel jacket of the cylindrical furnace is lined with several layers of insulating and fireproof bricks. The sulfur burner is located on the front face of the furnace chamber and the waste heat boiler connected directly to the gas discharge side opposite. If the combustion gases are processed to 100 % SO_2 or sulfites, dried air is sucked in directly from the environment. A small amount of SO_3 is formed during sulfur combustion, and, if moist air is used, is converted into sulfuric acid. Severe corrosion may occur if the temperature falls below the dew point, especially during subsequent cooling of the combustion gases in the downstream steam boiler.

Even today, SO_2 is still produced by the oldest known process employed by IG Farben.

Solid sulfur is introduced into gaseous oleum at about 383 K (110 °C) in a reactor. At the same time, preheated 26–30 % oleum is fed into the lower part of the reactor. The oleum rises against the slowly falling sulfur; the spent oleum containing 1–5 % free SO_3 being removed from the top of the reactor. The SO_2 formed in the reactor

still contains about 5–10 % by volume SO_3 , which is converted into further SO_2 in a subsequent column.

In modern processes, the sulfur trioxide and sulfur are preferably used in liquid form. Either oleum with a very low SO_3 content, a liquid mixture of SO_2 and SO_3 under pressure or liquid sulfur is used as the reaction medium [1].

In recent times, sulfur dioxide has been produced from waste sulfuric acid and sulfates, from waste industrial gases containing hydrogen sulfide, and from flue gases from power stations. About 6.36 kJ/t H_2SO_4 (calculated as 100 % H_2SO_4) are required for cleavage of 70 % acid at 1,273 K (1,000 °C) under oxidizing conditions. The theoretical process steps and the associated energy consumption are listed in [8].

The theoretical energy requirement mentioned of 6.36 kJ/t H_2SO_4 only applies, however, under conditions of indirect heat transfer. Since no corrosion-resistant materials are available for the absolutely essential heat exchangers under these conditions, in practice the heat required for acid cleavage is supplied directly by the hot flue gases from fossil fuels. In this case, the heat requirement is far greater than with indirect heating, since the flue gases have to be heated up to a cleavage temperature of 1,273 K (1,000 °C). As already mentioned above, most of the heat supplied can be recovered during cooling of the gases emerging from the cleavage furnace between about 1,273 K (1,000 °C) and 623 K (350 °C) [1].

The energy requirement for acid cleavage increases greatly as the H_2SO_4 concentration decreases, in relation to the amount of water to be evaporated, and for this reason the waste sulfuric acid should have a concentration of 60–75 %.

The flow chart of a modern waste acid treatment plant is shown in Figure 5. The actual cleavage plant consists of the cleavage furnace and the waste heat system. A gas purification plant for further cooling and purification of the cleavage gases and a twin catalysis plant for generation of concentrated sulfuric acid and oleum are installed downstream [1].

The waste acid is introduced at the top of the vertical, masonry-lined furnace and finely distributed with a rotary atomizer. Cold air serves as the atomizing agent and is blown in under a pressure of 0.135 MPa. Heating oil or gas is burned in several combustion chambers on the sides around the top part of the cleavage furnace. The spatial separation between the combustion chamber and cleavage furnace allows the fuel to be mixed and burned completely with the combustion air outside the actual acid cleavage zone.

The air used for the combustion is introduced in excess (air factor 1.1–1.3), since the oxygen released during the acid cleavage is, in general, not sufficient to guarantee complete combustion of the oxidizable inorganic and organic constituents.

The flue gases enter tangentially in the combustion chamber plane of the cleavage furnace at about 2,073 K (1,800 °C) and release heat into the upper part of the furnace here by radiation. The essential heat transfer to the acid takes place by intensive mixing due to the formation of eddies close to the discharge openings of the combustion chambers. The required acid cleavage temperature of 1,273 K (1,000 °C) is established by adjusting the amount of fuel and air.

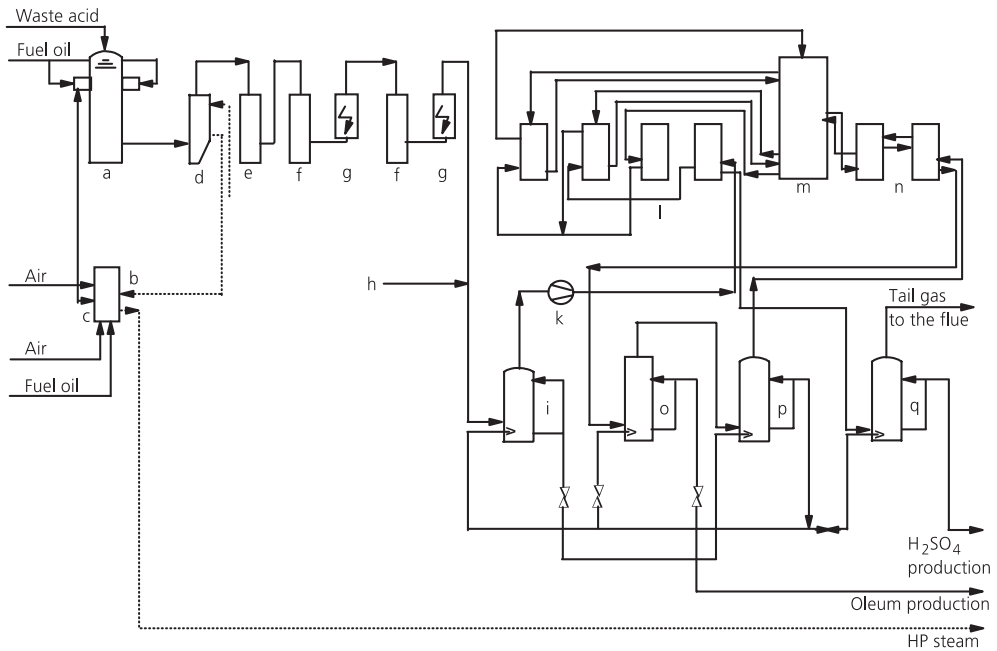


Figure 5: Sulfuric acid regeneration plant with thermal cleavage of waste acid, gas purification and a contact plant with oleum production [1]

- | | |
|----------------------|--------------------------------|
| a) cleavage furnace | i) dryer |
| b) air preheater | k) fan |
| c) superheater | l) gas heat exchanger |
| d) waste heat boiler | m) diluting air |
| e) Venturi washer | n) intermediate heat exchanger |
| f) gas cooler | o) oleum absorber |
| g) wet electrofilter | p) intermediate absorber |
| h) contact boiler | q) final absorber |

Various waste heat systems are used, depending on the way in which the energy recovered is used. In the treatment plant shown in Figure 5, 360 t 65 % waste sulfuric acid can be processed daily. This process concept is particularly suitable for plants producing more than 100 t H_2SO_4 daily [1, 8].

This brief and incomplete overview of the possibilities of sulfur dioxide production provides an insight into the diversity of the exposure of materials to corrosion during such processes. Other means of producing sulfur dioxide, not mentioned here, include the absorption processes, which employ media capable of absorbing several times the amount of SO_2 absorbed by water – organic amines being an example. These solutions present problems (solvents), especially if plastics are used.

A problem of great interest worldwide in recent times is the removal of sulfur dioxide from all types of waste gases, i.e. flue gas desulfurization.

– Flue gas desulfurization plants –

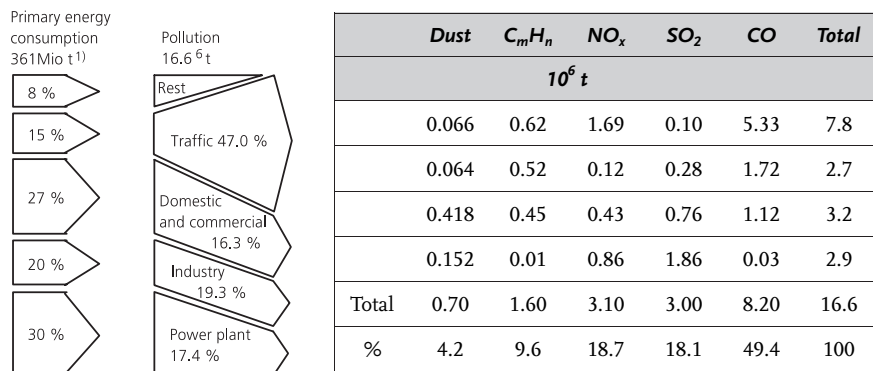
The total amount of pollutants in the Federal Republic of Germany in 1982 was about 16.6 million tonnes. It should be remembered however, that about 50 % of emissions come from neighboring countries. On the other hand, of course, some of the emissions from the Federal Republic pass into other countries. Table 4 gives a breakdown of the emissions.

To reduce emissions from power stations, the Large-Scale Furnace Legislation (GfAVO) came into force in the Federal Republic of Germany on 1. 6. 1983 (Bundesgesetzblatt, Part I, No. 26 of 25. 6. 1983). More than 70 processes are known worldwide for flue gas desulfurization. The most flue gas desulfurization plants are located in Japan and in the USA.

In Japan, the waste gases from boiler plants fired with heavy oil are mainly desulfurized [11]. Since other pollutants, such as nitrogen oxides, must also be removed as well as sulfur dioxide, it should not be forgotten that the experiences of nitrogen oxide deposition in Japan have so far been obtained only on dry-fired boilers. There are, as yet, no results available for German coal, in particular ballast coal or brown coal [10].

In the USA, the waste gas desulfurization plants are usually installed in association with coal-fired power stations. It has been found in practice that it is more difficult to operate flue gas desulfurization plants with coal-fired plants than with oil-fired plants [11].

In contrast to hard coal, the fuel composition of brown coal is subject to relatively wide variations. The sulfur and calcium contents vary largely. The sulfur content is, on average, 0.3 %, and the SO_2 content in the flue gas is thus about $1,500 \text{ mg/m}^3$. The maximum value here can be $7,000 \text{ mg/m}^3$ [10].



1) coal equivalents

Table 4: Primary energy use and emissions of pollutants in the Federal Republic of Germany in 1982 [10]

Table 5 summarizes the selected threshold values of emissions from TA-Luft (Technical Instructions on Clean Air).

Substance	Emission threshold values		Flow
	mg/m³ 2)		kg/h
	TA-Luft¹⁾	Continuous require- ments	After which TA-Luft requires continuing measurement
HCl	30	10 to 30	3
SO ₂ /SO ₃	500	30 to 50	50
H ₂ S	5	2 to 5	1
Cl ₂	5	2 to 5	1
NH ₃	–	10 to 80	–
CH ₃ NH ₂	20	–	1 ³⁾
NH ₄ Cl	50	30 to 50	2 to 5
(NH ₄) ₂ SO ₃	50	30 to 50	2 to 5

1) April 1986 version [1]

2) Commonly interpreted today as mg/m³_N (dry)

3) Stated as total carbon (TOC)

Table 5: Selection of emission threshold values from TA-Luft (Technical Instruction on Clean Air) [12]

The values to which waste air purification plants must currently be designed are quoted in the second column of this table. When these values are compared with the TA-Luft values, it is striking, especially in the example of SO₂, that the value achieved in practice is significantly below the threshold values required [12].

A distinction is made in principle between dry and wet flue gas desulfurization processes. The flue gas desulfurization plants currently installed throughout the world operate almost exclusively by the wet process, since the technology of wet dust removal from large quantities of gas, known already for more than 70 years, could be called upon in the development of these processes [11]. See also Section A 21.

A characteristic feature of the dry processes is that the flue gases are not cooled, or are cooled only to 338–343 K (65–70 °C). In the case of processes without regeneration, the product to be disposed of is formed from the absorption masses together with the pollutants deposited from the flue gases. Their advantage is that they can be operated without effluent.

In regeneration processes, the agent charged with the pollutants is regenerated and used again for renewed charging. The pollutants deposited from the flue gases are released in these processes and processed further to end products.

Either quicklime (CaO), calcium hydroxide ($\text{Ca}(\text{OH})_2$), limestone (CaCO_3) or ammonia (NH_3) can be used as absorbants in the wet processes without regeneration. The end product is gypsum ($\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$) or ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$). The ammonia process is anhydrous.

<i>Dry process</i>			<i>Wet process</i>			
– regeneration –						
without		with	without		with	
– absorbent –						
Dry lime	lime suspensions	activated coke (adsorption)	quicklime calcium hydroxide limestone flour	ammonia	sodium or potassium hydroxide	sodium sulfite
– type of regeneration –						
–	–	thermal	–	–	with lime	thermal
– process temperature –						
403 K (130 °C)	338–343 K (65 – 70 °C)	403 K (130 °C)	319–325 K (46 – 52 °C)			
– intermediate or end product –						
Calcium sulfite	calcium sulfite	SO_2 -rich gas	gypsum	ammonium sulfate	gypsum	SO_2 (gas)
– further use –						
Wet FGD dumping sewage sludge stabilization	dumping sewage sludge stabilization calcium sulfate anhydrite	sulfur sulfuric acid SO_2 (liquid)	cement and gypsum industry	fertilizer	cement and gypsum industry	sulfur sulfuric acid SO_2 (liquid)
– effluent discharge –						
No	no	yes, and dumping	yes	no	yes	yes

Table 6: Overview of the most widely known flue gas desulfurization processes [10]

Table 6 contains an overview of the most widely known flue gas desulfurization processes.

Alongside the process procedure and its reliable implementation, the corresponding end products are of not insignificant importance to the environment, especially

their disposal. It is not certain whether end products, such as gypsum, artificial fertilizer, sulfur, sulfuric acid or others, can be used industrially or kept inexpensively on dumps [10].

– Use –

About 98 % of the SO_2 employed industrially is used for sulfuric acid production [1]. This means that the demand for sulfur dioxide for other purposes is low. It is sometimes met by combustion of sulfur by the user directly or by delivery of 100 % liquid sulfur dioxide. The very large quantities of sulfur dioxide formed, for example, during combustion of fossil fuels (see – Flue gas desulfurization plants –) are currently converted into other products at great industrial expense.

Apart from production of sulfuric acid, sulfur dioxide is used in the following branches of industry:

- in the cellulose industry for the production of digestion solutions for sulfite cellulose,
- in sodium chlorate reduction for chlorine dioxide production,
- in combination bleaches for conversion of peroxide before hydrosulfite bleaching,
- as “antichlorine”, in particular in sulfate cellulose factories following chlorine bleaching,
- in the chemical and pharmaceutical industry for production of sulfites, bisulfites, disulfites, thiosulfates and dithionites as well as salts of hydroxyalkanesulfonic acid,
- for production of alkanesulfonates by sulfoxidation or sulfochlorination,
- for production of gelatin and glue,
- as a reducing agent or solvent,
- for chemical reprocessing of manganese ores and recovery of, for example, cobalt, selenium and tellurium from waste products,
- in the textile industry as a bleaching agent [1].

In wood, wool, paper and other substances, sulfur dioxide reduces the dyestuffs to colorless products. The use of SO_2 for bleaching these substances, not possible with chlorine, is based on its reducing action [4].

The leather industry also uses SO_2 as a bleaching agent. In the foodstuffs industry it is used as a preservative and disinfectant, as a sterilizing agent in breweries for regulation of fermentation, and as a preservative in the wine industry. Its use in the foodstuffs industry is not entirely without objection (see – Toxicology –) [2].

Sulfur dioxide is used in the water industry for dechlorination of chlorinated water and effluent and was previously used as a refrigerant [1, 2].

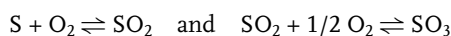
Another use is in agriculture, amongst other things as preservative for silo fodder (2–3 kg liquid SO_2 per t silo grass) and pest control agent [2].

– Corrosive action –

The corrosive action of sulfur dioxide towards the materials used in chemical engineering is determined by the particular state in which it exists and its purity. Pure, liquid, anhydrous sulfur dioxide hardly attacks metallic materials, if at all, unless it is capable of dissolving the metal under the prevailing conditions. The corrosive attack increases with water content and with the increasing electrical conductivity of the medium, and also as a result of any reaction products formed.

Similar behavior can be expected in gaseous sulfur dioxide. No corrosive attack by dry sulfur dioxide occurs on metals at normal and slightly increased temperatures, since sulfur dioxide is very stable, as mentioned above. Increasing aggressiveness is likely as the water content and impurities increase.

High-temperature corrosion by sulfur dioxide on various materials depends on their resistance to and reaction with SO_2 under the prevailing conditions. During production of sulfur dioxide, for example, by combustion of sulfur or fossil fuels, some of the sulfur or some of the sulfur contained in the fuel reacts with oxygen in the air in accordance with the equations:

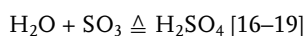


The thermodynamic equilibrium of this reaction at 1,473 K (1,200 °C) lies almost completely on the side of SO_2 , and at 673 K (400 °C) on the side of SO_3 .

The following factors play a role in SO_3 formation and influence the reaction kinetics:

- the sulfur content of the fuel,
- the excess air,
- the flue gas temperature,
- the residence time at a certain temperature range or temperature,
- the amount and distribution of catalytic metal oxides and
- the amount of additives.

For corrosion, it is important to prevent SO_3 formation, since, below 853 K (580 °C), it reacts with the steam almost always present in accordance with the following equation:



Combustion with a slight excess of air has proved to be an effective measure.

It has been found that conversion of SO_2 into SO_3 is low in the presence of a small excess of air, as can be seen from Figure 6. For this reason, excess air values of 1.01 to 1.03 are maintained in oil-fired plants, in order to avoid low-temperature corrosion (corrosion below the dew point of the gas mixture) and the discharge of acid agglomerates both at low waste gas temperatures and otherwise [17]. In practice, these conditions can be met only if the burners achieve high-energy mixing and burning and the fuel/air ratio is adjusted exactly, so that the amount of soot and the CO content can be kept low.

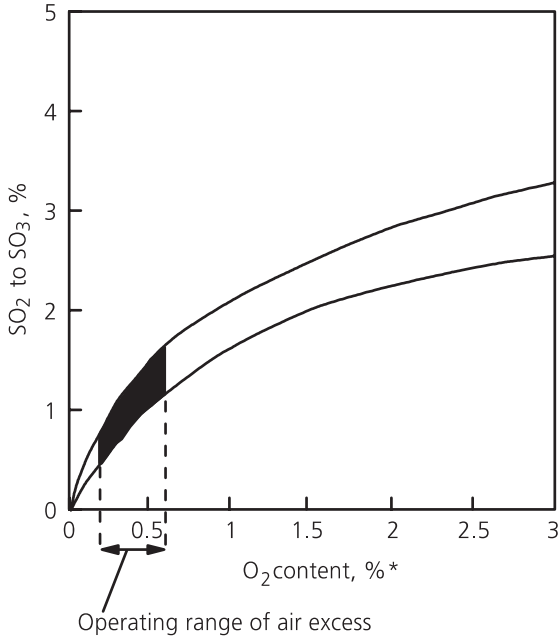


Figure 6: Conversion of SO_2 to SO_3 in oil-fired plants [17]

* percent by volume

Figure 7 shows the flue gas composition as a function of the fuel/air ratio in an oil-heated boiler for a flue gas temperature of 1,473 K (1,200 °C). With a virtually stoichiometric combustion, only very little SO_3 is formed, the amount rising as the excess air increases ($l > 1$), up to about 10 ppm at $l = 1.05$. If $l < 1$ (oxygen deficiency), the CO content increases due to incomplete combustion. Severe carbonic acid corrosion may occur in these cases due to formation of condensate. The residence time of the reaction gas mixture in the temperature range between 1,473 and 673 K (1,200 and 400 °C) is critical for the conversion of SO_2 into SO_3 . In steam generators this is between 4 and 6 seconds and is, therefore, too short to achieve conversion of SO_2 into SO_3 .

The reaction also proceeds rapidly below 1,173 K (900 °C) with a catalyst. Metal oxides of vanadium (V_2O_5), iron (Fe_2O_3), nickel and alkaline earth metals act as catalysts. Heating surfaces in the temperature range stated can also have the same effect. However, these are not the only possibilities for promoting SO_3 and hence sulfuric acid formation.

Figure 8 shows the formation of sulfuric acid (H_2SO_4) as a function of temperature. As can be seen from this graph, the formation of acid is almost complete at 473 K (200 °C).

The dew point of the gas mixture can be defined as that temperature at which the first liquid precipitate forms on the surface of the medium. The sulfuric acid-water vapor phase diagram (Figure 9), shown for reasons of expediency here, illustrates that a condensate containing about 80 % H_2SO_4 is formed at a dew point of 413 K