7.17 Sulphuric acid production

7.17.1 Coverage

The production of sulphuric acid (H_2SO_4) is in terms of quantities the most important production of the industrial chemical production. The production of H_2SO_4 varies from the SO_2 sources.
The emissions to the atmosphere from sulphuric acid production which cause greatest concern are sulphur dioxide (SO_2) emissions. This chapter covers the chemical production of sulphuric acid.

7.17.2 Emission sources

H_2SO_4 is produced from sulphur dioxide or elemental sulphur. Elemental sulphur is derived from desulphurisation of natural gas or crude oil. SO_2 is derived from flue gas process, e.g. SO_2 gases from sulphur, the roasting of zinc and /or lead minerals, regeneration of spent acids, non ferrous metal production, or waste gas incineration...
SO_2 is first oxidised on catalysts to SO_3. Catalysts used are based on vanadium compounds, platinum and iron oxides. [6]
SO_3 is then absorbed in H_2SO_4 to form sulphuric acid. High SO_2 emission levels come from this part of the process; hence measures to reduce SO_2 emissions have to be used.

7.17.3 BAT, Associated Emission Levels (AEL)

SO_2: [1]

The major SO_2 emissions come from the absorption process tail gas. SO_2 emissions depend on the conversion rate of the process. Process optimisation can be considered as the best available technique to reduce emissions.
Different techniques to increase SO_2 conversion rate can be combined in order to achieve BAT associated emission levels.
A double contact/double absorption process improves the conversion yield of SO_2 from the tail gas. A change from a single absorption to a double absorption can significantly reduce SO_2 emissions.
The addition of a fifth bed catalyst in the double contact process can increase the conversion rate to 99.9 %. This technique is generally applicable for double contact plants, provided that sufficient room is available [1]. Usually applying double contact process maximum conversion rate is 99.8 % in a steady-state operation, maximum conversion rate 99,6% under transient operation conditions. But this technique's application in an existing plant has two main difficulties: the high cost of the investment and the high cost of the operation, owing to the need of external heating, owing to the difficulty of reaching the proper temperatures for the operation of catalyst and to the fluodynamic characteristics of the installed blowers [6].
The use of a Cs promoted catalyst can also increase the conversion rate of SO_2. Indeed, Cs promoted catalysts can be used at lower temperature (380 – 620°C) than conventional catalysts (420 – 660°C)
The replacement of brick-arch converters, too porous, can lead to an increase of SO_2 conversion rate.
The use of wet catalysis process enables the conversion of wet SO_2 gases.
Finally, a regular maintenance of utilities and replacement of catalysts is necessary to maintain a high conversion rate.
Secondary measures can also be applied;
Tail gas can be scrubbed using an aqueous ZnO solution or NH_3 solution, or other alkaline solutions such as sodium hydroxide, as well as hydrogen peroxide. These scrubbing can provide by-products that can be used on-site or sold. [4]**Erreur ! Source du renvoi introuvable.**

The BAT to reduce SO_2 emissions is a combination of the formerly cited processes and reduction techniques permitting to achieve the emission levels detailed in the following table.
The following table gives an overview of BAT associated SO_2 emission levels for sulphuric acid production.

Table 1: Associated SO_2 emission levels with BAT to reduce emissions in sulphuric acid production.

Emission source	Techniques	Associated emission level with BAT (mg/Nm^3)[1,2]
sulphuric acid production	Sulphur burning, double contact/double absorption	Existing installations : 30-680 New installations : 30-340
	Other double contact/double absorption	200-680
	Single contact/single absorption	100-450
	other	14-170

[1] This level might include the effect of tail gas scrubbing.
[2] Expressed as daily average value.

7.17.4 Emerging techniques

No data available

7.17.5 Cost data for emission reduction techniques

The addition of a fifth bed to a double contact process needs an investment of about 1 million euros. The specific cost related to SO_2 reduction is 629 euros per ton SO_2 reduced. [1]

The investment cost of the application of promoted-Cs catalyst in a double contact process is 21 700 eur/y more than the original investment for traditional catalyst. The specific cost related to SO_2 reduction is 12 euros per ton SO_2 reduced. This cost increases to 930 euros per ton SO_2 reduced for a single contact process. [1]

The following table gives an overview of the costs and SO_2 conversion rate for different abatement techniques in sulphuric acid production [8].

Table 2: Cost and operational data of techniques used to control SO_2 emissions in sulphuric acid production.

Nr.	Capacity ($t\ H_2SO_4/d$)	% SO_2 content	Construction		SO_2-Conversion average (%)		Costs		SO_2 avoided (t/year)	Annuelised costs (€/year)	SO_2 unabeted (t/year)
							€/t SO_2	€/t H_2SO_4			
			before	after	before	after	abated	additionaly			
	250	5 - 7	4 bed SC/SA	Base case A1	98.00	-	0	0	0	0	1143
3			4 bed SC/SA	+ Cs in bed 4	98.00	99.10	3	0.02	628	1 763	
1			4 bed SC/SA	4 bed DC/DA	98.00	99.60	1 317	13.76	914	1 203 985	
2			4 bed SC/SA	4 bed DC/DA + Cs in bed 4	98.00	99.70	1 159	12.87	971	1 125 848	
4			4 bed SC/SA	+ TGS Peracidox	98.00	99.87	1 048	12.80	1 068	1 119 881	
5			4 bed SC/SA	+ TGS (alkaline)	98.00	99.87	1 286	15.70	1 068	1 373 446	
		9 - 12	4 bed DC/DA	Base case A2	99.60	-	0	0	0	0	228
6			4 bed DC/DA	+ Cs in bed 4	99.60	99.70	367	0.24	57	20 858	
7			4 bed DC/DA	5 bed DC/DA + Cs in bed 5	99.60	99.80	3 100	4.03	114	352 656	
8			4 bed DC/DA	+ TGS Peracidox	99.60	99.94	3 910	8.68	194	759 562	
9			4 bed DC/DA	+ TGS (alkaline)	99.60	99.94	6 636	14.73	194	1 287 390	
	500	5 - 7	4 bed SC/SA	Base case B1	98.00	-	0	0	0	0	2286
12			4 bed SC/SA	+ Cs in bed 4	98.00	99.10	5	0.04	1 257	6 285	
10			4 bed SC/SA	4 bed DC/DA	98.00	99.60	867	9.06	1 829	1 584 685	
11			4 bed SC/SA	4 bed DC/DA + Cs in bed 4	98.00	99.70	835	9.27	1 943	1 622 590	
13			4 bed SC/SA	+ TGS Peracidox	98.00	99.87	718	8.77	2 137	1 535 220	
14			4 bed SC/SA	+ TGS (alkaline)	98.00	99.87	883	10.78	2 137	1 886 839	
		9 - 12	4 bed DC/DA	Base cas C1	99.60	-	0	0	0	0	457
15			4 bed DC/DA	+ Cs in bed 4	99.60	99.70	363	0.24	114	41 278	
16			4 bed DC/DA	5 bed DC/DA + Cs in bed 5	99.60	99.80	1 559	2.03	228	354 762	
17			4 bed DC/DA	+ TGS Peracidox	99.60	99.94	2 209	4.90	389	858 349	
18			4 bed DC/DA	+ TGS (alkaline)	99.60	99.94	4 591	10.19	389	1 783 465	
	1000	9 - 12	4 bed DC/DA	Base Case C2	99.60	-	0	0	0	0	914
19			4 bed DC/DA	+ Cs in bed 4	99.60	99.70	356	0.23	228	81 023	
20			4 bed DC/DA	5 bed DC/DA + Cs in bed 5	99.60	99.80	1 020	1.33	455	464 258	
21			4 bed DC/DA	+ TGS Peracidox	99.60	99.94	1 359	3.02	777	1 055 922	
22			4 bed DC/DA	+ TGS (alkaline)	99.60	99.94	3 432	7.62	777	2 667 020	

Hypothesis:

- The conversion rate depends on specifications (design, installations, concentration, source of SO2). Precision 0,1%.
- SO_2 content: 5 - 7%: calculated with 5% and 9 - 12% calculated with 10%,
- O_2 content: 5 - 7% SO2 + 6 - 9% O2 and 9 - 12% SO2 + 8 - 11% O2,
- lifetime for all installations: 10 years,
- fixed operation costs: 3%,
- interest rate: 4%,
- price H_2SO_4: 20€/t ex works
- labour costs: 37 k€/man-year
- utilities for TGS Peracidox and alkaline Absorptions: +30% capital investment costs
- warranted SO_2-content after TGS: < 200 mg SO_2/Nm^3 = < 70 ppm SO_2
- steam price: 10€/t
- SC = single contact ,SA = single absorption, DC = double contact, DA = double absorption

7.17.6 References used in chapter 7.17

[1] Reference document on Best Available Techniques for the manufactures of large volume chemicals – ammonia, acids and fertilizers, August 2007.

[2] Comments from Birgit Brahner, German Federal Environment Agency, 12/2008.

[3] "Compilation of the answers-to-questions-and proposal of EGTEI secretariat.doc",EGTEI, 02/2009.

[4] Comments from Erik Kiekens, PVS, European sulphuric acid association, March 2009.

[5] Comments from Dawn Christensen, Ineos, European sulphuric acid association, March 2009.

[6] Comments from Aldo Zucca, Portovesme, European sulphuric acid association, March 2009.

[7] Comments from Thomas Krutzler, UBA Austria, March 2009.

[8] Retrofitting of old plants, ESA expert group, May 2009.