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EXERGY ANALYSIS OF PROCESSING SO_2-CONTAINING GASES IN METALLURGY INTO SULPHURIC ACID AND SULPHUR

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Abstract

An energy study has been conducted on the process of making sulphuric acid (in two ways: by one-stage and two-stage conversion) and the process of making sulphur from SO_2-containing gases resulting from the pyrometallurgical production of copper. The exergy method of thermodynamic analysis has been used as a method of investigation. The general and relative exergy characteristics of the processes have been determined.

The results of the investigation show higher exergy efficiency of the processes of making sulphuric acid (in both ways) than that of the process of making sulphur from SO_2-containing metallurgy gases.

Keywords: exergy analysis, SO_2-containing metallurgical gases, sulphuric acid production, sulphur production

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1. Introduction

The waste sulphur-containing gases from winning non-ferrous metals from sulfide ores are used mainly for the production of sulphuric acid. However the great supply and low market demand for sulphuric acid, as well as the strict environmental standards which modern production should meet, require a search for new, optimized from technical and economical point of view, methods of processing these gases. In this connection, the making of sulphur from sulphur-containing gasses (especially those with high concentration) is becoming an important issue because unlike sulphuric acid, sulphur is easier to transport, keep on stock and sell.

The cost of the obtained sulphur is high. However, numerous investigations and the practical implementation of different varieties of this process point to the great existing possibilities for its improvement and optimization in the direction of making it an economically efficient one [1-10]. The main driving motive for these studies is the reduction of energy consumption in the process of production.

Finding an optimal energy solution for controlling the processes is of particular importance. It requires a very precise energy-technological analysis of both, the existing methods of sulphuric acid production from SO_2-containing gases and the methods for processing the latter into elemental sulphur.

2. Results

Having in mind the considerations mentioned so far, a study was conducted aiming at an energy evaluation of the process of making sulphuric acid (in two ways: by one-stage and two-stage conversion) and of the process of making sulphur from SO_2-containing gases. The exergy method of thermodynamic analysis was used as a method of investigation. The data necessary for the analyses of the process of making sulphuric acid are taken directly from the functioning technological units of Copper Extraction Plant in the town of Pirdop, Bulgaria. The data for the analysis of the process of making sulphur are taken from references [7].

In spite of differences in the scale of processes, the quality of input materials, and the dynamics of the processes, the conclusions are applicable and can be used for chemico-technological studies in this field due to comparative character of the results.

Fig.1 and Fig.2 present the process flow charts of the processes of sulphuric acid production by one-stage and two-stage conversion, by which the analysis was made.

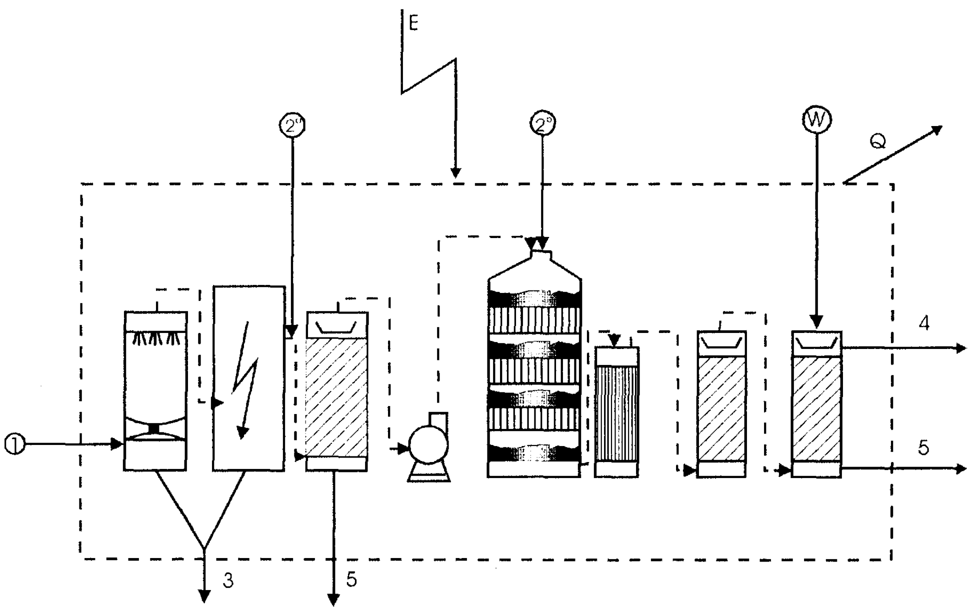

Fig.1. Chart of the process of making sulphuric acid by one-stage convertion: 1-dust containing gas; 2^a, 2^b-air; 3-dust; 4-off gasses; 5-sulphuric acid; W-water; E-electric energy; Q-heat exchange with environment.

The model chart used to study the process of making sulphur from SO_2-containing gases is the one of the Metallurgy Plant in Norillsk,Russia [7]. The selection of this very process was made on the following basis: the technology is implemented on industrial scale and it ensures high degree of utilization of the sulphur-containing gases - up to 99.5%; the installation can process waste metallurgical gases with different content of SO_2. Fig.3

shows a generalized chart of the way the analysis was made. The process includes reduction of SO_2 with methane, followed by processing the reduced gas, using Claus's method in two catalytical stages. The level of conversion of SO_2 reaches 79%. It is also possible to include a third, so called "sulphren" process in which in three catalytical reactors all the residual sulphur compounds are turned into sulphur and the extent of conversion is increased up to 99.5%. As there is a lack of detailed technological data for the separate metallurgical equipment units, a generalized analysis was made, not including the "sulphren" process.

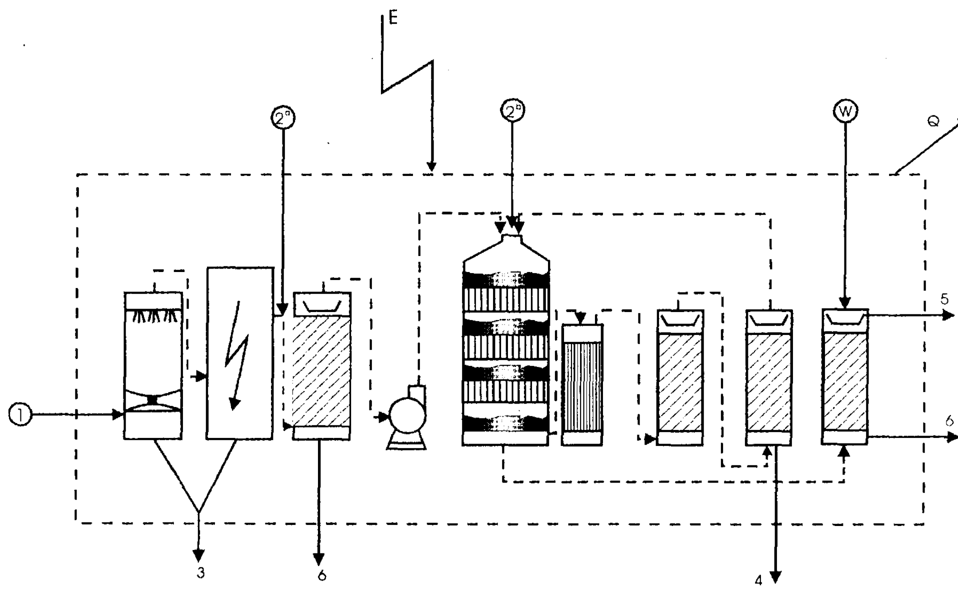

Fig. 2. Chart of the process of making sulphuric acid by two-stage convention: 1-dust containing gas; 2^a, 2^b-air; 3-dust; 4-oleum; 5-off gasses; 6-sulphuric acid; W-water; E-electric energy; Q-heat exchange with environment.

Tables 1 - 3 present the parameters of the input and output gas flows. The material balance is calculated for $100m^3$ input of SO_2-containing gas and is presented in Tables 4 - 6.

An enthalpy method (described in detail in [11]) was applied for calculating the energy balance because it has a number of advantages compared to the classical thermal one. When determining the values of the relative enthalpies of the different components of flows, the standard substances suggested in [11] were accepted, namely: O_2, N_2, SO_2, CO_2, H_2O-vapour. Under standard conditions the latter have an enthalpy equal to zero (P = 1atm and T_o = 298,15K).

Table 1. Parameters of the gas flows in the process of making sulphuric acid by one-stage conversion of SO_2.

Flow	Components, %					Temperature, °C
	N_2	O_2	SO_2	SO_3	H_2O	
1 - SO_2 - gases	77.20	11.72	6.28	0.30	4.50	250
2 - air	79.00	21.00	-	-	-	25
4 -off-gases	88.31	11.48	0.20	0.01	-	50

Table 2. Parameters of the gas flows in the process of making sulphuric acid by two-stage conversion of SO_2.

Flow	Components, %						Temperature, °C
	N_2	O_2	SO_2	SO_3	CO_2	H_2O	
1 - SO_2 gases	79.42	9.00	8.00	0.08	1.50	2.00	375
2 - air	79.00	21.00	-	-	-	-	25
5 -off-gases	90.14	8.36	0.05	0.01	1.44	-	50

Table 3. Parameters of the gas flows in the process of making sulphur from SO_2-containing gases.

Flow	Components, %									Temperature, °C
	N_2	O_2	SO_2	CO_2	H_2	CO	H_2S	COS	H_2O	
1-SO_2 - gas	69.4	17.4	11.4	1.8	-	-	-	-	-	25
5-off-gas	57.5	1.1	1.2	8.9	1.9	4.8	0.9	0.3	23.4	230
gas after "sulphren"	77.24	1.65	0.04	19.73	0.85	0.37	0.12	-	-	140

Based on the material balances and using the values of the relative enthalpies of separate components (of separate flows respectively), the energy balances are made using the above mentioned methods. They are presented by the following equations:

- for one-stage conversion into sulphuric acid

$$H_1 + H_{2a} + H_{2b} + W + E = H_3 + H_4 + H_5 + Q \quad (1)$$

- for two-stage conversion into sulphuric acid

$$H_1 + H_{2a} + H_{2b} + W + E = H_3 + H_5 + H_6 + Q \quad (2)$$

- for the process of making sulphur

$$H_1 + H_2 + H_3 = H_4 + H_5 + Q \quad (3)$$

H stands for the enthalpy of a particular flow, *E* stands for the input energy in the system, *Q* is the heat exchanged with the environment, *W* is the water input in the system during the absorption.

Table 4. Material balance of the process of making sulphuric acid by one-stage conversion of SO_2.

Input			Output		
Flow	kg	%	Flow	kg	%
1 - SO_2 gases	136.2	86.9	3 - dust	0.01	0
2^a - air	1.9	1.2	4 -off-gases	130.2	83.1
2^b - air	13.7	8.7	5 - H_2SO_4	26.5	16.9
W - water	4.9	3.2			
Total	156.7	100.0	Total	156.7	100.0

Table 5. Material balance of the process of making sulphuric acid by two-stage conversion of SO_2.

Input			Output		
Flow	kg	%	Flow	kg	%
1 - SO2.- gases	139.9	82.4	3 - dust	0.02	0
2à - air	3.7	2.2	5 -off-gases	134.9	79.5
2b - air	19.7	11.6	6 - H2SO4	34.8	20.5
W - water	6.4	3.8			
Total	169.7	100.0	Total	169.7	100.0

Table 6. Material balance of the process of making sulphur from SO_2-containing gases.

Input			Output		
Flow	kg	%	Flow	kg	%
1 - SO_2 - gases	147.8	93.1	4 - sulphur	12.1	7.6
3 - natural gas	10.9	6.9	5 -off-gases	146.6	92.4
Total	158.7	100.0	Total	158.7	100.0

The energy balances are given in Tables 7 -9.

The composing of the exergy balances is done by a method described in detail in [12], using the reference level proposed by Szargut J. [12] according to the equations:

- for one-stage conversion and production of sulphuric acid

$$\varepsilon_1 + \varepsilon_{2a} + \varepsilon_{2b} + W + E = \varepsilon_3 + \varepsilon_4 + \varepsilon_5 + \varepsilon_q + D \qquad (4)$$

- for two-stage conversion and production of sulphuric acid

$$\varepsilon_1 + \varepsilon_{2a} + \varepsilon_{2b} + W + E = \varepsilon_3 + \varepsilon_5 + \varepsilon_6 + \varepsilon_q + D \qquad (5)$$

- for the process of production of sulphur

$$\varepsilon_1 + \varepsilon_2 + \varepsilon_3 = \varepsilon_4 + \varepsilon_5 + \varepsilon_q + D \qquad (6)$$

ε is the exergy of a particular flow, D is the internal exergy losses.

The exergy balances are given in Tables 10 - 12 and graphically represented by Grassman's diagrams in Figs 4 - 6.

Based on the balance data the exergy efficiency for each installation can be calculated:

$$\eta = \varepsilon_{ef} / \Sigma\varepsilon \qquad (7)$$

where ε_{ef} is the utilized exergy of final products leaving the system, $\Sigma\varepsilon$ is the exergy input into the system. For the process of one-stage conversion η is 36,5%, while for the process of making sulphuric acid by the two-stage conversion η is 36,3%, and for the process of making sulphur from SO_2-containing gases = 27,1%.

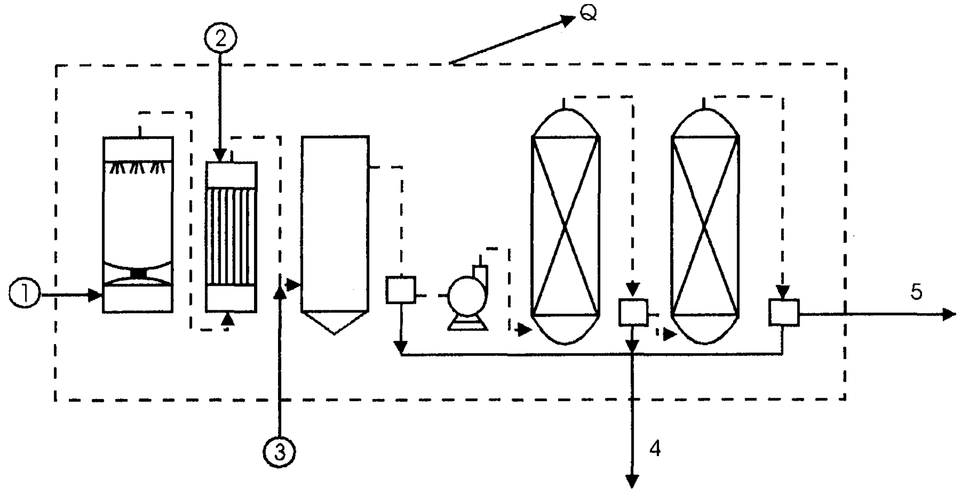

Fig. 3. Chart of the process of making sulphur from SO_2 - containing gases. 1-SO_2 - containing gas; 2-energy from heating of SO_2 - gases; 3-natural gas; 4-sulphur; 5-off -gases; Q-heat exchange with environment.

Table 7. Energy balance of the process of making sulphuric acid by one-stage conversion of SO_2.

Input Energy		Output Energy	
Flow	MJ	Flow	MJ
1 - SO_2 - gases	38.8	3 - dust	0
2^a - air	0	4 - off-gases	3.2
2^b - air	0	5 - H_2SO_4	-61.8
W - water	0	Q - heat losses	116.5
E - electric energy	19.1		
Total	57.9	Total	57.9

Table 7. Energy balance of the process of making sulphuric acid by two-stage conversion of SO_2.

Input Energy		Output Energy	
Flow	MJ	Flow	MJ
1 - SO_2 - gases	53.3	3 - dust	0
2^a - air	0	5 - off-gases	3.4
2^b - air	0	6 - H_2SO_4	- 81.3
W - water	0	Q - heat losses	156.3
E - electric energy	25.1		
Total	78.4	Total	78.4

Table 8. Energy balance of the process of making sulphuric acid by two-stage conversion of SO_2.

Input Energy		Output Energy	
Flow	MJ	Flow	MJ
1 - SO_2 - gases	53.3	3 - dust	0
2^a - air	0	5 - off-gases	3.4
2^b - air	0	6 - H_2SO_4	- 81.3
W - water	0	Q - heat losses	156.3
E - electric energy	25.1		
Total	78.4	Total	78.4

Table 9. Energy balance of the process of making sulphur from SO_2-containing gases.

Input Energy			Output Energy		
Flow	MJ	%	Flow	MJ	%
1 - SO_2 - gases	0	0	4 - sulphur	134.1	22.0
2 - energy from heating	198.3	32.5	5 -off-gases	226.6	37.1
3 -natural gas	412.1	67.5	Q - heat losses	249.7	40.9
Total	610.4	100.0	Total	610.4	100.0

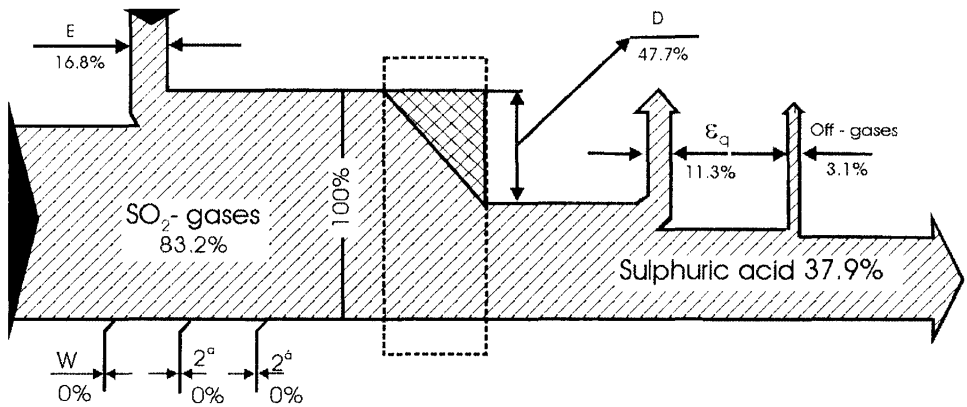

Fig. 4. *Grassman's diagram of the process of making sulphuric acid by one-stage convertion: 2^a, 2^b - air; W-water; E-electric energy; D-internal exergy losses; ε_q-heat exchange with environment.*

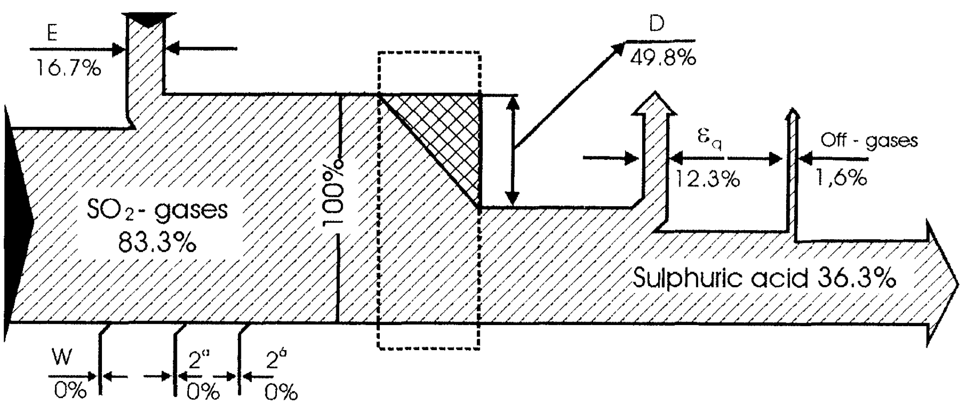

Fig. 5. *Grassman's diagram of the process of making sulphuric acid by two-stage convertion: 2^a, 2^b - air; W-water; E-electric energy; D-internal exergy losses; ε_q-heat exchange with environment.*

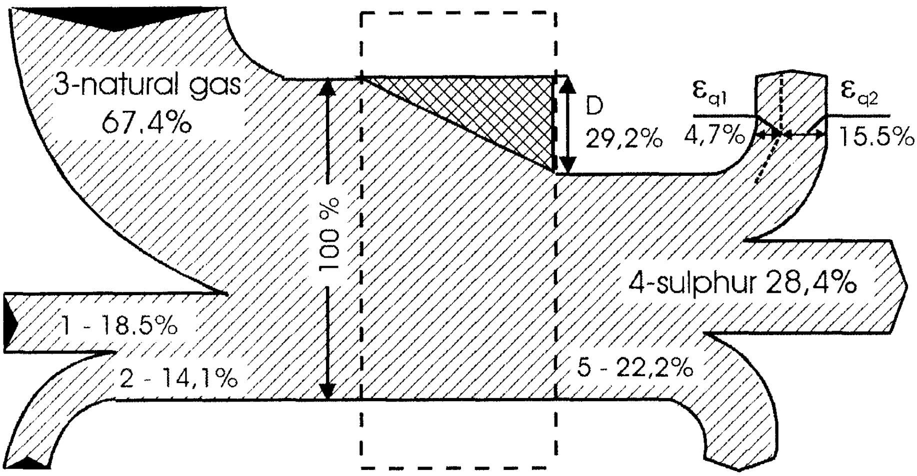

Fig. 6. Grassman's diagram of the process of making sulphur from SO_2-containing gases: 1-SO_2 - containing gases; 2-energy from heating of SO_2 - gases; 5-off - gases; D-internal exergy losses; ε_{q1}-heat exchange with environment; ε_{q2}-heat discharged during the cooling of gases after the reduction column.

Table 10. Exergy balance of the process of making sulphuric acid by one-stage conversion of SO_2.

Input Exergy			Output Exergy		
Flow	MJ	%	Flow	MJ	%
1 - SO_2 - gases	94.1	83.2	3 - dust	0	0
2^a - air	0	0	4 - off-gases	3.5	3.1
2^b - air	0	0	5 - H_2SO_4	42.9	37.9
W - water	0	0	ε_q	12.8	11.3
			D - internal losses		
E - electric energy	19.1	16.8	intrinsic	41.3	36.5
			other	12.7	11.2
Total	113.2	100.0	Total	113.2	100.0

Table 11. Exergy balance of the process of making sulphuric acid by two-stage conversion of SO_2.

Input Exergy			Output Exergy		
Flow	MJ	%	Flow	MJ	%
1 - SO_2 - gases	124.7	83.3	3 - dust	0	0
2^a - air	0	0	5 -off-gases	2.4	1.6
2^b - air	0	0	6 - H_2SO_4	54.3	36.3
W - water	0	0	ε_q	18.5	12.3
E - electric energy	25.1	16.7	D - internal losses		
			intrinsic	54.4	36.3
			other	20.2	13.5
Total	149.8	100.0	Total	149.8	100.0

Table 12. Exergy balance of the process of making sulphur from SO_2-containing gases.

Input Exergy			Output Exergy		
Flow	MJ	%	Flow	MJ	%
1 - SO_2 - gases	155.6	18.5	4 - sulphur	238.9	28.4
2 - energy from heating	118.6	14.1	5 - off-gases	186.7	22.2
3 - natural gas	566.9	67.4	ε_q	169.9	20.2
			D	245.6	29.2
Total	841.1	100.0	Total	841.1	100.0

3. Discussion

The processes of making sulphuric acid in the Copper Extraction Plant in the town of Pirdop, Bulgaria, both by one and two-stage conversion of waste SO2-containing metallurgical gases in copper smelting can be defined as relatively inefficient from the viewpoint of exergy balance.

The losses of useable energy are mainly internal: 47,7% in the one-stage and 49,8% in the two-stage conversion, and they occur due to the irreversible character of the processes which take place in the reactors themselves. The detailed internal losses (36,5% in the one-stage and 36,3% in the two-stage conversion - Table 10 and 11) point on the controlling role of the so called intrinsic exergy losses, *i.e.* those connected to the chemical process itself during which the exergy of the SO_2-containing gas turns consecutively into exergy of the oxidized gas and later into exergy of the final product: H_2SO_4.

The other internal irreversible losses are also great (11,2% in the one-stage and 13,5% in the two-stage conversion). They are due to the transformation of exergy in the irreversible processes of friction, heat exchange due to differences in temperature and concentration, expansion, fusion, distribution into flows with different thermodynamical parameters, evaporation, condensation, *etc.*

The external losses in both installations for sulphuric acid production are high. The diagrams presented (Fig. 4 and 5) show separately the exergy losses due to the emission of residual gases into the environment (3,1%, resp. 1,6%) and the other external losses, about 12% which are given in total and are not specified in details. The latter are due to the necessary heat exchange with the environment, no utilization of the exergy of the main flows, *etc.* These losses are related to the main thermo-technical equipment: reactors, absorbers and acid coolers.

Although the overall exergy efficiency is almost the same for both installations, there still is a difference in the distribution of losses and predominantly of the external ones. This is in a direct relation to the anthropogenic influence of the production process on the environment. The exergy of the gases emitted of of the installation is considerable, especially in the case of the one-stage conversion. The exergy depends mainly on the residual quantities of SO_2 and SO_3. In other words, there is a considerable exergy gradient in the zone of the industrial installation. This gradient facilitates dissipation of energy into the environment.

The process of making sulphur from SO_2-containing gases cannot be put on the list of exergy effective processes either (Fig.6). The internal losses are smaller (about 30% of the energy input in the process) compared to the ones in the process of making sulphuric acid, but only in case of incomplete technological cycle. If only the intrinsic losses during the "sulphren" process are added, *i.e.* those of the chemical transformation of the residual sulphur compounds in the outflowing gases (Flow 5 in Fig.6) into sulphur, then the total internal losses for the whole process will reach 36-37%.

The multistage nature of the process is a reason for considerable external exergy losses; 15.5% of them are due to the not utilized physical exergy of gas flows or their transfer from one piece of equipment to another. The total external losses due to heat exchange between the basic equipment and environment are 4,7%. It is also very difficult to utilize thoroughly the exergy of the outgoing gases (Flow 5) which will additionally increase the external losses. The analysis of this flow - a secondary source - should therefore be done in two ways: its utilization as a source of substances and energy, as well as its anthropogenic influence on the environment.

The consumption of primary energy sources for the production of sulphur is very high. The exergy of natural gas - deoxidizer is over threefold higher than the one of the main sources - the waste SO_2-containing gases. If the consumption of electricity is added to this, the total relative exergy consumption of the process is 4.5, compared to 0.2 in the processes of making sulphuric acid. Relative exergy consumption can be defined as the ratio between the additional exergy brought into a certain technological process to the exergy of the input material (in our case SO_2-containing gases).

The comparative analysis made for processing the SO_2-containing gases into H_2SO_4 and into sulphur confirms the energy advantages of the process of making H_2SO_4. That is due to the nature of the processes which take place: autothermal oxidation of SO_2 into SO_3 with a minimal consumption of primary energy sources in the production of sulphuric acid and reduction of SO_2 into elemental sulphur following complex chemical and technological models and great consumption of primary energy sources.

However, the problems arising from the great supply of sulphuric acid on international markets, and the resulting low prices, as well as the necessity to comply with the environmental standards put forward the need of carrying out a systematic energy analysis of the different processes of producing elemental sulphur from SO_2-containing gases. This study should give a solution to the following problems: improvement and optimisation of the reduction processes of SO_2, CHS and CS_2 into H_2S, the process of conversion of H_2S to sulphur; utilization of the secondary energy sources and reduction of the external exergy losses with the different flows, optimisation of the structure of the heat exchange system which treats the gasses in making sulphur; a study of the effect of the use of natural gas and of natural gas converted to (H_2 + CO) upon energy efficiency; optimisation of the structure of the technological flowchart of Claus's method aiming at high yield of sulphur and allowable concentration for content of SO_2 and H_2S in waste gases

The issues mentioned are subjects of our future studies.

4. Conclusions

The energy study of the processes of production of sulphuric acid and sulphur from SO_2-containing metallurgy gases is made by using the exergy method of thermodynamic analysis. The general and relative exergy characteristics of the processes are determined.

The results of the study show that:

1. The total exergy efficiency of the processes of making sulphuric acid by one- and two-stage conversion is nearly the same. The exergy efficiency is 35-36%. There is a difference in the distribution of the external losses which is directly related to the anthropogenic influence of the particular processes on the environment.

2. The process of making sulphur is ineffective from exergy point of view. The exergy efficiency is under 30%. There are considerable internal and external losses.
3. Some possible ways of increasing the exergy efficiency of the processes could be the following:
- Improving the parameters of the chemical processes in the main reactors (reduction columns and Claus-units) and thus reducing the exergy consumption of the system.
- Economy of the secondary energy sources by limiting the external exergy losses and mainly by utilization of the physical exergy of the gas flows and of the gases leaving the installation.

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