

# The influence of the catalyst worktime on SO<sub>2</sub> emission quantity from the sulfuric acid system and the catalyst waste material

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The catalytic process of SO<sub>2</sub> to SO<sub>3</sub> oxidation is the main step of sulfuric (VI) acid formation. The sustained catalyst operating due to its structural and textural modifications could disturb the process course. This paper includes the influence of the vanadic catalyst worktime on SO<sub>2</sub> emission and the expected amount of the obtained waste material of the inactivated catalyst.

**Keywords:** vanadic catalyst, inactivation, SO<sub>2</sub> emission, industrial waste material.

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## INTRODUCTION

The SO<sub>2</sub> to SO<sub>3</sub> oxidation process progresses with the vanadic catalyst participation that is responsible for the thermodynamic process capacity and ipso facto the SO<sub>2</sub> emission amount to the atmosphere. The catalyst active phase is formed by vanadium and potassium compounds like K<sub>2</sub>SO<sub>4</sub>:V<sub>2</sub>O<sub>5</sub> and K<sub>2</sub>S<sub>2</sub>O<sub>7</sub>:V<sub>2</sub>O<sub>5</sub> that have precisely matched the molar ratio K<sub>2</sub>O:V<sub>2</sub>O<sub>5</sub> and it depends on the type of the used silica carrier. The active phase is sometimes modified by sodium or cesium compounds<sup>1</sup>.

The catalyst that is operated under industrial conditions, is inactivated, which is estimated by the decrease of the SO<sub>2</sub> oxidation reaction rate. The inactivation is caused by the structural and textural changes of the catalyst that lead to the active phase recrystallization. The observed modification depends on the conditions and the catalyst worktime, and it provokes the catalyst complement or its partial elimination from the operating.

The general tendency of the production cycle increasing in sulfuric acid plants has been lately observed. It especially concerns the metallurgic systems, which work in connection with the operation of the metallurgic part of productive complexes. In such systems all standstills of sulfuric acid plants lead to the discontinuation of the copper production process. Since the production cycle extension is always accompanied by the increased emission of sulfur compounds, therefore it is necessary to examine and optimize all parameters of the production process run in sulfuric acid plants during the whole production cycle. The control purpose is the stabilization of sulfur compound emission according to emission limits. The optimization technique is recommended by BAT directions.

The optimization of the manufacturing process is approached in different ways. The method based on: the examination of the heat exchange node effectiveness and the conditioning in the contact-absorptive node, as well as the estimation of real kinetic parameters of the SO<sub>2</sub> oxidation process during the industrial manufacturing process, was developed in Poland. The catalyst distribution at each converter bed is calculated according to determined parameters, taking the present conditions under consideration. Then the optimal parameters of the contact-ab-

sorptive node are determined. Such technique allows the minimization of the sulfur compound emission. Moreover, it is also a basis of the prognostication of the catalyst amount that is necessary for each bed supplement. Ipso facto, it allows the defining of the amount of the forming waste material.

The optimization of the manufacturing process takes place in the Copper Smelter GŁOGÓW in the sulfuric acid system. This works converts gas that comes from copper ore roasting according to the shaftsman bake technology, which works like a multistage-process DK/DA - Figure 1. The system effectiveness is about 220 – 260 thousands tons MH/year. The catalyst that is operated in such a system is especially exposed to the increased inactivation due to the effectiveness of the process gas purification from danger impurities and the efficiency of the gas drying process. The effectiveness of the discussed installation is lower due to the applied technology of copper heat. It causes faster structural and textural catalyst modifications that lead to its premature inactivation.

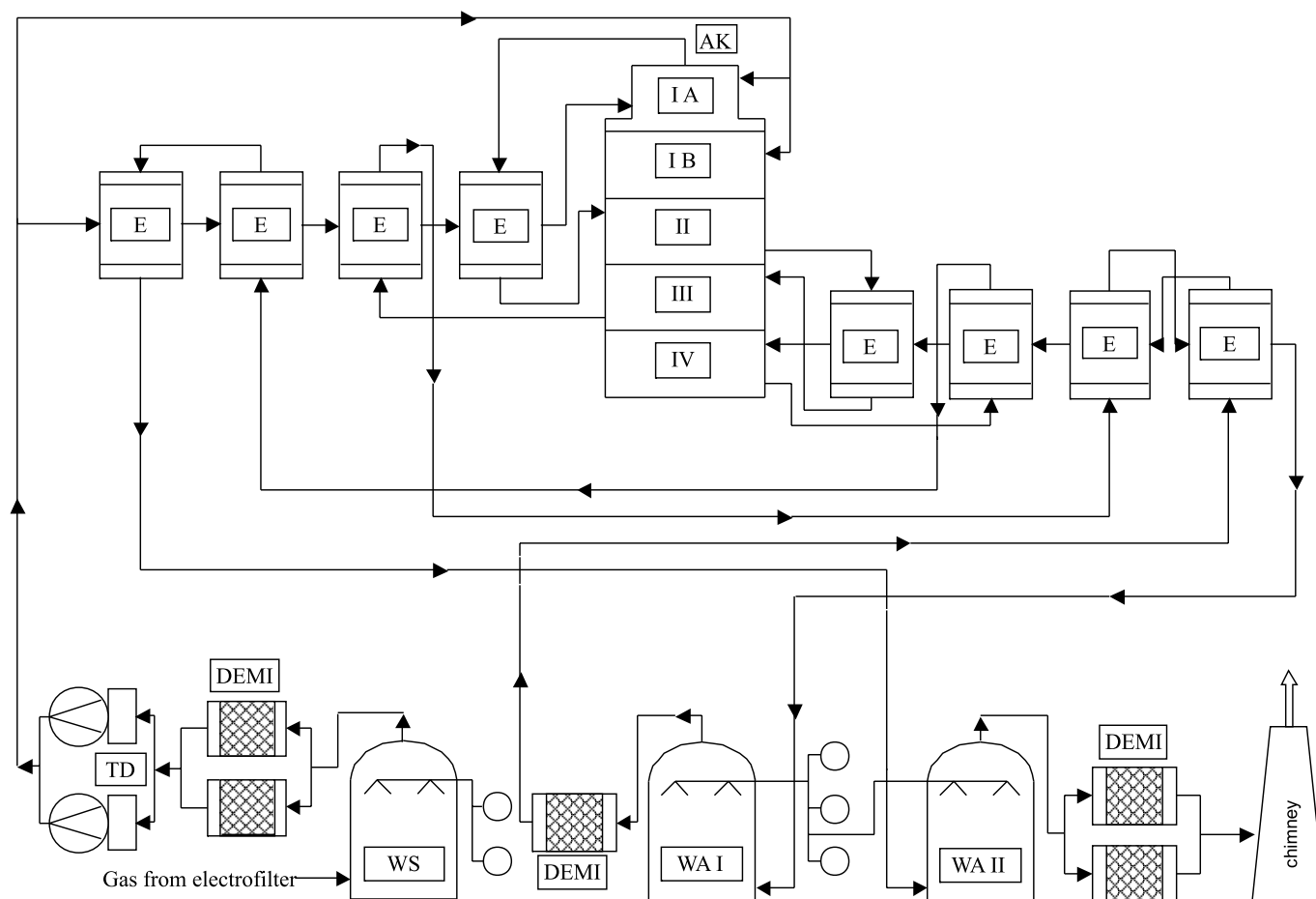
## THE RESEARCH PURPOSE

The main purpose of the studies was the estimation of the vanadic catalyst worktime influence on the SO<sub>2</sub> emission quantity to the atmosphere and the determination of the catalyst amount that is essential for the bed supplement in order to maintenance of optimum parameters of the sulfuric acid plant running (the waste material value).

Before the converter is loaded, the examination of the real reaction rate of SO<sub>2</sub> oxidation dependence on temperature  $r = f(t)$  and conversion  $r = f(x)$  was realized. Afterwards, on the basis of those studies, the calculation of the catalyst arrangement in the converter was done.

Starting with the first correction of the catalyst bed carrier, the productivity of the SO<sub>2</sub> oxidation process was carried out, based on sulfur dioxide concentration in the gas before and after the converter.

Later on the production process capacity on the basis of real kinetic parameters, taking under consideration the primary catalyst distribution, and optimal parameters of catalyst functioning was predicted. Thus the emission amount, which would be observed without accomplished modifications of the catalyst quantity at each bed, was



**Figure 1.** AK – converter, IA-IV – converter bed, E – exchanger, WS drying tower, WAI – interstage absorption tower, WAI I – final absorption tower, DEMI – demisters, TD – turbo-blower

determined. Such method was used because sulfur compound emission cannot be overdone under industrial conditions. The correction of the catalyst distribution hampers the estimation of real inactivation.

## RESULTS AND DISCUSSION

The initial catalyst distribution in the converter is collected in Table 1. The total volume of the used catalyst was 142 m<sup>3</sup>. After each year of the plant working, the average catalyst samples were collected from each bed.

**Table 1.** The initial catalyst distribution in the converter

Bed	Catalyst type	Project data	
		Shell height, m	Shell volume, m <sup>3</sup>
1	2	3	4
I	LP220	0.46	26
II	LP110	0.60	34
III	LP110	0.65	37
IV	LP110	0.80	45

SO<sub>2</sub> contents in the gas before the converter and the gas directed into the atmosphere was determined according to the industrial study methodology<sup>2</sup>. The examination of real kinetic parameters of SO<sub>2</sub> oxidation was operated in the technical apparatus equipped with the isothermal reactor with the internal gas circulation<sup>3</sup>. Such apparatus is used for the examination of fresh and operated catalysts. The kinetic studies were conducted for a sample that weighed 40.0 ± 0.1 g and the gas mixture contents corresponded with the industrial conditions (6% SO<sub>2</sub>, 14% O<sub>2</sub>, 80% N<sub>2</sub> and v = 0,3 Nm/s) – table 2.

On the basis of the determined reaction rates (r), the relative inactivation coefficient of the catalyst (η) was defined and the catalyst distribution at each bed was calculated.

$$\eta = \frac{r_0 - r}{r_0} \cdot 100$$

where: η – relative inactivation coefficient, %

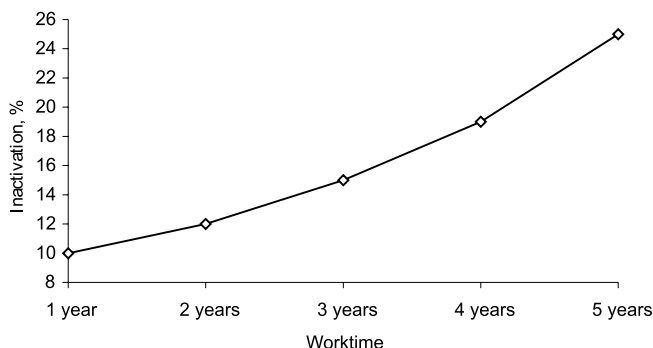
**Table 2.** The dependence of real reaction rate on temperature for I bed catalyst x<sub>w</sub>=0

Operating time	Reaction rate, 1/s											
	Temperature, °C											
	380	400	420	440	460	480	500	520	540	560	580	600
1	2	3	4	5	6	7	8	9	10	11	12	13
Fresh catalyst	0.01838	0.02430	0.03713	0.06008	0.07478	0.08258	0.08663	0.08738	0.08588	0.08363	0.08100	0.07875
1 year	0.01654	0.02187	0.03342	0.05407	0.06730	0.07432	0.07797	0.07864	0.07729	0.07527	0.07290	0.07088
2 years	0.01617	0.02138	0.03267	0.05287	0.06581	0.07267	0.07623	0.07689	0.07557	0.07359	0.07128	0.06930
3 years	0.01562	0.02066	0.03156	0.05107	0.06356	0.07019	0.07364	0.07427	0.07300	0.07109	0.06885	0.06694
4 years	0.01489	0.01968	0.03008	0.04866	0.06057	0.06689	0.07017	0.07078	0.06956	0.06774	0.06561	0.06379
5 years	0.01379	0.01823	0.02785	0.04506	0.05609	0.06194	0.06497	0.06554	0.06441	0.06272	0.06075	0.05906

$r_0$  – initial reaction rate at reference catalyst, 1/s

$r$  – reaction rate at catalyst after operating time, 1/s

The conducted investigations confirm the progressive inactivation of the operated catalyst. The relative inactivation of the I bed catalyst is about 10% after 1 year, 12% after 2 years, 15% after 3 years and it increases to 25% after 5 years of operating – figure 2.



**Figure 2.** The dependence of the catalyst inactivation at I bed on the catalyst worktime

The investigations demonstrated that the strongest inactivation was observed at I bed and the lowest one – at IV bed.

If the catalyst worktime increased, the capacity of SO<sub>2</sub> oxidation would decrease and the emission would increase – Figure 3.

The emission amount changes weren't caused by the gaseous SO<sub>2</sub> loading modification of the system because it worked with insignificant changes of gaseous SO<sub>2</sub> loading during an estimated period. The average SO<sub>2</sub> concentration in the gas directed into the converter was insignificant and it varied between 6 and 7.5% – Figure 4.

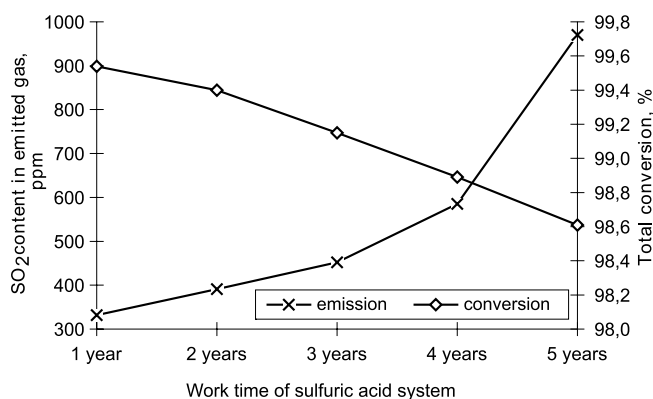
The computer simulation of SO<sub>2</sub> emission, relating to the catalyst inactivation increase, indicates its increase as the catalyst worktime increases. The average emission was 100 kg/h during the first operating year and it would increase up to 124 kg/h if the carrier correction weren't applied. The emission would increase systematically to 293 kg SO<sub>2</sub>/h in the following years that meant the annual emission of 2320 tons (0,293kg/h·24h·330days) – Figure 5.

Such optimization studies allow the determination of the vanadic catalyst amount that is necessary for the supplement at each bed of the converter in order to stabilize the process capacity – Table 3.

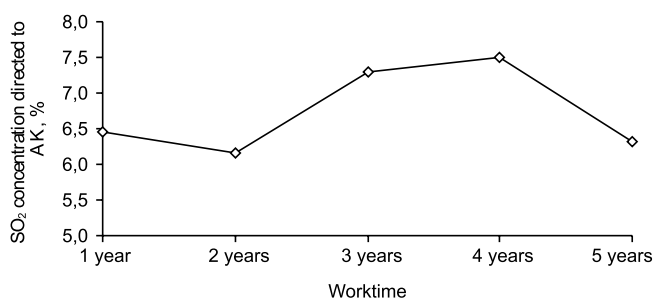
During the research period, the catalyst amount was increased (additional 12 m<sup>3</sup>).

## CONCLUSIONS

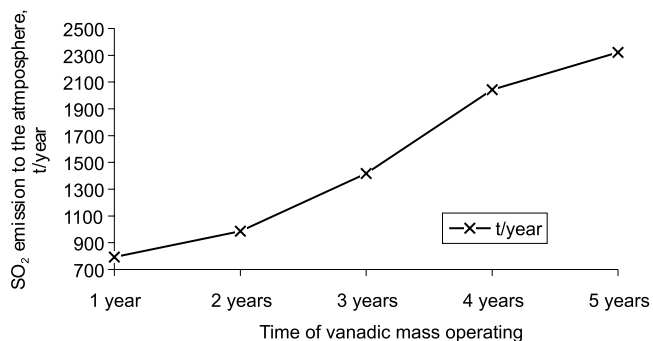
The production cycle extension of the sulfuric acid plant generates the danger for the environment and it results mostly from the emission of harmful sulfur compounds.



**Figure 3.** The dependence of SO<sub>2</sub> oxidation and the emission capacity on the catalyst worktime emitted



**Figure 4.** The average system loading by SO<sub>2</sub> gaseous



**Figure 5.** The amount of SO<sub>2</sub> emitted to the atmosphere

The conducted experiments demonstrate that the production cycle extending up to 5 years would lead to a six-time SO<sub>2</sub> emission increase to the atmosphere if proper corrections of the bed filling weren't applied.

The main reason of the problem discussed is the progressive catalyst inactivation during its worktime. The problem could be prevented by suitable corrections of the catalyst amount at each bed. The corrections are defined on the basis of real kinetic parameter studies for the operated catalyst.

Moreover, the sulfur compound emission to the atmosphere can be limited by the parameter optimization of the system during the production run. BAT directions require such technique.

**Table 3.** The catalyst amount oriented to the supplement at each bed

Bed	Catalyst type	Project data		The amount of completed catalyst during 5 years
		Shell height, m	Shell volume, m <sup>3</sup>	Shell volume, m <sup>3</sup>
1	2	3	4	
I	LP220	0.46	26	15
II	LP110	0.60	34	11
III	LP110	0.65	37	3
IV	LP110	0.80	45	14
Sum			142	43

The vanadic waste material is produced as a result of structural and textural modifications of the operated catalyst and its deposit is forbidden. The waste material quantity could be predicted on the basis of the kinetic process.

#### **ACKNOWLEDGMENTS**

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