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ALKALINE WASHING OF OFF-GASES FROM SULPHURIC ACID PLANTS

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Sulphuric acid manufacturing plants are one of the most important sources of air pollution in the chemical industry, due to the large number of widely scattered installations as well as to the amount of pollutants emitted into the atmosphere by each plant. Sulphuric acid is a principal intermediate in a variety of industries. Most of the sulphuric acid produced is consumed in the production of fertilisers, in particular of phosphatic fertilisers.

The overall production of H_2SO_4 and also the capacity of the individual plants have increased steadily.

The main source of air pollution in sulphuric acid plants are the off-gases, which contain varying amounts of harmful sulphur oxides, i.e. SO_2 and, to a lesser extent, also SO_3 and H_2SO_4 mist.

The SO_2 content in the off-gases from conventional contact process plants is 0.2-0.3 mol.%. The more obsolete plants emit up to 5% of the processed sulphur. The more recent installations usually employ some modification of the double catalytic oxidation and double absorption process, which brings about a considerable decrease in the SO_2 content in the off-gases; e.g. in Czechoslovakia this value is approximately 0.08 mol.%. As the capacity of the newly built plants will grow to some 1,000 - 2,000 t H_2SO_4/day, even this lowered SO_x concentration may become intolerable, particularly in certain heavily industrialized areas.

According to the regulations issued by the Czechoslovak authorities responsible for hygienic inspection, the maximum permissible amount of SO_2 emitted from sulphuric acid plants is 1.2 kg/t H_2SO_4 and its maximum content in off-gases is 110 ppm. The standards for SO_3 are 60 mg/m^3 and 0.22 kg SO_3/t of H_2SO_4 produced (as monohydrate).

A feasible way for the SO_x pollution abatement is alkaline washing of the sulphuric acid plant off-gases. The Research Institute of Inorganic Chemistry in Usti nad Labem, in co-operation with several manufacturing plants, has conducted research on processes and equipment for alkaline washing of H_2SO_4 off-gases for many years and three modifications based on the alkaline washing concept have been developed and proven in the commercial scale at the present time :

1. SO_2 absorption from off-gases combined with the production of $Na_2S_2O_4$;

2. SO_2 absorption from off-gases by ammonia with subsequent decomposition of the scrubbing liquors by HNO_3;

3. SO_2 absorption from off-gases by ammonia with subsequent decomposition of the scrubbing liquors by H_2SO_4.

The processes have been realized and proven in industrial plants. The processes 2 and 3 have been designed for and constructed in the 100,000 tpa H_2SO_4 plants at Lovosice (North Bohemian Chem.Works -SCHZ) and in Ostrava (Moravian Chem.Works - MCHZ) resp. The following description and discussion concern these two plants and their operation.

The process equipment is very similar in both units and its essential element is an absorption tower packed with vertically orientated helices, which have also been developed in the RIIC. According to the results of extensive testing of this type of absorbers, their use for alkaline washing enables to reduce the SO_2 content from an initial value of about 0.3 mol.% to 0.02 mol.% and, provided a reliable automatic control is incorporated, even to less than 0.01 mol.%.

<u>Alkaline washing of off-gases in the SCHZ Lovosice plant</u>

The flow-sheet of this industrial installation is shown in Fig.1. The main items of equipment are : two absorption towers connected in series (with respect to the gas flow), circulating liquor receiver, saturated solution tank, desorption column fitted with a steam heated boiler, recycled stream mixer, aqueous ammonia storage tank, decomposed solution (i.e. product) storage tank.

The reactions taking place in the process may be described as follows :

$$2NH_3 + H_2O + SO_2 = (NH_4)_2SO_3 \quad (1)$$

$$(NH_4)_2SO_3 + H_2O + SO_2 = 2NH_4HSO_3 \quad (2)$$

$$(NH_4)_2SO_3 + 2HNO_3 = 2NH_4NO_3 + SO_2 + H_2O \quad (3)$$

$$NH_4HSO_3 + HNO_3 = NH_4NO_3 + SO_2 + H_2O \quad (4)$$

$$2NO_3^- + 3HSO_3^- = 2NO + 3SO_4^{2-} + H^+ + H_2O \quad (5)$$

$$H^+ + 2NO_3^- + HSO_3^- = 2NO_2 + SO_4^{2-} + H_2O \quad (6)$$

$$NO_3^- + HSO_3^- + NH_4^+ = N_2 + H^+ + SO_4^{2-} + 2H_2O \quad (7)$$

The reactions (1) and (2) take place in the absorption towers, (3) and (4) in the desorption column and boiler. The decomposition may be accompanied by certain undesired reactions (5, 6, 7), which are brought about by higher temperatures and by exceeding the recommended nitric acid strength.

It has been verified experimentally that the reactions (5, 7) can be suppressed by lowering the concentration of HNO_3 to a determined value, depending on temperature. The assessed values of maximum HNO_3 concentration at a given temperature are as follows :

Temp. (°C)	107	103	98	89
Max. concn. of HNO_3 (wt.%)	0	5	10	20

These values of HNO_3 concentration must never be exceeded, not even locally. In practice, when 50% HNO_3 by weight is used, the concentration required for the desorption column operation is adjusted by mixing the acid with an aliquot portion of the cooled decomposed liquor (recycled stream).

A typical composition of the saturated absorption liquor and of the solution as obtained by its decomposition by HNO_3 is shown in Table 1.

Table 1

Component	Absorption liquor	Decomposed solution
SO_2 (kg/m^3)	300	1
NH_3 (kg/m^3)	130	
$(NH_4)_2SO_4$ (kg/m^3)	100	100
NH_4NO_3 (wt.%)	-	40

The decomposed solution is further processed within the SCHZ combine, viz. in the plant producing prilled calcium ammonium nitrate. Sulphur dioxide is delivered by pipeline to a chamber process sulphuric acid unit, still operating at Lovosice, where it is combined with the roaster gas stream prior to oxidation.

Some technico-economic characteristics of the process are given in Table 2.

Table 2

Volume of treated off-gas (m^3/hr)	40,000
Pressure drop over two absorption towers (mm of H_2O column)	140
Linear gas stream velocity in absorption towers (m/sec)	3.7
Inlet SO_2 concentration (mol.%)	0.25
Outlet SO_2 concentration (mol.%)	0.02
Overall NH_3 losses (%)	8
Steam consumption (t/tSO_2)	1.3
Manpower consumption (hr/day)	12
Plant cost (as % of investment costs of the whole sulphuric acid plant)	5
Costs balance (sum of credits for SO_2 and NH_4NO_3 - total production costs) (million Cz. crowns/year)	+ 0.25

Alkaline washing of off-gases in the MCHZ Ostrava plant.

The capacity of this unit is identical to that of the SCHZ Lovosice installation. The process flowsheet is shown in Fig.2. The absorption section differs from that in the Lovosice plant for each tower is equipped with an independent liquid loop and the scrubbing liquors are circulated in these two loops at different compositions.

Sulphuric acid is used to decompose the saturated absorption liquor; the process is carried out in a mixing reactor that is not heated and also the desorption of SO_2 is effected in a separate desorption column by air without heating. The necessary air for stripping SO_2 is supplied from the main blower of the H_2SO_4 plant. The gas leaving the stripping column is passed through a drier and the dry mixture of SO_2 with air is fed back to the sulphuric acid plant, where it is added to the gas stream entering the contact stage.

The reactions taking place in the absorption section proceed according to the same mechanism (equations (1) and (2)) as in the SCHZ unit. The decomposition by H_2SO_4 can be described by the following reactions :

$$(NH_4)_2SO_3 + H_2SO_4 = (NH_4)_2SO_4 + H_2O + SO_2 \quad (8)$$
$$2NH_4HSO_3 + H_2SO_4 = (NH_4)_2SO_4 + 2H_2O + 2SO_2 \quad (9)$$

No side reactions take place in this case.

The main reason for the use of air for SO_2 removal from the decomposed absorption liquor is to avoid serious corrosion problems, which would necessarily arise if the desorption was carried out by boiling. Air is by-passed from the main air duct of the sulphuric acid plant and joins the main gas stream again before it enters the contact stage; its SO_2 content is virtually the same as in the gas leaving the sulphur burning section (see Fig.11). Since an independent drying column is incorporated in the by-pass system, the rate of the by-passed air supply needs not to be controlled very accurately. The air system may operate without changes even when the process of the scrubbing liquor decomposition by H_2SO_4 is temporarily discontinued. This possibility is advantageously used to intensify SO_2 desorption from the decomposed scrubbing liquor : the decomposition itself is effected practically batchwise during a short period of time and the resulting solution is then allowed to circulate through the stripping column for a longer time. Consequently, the content of SO_2 remaining in the solution may be reduced to less than 0.1 g/l. This arrangement also contributes to a certain economic benefit of the process as it does not require any steam for SO_2 desorption.

A typical composition of the saturated absorption liquor and of the $(NH_4)_2SO_4$ solution from the decomposition and stripping sections is shown in Table 3.

Table 3

Component	Absorption liquor	Decomposed solution
NH_4HSO_3 (kg/m^3)	348	-
$(NH_4)_2SO_3$ (kg/m^3)	135	-
Free SO_2 (kg/m^3)	-	0.1
$(NH_4)_2SO_4$ (kg/m^3)	100	500

After the completion of the decomposition and stripping processes the remaining content of free sulphuric acid is neutralized by ammonia.

Some important technico-economic characteristics of the MCHZ Ostrava process are given in Table 4.

Table 4

Volume of treated off-gas (m^3/hr)	40,000
Linear gas velocity in absorption towers (m/sec)	3.7
Pressure drop over two absorption towers (mm of H_2O column)	140
Liquid rate in absorbers (m^3/m^2.hr)	2-3
Absorption efficiency (%)	85
Rate of air for stripping (m^3/hr)	500
Steam consumption (t/tSO_2)	0
Plant cost (as % of investment costs of the sulphuric acid plant)	4.0
Cost balance (sum of credits for SO_2 and $(NH_4)_2SO_4$ - total production costs) (million Cz.crowns/year)	+ 0.4

Process control

The regulation of the unit operation and adjusting and controlling of most of the process parameters are automatic. The instruments and control elements used in the control system are either currently available or have been specially developed for this purpose. The individual controls and their components (regulation drive and transmission systems, valves are mostly of Czechoslovakian provenience. The control systems used in both plants are similar.

Metering of aqueous ammonia to the absorption section is conducted manually by distance regulation of the control valve in accordance with the required performance of the absorbers.

Besides, an automatic ammonia dosing system was successfully tested. Its principle consists in continuous measuring of SO_2 tension over the absorption liquor and in automatic adjusting of SO_2 partial pressure to a preset value by regulating the rate of ammonia supply. This system, however, has not yet been adopted in the plants.

Constant density of the absorption liquor is maintained at a desired value by regulating the rate of make-up water by means of a pneumatic valve, whose adjustment is controlled by a pneumatic densimeter.

Liquid level in the circulating liquor receiver is adjusted automatically according to a pneumatic level indicator.

Automatic metering of HNO_3 for the decomposition of the scrubbing liquor is based on pH of the solution as measured by a foreign-made pH-meter. The rate of sulphuric acid supply (MCHZ Ostrava) is adjusted manually.

The supply of steam for the decomposition section in the Lovosice plant is controlled automatically on the basis of temperature in the desorption column. The rate of air for SO_2 stripping (Ostrava) is adjusted manually.

Absorber packed with orientated helices

This type of absorption apparatus is used in both processes discussed. The feature of the absorbers are wire helices (wire diameter 2-4 mm) mounted vertically in a supporting structure. The helix whorl diameter is 35-40 mm and the number of whorls per m of helix length is approximately 90. Packing density, i.e. number of helices per 1 m^2 of the absorber cross-section area is 400-600.

This special packing is superior to conventional kinds of packing (Rashig rings, Berl saddles, Intalox) in most operational conditions; in particular, they exhibit a lower hydraulic resistance (i.e. pressure drop over the packing), thorough utilization of the surface area, perfect self-distribution of liquid over the packing, and relatively long residence time of liquid on the helices.

A more detailed description of the helical packing and a discussion of its characteristics is the subject of a recently published paper (1).

The design of the packing arrangement and different ways of its assembling as well as of the construction of absorbers are illustrated in Figs. 3-10. A view of plant scale absorption towers is shown in Figs. 9 and 10.

Naturally, the use of absorbers fitted with helical packing is not limited to desulphurization. Recently, they have been successfully applied also for drying of chlorine by sulphuric acid in brine electrolysis plants, for the absorption of nitrous gases, and for cleaning of acidic emissions from various industrial operations (2).

Owing to their specific properties, the helical packing absorbers are best fitted for processes involving the treatment of very large volumes of gases, in which the concentration of the solute to be removed is relatively low, and where a low rate of scrubbing liquid, low pressure drop, countercurrent arrangement of the gas-liquid phases flow, and a high degree of flexibility in their performance (esp. with respect to the fluctuations in the feed gas rate) are required.

Conclusions

The extensive experience gained during the development, design, construction and operation of the plant-scale installations has proved that the SO_2 content in sulphuric acid plant off-gases can be controlled more efficiently by alkaline washing than by a double absorption process. The main advantage of the latter process is that no by-products are produced but in plants with a capacity of 300 t H_2SO_4/day and more the double absorption may not be an adequate solution of the air pollution problem.

Both the investment and production costs of the alkaline washing processes are lower and this approach could become the final solution for the abatement of air pollution caused by sulphuric acid plants, provided that also the remaining problems of automatic process control and, in particular, the question of by-products, are successfully solved.

Literature

(1) Klimecek R., Krivsky Z., and Veverka V., Brit. Chem. Eng. & Proc. Tech., 16, 1018, (1971).

(2) Klimecek R., Ochrana ovzdusi, 11, 173, (1970).

List of Figures

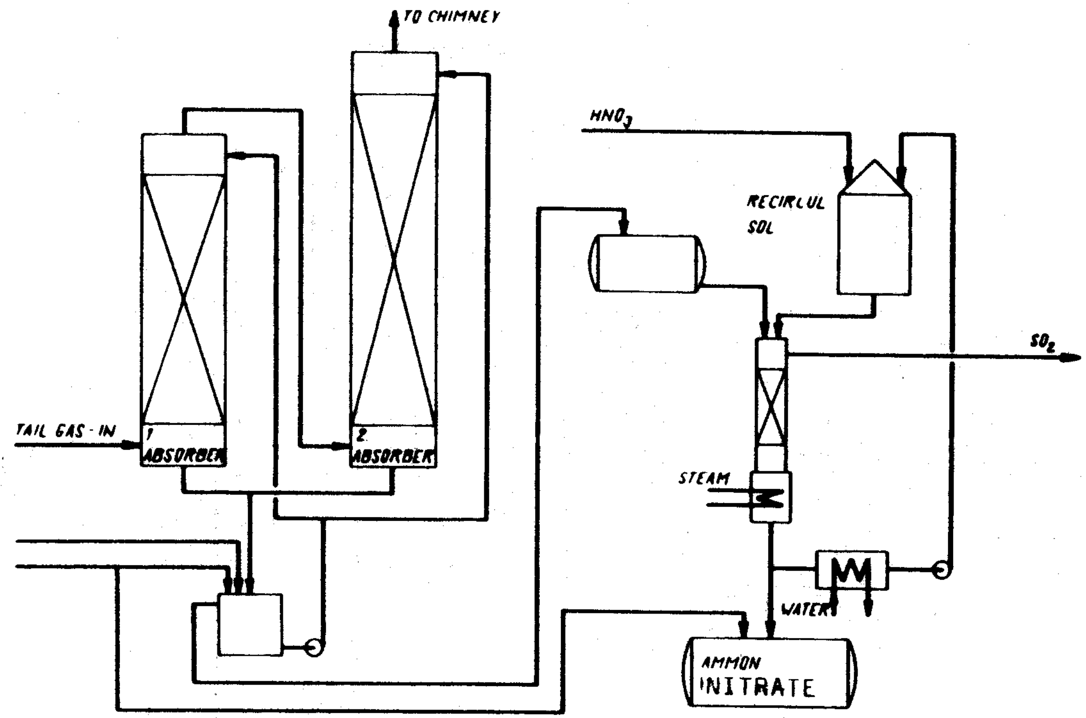

FIG 1 SO_2 RECOVERY UNIT AT SCHZ LOVOSICE

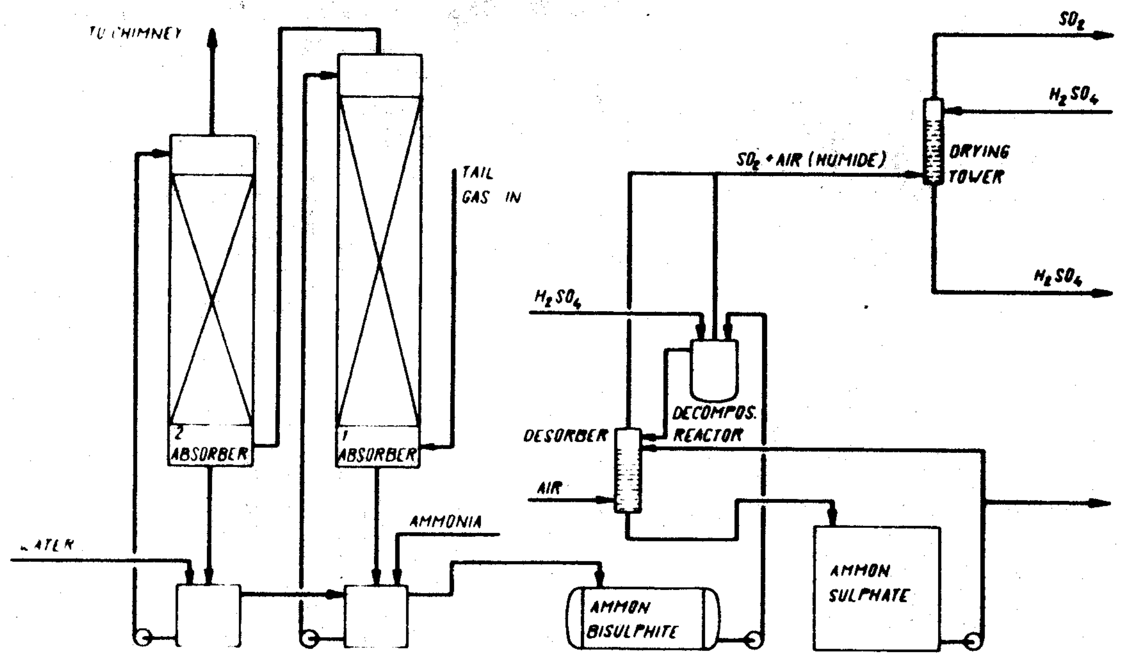

FIG 2 SO_2 RECOVERY UNIT AT MCHZ OSTRAVA

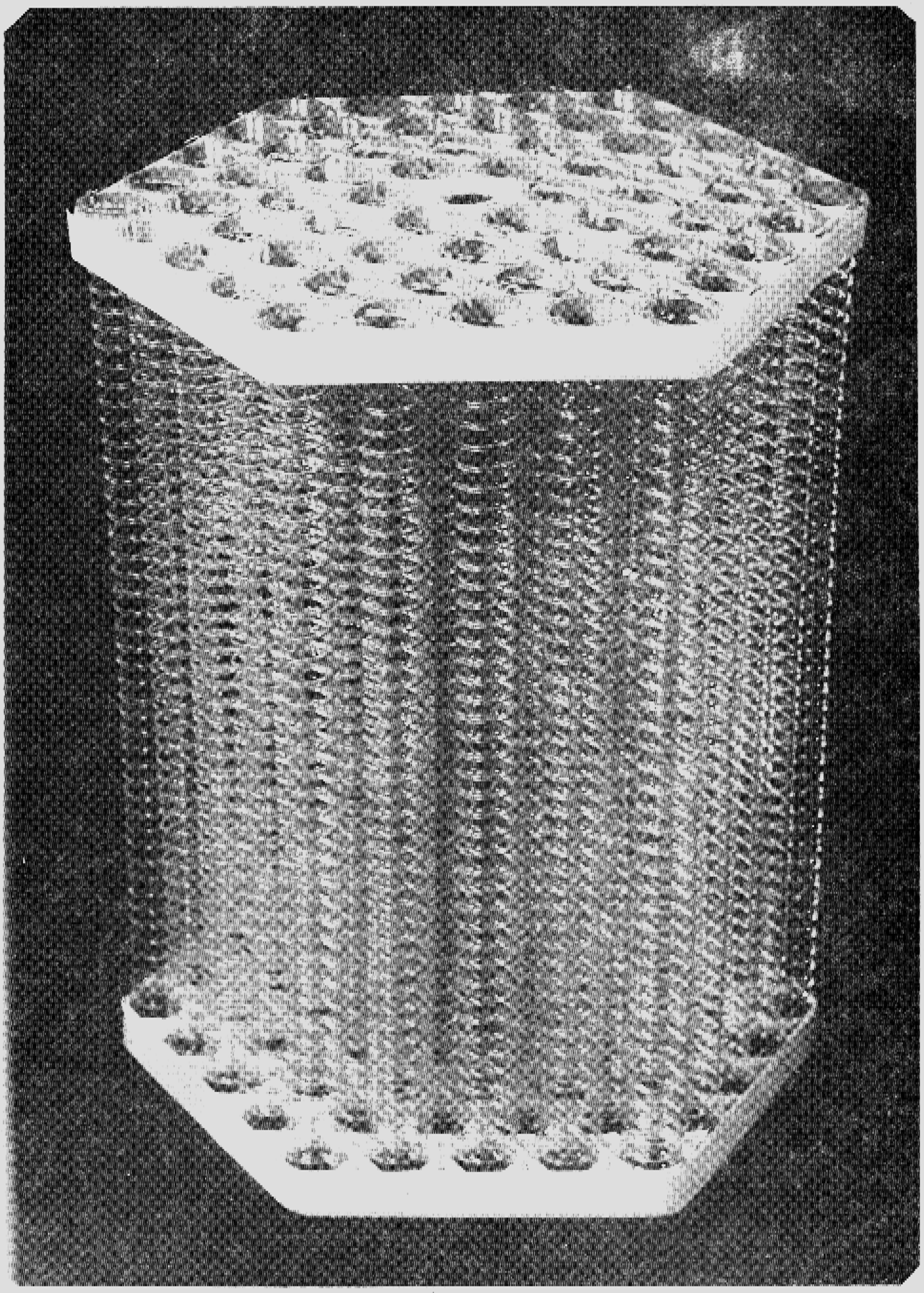

Fig. 3

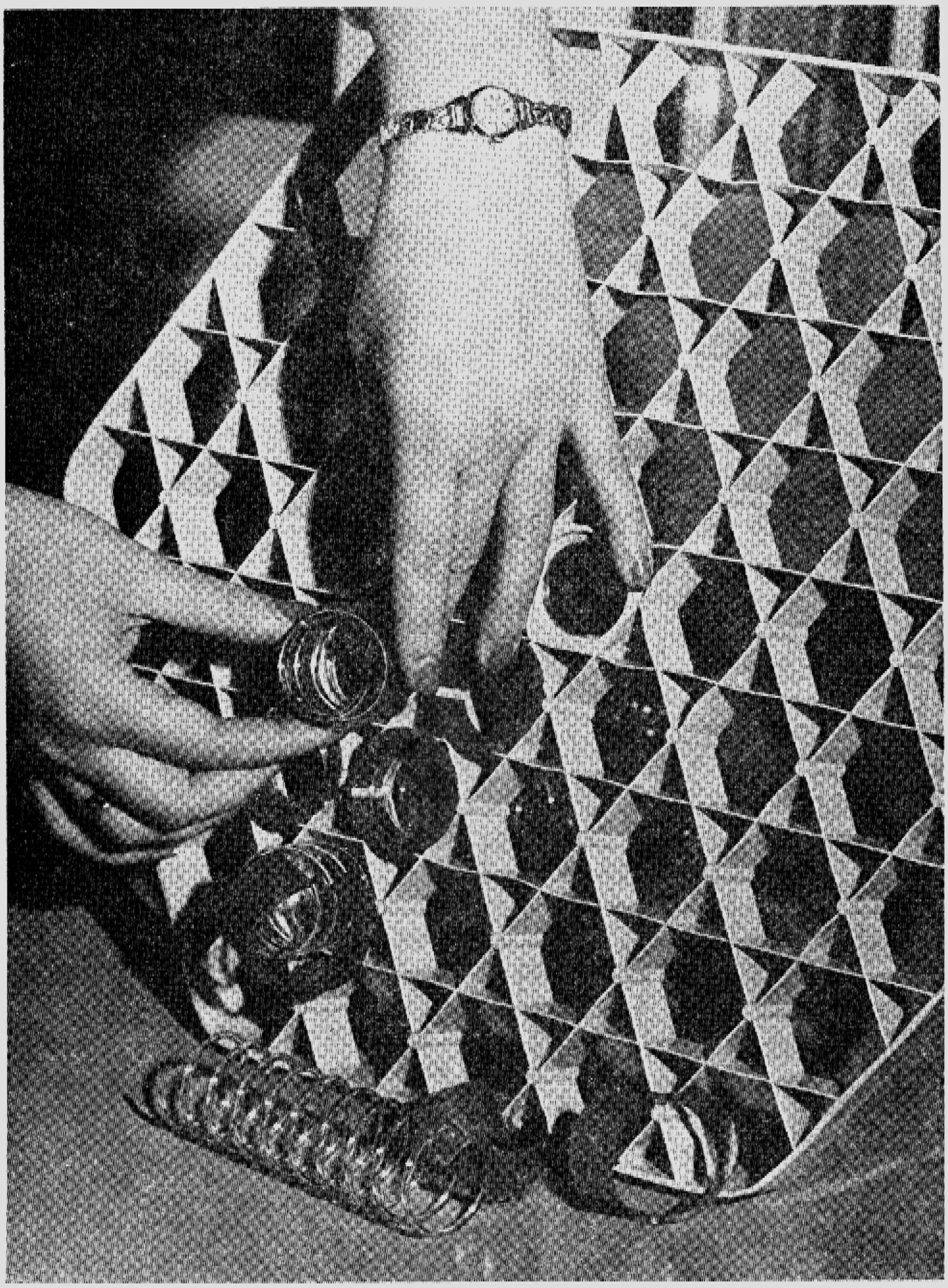

Fig. 4

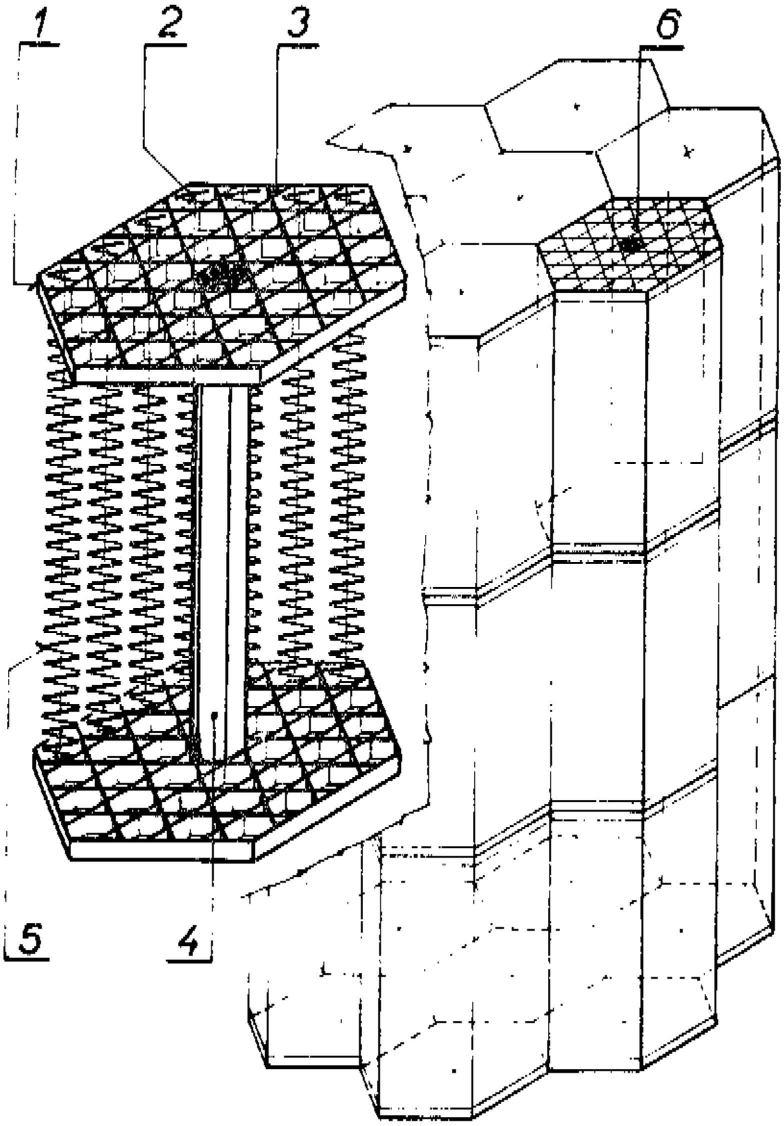

Fig. 5,6

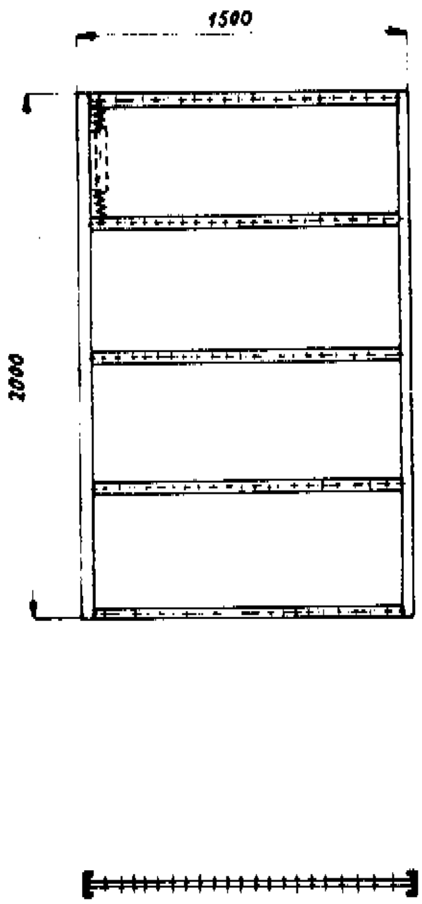

FIG. 7

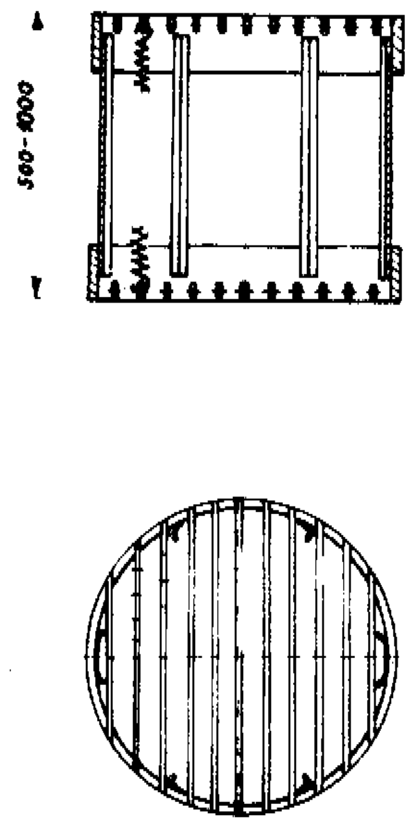

FIG. 8

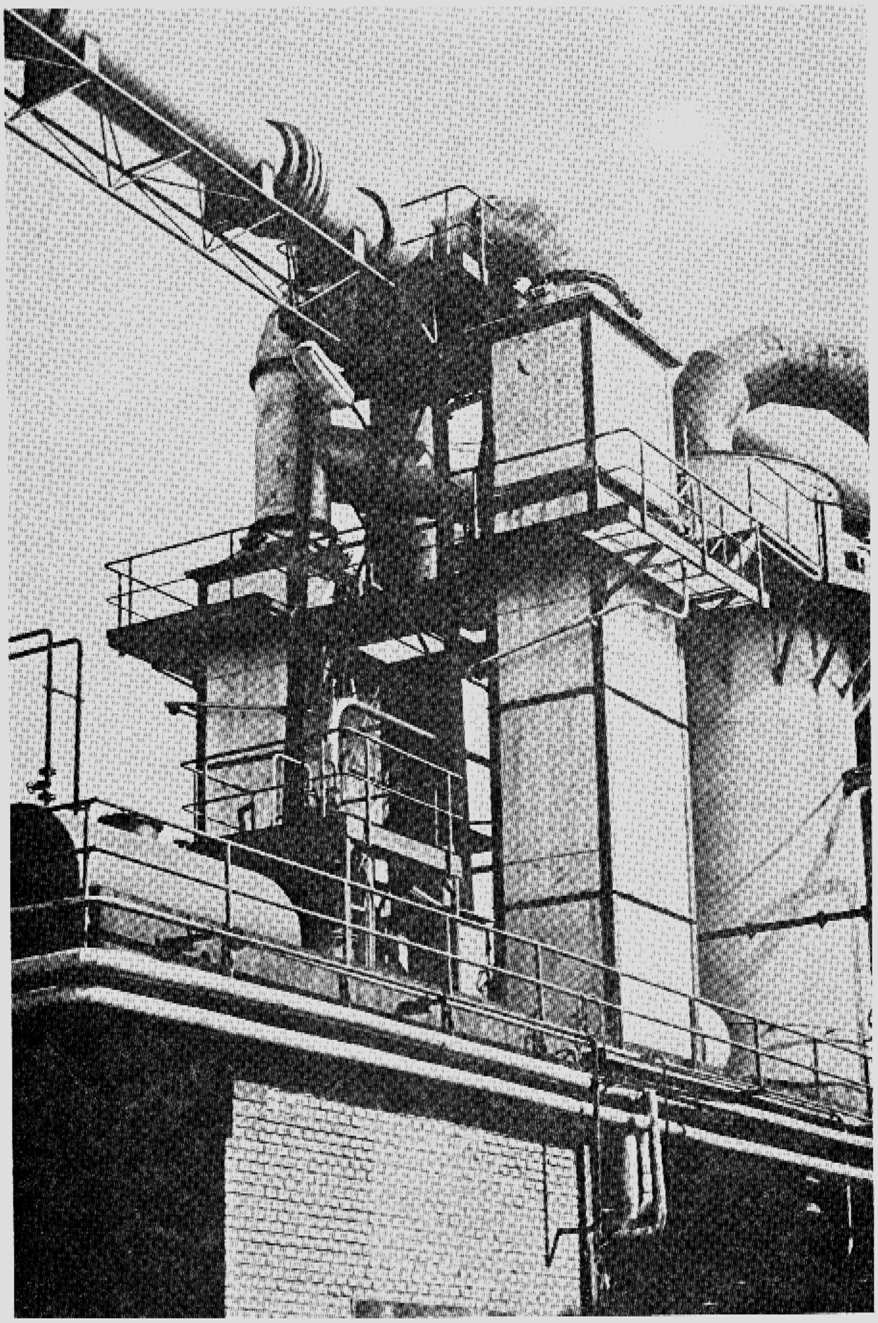

Fig. 9

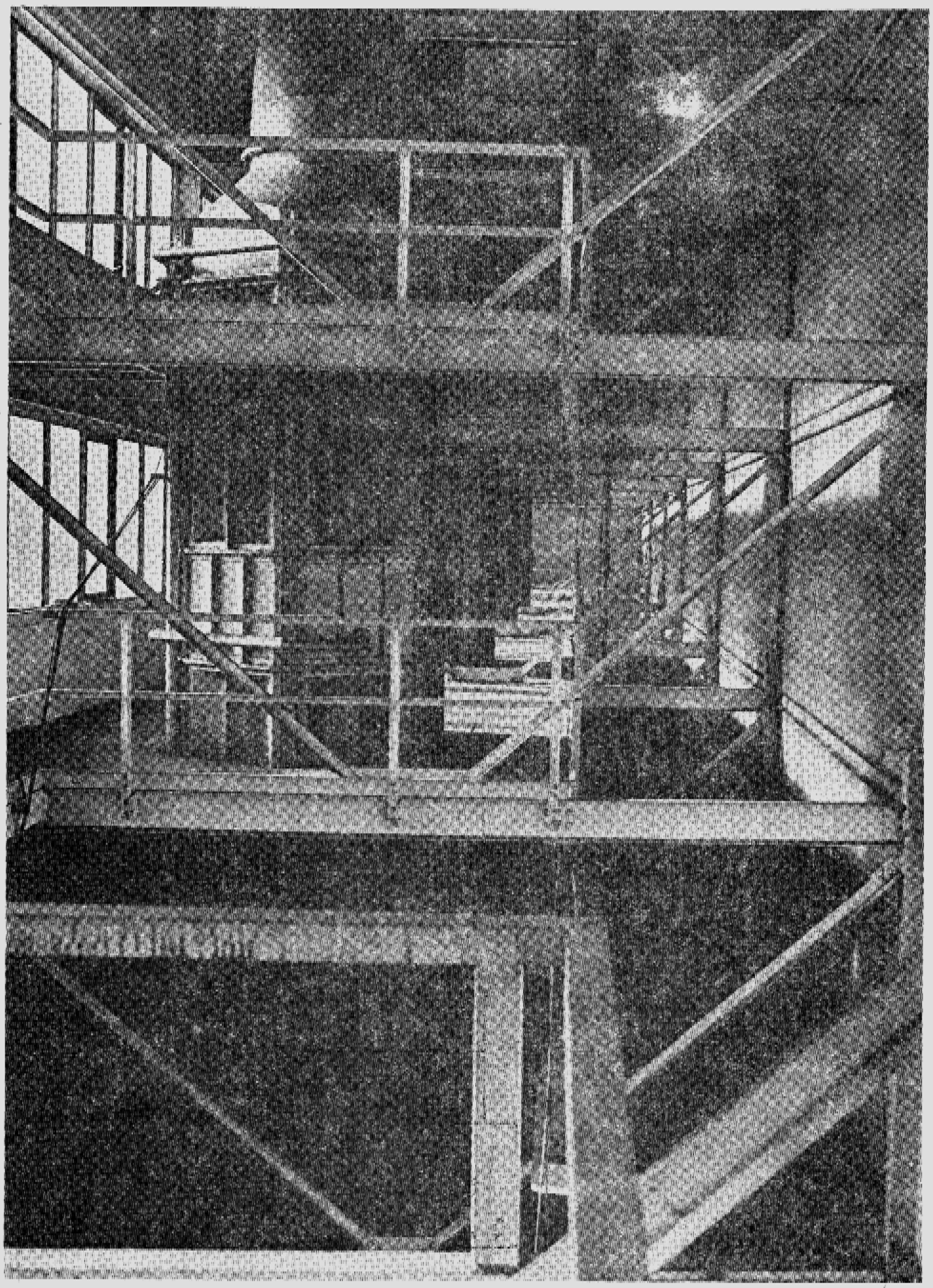

Fig. 10

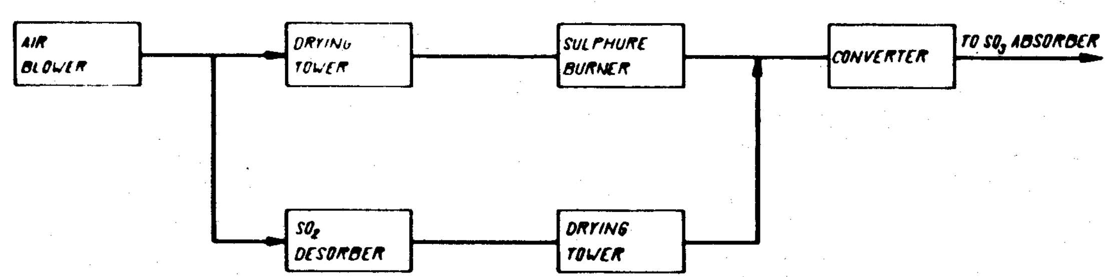

FIG 11 FLOW - SHEET OF AIR - BY - PASS FOR SO_2 DESORPTION

DISCUSSION

Mr. KLIMECEK (Research Institute of Inorganic Chemistry, Czechoslovakia)

The purpose of my project is to draw the attention of experts of phosphate fertilizer manufacture on the problems of atmospheric pollution associated with waste gases from sulphuric acid plants. Since most of the sulphuric acid produced is used to manufacture phosphate fertilizers, relevant atmospheric pollution problems are not unimportant ; the progress made in research work carried out at the Research Institute of Inorganic Chemistry at Usti and completed by the construction and the start up of two industrial units which are the subject of the written paper and one of which will be visited at Lovosice can be characterized as follows :

1. The SO_2 absorption problem using ammonia was solved by using an original piece of equipment developed for that purpose. The advantage of the vertical column with helix is in its relatively small size due to a high velocity of the gas flow with a small pressure drop and its spraying density.

2. Concerning the process of decomposition of absorbing solutions by nitric acid the possible way of working at high temperature while avoiding secondary reactions and, hence, nitrogen losses.

3. The total elimination of steam consumption in the process at Ostrava as a result of a new modification of the decomposition of absorbing solutions and SO_2 desorption by air. Nevertheless one cannot state that there is no open question left in that field ; a few still remain including the existence of by-products, probably the most important and cumbersome one. It is the only disadvantage of alkaline scrubbing as compared to double catalysis, which should be eliminated so that this method could gain the universal recognition it requires to solve the problem, since, from the point of view of efficiency of desulphuration, the scrubbing process ensures a higher level of purification of waste gases. Finally would delegates correct an error on page 23 - 9 fig 1, where ammonium nitrate should stand for ammonium sulphate.