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BY SULPHURIC ACID PLANTS

by

N. Popovici, D. Stanciu, T. Ciobanu

EDITED TRANSLATION

FTD-ID(RS)T-1686-79 29 January 1980

MICROFICHE NR: FTD-80-C-000157

CSB78125907

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English pages: 10

Source: Revista de Chimie, Vol. 28, Nr. 3, March 1977, pp. 263-267

Country of Origin: Romania
Translated by: SCITRAN
F33657-78-D-0619
Requester: PHE
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PREPARED BY:

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ABSTRACT

D.C. 628.512:661.25

The paper presents two processes developed on an industrial scale in Romania, having as a practical result the decrease in noxious gases emissions by sulphuric acid plants.

1. Retaining and use of SO_2 poor gases (as well as SO_3 gases in the mixture) by ammonia absorption.

2. Double absorption process in contact sulphuric acid plants.

The former process with licences patented in other countries as well, is based on the commonly known reaction of SO_2 fixing (possible SO_3 too) through ammonia absorption mainly as ammonium bisulphite which is further decomposed with H_3PO_4 or H_2SO_4. The process provides a retaining performance of 93–95 per cent and fits perfectly to a fertilizer plant requiring besides a low investment. The process has successfully been applied to an industrial unit under current operation, consisting of three absorption lines each processing 50.000 Nm^3/h with the desorption side in one circuit only. The double absorption process offers, in comparison with other similar processes known, the advantage of a high heat recovery, having a systematical and simplified layout of the gas circuits, thus permitting a close location of the contact units. These advantages make the application of the process possible even in the case of gas processing from the non-ferrous metallurgical works.

The recent explosive growth of industry has brought about some negative side effects among which pollution of the environment is one of the most important.

A very noxious compound present in the atmosphere in larger and larger quantities is sulphur dioxide. Sulphur dioxide results from the burning of fossil coals, hydrocarbons with sulphur and also from a number of industrial processes in energetics, non-ferrous metals, siderurgy and the chemical industry. In the latter the production of sulphuric acid is the main source.

The concentration of industry and energy reproduction in large units has modified large zones of our planet by creating ecological imbalances.

Aside from the air pollution due to SO_2, another side effect is the corrosive action on industrial installations, buildings and works of art.

The explosive industrialization of the last decades has brought a large increase in the production of sulphuric acid worldwide, which has surpassed 100 million tons/year. In order to decrease the production costs of sulphuric acid, useful in the production of fertilizers, large industrial installations with capacities of over 2,000 tons/day have been built. The creation of such industrial complexes for the production of fertilizers has resulted in a concentration of the production of sulphuric acid, with capacities of 3-4,000 tons/day being common. The upper limit of the conversion efficiency of SO_2 into SO_3 in classical installations is about 98%, and the degree of absorption is about 99.5%. Thus for a production of 4,000 tons/day of H_2SO_4, 45-65 tons of SO_2 and 15-17 tons of SO_3 are released in the atmosphere. This results in the creation around these plants of large zones, with high concentrations of noxious gases above the admissible limits, in which destructive effects on animal and plant life are observed. The deleterious effects of these emissions can be amplified by climatic factors, population density or the cumulative effects due to the presence in the atmosphere of NO_x or absorbant powders such as soot, carbon black, etc.

*

In order to decrease the SO_2 emissions by sulphuric acid plants, two processes have been used in Romania: - retaining and use of SO_2-poor gases (including SO_3 if present) through ammonia absorption

- catalytic conversion with double absorption.

1. Retaining and use of SO_2 poor gases through ammonia absorption

The process consists in ammonia absorption of SO_2 (and also SO_3). The solution obtained, mainly ammonia disulphate, is decomposed with H_3PO_4 or H_2SO_4. Gases rich in SO_2 which result from this decomposition are returned to the H_2SO_4 installation or can be used for other purposes. The acid solution of phosphate or sulphate of ammonia is turned into fertilizer. This process is the result of the collaboration between IPROCHIM and ICECHIM and is patented [11]. The process presents the following advantages:

- simple and easy to control
- efficiency of retaining of noxious compounds of 93-95%
- large sphere of application for various sources of residual gases: H_2SO_4 installations, thermoelectric power stations, siderurgy of nonferrous metals
- in the case of fertilizer plants which produce their own needs of H_2SO_4 the process can be easily adapted, the results of the retaining process being processed in the H_2SO_4 and respectively fertilizer installation. Thus the initial expenses and running costs are substantially reduced
- installations based on this process can be also used for sources of residual gases poor in SO_2, they require a small space and consumption of utilities
- an installation based on this process has been functioning

in Romania since 1971. This installation at the absorption of SO_2 stage, is composed of three fabrication lines each being connected to a H_2SO_4 installation which processes about 50,000 Nm^3/hour of residual gases. The desorption of SO_2 stage is realized on one fabrication line. The decomposition of the solutions of sulphate and disulphate of ammonia is done using phosphoric acid. The flow chart of the installation is shown in Figure 1 and a partial view showing the upper part of the absorption towers and evacuation stacks is shown in Figure 2.

Residual gases poor in SO_2 are introduced in the absorption installation through nozzles in which their speed can be modified over a broad range (22-70 m/s). At the outlet of the nozzle the gases, intimately mixed with the absorption fluid, enter a cylindrical column, protected against the acid, and their speed decreases to normal values. This change in speed results in breaking of the absorption liquid film on the inside of the nozzles, resulting in an advanced pulverization of the liquid. The absorption solution of sulphate-disulphate of ammonia is mixed with the appropriate amount of gaseous ammonia for neutralizing the absorbed SO_2. The ratio NH_3/SO_2 is between 0.38-0.35 which assures a high efficiency for the absorption of SO_2.

The intimate contact between SO_2 in the gases and large surface area of the droplets of sulphate-disulphate solution insures an absorption efficiency of 83-86%. The content of NH_4HSO_3 is increased through continually adding ammonia without decreasing the ratio NH_3/SO_2 below 0.34. The total content of SO_2 in solution is 350-400 g/SO_2/liter. In the collector vessel gases are separated from the absorption solution, and then are passed through a droplet separator and are released to the atmosphere through a stack. The gas pressure as it leaves the absorption column is about 25 mm H_2O. The absorption solution is removed from the absorption column with a centrifugal pump. It is partly recycled in the absorption column through the pulverizing jets, in order to insure the proper liquid-gas ratio; the rest goes to the buffer vessel of the desorption unit which is made out of rubberized OL.

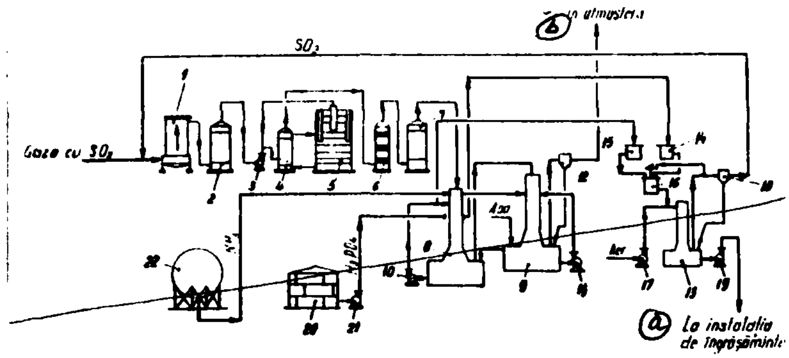

Figure 1. Flow chart of SO_2 retaining from residual gases in a sulphuric acid installation.

Key: 1--wet electrostatic filter; 2--drying tower; 3--blower; 4 and 6--heat exchangers; 5--oxidation chamber; 7--absorption tower; 8,9--absorption column; 10,11,19,21--pumps; 12,18--droplet retainers; 13--absorption column; 14,15--tanks; 16--mixing tank; 17--air blower; 20--H_3PO_4 tank; 22--ammonia tank.
(a) to fertilizer installation; (b) to atmosphere

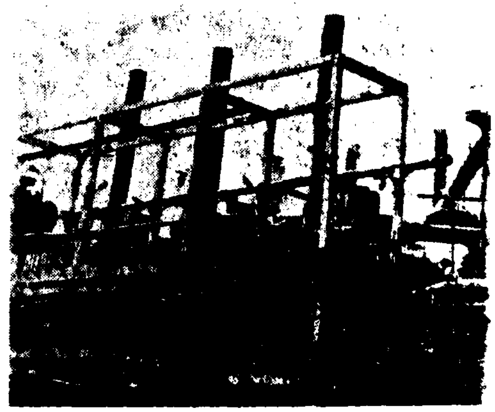

Figure 2. General view of the SO_2 absorption installation from residual gases.

The addition of gaseous ammonia is automatically adjusted through the pH of the absorption solution at the outlet of the pulverizing jets. It corresponds to a ratio SO_2 in sulphate/SO_2 in disulphate = 0.4 which allows a greater content of SO_2 in the absorption solution and an optimum absorption efficiency. The pH is a function of the SO_2 content of the gases and can be used to determine the amount of gaseous ammonia which has to be added to keep the pH to an optimum.

The density of the solution is kept between 1.27-1.29. It is monitored which allows to adjust the amount of water added in order to maintain an optimum concentration of the solution for the next phase. Concentration varies between 600-700 g salts/liter.

The solution thus obtained is constantly fed from the buffer vessel into an acid-resistant reactor where it is mixed with phosphoric acid. The molar ratio of phosphoric acid and ammonia ion must be at least 2 according to the reaction

$$NH_4HSO_3 + (NH_4)_2SO_3 + 6H_3PO_4 = 3NH_4H_2PO_4 + \\ + 3H_3PO_4 + 2SO_2 + 2H_2O.$$

The gaseous SO_2 formed is aspired through a collecting pipe. The solution enters at the top of the desorption column in the feeding compartment of the pulverizing jet. The column used for desorption is similar in construction with the absorption one. It is scaled to size according to the flow of liquid and gas. Air is used for pulverizing the warm solution of phosphoric acid and phosphate of ammonia. It enters the jets due to the vacuum of 130 mm of H_2O created by the blower of the H_2SO_4 installation at the return point of the desorbed SO_2 line.

The intimate contact between air and the warm acid solution of ammonia phosphate which contains dissolved SO_2 (released from the solution sulphate-disulphate) allows the desorption of SO_2. The gas obtained has 18% SO_2. The solution obtained after desorption contains monoammonia phosphate and the excess of H_3PO_4. It contains 50% P_2O_5 and has a ratio H_3PO_4/NH_3 of at least 2.2. After being cooled in the separation vessel it is pumped to the fertilizer installation.

After passing through a droplet separator the gases containing SO_2 are introduced in the H_2SO_4 installation, where they are mixed with the gases from the frying oven. The resultant flow of sulphurous gases after the desorption stage is about 1% of the total volume of gases containing 7-8% SO_2 in the H_2SO_4 installation. Thus the SO_2 concentration is increased by 0.1%.

TABLE 1

1 Nr. analizei	2 Concentraţia SO_2 în gaze la intrare	3 Concentraţia SO_2 în gaze la ieşire	4 Randament pH de desorbţie %	pH	5 Densitatea soluţiei g/cm³
1	0,423	0,074	82,5	5,8	1,15
2	0,405	0,070	82,7	6,9	1,23
3	0,366	0,068	81,5	5,8	1,25
4	0,390	0,062	84,1	5,8	1,25
5	0,396	0,099	75	5,6	1,23
6	0,377	0,042	77,5	5,6	1,24
7	0,390	0.08	83,2	5,7	1,19
8	0,458	0,085	81,4	5,5	1,18
9	0,377	0,072	80,4	5,6	1,19
10	0,349	0,068	80,5	5,6	1,13

Key: 1--No. of analysis; 2--SO_2 concentration at the intake; 3--SO_2 concentration at the outlet; 4--desorption efficiency %; 5--density of solution

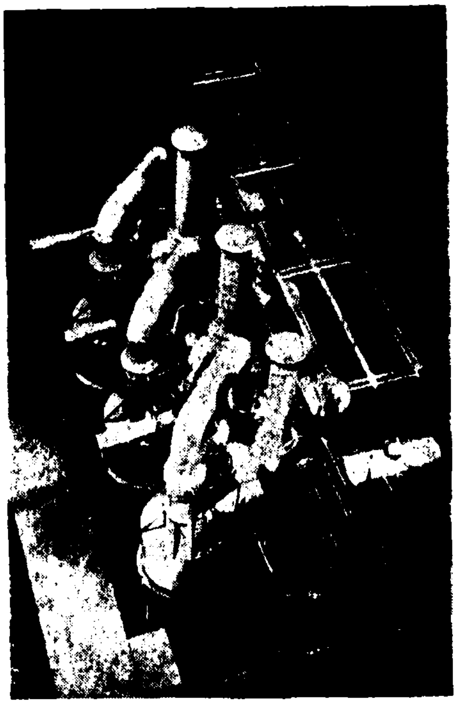

Figure 3. Scale model of an installation for retaining SO_2 from the exhaust gases of a sulphuric acid plant with a capacity of 3 x 50000 Nm^3/hr.

During the operation of this installation some of the parameter values determined on the pilot installation had to be adjusted. Table 1 gives some of the representative data obtained. When the data presented in Table 1 was taken the catalyst in the H_2SO_4 installation was used up, thus the residual gases had an increased concentration of SO_2. Despite this, working with only one absorption step, absorption efficiencies of 80% were obtained. We have noticed an increase of the concentration of sulphate ions in the absorption solution. This increase beyond a certain limit brings a decrease in the absorption efficiency of SO_2. Because such an occurrence is common, especially at the absorption of the final gases from the H_2SO_4 installation, in the new installation this phase is realized in two steps.

The amount of the fluorine drawn from the phosphoric acid during the desorption process was studied. Based on studies of fluorine poisoning of vanadium catalysts, and also on results obtained in the processing of nonferrous metal compounds containing fluorine, it seems that 2-3.3 mg F/Nm^3 in the gases containing SO_2 before the drying stage is acceptable in contact H_2SO_4 installations. The amount of F in the gases rich in SO_2 after desorption is determined by a number of factors:

- the origin and concentration of H_3PO_4
- desorption temperature
- the conditions under which the air degassing of the acid solution is done. As an example, using H_3PO_4 obtained from Kola apatite with 54% P_2O_5, the amount of F in the gases with 15% SO_2, obtained at desorption, was 2.07 g F/m^3, which represents 4.4% of the F in H_3PO_4. These gases pass through the purification stage of the H_2SO_4 installation. After mixing with the sulphurous gases from the main circuit of the installation the F content at contact stage is well below the admissible limit, and thus the contact mass is not affected.

Specific consumptions of such an installation for retaining and use of SO_2 poor gases per ton of SO_2 are

Materials* (used up)

- ammonia 0.004t
- phosphoric acid 0.003t

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* Materials are recuperated in the form of acid solution of ammonia phosphate. The consumption refers to possible losses through handling.

- electric energy 60 kWh
- steam (4 kgf/cm^2) 3.5t
- industrial water 5 m^3

2. Catalytic conversion with double absorption process for H_2SO_4 installations

Another process developed by IPROCHIM which is patented [15] is based on double catalysis with absorption. A number of variations of this method are known. They differ in the way the heat of reaction is recuperated and how the gases are heated after the intermediate absorption step in order to be brought to the starting temperature of the catalyst in the second conversion stage.

The IPROCHIM process uses gases with a 10% concentration of SO_2 and the temperature at the intake of the contact oven of 430°C.

The conversion reactor has four catalytic layers. The intermediate absorption stage is placed after the third catalytic layer.

It has the following advantages:

- improved recovery of heat. The gases after leaving the first contact stages enter the absorption with temperatures around 200°C. A large part of the heat of reaction is recovered in the form of steam at 40 ata, and also for heating the water which feeds the heat recovery system;
- the final heating of the gases which enter the second stage of contact is done by using the heat of gases after the first catalytic layer. The entropy of the system is minimum there which results in a smaller transfer surface in the heat exchanger;
- the contact system was simplified by reducing the number of technological circuits, thus the contact system is very compact;
- indirect air cooling, which complicates the heat recovery and diminishes the degree of use of heat of reaction, was eliminated. As can be seen from the diagram in Figure 4 after layer I of the

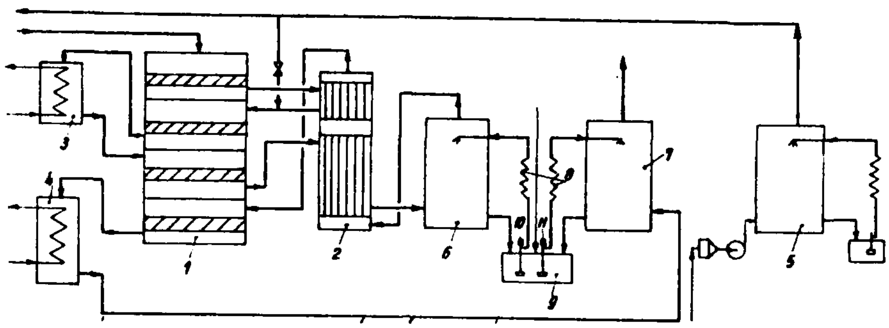

Figure 4. Flow diagram of the installation with double contact with intermediate absorption

Key: 1--oxidation oven; 2--heat exchanger; 3--auxiliary vaporizer; 4--economizer; 5--air drying tower; 6--intermediary absorption tower; 7--final absorption tower; 8--acid cooler; 9--acid tank; 10,11--pumps

contact oven 1, the heat is partially taken in the upper part of the heat exchanger 2, thus achieving the final heating of the gases coming from the first absorption stage which are then introduced in the layer IV of the contact oven;

after layer I the gas being hottest insures the optimum temperature gradient for this heating. The final cooling and adjusting of temperature at the intake of layer II is done with cold air. This dilutes the gas to an initial concentration of 8.8-8.3% SO_2. It also increases the ratio $O_2:SO_2$ which increases the speed of reaction and reduces the amount of catalyst in layers II and III with respect to the case in which the ratio $O_2:SO_2$ was kept at the value corresponding to the initial 10% SO_2 concentration;

- after layer II the heat is taken by the auxiliary vaporizer 3 to make steam. This has the advantage of a much higher coefficient of thermal transfer than for the case of gas-gas cooling. This vaporizer can function in parallel with the recovery boiler of the sulphur burning oven;

- after layer III the heat is used to partially heat the gases coming from the first absorption stage, which then enter the lower part of the heat exchanger 2;

- after layer IV the heat is taken up by economizer 4, to heat the water feeding the recovery boiler.

The investments for installations based on this process, for the same capacity, are 10-12% higher than for the simple contact process.

The conversion efficiency of SO_2 in SO_3 of 97-98% obtained up to now in sulphuric acid installations is no longer appropriate. The efficiency can be increased by using the process with double contact and intermediate absorption.

Presently the use of this scheme in H_2SO_4 installations using pyrites, and also for processing exhaust gases in nonferrous metals siderurgy is being studied. In the latter case all sources of gas including the very dilute ones have to be processed and conversion efficiencies as high as possible need to be obtained. Processing of these sources through the contact process raises special problems due to the number of sources which feed the same installation and the range of concentrations (0.5-12% SO_2).

Mixing the continuous sources with fairly steady concentration with the discontinuous oneswith small and variable concentrations results in variable concentrations and flows. The average SO_2 concentration is in some cases very low. In such a case the autothermicity of the conversion process cannot be achieved, and part of the dilute gases cannot be taken up by the H_2SO_4 installation for processing and is released in the atmosphere.

As we have shown, the decrease in the pollution due to the nonferrous metal plants can be achieved in the first place by processing all the gas sources including the dilute ones. Thus for new installations the patented process is used. One has to insure a high concentration of the steady sources and an optimum ratio of the flows from the continuous concentrated sources and the dilute continuous and discontinuous ones in order to achieve the autothermicity of the process.

If at the nonferrous metal plant sites only dilute sources of sulphurous gases are present, additional continuous and concentrated sources of sulphurous gases must be created in order to make the processing into H_2SO_4 possible. For this sulphur and pyrites are utilized as raw materials.

At some of the older installations using the simple contact process, due to lack of space, low SO_2 concentration or the impossibility of turning off the process long enough for the necessary modifications, it is not feasible technically and economically to switch to the double contact process. In such cases it is prefereable to change to the ammonia absorption process in order to decrease pollution.

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