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NEW TECHNOLOGY FOR THE REMOVAL AND REUSE OF NITROGEN OXIDES CONTAINED IN INDUSTRIAL GASES

A new technology enabling removal and reuse of nitrogen oxides carried by flue gases (25,000 m^3/h) from the manufacture of sulfuric acid by the mixed acid method is presented. The technology has been designed for the superphosphate department of an industrial plant manufacturing phosphatic fertilizers. Using the technology described eliminates sulfuric acid mist emission into the atmosphere and brings an abatement of nitric acid consumption by decreasing the amount of nitric acid required for the manufacture of 1 Mg of sulfuric acid from 21 kg to 6.5 kg only.

1. INTRODUCTION

Of the gaseous pollutants entering the atmosphere, nitrogen oxides create the greatest environmental nuisance. According to recent estimates, the annual emission of nitrogen oxides in Poland ranges within 1.5 and 2.0 million Mg [1]. About 0.4 to 0.7 million Mg of this pollutant come from industrial processes, primarily from chemical plants manufacturing nitric acid and mineral fertilizers, or sulfuric acid by the mixed acid method. The choice of an adequate removal technology (which is to be both efficient and economic) raises serious problems, because the flue gas volume to be treated is large and the amount of nitrogen oxides contained in it is small. Moreover, the economy of the method depends on the parameters of the gas to be treated and on the possibility of utilizing the end-product of the treatment process.

This paper presents a technology in which nitrogen oxides included in the flue gas stream released during sulfuric acid production can be removed and utilized. The object under study is a chemical plant which manufactures phosphatic fertilizers. Sulfuric acid is produced by the mixed acid method. One Mg of sulfuric acid produced requires approximately 21 kg of nitric acid to be used. A considerable portion of nitric acid entered the atmosphere in the form of nitrogen oxides. The gas

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stream emitted into the atmospheric air contained from 1 to 3 g NO_2/m^3, from 1 to 4 g NO/m^3, 0.25 g H_2SO_4/m^3, and from 4 to 8% O_2.

The environmental nuisance of the emission has been limited by modifying and intensifying the system of sulfuric acid production, by removing its mist prior to the main treatment process, and by nitrogen oxide absorption in solutions (taking into account the possible reuse of the treatment product for the needs of the plant).

2. INTENSIFICATION OF THE PROCESS

The removal of nitrogen oxides can be intensified by a) changing the technology of the sulfuric acid production process, b) applying a modified installation and sorbing solution for the absorption of nitrogen oxides from the gas stream leaving the system.

2.1. TECHNOLOGICAL CHANGES

There exist real possibilities to decrease the loss of nitrogen oxides in the course of the technological process and, consequently, to abate their emission into the atmosphere. This may be achieved in the following steps:

A. The process gases should be sufficiently oxidized before entering the Gay–Lussac absorption tower. This means that the process will be conducted under favourable conditions in the absorbing zone, at an influent NO/NO_2 ratio amounting to 1. Excess nitrogen dioxide (in relation to nitrogen oxide) must be avoided as otherwise the mixed acid vapour pressure will increase in the presence of nitric acid, thus decreasing the rate of nitrogen oxides absorption in sulfuric acid. When oxidation is insufficient, there will appear an excess of nitrogen oxide. Being practically acid-insoluble, this portion of nitrogen oxide passes to the flue gas stream and, consequently, enters the atmospehre, thus increasing the air pollution level.

B. The packing layer and the spraying rate should be increased without deteriorating the operating conditions. Effective spraying is possible to achieve only when maintaining an appropriate column depth/packing diameter ratio, and supplying an adequate quantity of the spraying liquid. Increasing the circulation of the liquid makes it possible to increase (to a certain extent) the amount of the component absorbed without changing the column size. The inherent disadvantage of such an approach is the increase in energy demand.

C. Absorption of nitrogen oxides in the Gay–Lussac tower should be carried out, using concentrated sulfuric acid which is delivered to the plant for the manufacture of phosphatic fertilizers. The process should consist of the following stages: a) absorption of nitogen oxides in concentrated sulfuric acid until the concentration of nitrosyl bisulfite approaches 5%, b) removal of nitrosyl bisulfite from the sulfuric acid leaving the sorption system and dissolution of the sulfuric acid to a concentration of about 75% in Glower towers, and c) passage of the acid to the department of superphosphate manufacture.

2.2. REMOVAL OF NITROGEN OXIDES FROM PROCESS GASES

Although a wide variety of methods are available for abating nitrogen oxide emissions [2], [3], a universal successful method does not exist. Analysis of literature data shows that the economics of the treatment method depends on the parameters of the waste gas and on the possible reuse of the absorption product at the source of origin. The Institute of Environment Protection Engineering, Technical University of Wrocław, has been interested in solving the nitrogen oxide removal problem for may years [4]–[8]. The investigations conducted there have aimed at determining the most significant parameters for the removal of nitrogen oxides from process gases by making use of such sorbing solutions that create favourable conditions for the reuse of the absorption products in the plant. Of the various treatment systems tested, packed columns were found to be best suited for the removal of nitrogen oxides from the waste gases produced during the manufacture of sulfuric acid by the mixed acid method. The columns are simple in design, safe in operation, and may work in a wide range of liquid-phase and gas-phase loading.

3. REMOVAL OF SULFURIC ACID MIST

Sulfuric acid mist removal was investigated in a prototype system with 25,000 m^3 of gas per hour capacity, operated in a chemical plant manufacturing phosphatic fertilizers. The study involved a single-layer demister consisting of glass wool and a double-layer demister consisting of I-15M-type polyethylene rings and wool glass, respectively. Examples of removal efficiency achieved with the two demisters are listed in table. As shown by these data, the efficiency of sulfuric acid mist removal for the double-layer demister averages more than 85%. And this efficiency enables 74% sulfuric acid amounts approaching 25 dm^3/h (1 Mg/day).

The authors' own studies [9]–[11] made it possible to develop a technology of removing and utilizing nitrogen oxides carried by waste gases from the manufacture of sulfuric acid by the mixed acid method. The technology has been designed for the superphosphate department. Thus, we have a practical example of how to abate the release of nitrogen oxides into the atmosphere at minimum expenditure and by taking advantage of local facilities. The technology itself makes use of an apparatus which is simple in design and easy to handle. The end-product of the treatment process is fit for reuse at the source of origin and may become a valuable starting material for the primary production line of the plant.

Table

Efficiency of sulfuric acid mist removal

Single-layer demister			Double-layer demister		
SO_4^{-2} concentration mg/m^3		Removal efficiency %	SO_4^{-2} concentration mg/m^3		Removal efficiency %
Influent	Effluent		Influent	Effluent	
1747.8	804.0	54.0	1780.0	265.7	85.1
1783.9	801.0	55.1	1884.3	247.1	86.9
1738.1	803.0	53.8	2081.7	272.7	86.9
1701.5	815.0	52.1	2149.6	288.0	86.6
1851.0	796.0	57.0	1970.6	295.6	85.0
1777.8	800.0	55.0	1880.7	242.6	87.1
1797.3	798.0	55.6	2390.0	272.5	88.6
1744.6	813.0	53.4	1936.1	286.2	85.2
1765.0	806.0	54.1	2320.6	241.3	89.6
1764.3	801.0	54.6	2400.4	220.8	90.8

The technology of interest [11] involves the following processes conducted in three different units:

A. PRE-SCRUBBER

Absorption of residual sulfuric acid mist:

$$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O.$$

Oxidation of nitrogen oxide:

$$NO + \tfrac{1}{2}O_2 \rightarrow NO_2.$$

Pre-absorption of nitrogen oxide:

$$2NO_2 + 2NaOH \rightarrow NaNO_3 + NaNO_2 + H_2O.$$

B. ABSORBER

Absorption of nitrogen oxides:

$$NO + NO_2 + Na_2CO_3 \rightarrow 2NaNO_2 + CO_2.$$

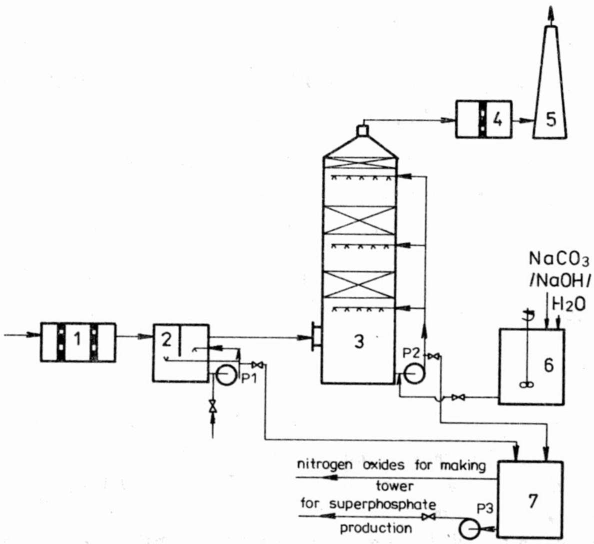
C. REACTOR

Regeneration of the effluent from sorption:

$$2NaNO_2 + H_2SO_4 \rightarrow Na_2SO_4 + N_2O_3 + H_2O.$$

The nitrogen oxides released via this route are passed to the production line. The solution contained in the reactor is sent to the superphosphate department to be used for the degradation of phosphorites. The technology has been developed for the following parameters:

gas flow rate, 25,000 m^3/h,
gas temperature, 310 K,
sulfuric acid mist concentration, $c_{H_2SO_4} = 0.2\text{–}0.3\ g/m^3$,
nitrogen oxide concentration, $c_{N_2O_5} = 5.55\ g/m^3$,
sorbing solution concentration in the pre-scrubber, 1–2% wt. NaOH,
sorbing solution concentration in the absorber, 10% wt. Na_2CO_3,
spraying rate, 20 $m^3/m^2 \cdot h$,
efficiency of removal, $\eta_{H_2SO_4} = 100\%$, $\eta_{N_2O_3} = 90.0\%$.
The technological system for the removal of nitrogen oxides is shown in figure.



Technological system for removal and reuse of nitrogen oxides contained in the waste gas

The waste gas leaving the single-layer demister *1* passes to the pre-scrubber *2* for humidification, complete removal of residual sulfuric acid mist, oxidation of nitrogen oxide, and pre-absorption of nitrogen oxides in alkaline sodium hydroxide solution (1–2% wt.). The sorbing solution circulates in a closed system (pump P1, pneumatic nozzles DP) until pH approaches 7.5. Half of the sorbing solution is then passed to the storage tank *7*, and the pre-scrubber is fed with a fresh sorbing solution. Following pre-treatment in the pre-scrubber, the gas stream enters the absorption column *3* packed with I-15N polypropylene rings (two layers). After spraying with sodium carbonate solution (10% wt.) in counter-current, the gases pass through a single-layer demister *4* to enter the atmosphere after passage through stack *5*. Sodium carbonate solution is prepared in tank *6*. Fresh portions are pumped (P2) to the nozzles which provide spraying of the absorption column. Circulating up to the moment at which pH approaches 7.5, the sorbing solution enters the storage tank *7*, wherein the effluent from the pre-scrubber and from the absorption column is being stored. From there, the sorbing solution is sent (through pump P3) to the reactor belonging to the production line and is treated with 75% sulfuric acid until a complete degradation of nitrites is achieved. Nitrogen oxides released in the course of the degradation process are passed to the production line as a substitute for nitric acid. The effluent from regeneration is sent to the superphosphate department.

The technology proposed in this paper may also involve other types of sorbing solutions which are in use in the given plant [8].

4. SUMMARY

1. The technology proposed not only abates environmental pollution, but also has the inherent advantage of being economic.

2. It is advantageous to send the nitrogen oxide containing waste gases to a double-layer demister before they are passed to the absorption column. In this way, it is possible to recover 74% sulfuric acid in amounts approaching 1 Mg/d.

3. The technology eliminates sulfuric acid emission and abates the quantity of nitric acid required for the manufacture of 1 Mg of sulfuric acid from 21 kg to only 6.5 kg.

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NOWA TECHNOLOGIA USUWANIA I UTYLIZACJI TLENKÓW AZOTU Z ODLOTOWYCH GAZÓW PRZEMYSŁOWYCH

Przedstawiono nową technologię usuwania i utylizacji tlenków azotu z gazów odlotowych (25,000 m^3/h) po produkcji kwasu siarkowego metodą nitrozową (w odniesieniu do oddziału superfosfatu w fabryce nawozów fosforowych). Technologia ta pozwala całkowicie ograniczyć emisję mgły kwasu siarkowego oraz obniżyć z 21 kg do 6,5 kg zużycie kwasu azotowego potrzebnego do wyprodukowania 1 Mg kwasu siarkowego.

НОВАЯ ТЕХНОЛОГИЯ УДАЛЕНИЯ И УТИЛИЗАЦИИ АЗОТНЫХ КИСЛОТ ИЗ ОТХОДЯЩИХ ПРОМЫШЛЕННЫХ ГАЗОВ

Представлена новая технология удаления и утилизации азотных кислот из отходящих газов (25000 $м^3$/час) после производства серной кислоты нитрозным методом (по отношению к отделению суперфосфата на заводе фосфорных удобрений). Эта технология позволяет полностью ограничить эмиссию тумана серной кислоты, а также понизить с 21 кг до 6,5 кг потребление азотной кислоты, нужной для произведения 1 Мг серной кислоты.