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## ON THE REMOVAL AND REUSE OF NITRIC OXIDES FROM PROCESS GASES OF SULPHURIC ACID PRODUCTION

Absorption (both acidic and alkaline) of nitrogen oxides and sulphuric acid mist following production of sulphuric acid by the mixed acid method was investigated. The experiments were run under laboratory ( $2.5 \text{ m}^3/\text{h}$ ), semitechnical ( $2500 \text{ m}^3/\text{h}$ ) and full industrial ( $25,000 \text{ m}^3/\text{h}$ ) conditions.

Three possible reuses of the effluent from alkaline absorption were examined. The performance of a full-industrial-scale system (operated since 1982), which has been designed for the purification of waste gases, is of interest. The system involves absorption in sodium hydroxide solution and enables reuse of the sorption effluent by chemical degradation with sulphuric acid.

### 1. INTRODUCTION

There is no doubt that chemical industry belongs to the main class of primary pollution sources. Of extreme importance to the environment are nitrogen oxide emissions from industrial plants manufacturing nitric acid and mineral fertilizers, or sulphuric acid by the mixed acid method, because the resulting environmental impacts are much more varied and substantial than is generally realized.

Among the methods that have been used so far for the removal of nitrogen oxides from flue gases, we may distinguish the following processes: catalytic reduction, flame reduction, adsorption and absorption. However, the choice of an economically optimum method depends on the parameters of the gas to be treated and on the possibility of reusing the sorption products. Acidic absorption [1]–[7] and alkaline absorption [7]–[12] are the treatment procedures that seem to be

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best suited for the removal of nitrogen oxides from waste gases generated during production of sulphuric acid by the mixed acid method.

The study reported deals with absorption of nitrogen oxides and sulphuric acid mist following production of sulphuric acid in the manufacture of superphosphate. The yearly output of the superphosphate plant amounts to 260,000 Mg at an annual sulphuric acid demand of 90,000 Mg. Of this total, some 70,000 Mg of sulphuric acid are produced on the spot by the mixed acid method. To generate 1 Mg of sulphuric acid it is necessary to use about 21 kg of nitric acid. A major part of the latter is released into the atmosphere in the form of nitrogen oxides. The gas emitted into the atmosphere contains 1 to 3 g  $\text{NO}_2/\text{m}^3$ , 1 to 4 g  $\text{NO}/\text{m}^3$ , 0.5 g  $\text{H}_2\text{SO}_4/\text{m}^3$ , and 4 to 8%  $\text{O}_2$ . A modernization of the object will increase its yearly output to a total of 500,000 Mg, accounting for a twofold increment in sulphuric acid demand. Thus, the abatement of nitrogen oxides emission will become a problem of vital importance.

Three methods are accepted as applying for this purpose: modernization of the system for sulphuric acid production, intensification of the process itself, and purification of the outlet gases from the absorption process.

The need for efficient removal of nitrogen oxides from process gases generated during manufacture of sulphuric acid has directed the attention of many investigators and engineers to absorption in an acidic or in an alkaline medium. In this study, absorption was investigated in three different media: sulphuric acid, water and diluted solutions of acids, sodium hydroxide. The experiments were run under laboratory ( $2.5 \text{ m}^3/\text{h}$ ), semitechnical ( $2500 \text{ m}^3/\text{h}$ ), and full industrial ( $25,000 \text{ m}^3/\text{h}$ ) conditions, using actual process gases from the production of sulphuric acid by the mixed acid method.

## 2. EXPERIMENTAL

1. Absorption in sulphuric acid. The ability of sulphuric acid to sorb nitrogen oxides is widely known in engineering practice (processes occurring in Gay-Lussac towers during production of sulphuric acid by the mixed acid method). The objective of the experiments reported here was to ensure whether concentrated sulphuric acid delivered to the superphosphate manufacturing plant might be used for our purpose.

The adopted production cycle was as follows: a) adsorption of nitrogen oxides in concentrated sulphuric acid until the concentration of mixed acids has reached about 5%, b) removal of mixed acids from absorption sulphuric acid and dilution of sulphuric acid in Glower towers to a concentration of about 75%, c) transfer of sulphuric acid (after removal of nitrogen oxides) to the superphosphate manufacturing plant.

Economic considerations show that the plant is supplied with an annual amount of approximately 21,000 Mg of concentrated sulphuric acid. The application of the method suggested will increase the annual sulphuric acid demand to a total of 25,000 Mg.

2. Absorption in water and diluted solutions of acids. The factory uses about 100 Mg of technological water a day for the production of sulphuric acid. The aim of our study was to test whether or not this water might be utilized for removing sulphuric acid mist and nitrogen oxides from the waste gases. If so, the circulation of the water should be somewhat changed: a) the outlet gas absorber should be fed with water continually or intermittently; b) the solution obtained from outlet gas purification contains a mixture of nitric, nitrous and sulphuric acids of a total concentration ranging between 2 and 10% (which depends on the composition of the outlet gases and the treatment efficiency). This mixture might be sent to the Glower and production towers as a substitute of technological water.

3. Absorption in sodium hydroxide. The objective of the experiments was to solve some technological problems associated with the corrosive action of the solutions obtained from absorption in water. Possible applications of the solutions obtained from sorption in sodium hydroxide were also considered.

### 2.1. LABORATORY TESTS

The experiments aimed at verifying (under comparable conditions) the efficiency of nitrogen oxides absorption in sulphuric acid or sodium hydroxide solutions and determining the sorption capacity of the solutions. The concentrations of the sulphuric acid and sodium hydroxide solutions used in the experiments were 40 to 95% and 0.1 to 5.0 mol/dm<sup>3</sup>, respectively. Figure 1 gives the relationship between

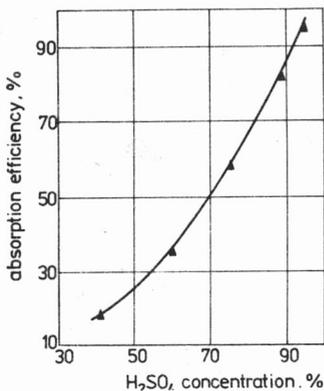


Fig. 1. Efficiency of nitrogen oxides absorption versus sulphuric acid concentration

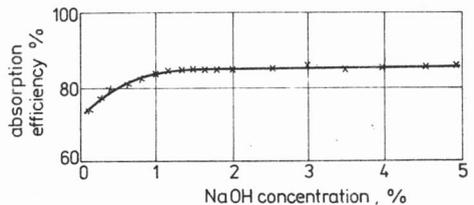


Fig. 2. Efficiency of nitrogen oxides absorption versus concentration of sodium hydroxide solution

nitrogen oxides absorption efficiency and sulphuric acid concentration. The relationship between nitrogen oxides absorption efficiency and the concentration of sodium hydroxide solution is plotted in fig. 2. The sorption capacity of concentrated sulphuric acid solutions was investigated in order to determine the sulphuric acid demand. The highest sorption capacity was obtained for 95% sulphuric acid. It amounted to  $110.3 \text{ kg N}_2\text{O}_5/\text{m}^3 \text{ H}_2\text{SO}_4$  which is equivalent to the average sorption efficiency of 88.7%. The sorption capacity of NaOH solutions approached the theoretical value by amounting to  $53 \text{ kg N}_2\text{O}_5/\text{m}^3 \text{ 1 mol NaOH}$ .

## 2.2. SEMITECHNICAL INVESTIGATIONS

The experimental system is shown in fig. 3. A fan 1 directs the stack flue gases to the spraying column 2 in which sulphuric acid droplets are separated and small

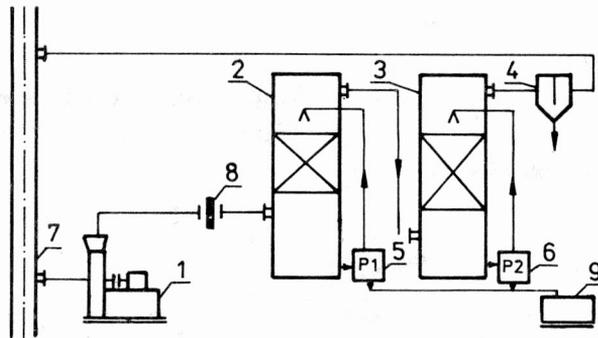


Fig. 3. Semitechnical system for the absorption of nitrogen oxides from waste gases

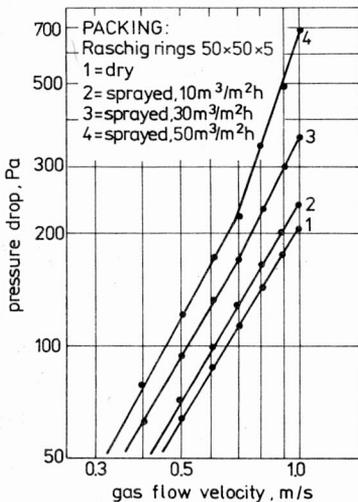


Fig. 4. Pressure drop on the packing as a function of gas flow velocity and spraying density

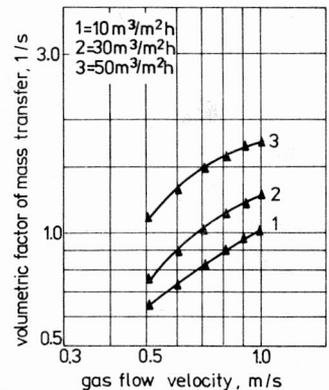


Fig. 5. Rate of sulphuric acid mist absorption in water and diluted acids

amounts of nitrogen oxides are sorbed. The actual purification process occurs in a packed column 3 (the packing is 2 m high) with bottom supply of the wetting solution circulating in a closed cycle. Figure 4 shows the dependence of gas flow resistance on spraying density and gas velocity in the packed column.

The experimental results for the absorption of sulphuric acid mist and nitrogen oxides in technological water (with concentration of acids increasing up to 10%) are plotted in figs. 5 and 6. In these plots the volumetric factor of mass transfer was shown as a function of spraying density and gas flow velocity. It should be noted that appropriate anticorrosive measures had been taken.

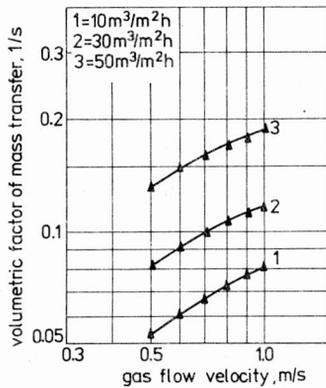


Fig. 6. Rate of nitrogen oxides absorption in water and diluted acids

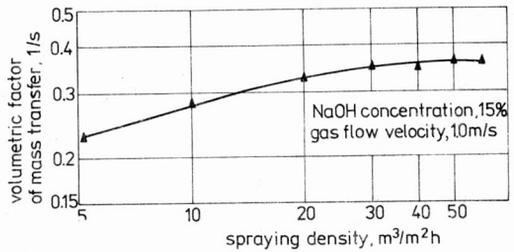


Fig. 7. Rate of nitrogen oxides absorption in sodium hydroxide solution

During absorption of sulphuric acid mist and nitrogen oxides in the sodium hydroxide solution two circulation cycles of the sorbing medium were adopted. Column 2 was sprayed with 5% NaOH solution, while column 3 was fed with 15% NaOH. The results are given in fig. 7. The process yielded complete removal of sulphuric acid. 50% efficiency was achieved for the absorption of nitrogen oxides at a gas flow velocity of 1 m/s and a spraying density of 20 m³/m² h.

### 2.3. FULL INDUSTRIAL SCALE INVESTIGATIONS

The objective was to check the results obtained under laboratory and semitechnical conditions and to produce appropriate quantities of the solutions for their utilization. The industrial system is shown in fig. 8. The process parameters were the following: gas flow rate, 25,000 m³/h; average N<sub>2</sub>O<sub>3</sub> concentration in the gases, 5.4 g/m³; rate of spraying with the sorbing medium, 150 m³/h; volume of the sorbing medium in the system, 20 m³; height of packing, 2 m; NaOH concentration, 15%; H<sub>2</sub>SO<sub>4</sub> concentration, 90%; gas temperature, 303–310 K; duration of experiments, 24 h. Average concentrations of nitrogen oxides and

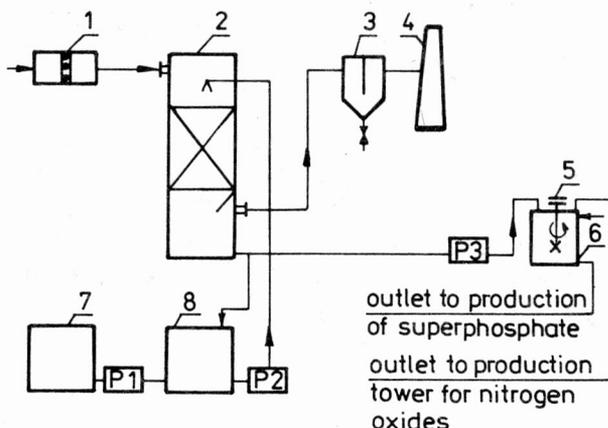


Fig. 8. Full-industrial-scale system for reuse of nitrogen oxides

sulphuric acid mist were measured before and after passing through the absorber. Determinations were also carried out for the concentration and volume of the sorption effluent.

The efficiencies were as follows: 50% for nitrogen oxides and 85% for sulphuric acid mist by absorption in concentrated sulphuric acid, 23% for nitrogen oxides and 90% for sulphuric acid mist by absorption in water and diluted acid solutions, 50% for nitrogen oxides and 93% for sulphuric acid mist by absorption in sodium hydroxide.

### 3. REUSE OF SORPTION EFFLUENTS

An appropriate management of the sorption effluent has become a problem of vital importance in the treatment of process gases. An optimal solution to this problem is the application of a no-waste technology, but so far, such a solution has belonged to the sphere of wishful thinking. To change this situation, we have tested some possible reuses of the effluents from acidic and alkaline absorption.

1. The effluent from absorption in concentrated sulphuric acid (90 to 95%  $H_2SO_4$  and 5% mixed acids) was sent to the system of sulphuric acid production in which it was subject to denitration and dilution. There may be only two factors limiting the reuse of the effluent — the capacity of the production system and the necessity of denitrating additional amounts of concentrated sulphuric acid.

2. The effluent from absorption in water and diluted solutions of acids (10%  $H_2SO_4$ ,  $HNO_3$ , and  $HNO_2$  solution) was closed to the system of sulphuric acid production. Apart from anticorrosive measures, no preventive actions need be undertaken prior to the reuse of this effluent.

3. For the effluent from absorption in sodium hydroxide, which contains  $\text{NaNO}_2$ ,  $\text{NaNO}_3$  and  $\text{Na}_2\text{SO}_4$ , three methods of utilization were investigated:

A. The effluent was passed to the production tower as a substitute of water and nitric acid; the method has the following advantages: nitric acid demand can be decreased from 21.5 kg  $\text{HNO}_3/\text{Mg H}_2\text{SO}_4$  to 14.5 kg  $\text{HNO}_3/\text{Mg H}_2\text{SO}_4$ , whereas  $\text{Na}_2\text{SO}_4$  in the acid produced reaches a concentration of 11.5 g  $\text{Na}_2\text{SO}_4/\text{kg H}_2\text{SO}_4$ .

B. The effluent was subject to electrodialysis. Following completion of the process, 10–15% sulphuric acid (containing small amounts of nitric acid) was removed routinely from the anode chamber. Sodium hydroxide solution contained in the cathode chamber was passed to the absorption column continually or intermittently. The electrodialysis process was investigated on a large laboratory scale.

C. Chemical decomposition of sodium nitrite was achieved by treatment with sulphuric acid. The effluent was passed to reactors and treated with excess sulphuric acid. Evolving nitrogen oxides flowed to the production tower, whereas the solution from the reactors was pumped to the superphosphate department in which it was used for chemical degradation of phosphorites.

#### 4. SUMMARY

The full-industrial-scale system for the separation of sulphuric acid mist and nitrogen oxides from waste gases (fig. 8) has been operated since January 1982. The gases flow through a filter 1 to separate sulphuric acid droplets and mist. From there, they are sent (in parallel flow with the sodium hydroxide solution) to the absorption column 2. Purified gases leaving the absorption column flow through a droplet separator 3 to enter the atmosphere after having passed through the stack 4. The sodium hydroxide solution is prepared in tank 7; then, some part of it is sent to tank 8. From there, the solution is pumped to the sprayer of the column. After neutralization, the effluent is pumped to reactor 6 and treated with 75% sulphuric acid solution, until a complete chemical decomposition of nitrites has been achieved. Nitrogen oxides released during decomposition are passed to the production tower, and the solution is sent to the system manufacturing superphosphate.

The application of the treatment process and methods of reusing the effluent, which are discussed in this paper, brings about a considerable decrease in the total emission of pollutants generated during sulphuric acid production by the mixed acid method.

The efficiency of nitrogen oxides absorption in the installation operated in the superphosphate manufacturing plant can be improved by the intensification of the absorption process.

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### USUWANIE I UTYLIZACJA TLENKÓW AZOTU Z GAZÓW PROCESOWYCH PO PRODUKCJI KWASU SIARKOWEGO

Przedstawiono wyniki badań kwaśnej i alkalicznej absorpcji tlenków azotu i mgły kwasu siarkowego z gazów po produkcji kwasu siarkowego metodą nitrozową. Doświadczenia prowadzono w skali laboratoryjnej (2.5 m<sup>3</sup>/h), półtechnicznej (2500 m<sup>3</sup>/h) i przemysłowej (25000 m<sup>3</sup>/h). Przebadano również trzy warianty utylizacji roztworów po absorpcji alkalicznej. Omówiono pełnoprzemysłową instalację do oczyszczania gazów odlotowych. Pracuje ona od stycznia 1982 r., a podstawą jej działania jest absorpcja w roztworze wodorotlenku sodowego i utylizacja roztworów posorpcyjnych przez rozkład kwasem siarkowym.

### УДАЛЕНИЕ И УТИЛИЗАЦИЯ ОКИСЕЙ АЗОТА ИЗ ПРОЦЕССУАЛЬНЫХ ГАЗОВ ПОСЛЕ ПРОИЗВОДСТВА СЕРНОЙ КИСЛОТЫ

Представлены результаты исследований кислой и щелочной абсорбции окисей азота и тумана серной кислоты из газов после производства серной кислоты нитрозным методом. Исследования проводились в лабораторном масштабе 2,5 м<sup>3</sup>/ч, полутехническом — 2500 м<sup>3</sup>/ч и полнопромышленном — 25000 м<sup>3</sup>/ч. Исследованы также три варианта утилизации растворов после щелочной абсорбции. Обсуждена полнопромышленная установка, очищающая отходящие газы, работающая с января 1982 г. на базе процесса абсорбции в растворе гидроокиси натрия, а также утилизацию послесорбционных растворов путём разложения серной кислотой.