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NEW HONEYCOMB CATALYSTS FOR SCR NOx ABATEMENT

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RESUME

ESPINDESA a construit jusqu'ici 7 réacteurs catalytiques industriels pour l'abattement de NOx SCR des unités d'acide nitrique. Dans tous les cas, le catalyseur était constitué de granules d'oxyde métallique sur support céramique. Le principal inconvénient du système était la baisse de pression à travers le lit de catalyse qui entraînait une consommation considérable d'énergie ou une réduction de la productivité de l'unité d'acide nitrique.

ESPINDESA a récemment mis au point deux catalyseurs en forme de nid d'abeilles pour l'abattement de NOx SCR dans les unités d'acide nitrique qui fonctionnent à 200-300°C ou 300-400°C respectivement.

Les deux catalyseurs utilisent l'ammoniac comme réducteur. L'emploi de l'un ou de l'autre catalyseur dépend de la température des gaz de queue de l'unité d'acide nitrique, ce qui évite la nécessité d'échangeurs de chaleur onéreux.

La structure en nid d'abeilles réduit notablement la baisse de pression des gaz à travers le lit de catalyse. Les essais ont montré que les rendements de catalyse sont équivalents à ceux des catalyseurs granulés.

A notre connaissance, les catalyseurs ESPINDESA sont les premiers catalyseurs de réduction sélective pour les unités d'acide nitrique en forme de nid d'abeilles. Le premier réacteur industriel est construit pour une unité en Espagne et devrait fonctionner à la fin de 1994.

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1. INTRODUCTION

The overall emission of anthropogenic nitrogen oxides to the atmosphere is estimated to be in the order of 50 million tons per year of which almost half (see Figure 1) is due to transport, one third to combustion boilers and around one fifth to industry process plants.

Those NOx are responsible of acid rain, persistent smog, etc. For those reasons the environmental standards all over the world try to be more and more strict. For instance, the European Union is trying to reduce the present values of 30-40 kg of NOx per person per year to 10-20 kg which is considered as the range the European ecosystem can bear.

Of those huge emissions, only 1.3% is considered due to nitric acid plants but as their NOx emissions are concentrated and give a typical brownish-red colour to the stack gases most of the countries attempt to reduce the nitric acid plant emissions to limits which differ from one country to the other although a value of 200 ppm of NOx might be considered as typical.

Of the different abatement processes available, only secondary absorption in water, chemical absorption with alkalies and catalytic reduction, are used in the industry, the last one being, by far, the most widely used.

2. CATALYTIC REDUCTION OF NOx

Catalytic reduction is used in transport, boilers and industry.

Two different types of catalytic reduction systems are used in practice: non-selective (NSCR) and selective (SCR):

An example of NSCR is the well-known catalyst cartridges made of precious metals (Pt, Pd, etc.) deposited on ceramic substrates used in exhaust gases of spark-ignition internal combustion engine of automobile or light trucks to abate the small concentrations of hydrocarbons and CO from incomplete combustion of fuel and of NOx from nitrogen fixation at the high temperature of combustion. These catalyst achieve nearly complete oxidation of CO and hydrocarbons and simultaneously a good control of NOx.

For many years, NSCR has also been used in nitric acid plants for partial abatement of the nitrogen oxides and to decolorize the fumes by reacting the NOx and O_2 in the presence of a catalyst made of promoted platinum or palladium with fuels such as hydrogen, natural gas, naphta, etc. The sequence of the reactions is:

$$4\ NO_2 + CH_4 \longrightarrow 4\ NO + CO_2 + 2\ H_2O$$
$$2\ O_2 + CH_4 \longrightarrow CO_2 + 2\ H_2O$$
$$4\ NO + CH_4 \longrightarrow 2\ N_2 + CO_2 + 2\ H_2O$$

The competing reaction of CH_4 with oxygen is preferred to the reduction reaction of NO to N_2 and usually concurrent with the decolourizing reaction in reducing NO_2 (red coloured) to NO (colourless). Thus, to "totally abate", reducing a typical nitric acid plant tail gas to 200 ppm or less, oxygen must be first reacted from the tail gas. As the reactor operates adiabatically, the heat of reaction (combustion with oxygen) heats up the tail gas about 140°C for each 1% O_2 in the tail gas. Therefore the abator ΔT could be 280-420°C in the case of 2-3% O_2 not including the heat of reaction for NOx reduction. The temperature rise encountered in NSCR during total abating has major implications when designing and/or retrofitting units. Heat recovery and temperature limitations of equipments such as boilers and power recovery expanders must be considered.

Those problems are avoided in SCR reduction, which has become the most common technique to totally abate NOx in nitric acid plants.

3. SELECTIVE CATALYTIC REDUCTION OF NOx

The term selective makes reference to the fact that in the presence of a catalyst, a reducing agent (commonly NH_3) reacts preferentially with the NOx without concurrent combustion of the oxygen which is more abundant than NOx in nitric acid plant tail gases.

The main chemical reactions involved are described by the following equations:

$$6\ NO_2 + 8\ NH_3 \longrightarrow 7\ N_2 + 12\ H_2O$$
$$4\ NO + 4\ NH_3 + O_2 \longrightarrow 4\ N_2 + 6\ H_2O$$

Thus, the expected ammonia consumption is directly proportional to the inlet NOx concentration and varies with the state of oxidation as well. Most of the references indicate that the ammonia requirement with SCR is near stoichiometric and typically is a 1:1 molar ratio NH_3:NOx. For the reduction of nominally 2000 ppm a ΔT of about 30-35°C can be expected.

In the temperature range from 200 to 450°C conversion of NOx to harmless nitrogen and water can be highly selective if adequate catalysts are used. Depending upon the temperature profile of the tail gases, the SCR technique can be adapted to any nitric acid plant either upstream or downstream the expansion turbine.

Catalysts for SCR use to be made of oxides of metals such as V, Ti, Cu, Cr, Ni, Fe over ceramic support, usually prepared as granules or pellets. Some sources indicate that catalysts made of precious metals "modified" type are also used for SCR.

The main drawback of those catalysts is the high pressure drop through the bed, what increases the energy consumption of the plant and/or reduces the nitric acid production. Even in cases where the temperature profile of the gases obliges to locate the SCR unit downstream the expander, the pressure drop may be a severe drawback.

4. THE NEW HONEYCOMB ESPINDESA SCR CATALYST

The above limitations lead ESPINDESA to develop catalysts of very low pressure drop and active in the wide temperature range usually found in nitric acid plants tail gases.

Firstly, we developed a low priced ceramic honeycomb support. Its surface to volume ratio is very high (above 1000 m^2/m^3 what means that very compact abators may be designed). The support element dimensions are 100 mm x 100 mm x (250-750 mm). The length of the honeycomb monoliths can be adjusted to have an optimum design of the reactor.

The support is to be mechanically strong and resistant to temperature fluctuations but at the same time needs to have a high open cross-sectional area what requires very thin walls.

As ESPINDESA has designed and supplied catalyst for 8 SCR nitric acid NOx abators we had developed two different granular catalysts operating in the ranges 200-300°C and 280-400°C. Those catalysts were used as the basis for the development of the new catalysts which were made by fixing the active elements of the old catalysts to the new honeycomb support. Laboratory and pilot plant tests have shown that the NOx abatement efficiency is as high as with the pelleted or granular catalysts, while its pressure drop is almost negligible.

5. THE DESIGN OF THE FIRST SCR HONEYCOMB CATALYST ABATOR

The design of an adiabatic abator incorporating honeycomb catalyst depends of:

- Activity constant of the catalyst
- Tail gas inlet NOx concentration
- Degree of NOx abatement to be achieved
- Flow of gases to be treated
- Concentration of O_2 in the tail gas
- Velocity of the gases through the catalyst (for honeycomb catalysts: much higher than granular catalysts)

Figure 2 illustrates the configuration of the reactor and summarizes the flow diagram:

a. After the ammonia and tail gases have been completely mixed, the flow of gases reach a flow straightener placed in the top of the reactor. (The almost negligible pressure drop when the gases flow through the catalyst oblige to a careful design of the flow pattern).

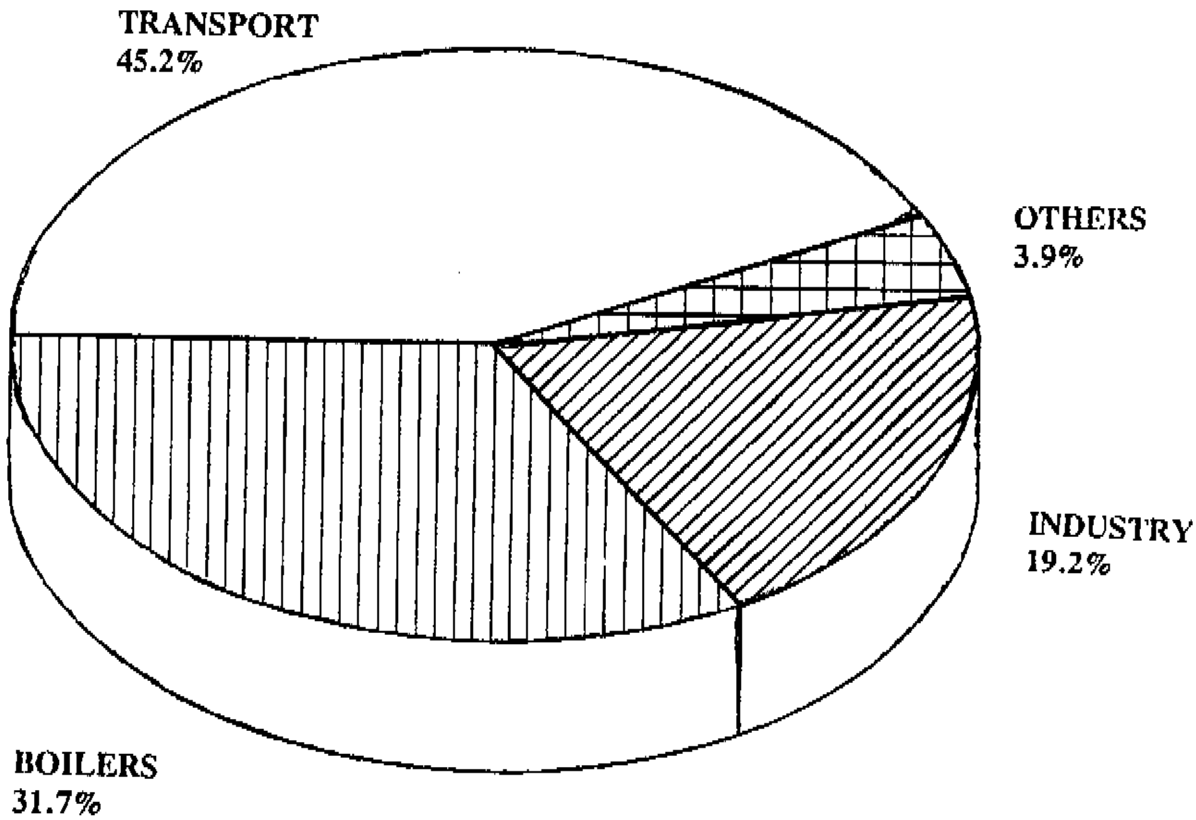
b. Downstream the straightener several layers of catalyst modules perform most of the NOx abatement. The number of layers and the length of the catalyst cartridges vary depending upon the degree of abatement of NOx which is to be achieved.

c. On top of the last catalyst layer secondary ammonia is injected. On the average 90% of the total ammonia flow goes to the primary injection point and the balance to the secondary.

At the time of this writing the first unit incorporating the new honeycomb catalyst is being erected. Commissioning is scheduled for late 1994. The unit contains 940 litres of catalyst shaped as monolytes sized 100 mm x 100 mm x 350 mm.

FIGURE 1

WORLD NOx EMISSION BY ANTHROPOGENIC SOURCES



TOTAL NOx EMISSION: 50,000,000 TONS/YEAR

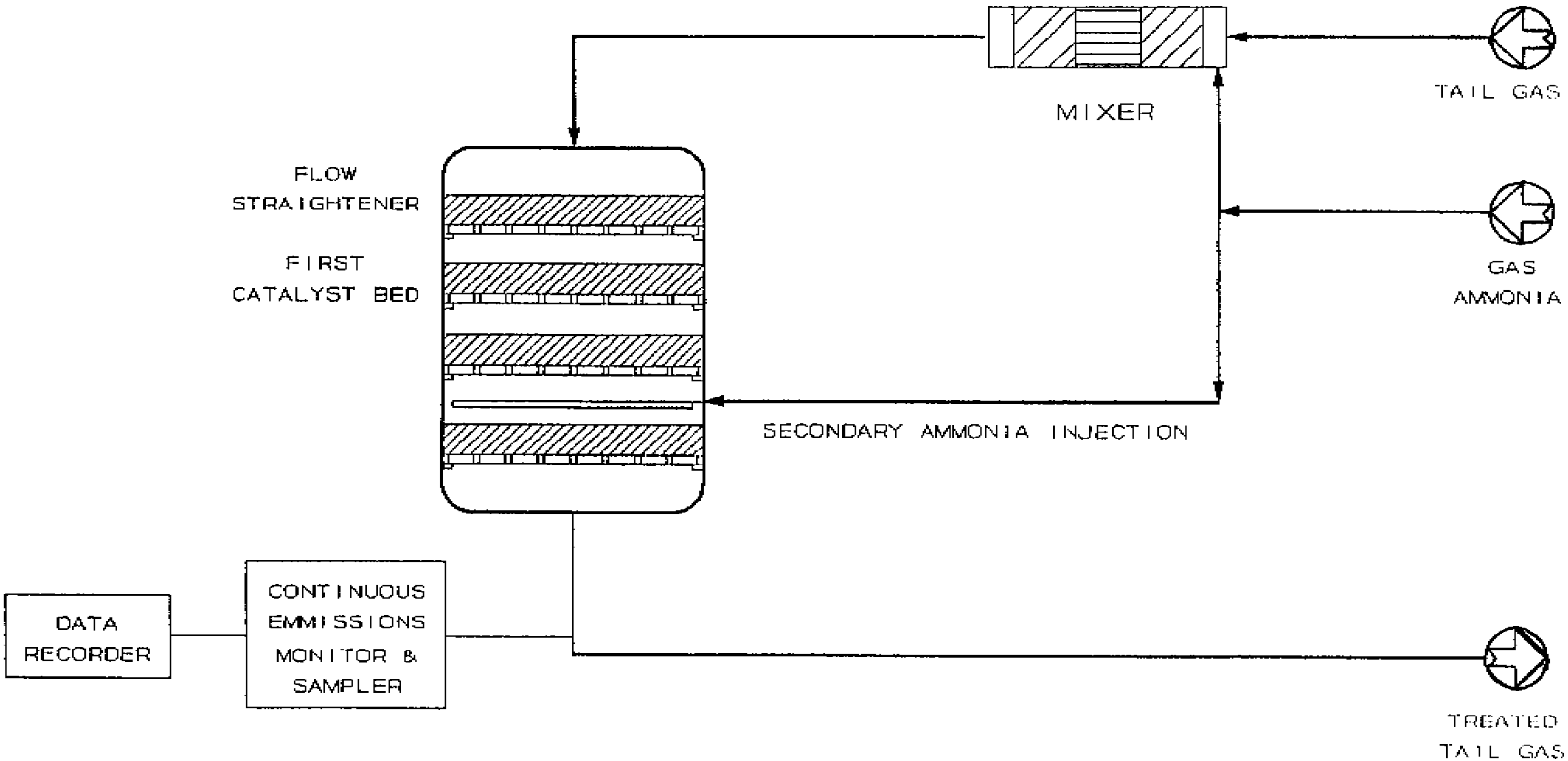


FIGURE 2

SCR NOx ABATEMENT UNIT