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REDUCTION OF NO_X IN LOW PRESSURE NITRIC ACID PLANTS

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Abstract

NO_X emissions of low pressure nitric acid plants are difficult to reduce economically.

This paper describes a system to reduce NO_X emissions by absorbing them with sulphuric acid at low pressure and low temperature. Part of the NO_X react with sulphuric acid to form nitroxil-sulphuric acid and another part are dissolved in the liquid phase.

The resulting liquid is heated and the NO_X are stripped by air and steam and reintroduced in the nitric acid plant.

Investment and operating data of a 300 MTD plant operating at 2 kg/cm^2 are shown. NO_X reduction over 90% is achieved. Economics of the process seem very promising.

INTRODUCTION

The growing preoccupation of the public opinion about the problems of environmental pollution has forced governments to put pressure on the chemical industry regulating the level of nitrogen oxides sent into the atmosphere.

Although the greater quantity of nitrogen oxides are produced by combustion engines, industrial boilers and power plants, most attention has been centred on the ugly plumes of brown fumes of the nitric acid plants due to the elevated local concentration existing in the point of emission and to their proximity to urban settlements.

The legislation in industrialised countries has made mandatory values as low as 200 ppm NO_X (expressed as NO_2) for new plants, placing in a critical situation those plants constructed before the decade of the $70's^{S}$, whose design was 2500 ppm of NO_X in the tail gas.

THE ABSORPTION SYSTEM OF NITROGEN OXIDES

The process of oxido-absorption is carried out in tray columns where the gas travels in countercurrent to the liquid, so that the NO_X is recovered in the form of diluted nitric acid.

In contrast to the absorption of SO_3 in water, which is quick, complete and irreversible, the reactions of the oxido-absorption of nitrogen oxides are slow and they are closely linked with the pressure and temperature conditions to those that are being made.

Oxido reaction	$NO + {}^{1/2}O_2 \dashrightarrow NO_2$ (1)
Absorption reaction	$3NO_2 + H_2O \dashrightarrow 2HNO_3 + NO$ (2)
Oxido-absorption reaction	$NO + {}^{1/2}O_2 + {}^{1/3}H_2O \dashrightarrow {}^{2/3} NHO_3 + {}^{1/3}NO$ (3)

The speed of reaction (1) is relatively slow and proportionally irreversible to the temperature of absorption, so that it is found in the cold parts of the plant and in the absorber when there is an excess of oxygen over the stoichiometric amount.

On the other hand, the reaction (2), like all the processes of absorption, is favoured by the pressure, but as a consequence of this, for every three mols of nitrogen dioxide absorbed a new mol of nitric oxide is produced and so a new oxidation cycle has to be initiated.

This process of absorption is inherently inefficient so we can come to the following conclusions:

a) The rate of oxidation of NO increases in low temperatures and high pressure.

b) The physical absorption of the gas increases with pressure.

c) Consequently the concentration of acid increases with pressure and at the same time the content of NO_x in the tail gas decreases.

In this way, the simplest method of reducing the content of NO_x in the tail gas consists in carrying out the absorption at high pressure and, following this line, all plants installed in recent years operate at 9-12 Atm. with values inferior to 200 ppm in the tail gas.

Unfortunately this solution couldn't be applied to the old plants which operate at a medium pressure of 2-4 Atm. and which, on the other hand, have been made to improve their capacity of production at the expense of increasing the emission of NO_x and reducing the concentration of the nitric acid produced.

PROCESSES FOR THE ELIMINATION OF NO_x

Within the multitude of existing processes we can make the following classification:

1) Process destroying of NO_x in N_2 and H_2O by reductive incineration of selective catalysis.

2) Physical adsorption process over zeolites or molecular sieves.

3) Chemical absorption process using alkaline or acid aqueous solutions.

The process of destroying NO_x in some cases allows the colourisation of gas instead of the reduction of content in nitrogen oxides (conversion of yellows NO_2 in decolored NO) and in other cases produces considerable quantities of colour, endangering the catalyst unless the reaction is carried out in various stages with intermediate refrigeration.

The physical adsorption presents problems in the regeneration of the molecular sieves and involves a high investment.

On the other hand, the chemical absorption process eliminates the effluent gases like solutions presenting few possibilities of commercialisation or the elimination of the effluent liquids and also a high cost of operation.

The object of this paper is to present the research carried out in the FESA factory in Seville using an absorption process of NO_x over concentrated sulphuric acid and the posterior desorption of the nitrogen oxides, which are recycled to the process, so that, not only is the gas cleaned, but the overall efficiency of the plant is improved.

SULPHURIC ACID ABSORPTION

The basic aspect of this process is based on the mechanism developed by Gay-Lussac for the sulphuric acid plants by the method of lead cameras where the reaction between the nitrogen oxides and the sulphuric acid was carried out with the formation of nitroxilsulphuric acid.

$$NO + NO_2 = N_2O_3 \quad (4)$$

$$NO + NO_2 + H_2O = 2NO_2H \quad (5)$$

$$N_2O_3 + 2H_2SO_4 = 2HSO_4NO + H_2O \quad (6)$$

$$2NO_2H + 2H_2SO4 = 2HSO_4NO + 2H_2O \quad (7)$$

The reactions (4) and (5) are quickly established in the gaseous phase, while (6) and (7) take place in the gas-liquid interphase and, depending on the solubility of the gases in the interphase and the speed of reaction in the operation system, it allows them to move to the right or to the left, being the high pressure, the low temperature and the greater concentration of sulphuric acid the conditions which move the equilibrium towards the right.

The chemical reaction favours and increases the absorption of nitrous gas, extending the transference effect by molecular diffusion and making this process more efficient than other absorption processes.

On the other hand, the high temperature and a reduction in the partial pressure of the nitrous gas moves the balance of reactions (6) and (7) towards the left allowing the regeneration of the sulphuric acid.

In the flow diagram of figure 1 the process of absorption with sulphuric acid applied by FESA can be seen combined with the process of desorption (denitration), which has been installed in Seville for the recovery and recycling of the nitrous gas of the nitric acid plant using the technology of SCHOTT A.G.

In the absorption phase the gas goes through a condenser separator, enters the absorption tower where it travels countercurrent to the sulphuric acid 75-80% weight, which the nitrogen oxides retain due to the formation of nitroxilsulphuric acid.

The reaction is slightly exotermic so it requires the refrigeration of the acid in recirculation.

The outgoing gas of the tower is passed through a scrubber-separator before being sent to the expansion turbine of the plant.

The efficiency of the absorption is proportional to operation pressure and, in the case of the Seville factory, the performance of recovery of nitrogen oxides is higher to 85% working at 2.8 Bar abs.

DESORPTION OF NITROGEN OXIDES

As has been mentioned above, the desorption of nitrogen oxides is carried out at low pressure and high temperature, for this reason in this stage, the denitration process of the residuary acids of the fabrication of explosives has been used.

The desorption is carried out at a pressure of 500 mbar abs. and the boiling temperature or the sulphuric acid, 170° C, producing the stripper of the nitrous oxides thanks to the injection of steam at the bottom of the tower.

The denitrated acid is cooled at first with the acid the desorption tower provides and finally with the refrigeration water before being recycled to the absorption tower.

The nitrous gas which comes out of the top of the tower is cooled separating the nitric acid condensers before being compressed and recycled to the absorption tower of the nitric acid plant.

OPERATION EXPERIENCES

The practise test carried for the functioning of this absorption process were done in a pilot plant constructed in PVC + FR 0,9 mts in diameter and using a packed of relleretes of 1" of polypropylene.

The tests took place with a gas rate of 1500 m^3/h and 2,8 bar abs of pressure.

The desorption in a unit of denitration of glass constructed by SCHOTT.

Absorption conditions

Gas volume	1500 m^3/g
Pressure	2,8 bar abs.
Acid temperature inlet	30° C
Acid temperature outlet	35° C
NO_x on inlet gas	3200-3500 ppm
NO_x on outlet gas	400-500 ppm
Concentration H_2SO_4	75-80% w/w

Desorption conditions

Pressure	500 mbar abs
Temperature	170° C
HNO_2 on entry Sulphuric Acid	1,5-2,0% w/w
HNO_2 on exit Sulphuric Acid	0,3% w/w

ADVANTAGES OF THE PROCESS

Compared with other absorption processes, the advantages which the absorption in sulphuric acid with recovery of nitrogen oxides present are as follows:

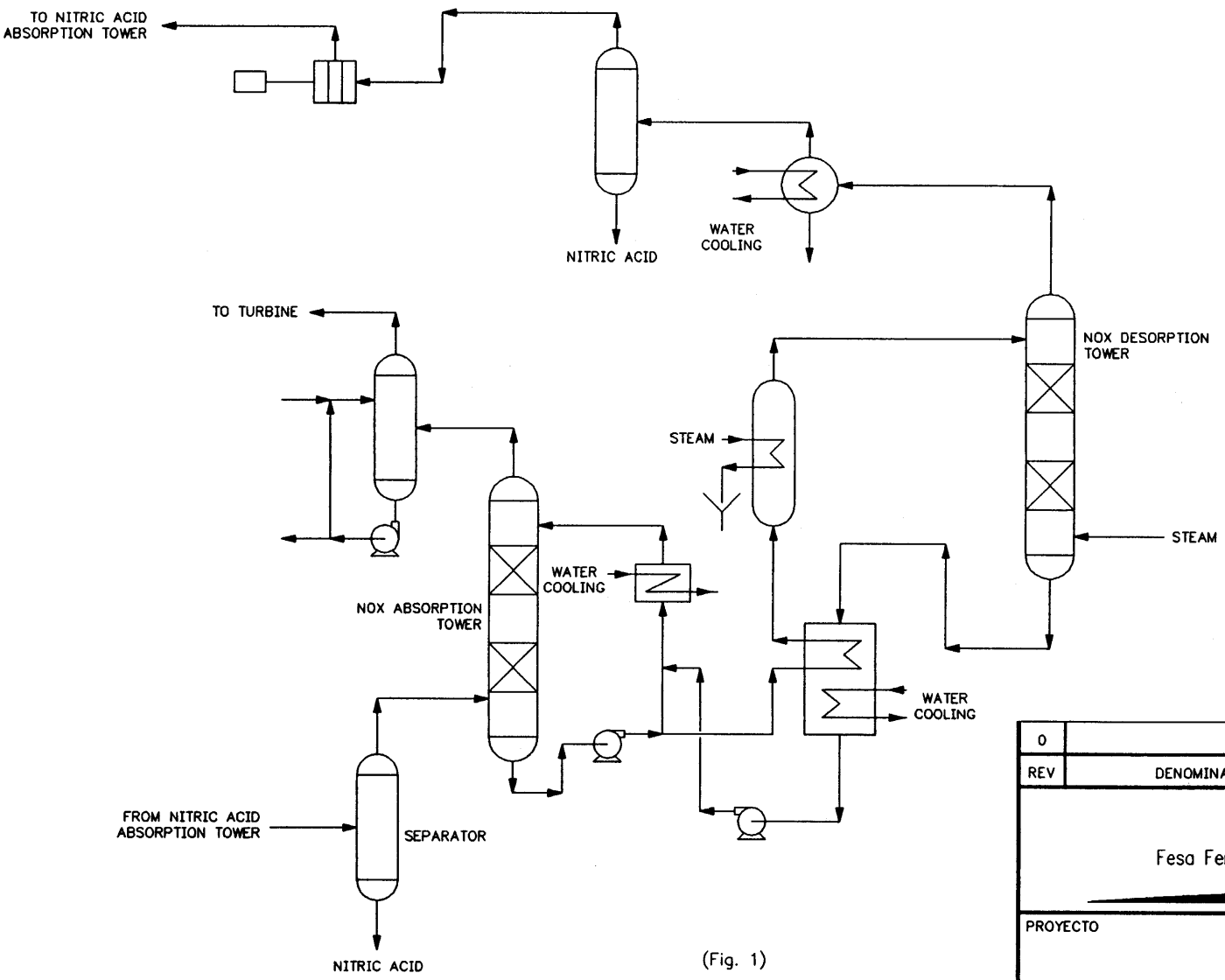
. The investment is similar to that of any chemical absorption with recovery or effluent liquid.

. It does not produce effluent liquids which are difficult to commercialise.

. The operative costs (energy, steam, cooling water) are compensated by the equivalent nitric acid due to the recycle of the nitrogen oxides of the process.

. There is no limitation to the production capacity because it has a very low pressure drop (200 mm c.a.).

At present a scale-up operation of the unit has been undertaken to process all the gas of the nitric acid plant, 40.000 m^3/h and hopes that the plant will come into service in the first term of 1991.



(Fig. 1)

REV	DENOMINACION	FECHA	DIB.	COMP.
0		21/05/90		

Fesa

Fesa Fertilizantes Españoles S.A.
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PROYECTO: ABATIMIENTO NOX

TITULO: ESQUEMA DE PROCESO

ESCALA	PLANO N° 102-90-P-001	REV. 0