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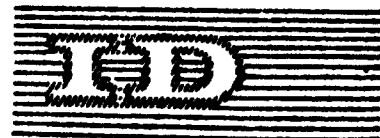
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NOTES ON THE ELIMINATION OF NO_x IN TAIL-GAS
IN MEDIUM-PRESSURE NITRIC ACID PLANTS

PRELIMINARY STUDY OF A NEW ABSORPTION
PROCESS ^{1/}

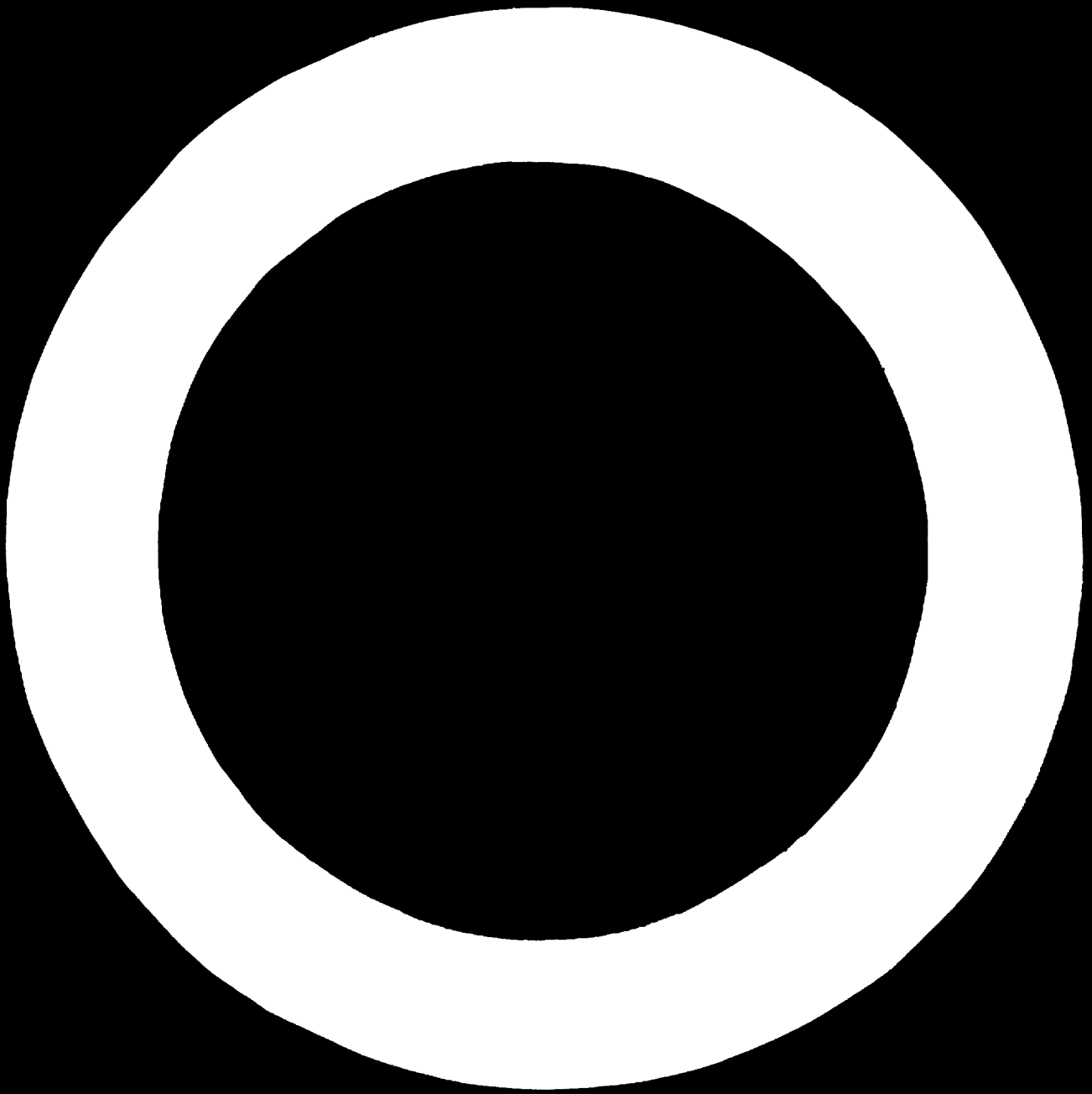
by

D. Joaquin Olivares ^{*/}

^{*/} Union Explosivos Rio Tinto, S.A.

^{1/} The views and opinions expressed in this paper are those of the author and do not necessarily reflect the views of the Secretariat of UNIDO.

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INTRODUCTION

The present study is concerned with nitric acid plants working at medium pressure (2-4 kg/cm²) which were designed before the growing use in Europe of high-pressure technology coincident with the appearance of ever stricter anti-pollution regulations, specifically since 1964 or 1965.

We refer to truly European processes, like Montecatini, Pintsch Bamag and Stamicarbon, among others.

Most of these plants, which are particularly numerous in Europe, are continuing to function with operational improvements which, in many of them, have allowed increases in capacity beyond what the designs provided for; they are of considerable economic interest as the acid they produce (50-55 per cent concentration) is used almost wholly for the production of ammonium nitrate (fertilizers).

This increase over rated capacity has been possible, within the limits of each case, of the expense of the concentration of the acid produced, and the efficiency of absorption of the gases in the water at the pressure concerned.

The lower concentration of the acid obtained is no obstacle to the production of ammonium nitrate, as in most chemical plants it is cheaper to concentrate the nitrate solution rather than the acid itself.

Nevertheless, the growing preoccupation of Governments and the world at large with problems of environmental pollution has encouraged great interest in reducing or eliminating NO_x emission in medium-pressure nitric acid plants, in spite of the fact that the amount of NO_x emitted from these plants is minimal in comparison with other sources of pollution (thermal power plants, motor vehicles, etc.).

After an analysis of problems of installation and of basic features of this type of nitric acid plant, it will be shown in the course of this study that there are serious economic difficulties to be solved in connexion with the emission of NO_x into the atmosphere if the regulations are to be applied that are being formulated by the competent organs in almost all industrialized countries.

The optimization possibilities for these plants and the preliminary experience gained with the development of an absorption process using an aqueous urea solution are also described.

1. General considerations regarding the technology of nitric acid production at medium pressure

We refer, of course, to the method of obtaining nitric acid in two phases: catalytic oxidation of the ammonia, and oxidation-absorption of the combustion gases. We consider only the case where the plant in question operates at practically constant pressure - that is, taking into account only the pressure loss of the various units in the course of the process.

The basic stages of the process in a medium-pressure nitric acid plant are as follows:

- (a) Combustion of the air/ammonia mixture at 4 kg/cm^2 absolute pressure;
- (b) Gradual cooling of the combustion gases to promote the oxidation of the NO;
- (c) Condensation of weak acid before absorption;
- (d) Absorption over water in a plate tower;
- (e) Reheating of the unabsorbed tail-gas;
- (f) Recovery of the tail-gas energy in an expansion turbine coupled to the air compressor shaft;
- (g) Full utilization of the steam produced in the waste-heat boiler of the reactor, in a condensing turbine that is also coupled to the air compressor shaft.

The acid concentration that can be obtained in practice with this type of process is up to 55-57 per cent, depending on the efficiency of the absorption stage. If the acid is to be used afterwards to obtain ammonium nitrate, this concentration can be lowered to 50 per cent, which usually allows increases in capacity, the design of the air compressor and the absorption process permitting; this is the case in most plants.

Apart from this, the choice of a medium-pressure process for the production of nitric acid has various advantages:

- (a) Working with a catalyst (Pt/Rh) gauze temperature of about 850°C , a high rate of conversion of NH_3 into NO is obtained, making an air pre-heater unnecessary.
- (b) The velocity of the gases through the catalyst is very low (about 2 m/sec) and catalyst losses are therefore moderate ($100-150 \text{ mg/tonne of HNO}_3$).
- (c) A Lamont-type boiler at the exit of the burner permits the production of steam sufficient in quantity and reheating temperature of power the plant's air compressor. (The defects of this apparatus, until the problems were finally solved, were one of the weak points of this type of plant.)

- (d) As the boiling point of NH_3 is lower than 20°C at $4-5 \text{ kg/cm}^2$ absolute pressure, evaporation can be effected with refrigeration water coming from the absorption towers, simply and economically.
- (e) Over-all efficiency usually exceeds 95 per cent.
- (f) Medium-pressure processes usually offer great flexibility in terms of capacity and concentration of the acid produced.

Among the most notable disadvantages of these plants - apart from design problems relating to the waste-heat boiler (vertical position, centred with the Pt/Rh gauzes) - is the low absorption efficiency, which leads to tail-gas with a concentration of about 0.25 per cent by volume of NO_x . This value increases if the plant has allowed optimization of production at the expense of product concentration. In any case it is difficult and expensive to adapt the design of these plants to NO_x emissions restricted by law to 2,500 parts per million (ppm), in line with the recent trend in most industrialized countries.

There is another interesting aspect of the subject of NO_x emissions in medium-pressure nitric acid plants, connected with purely economic considerations peculiar to this technology. One may say that the two cost items that substantially affect the production of nitric acid are the amortization of the investment (assumed to be short-term) and the cost of the basic ammonia. This is the reason for the boom in high-pressure plants ($7-12 \text{ kg/cm}^2$ absolute pressure), which, with lower installation costs and lower prices for ammonia on the world market, have tended to replace those working with medium pressure, in spite of their advantages - greater over-all conversion efficiency, and smaller catalyst losses. Besides, the high-pressure plants, with their greater absorption efficiency, permit NO_x emissions into the atmosphere of about 500 ppm or even less, especially if they are redesigned with catalytic abatement units (F.A.U.), which are difficult or impossible to combine with medium-pressure plants of older design (more than five years old).

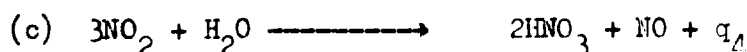
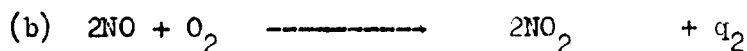
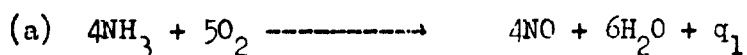
Recently, many economic comparisons have been made between medium-pressure and high-pressure processes for the production of nitric acid, and in Europe the former are in fact being replaced by the latter; but given the present world shortage of raw materials, or at least the shortage of naphtha for the production of ammonia, there is reason to expect that, if the price of this basic product for the production of nitric acid continues to increase, there may be a new trend in nitric acid technology towards medium-pressure processes. (It must be remembered that nearly 80 per cent of world production of nitric acid is used for fertilizers).

If anti-pollution regulations continue to be so strict, it is not certain that catalytic NOx abatement (F.A.U.) will be as easily applicable to medium-pressure plants as to high-pressure plants, at any rate without important economic effects.

In that case, our work should be of great interest to medium-pressure plants that are in operation at present and are having difficulties in complying with anti-pollution regulations.

2. Tail-gas pollution abatement problems at a nitric acid plant designed without taking into account this factor

The three stages of nitric acid production are, of course, as follows:



The combustion reaction (a) is so rapid that the controlling variable is the velocity of the ammonia when it reaches the catalyst surface. Therefore, processes operating at low pressure can achieve good conversion rates with a small quantity of catalyst (less than 0.5 grammes/m³ of mixture), and also lower platinum losses. Otherwise, pressure is not a variable that controls the process.

The (b) reactions are of paramount importance in the process, because the greater part of the NO must be oxidized when it reaches the absorption towers in order to start the absorption process (phase c). As these are exothermic reactions the gases must be suitably cooled at the outlet of the reactor (see diagram No.1), in a series of heat exchangers, whose dimensions must be very carefully calculated, for reasons which will be seen below.

The NO oxidation reaction is a homogeneous, third-order reaction described by Bodenstein by means of the equation:

$$-\frac{d(\text{NO})}{dt} = K(\text{NO})^2(\text{O}_2) - K'(\text{NO}_2)^2$$

but this reaction is unusual in that - unlike most homogeneous reactions - its velocity is lower when the temperature is higher. Moreover, the effect of pressure on this reaction is peculiar because, if the time necessary for a certain amount of gas to pass

to pass through a reactor increases directly with the pressure, it follows that the volume necessary to produce a certain rate of oxidation of NO to NO₂ is inversely proportional to the cube of the pressure. This means that the time the gas spends in the heat exchangers must be optimized for each pressure, depending on the gas flow.

The purpose of all this was to show that, if a medium-pressure nitric acid plant (in high-pressure plants, naturally, the time spent in the heat exchanger has less influence) permits an increase of load in the reactor, one must optimize the set of exchangers after the reactor, since otherwise the NO will not oxidize, and the NO_x content in the tail-gas will increase independently of the original design of the absorption process.

We come now to reaction (c), the absorption of NO₂ in water, followed by the desorption of NO and the production of nitric acid. This NO must be reoxidized with the remaining O₂ in the gas and in the inter-plate compartments of the column, with the same mechanism as described in the "oxidation" phase.

That is to say that the low temperatures promote the absorption of NO₂ in water in the presence of excess oxygen, for which reason the plate liquid must be suitably refrigerated.

As to the influence of pressure on the absorption mechanism, it is clear that pressure also promotes absorption, for various reasons:

- (i) The speed of NO oxidation increases with the pressure.
- (ii) The rate of physical absorption of a gas in a liquid increases with the pressure.
- (iii) The concentration of the acid obtained increases with the pressure.

This is the main advantage of high-pressure plants (inasmuch as the investment is lower) over medium-pressure plants, for the same production capacity and requirements regarding tail-gas composition.

Without pursuing the subject further, it is clear that improving the absorption of a nitric acid plant and thus reducing the quantities of NO_x emitted into the atmosphere is only possible by increasing the pressure (mixed process) or the number of plates, with the consequent investment cost. Both solutions are far from being economic in most cases.

If the plant in question permits the optimization of the oxidation phase, it may be possible to improve the absorption without increasing the number of plates, by increasing their refrigeration.

Let us now consider the fact that most medium-pressure plants which were in operation before 1965 make use of the heat content of the tail-gas, after heating with the process gas (see diagram), in a turbo-expander coupled to the air compressor shaft. But this recovery usually amounts to about 25 per cent of the motive power of the machine, for two reasons:

- (i) The temperature of the tail-gas at the absorption outlet is about 40°C , and it enters the expander at some 100°C after reheating in the exchanger.
- (ii) The pressure of the tail-gas is naturally low (2.5 to 3.0 kg/cm^2).

Suppose we wish to couple an F.A.U. to one of these medium-pressure plants; the abatement unit must be located before the expander, but the gas must be cooled to the design temperature of the machine. If the F.A.U. is only colour-removing ($\text{NO}_2 \rightarrow \text{NO}$) nothing will have been achieved, because re-oxidation is immediate at this temperature; on the other hand, if the F.A.U. is one producing total abatement, the plant must be provided with a heat recovery system; however, this will clearly not be economic in view of the investment it would require.

There are medium-pressure plants with incorporated F.A.U., but they were designed in such a way that the expander provides 80 per cent of the motive power for the compressor - that is, the plant's energy recovery takes place at the tail and not at the head (boiler), as is the case in most plants built before 1965.

The possibilities of coupling an F.A.U. to an old medium-pressure plant depend on using NH_3 as fuel, since high temperatures are then not needed for the NO_x abatement (the O_2 does not react), but these F.A.U. processes have not been tested industrially to a reliable extent.

Another way of eliminating NO_x in the tail-gases of a plant of this type is washing by absorption with alkaline lye, which is feasible, has been tried out, and might be economic in comparison with other alternatives, although it presents the additional problem of the evacuation of nitrous solutions and of the resulting water pollution, besides the fact that it does not recover acid.

Molecular sieves have been used for some years to purify tail-gases in nitric acid plants; and they have the advantage of being a regenerative system, with nitric acid recovery; however, the required investment is high - to be specific, it is about 10 per cent more than for absorption in water and 30 per cent more than for catalytic reduction.

As we shall see in the following paragraph, an economic comparison of the three most attractive types of solution (absorption in water, F.A.U. catalytic combustion and molecular sieves) shows that a medium-pressure nitric acid plant designed without tail-gas abatement can only be made to operate without polluting the atmosphere by suitably optimizing the oxidation (if the load has been increased beyond what was envisaged in the design) and increasing the number of plates installed for absorption, a solution which also recovers nitric acid and improves efficiency.

Let us assume that a nitric acid plant of 300 tonnes a day is operating with a tail-gas containing 3,500 ppm by volume of NOx and we wish to bring about an abatement leaving only 500 ppm by volume of nitrous gases. Either of the recovering systems (absorption and molecular sieves) will give about 7 Tm of HNO₃, while catalytic combustion only recovers steam (1 Tm/Tm of HNO₃), though with an additional fuel consumption equivalent to 600 kcal/Tm of HNO₃. The investment figures for the three processes - absorption, F.A.U. and molecular sieves - are in the proportion 1.15:1:1.26, for turn-key plants.

If we convert the preceding economic comparison into cost prices of nitric acid produced, we find that tail-gas abatement using a supplementary column for absorption in water gives more economical costs than the other two systems, provided that the acid is recovered.

	<u>Without acid recovery</u>	<u>With Acid Recovery</u>
Absorption	1.00	1
F.A.U.	0.98	2.04
Molecular sieves	2.06	3.07

3. Basic ideas for the development of a process for the absorption of NOx in tail-gas using urea solution

The action of urea on the development of nitrogen oxides, which results from the reaction or acidulation of natural phosphate with nitric acid, is well known. It is also established that the possible decomposition of ammonium nitrate and ammonium nitrosulphate can be prevented merely by adding small quantities of urea.

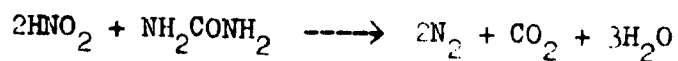
The chemical mechanism of this reaction appears to be the result of a breaking down of the urea into CO₂ and N₂ through the action of nitrogen oxides in an acid medium.

There are various patents in existence which support this reaction but they are based on experiments too limited in scale to yield as yet conclusive findings as to its effective use on an industrial scale and more specifically in nitric acid plants with a high emission of tail-gases (40,000-50,000 m³STP/h) and relatively low concentrations of NOx (0.2 to 0.4 per cent by volume).

Although the ideas contained in these patents are applied, through the extrapolation of data, to an actual nitric acid plant, it is found, as we shall see later, that there is no possibility of their industrial application without the relevant additional studies being carried out.

This study describes experiments conducted on the absorption of NOx with aqueous urea solutions using a small-scale model, and the foundations are laid for experiments in a pilot plant which are described and which will provide the necessary basis for application on an industrial scale.

The reaction which is in principle accepted for the process is the following:



which requires a urea consumption of 5.35 grammes for each m³STP of tail-gas from a nitric acid plant containing 0.4 per cent NOx (assuming 75 per cent NO₂ + 25 per cent NO). This presupposes a consumption of urea in the region of 6,500 kg/day for a conventional nitric acid plant producing 250-300 tonnes/day.

Nevertheless, the reaction in question does not appear to be so simple, since the estimated consumption of urea is much smaller than that recorded. This may be due to the fact that urea reacts only with a specific nitrogen oxide (there are several present) or to the fact that there is a certain catalytic action.

In any event, it has been found on a laboratory scale that there is a "decoloration" of the gases and a minimal consumption of urea, reasons which we feel justify undertaking an investigation which could yield practical conclusions applicable to a medium-pressure nitric acid plant when tail-gas cannot be purified by other processes.

3.1 Critical assessment of patents

As already noted, there are several patents based on experiments conducted on a limited scale which transpose the results obtained to substantial gas flows with a low concentration of NOx. These are not in practice applicable for technical considerations which we shall examine later.

Nevertheless, they present considerable interest as the urea consumption recorded is almost half the stoichiometric value, which corroborates our theory either of the existence of a catalytic effect or of the mere absorption (decomposition) of the coloured nitrogen oxides present in the tail-gas of a nitric acid plant.

Referring specifically to the work of A. Warshaw (US Pat. 3565575) which deals with the reaction of urea with NOx in the filling tower, we see that the installation would work with 0.2615 kg of 10 per cent urea solution for each kilogramme of gas to be purified; that is, an installation for the purification of an emission of 45,000 m³STP of tail-gas containing 0.2 to 0.5 per cent NOx would require 13.5 m³/h of 10 per cent aqueous urea solution. The addition of urea recorded is 3 grammes/m³STP of gas, or in other words 3.25 tonnes/day of urea which is practically 50 per cent of the stoichiometric value.

If we use this data to apply the LEVA graph and obtain the filling rate factor, we see that here, working at the upper load limit (that is, almost flood level), we obtain a filling factor of $F = 3$ which corresponds to a filling rate that is not at all normal. In other words, the L/G value in the assumed washing column is extraordinarily low.

Especially in the light of the low L/G ratio, one might of course consider increasing L at the expense of greater recirculation, but it was decided to programme a series of experiments designed to develop a process best applicable to industrial conditions.

3.2. Experiments conducted with a filling model

The gas to be purified with the absorption model issued from a medium-pressure nitric acid installation and had an NOx content in the order of 0.45 per cent by volume.

The urea solution used contained a small quantity of sulphuric acid and urea in the proportion of 10 per cent by weight.

The specifications of the model are as follows:

Diameter 10 cm

Height of filling 60 cm

Raschig rings 1 cm

A diagram of the installation is annexed (No. 2); the materials used were INOX 304L and PVC.

Tests were conducted varying gas and liquid emissions in a range of values permissible for the installation with which we were working, giving the results attached in table 1.

The analyses carried out were the following:

Gas entering and leaving the tower (absolute NOx absorbed);

Aqueous urea solution.

The analytical determinations of NOx were carried out by the hydrogen peroxide method, in order to avoid false findings due to the presence of CO₂ in the gas.

Analysis of the urea was done by visible spectrophotometry using p-dimethylaminobenzaldehyde as a reagent.

The consumption of urea noted (see table 1) is really small, almost beyond the accuracy range of the analytical process used, which shows that it is possible that the mechanism does not consist merely of absorption by chemical reaction. This assumed lack of analytical precision, in spite of the precautions taken, affects the related data on urea consumption.

It should also be noted that we have not taken into account the influence which the nitrous gases dissolved in the process might have on the colorimetry of the urea. This might be insignificant, but it will be studied at a later stage.

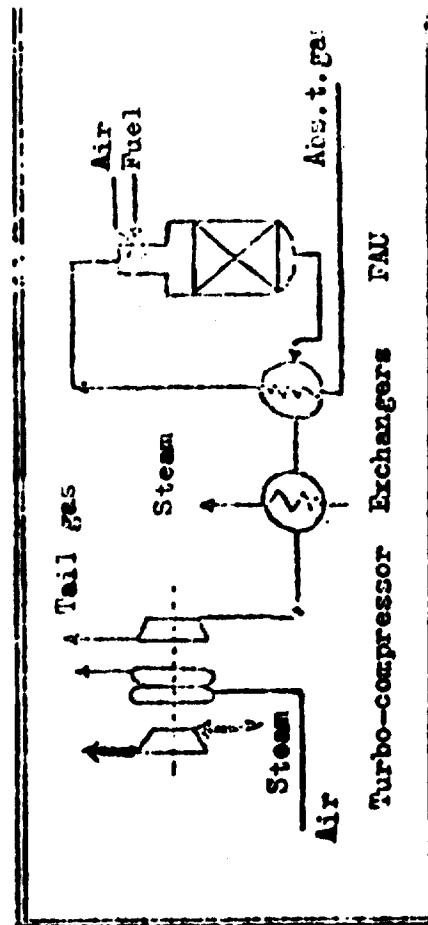
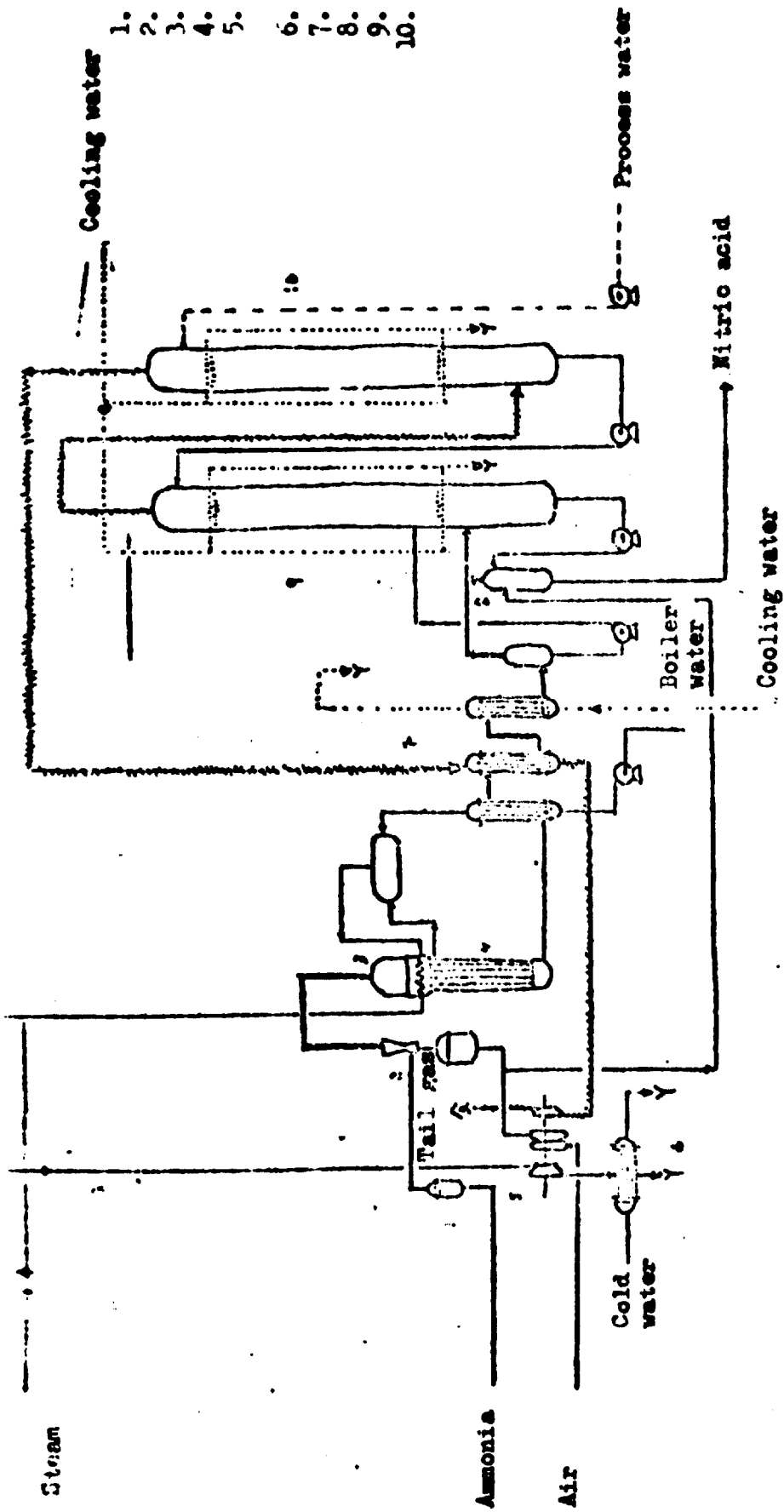
The results obtained are also expressed in graphic form where the influence of gas flow on the percentage of absolute NOx abated for L = constant is expressed in litres/sec.

The conclusions of the study conducted may be summarized as follows:

1. The purity of the gas is in the region of 1,500-2,500 ppm starting with 4,500-5,000 ppm NOx, and 1,000-1,200 ppm starting with tail-gas containing 2,500-3,000 ppm NOx.
2. The influence of liquid emissions on the percentage of absolute NOx absorbed is relatively small.
3. With large liquid emissions, the absorption appears to be more physical than chemical (small relative consumption of urea).
4. The small liquid emissions observed point in the direction of a plate tower, as was concluded in the above criticism of patents (see 3.1).

The study will be pursued with a pilot tower "on line" in a medium-pressure nitric acid plant, designed in accordance with plant conditions and on the basis of the results of the experiments conducted.

1. Filter
2. Filter and mixer
3. Reactor
4. Boiler
5. Turbo-compressor and expander
6. Condenser
7. Oxidation exchangers
8. Oxidation tower
9. Acid absorption tower
10. Water absorption tower



DIACRAM No. 1

Medium-pressure nitric acid plant

Detail of coupling of an FAU

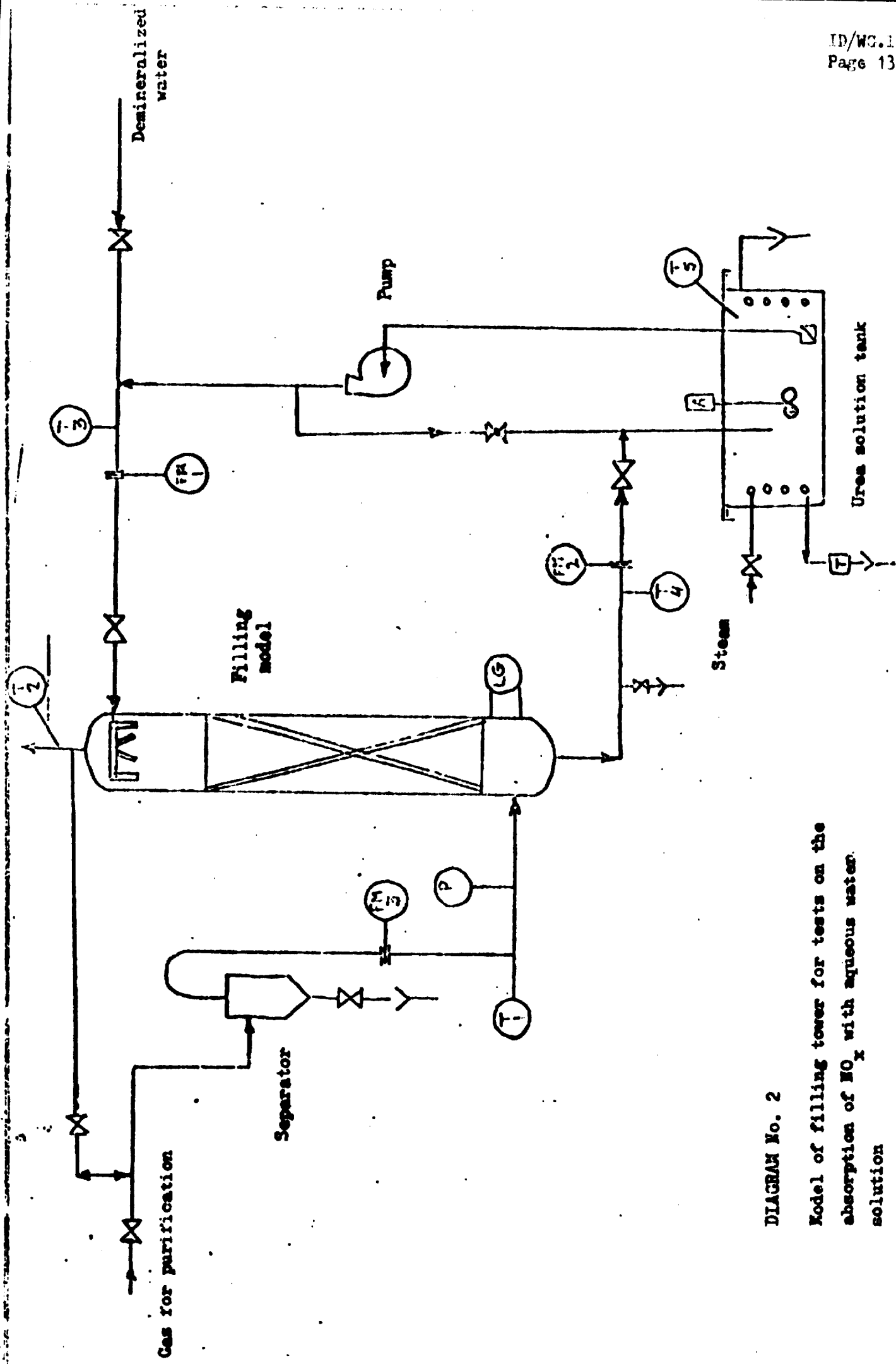


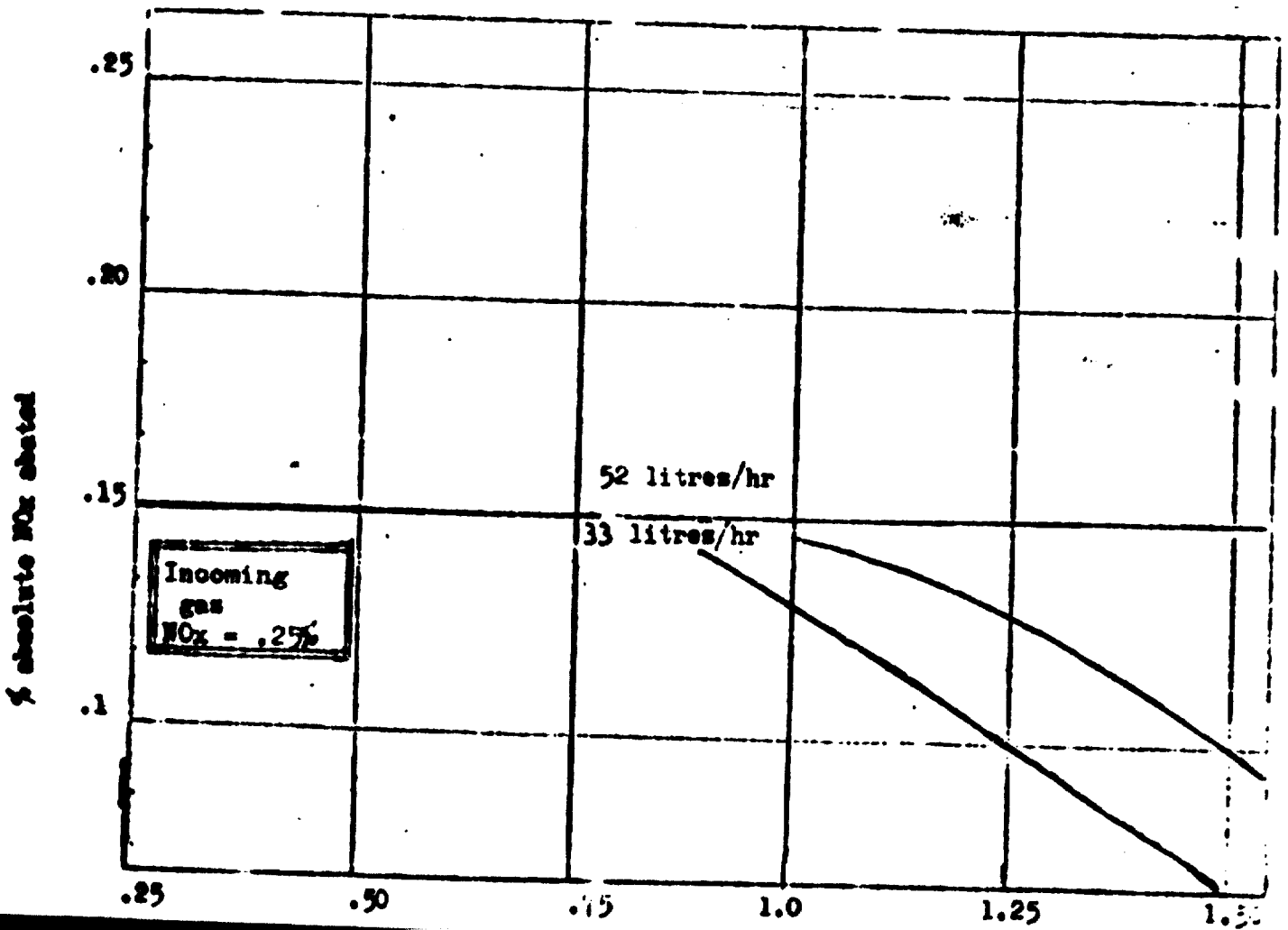
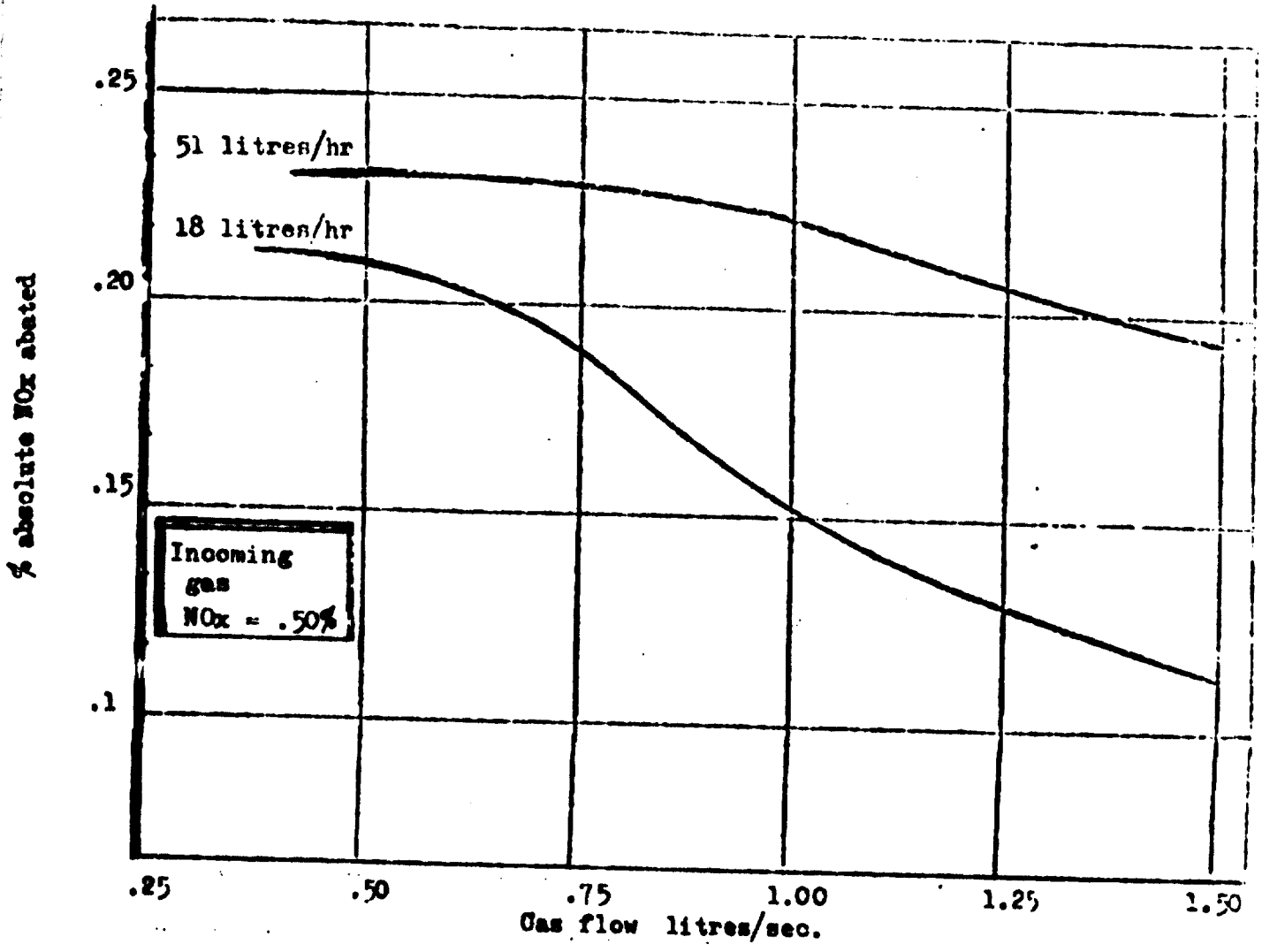
DIAGRAM No. 2

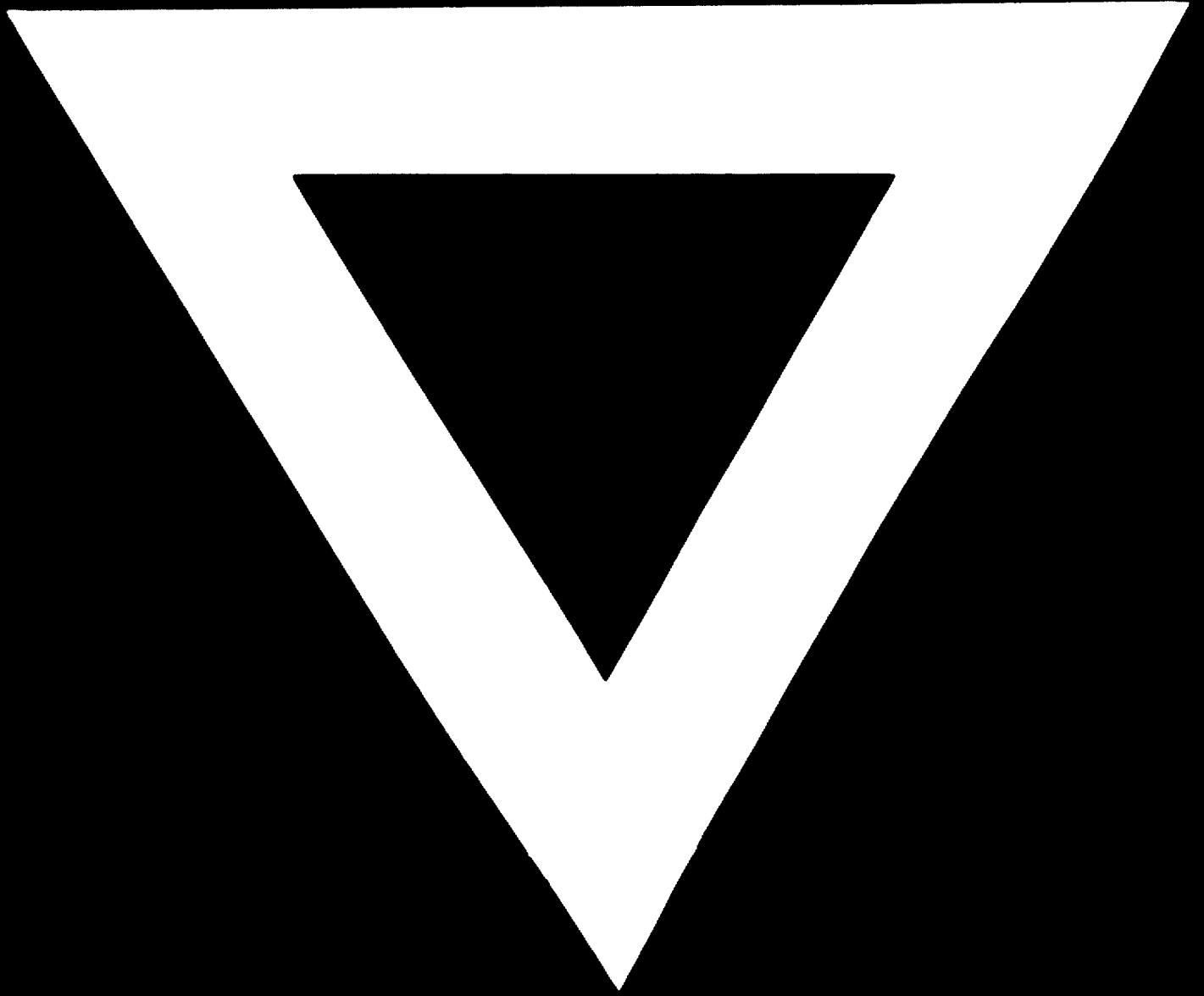
Model of filling tower for tests on the absorption of NO_x with aqueous water solution

TABLE No. 1

TABLE OF RESULTS. ABSORPTION OF NOx WITH UREA SOLUTION IN ROTEL TOWER

Gas flow l/sec.	Liquid flow l/h	% NOx Incoming	% NOx Outgoing	% Urea Incoming	% Urea Outgoing	% Absolute NOx	P. Urea/ P. abs. NOx	Residence time sec	Velocity of gas in the bottom m/sec.
0.50	19	0.48	0.27	10.46	10.20	0.21	7.66	2.54	2.57
0.50	49	0.48	0.26	10.73	10.77	0.22	11.40	3.46	2.77
0.75	33	0.46	0.27	10.66	10.66	0.22	0	2.35	2.63
0.75	51	0.53	0.27	10.73	10.80	0.26	5.50	2.22	2.45
1.00	15	0.44	0.22	10.46	10.40	0.25	0.78	1.77	2.40
1.00	52	0.54	0.32	10.66	10.66	0.22	0	1.75	1.74
1.25	33	0.25	0.25	10.46	10.00	0.10	19.6	1.42	1.53
1.25	52.5	0.25	0.12	10.73	10.55	0.13	3.70	1.41	1.37
1.50	33	0.25	0.25	10.46	10.05	0.05	22.0	1.13	1.07
1.50	52.5	0.25	0.15	10.73	10.73	0.10	0	1.18	1.11





74.10.1