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**In 1982, the name of the International Superphosphate Manufacturers' Associations (ISMA) was changed to International Fertilizer Industry Association (IFA).*

DYNAMICS OF REACTIONS AND OPTIMISATION IN SULPHURIC
ACID PLANTS USING THE NITROGEN OXIDES PROCESS.

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SUMMARY :

The influence of concentration and temperature during the slowest phase of the whole process - the NO reoxidation - is analysed.

The conditions in the reaction towers are examined together with the effect of the gas velocity and the liquid flow. Optimum values are then defined for the operational parameters of the reaction towers, taking into account corrosion and process stability.

Finally, the influence of temperature and reaction time on the consumption of nitric acid, this being bound up with the working capacity of the plant, is described.

1. INTRODUCTION :

In a previous paper (I) we began an analysis of the dynamics of the chemical reactions which take place in an intensive H_2SO_4 production unit using the nitrogen oxides process.

Apart from the strictly technical factors which argue for a re-evaluation of this type of process, it should be emphasised that, for plants of limited capacity, it is really competitive with the contact process, especially when the H_2SO_4 is only for superphosphate production.

The cost of a 100 tons/day tower process plant on a 100% H_2SO_4 basis, excluding the SO_2 production unit, is, according to DURAND (II), more than two and a half times less than that of a contact plant. Since, in Italy at least, raw material costs account for more than the 75% of the production costs, it is clear that the heavy incidence of capital depreciation on contact process plants is an argument against their use when an acid of less than 75% concentration is required.

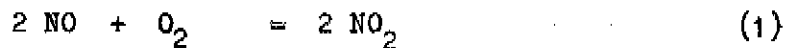
All economic considerations aside, it seems to us worthwhile to go more deeply into the dynamics of the reactions which take place in a nitrogen oxide process plant with the aim of defining the optimum operating conditions.

The operational data which we shall describe bellow refer to a 45 tons/day 75% H_2SO_4 plant, resulting from the collaboration between one of the authors and SALSAS-SERRA. Fig. 1. shows the plant

schematically and the values of the main parameters are indicated. Although the plant, installed in 1958 at the factory of Fabbrica Perfosfati Cerea, is similar in some respects to the classical Techno-chemie plants, it differs in respect of its greater simplicity and slightly lower range of working temperature. During 10 years of operation a very large quantity of data has been collected which checks the validity of the hypotheses initially advanced by KACHKAROFF and subsequently developed by SALSAS-SERRA (III).

2. REACTIONS IN THE GASEOUS PHASE

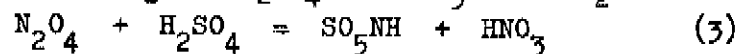
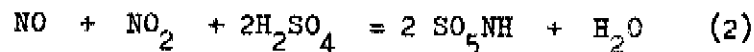
Following the KACHKAROFF theory, SALSAS-SERRA has stated (IV) that the phases which control the overall H_2SO_4 production process are the absorption of the SO_2 in H_2SO_4 and the reoxidation of NO according to the following reaction:



In 1932, SZEGO and LOMBARDI (V) measured the absorption rate of SO_2 , N_2O_3 , and N_2O_4 in H_2SO_4 at different concentrations (Fig.2).

From Fig.2 it may be seen that according to PETERSEN (VI), the slowest phase of the absorption process is that relative to SO_2 : at the concentration levels of H_2SO_4 normally found in an intensive plant, the absorption rate constant is some three times lower than that for N_2O_3 .

However, it should be emphasised that it is not the absorption of N_2O_3 but rather its preliminary phase (reaction 1) which is the slowest step of the process. In fact, the nitrogen oxides are absorbed according to the following scheme:



Thus the ratio NO/NO_2 should be as close to unity as possible.

We have pointed out (I) that an excess of NO_2 , although absorbed according to reaction (3), causes an appreciable increase in the vapour pressure of the liquid phase, as shown in Figure 3.

3. REACTION TOWERS FLUODYNAMICS

As has already been pointed out, the slowest step of the whole process is a gaseous phase reaction; to encourage it, the transport coefficient at the interphase can be improved increasing the gas velocity. This could be allowed because the operating conditions in the towers do not approach flooding conditions. With the following operating data:

- Section of the reactor

$$10 \text{ m}^2$$

- Gas flow

$$G = 400 \text{ Kg/h m}^2$$

- Liquid flow	9000 Kg/h m ²
- Gas density at about 100°C	1 Kg/m ³
- Liquid density at 55°C	1800 Kg/m ³
- Viscosity of the liquid at 55°C	8 cps

using the generalized plot of SHERWOOD et Al. (VIII), and taking into account that, the average dimension of the Raschig rings is 150 mm, it is found that flooding would result only for a gas flow 25 times greater than the actual flow. Since, after TAECKER and HOUGEN (IX), the mass-transfer coefficient in the gas phase K_G is:

$$K_G \propto G^{0.6} \quad (4)$$

a 10% increase in the velocity of the gases brings an increase in K_G of only about 6%. That is to say, the increased exchange at the interphase is not ever sufficient to compensate the reduction in residence time of the gases in the reactors. On the contrary, the pressure drop, being proportional to the square of the velocity, increase by some 20%. Thus, it may be concluded that increasing the flow of the gases beyond 400 Kg/h m² the plant efficiency diminishes. Lower flow values reduce the consumption of HNO₃, but also diminish the working capacity of the plant, assuming that it is not possible to vary the composition of the gases on entry to the Glover tower.

On the other hand, the liquid flow, which has the additional task of cooling the gases as much as possible, is an important factor in increasing the rate constant of the reaction (1) (I). Increasing the liquid flow decreases the temperature throughout the whole plant.

Since the following relationship holds:

$$h \propto Q^{0.8} \quad (5)$$

h = heat-transfer coefficient;

Q = volumetric flow of the liquid;

an increase of 10% in liquid flow increases h of about 8%. Depending on the cooling system used, this gives an increase in the overall heat transfer coefficient varying between 4 and 7% (X). In other words, with constant consumption of cooling water, the temperatures in the plant are appreciably diminished. A reduction of 3 to 4°C in temperature of the effluent gases at the stack means a reduction of about 20% in the consumption of HNO₃.

4. CONCENTRATION OF THE ACID CIRCULATING IN THE REACTORS

KACHKAROFF suggests that the major part of the NO is re-oxidised to NO₂ at the gas-liquid interface according to the reaction:



The NO which passes the inter face is oxidised only slowly because of its dilution in the gases.

The composition of the gases on entry to the Glover tower is strictly bound up with the functioning of the sulphurous raw materials roasters. Increasing the content of O_2 in order to encourage the reaction (1) leads to a dilution of the combustion gas in N_2 , which diminishes the efficiency of absorption of the towers. For these reasons, since it is not advisable to increase the O_2 content, it is necessary to increase the concentration of nitrogen oxide,

Figure 4 shows the temperature effect for a gas containing 2% of NO and 6.5% of O_2 , and the effect of the initial concentration of NO for a gas at $60^\circ C$ on the reaction time.

It has been shown (1) that the optimum value for the molar concentration of N_2O_3 in the liquid phase is 0.06, corresponding to about 150 g/l of N_2O_3 in 84% H_2SO_4 , a much higher concentration than that attained in chamber plants. The diagram shown in Figure 5, developed by SALSAS-SERRA (3), has proved to be a very useful guide in the running of intensive plants which use this process. The diagram shows:

- a series of curves (broken lines) parametric in the rate constant;
- a curve N defining the points where the ratio between active nitrosity and total nitrosity is at a maximum;
- two other curves indicating where this ratio has the values 0.95 and 0.55 of the maximum value respectively.

The distinction between active nitrosity and total nitrosity, first introduced by SALSAS-SERRA to explain the different behaviour of the circulating acid at different concentration levels, serves also, therefore to define the range of the working conditions of the reactors. Outside the two limiting values of 0.55N and 0.95N, considerable difficulties are encountered. For example, above the higher curve, in addition to a decrease in the reaction rate, abnormal reactions occur with irreversible decomposition of the nitrogen oxides. Furthermore, it has been observed that, in these conditions, intense corrosion of the steel takes place. The reduction in reaction rate displaces the reaction towards the downstream end of the plant, with consequent losses of SO_2 to the stack.

The more closely the operating conditions approach the curve 0.95N, the more the reaction is displaced towards the upstream end of the plant; with the same N_2O_3 content, dilution is greater and denitrification more intense. As well the process instability, resulting from the increased reaction velocity, the HNO_3 consumption is higher.

As a result of this fact, it is necessary to restrict the working conditions of the reactors to the range between the two curves

0.55N and 0.95N as illustrated (cross hatching) in Figure 6. Clearly, this refers to the average values for the four reactors since each particular situation is different (see Figure 6). The different composition of the circulating acid in the four reactors is readily explained when it is considered that there is a considerable diminution in temperature between the first and second reactors to permit the N_2O_3 to be absorbed more easily, and because the O_2 and NO contents are still high. Finally, the gradual dilution of the gases and the slight decrease of temperature in the third and then in the fourth reactor explain the reduction in nitrosity.

5. OPERATIONAL POSSIBILITIES AND CONSUMPTIONS

In recent experiments we have varied the working conditions of the reactors to a quite considerable extent, confirming the SALSAS-SERRA hypotheses. We have observed the running stability of the plant over the whole area examined only while the average composition of the strong circulating acid is maintained within the cross-hatched zone of Figure 6.

In no case did the control of the plant present difficulties: the response time was always less than 30 minutes. From this point of view, it was certainly helpful to use HNO_3 directly instead of NH_3 , since this permits rapid adjustments and also avoids initial dilution of the nitrogen oxides. As to HNO_3 consumption, this is strictly related with the temperature and the concentration of the weak circulating acid. With $35^\circ C$ temperature of the gas at the Gay-Lussac exit the consumption is $1.0 \text{ Kg } HNO_3 \text{ } 100\%/q \text{ } H_2SO_4 \text{ } 100\%$, with a production of about $110 \text{ Kg } H_2SO_4 \text{ } 75\%/m^3 \text{ day}$.

Figure 7 shows HNO_3 consumption as a function of the exit temperature of the gases at the stack; the lower curve refers to a run with a residence time 1.5 times longer than that for the higher curve.

A careful analysis of oxidising agent consumption cannot disregard the time of contact; with a time 1.5 times greater than the actual one, the average consumption is reduced to $0.67 \text{ Kg } HNO_3 \text{ } 100\%/q \text{ } H_2SO_4 \text{ } 100\%$, with a production of $74 \text{ Kg } H_2SO_4 \text{ } 75\%/m^3 \text{ day}$.

Figure 8 shows oxidising agent consumption in relation to the production of the plant. A value for a similar plant at Granville (France) has also been included.

Table I shows the distribution of oxidising agent losses; the data for chamber plants are after BENKOVSKII (XII).

Nitric Acid Losses	Table I	
	Chamber Plant	Tower Plant
In the produced H_2SO_4	5%	8%
For incomplete oxidation of NO	55%	62%
At absorption	40%	30%

In a tower plant, a smaller dilution of the H_2SO_4 causes a smaller denitration effect in the Glover tower. For this reason the loss of oxidising agent in the produced acid is greater than in the chamber plant. Furthermore, the shorter residence time increases the losses by incomplete oxidation of NO; this is to some extent offset by the lower temperature regime. On the other hand, losses by absorption are lowered by the increased circulation of the weak circulating acid in the Gay-Lussac towers.

6. CONCLUSION

Stability in operation can be attained and corrosion avoided in a tower installation by careful control of operating conditions.

Optimum working parameters are strongly dependent on the recirculation of the acid in all the towers and on the efficiency of the refrigerants.

HNO_3 consumption is strictly in accordance with the temperature regime and the residence time in the plant. It follows that, unless it is possible to vary the composition of the gases on entry to the Glover tower, increasing the plant capacity requires an increase in the consumption of HNO_3 .

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FIGURE I

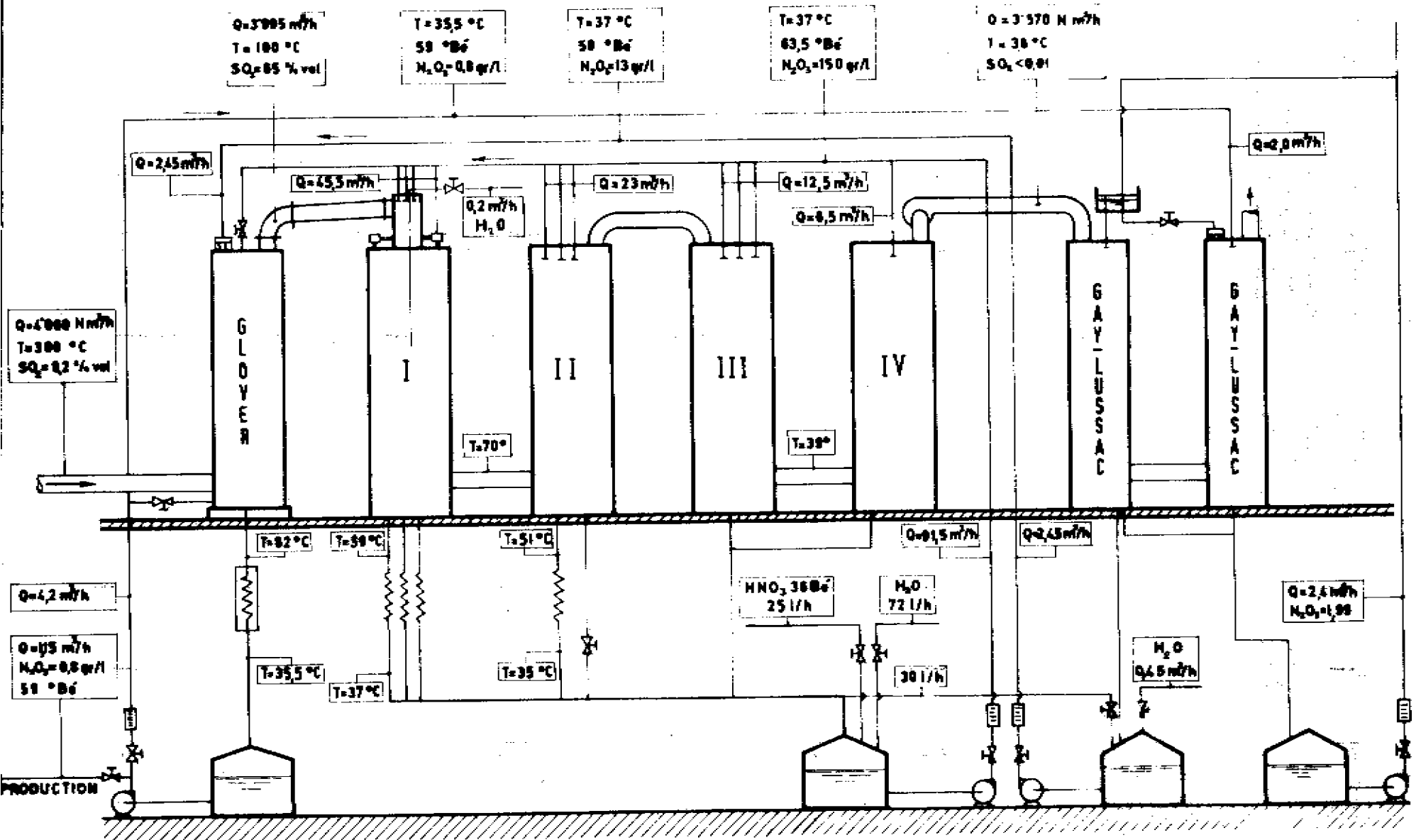


FIGURE 2

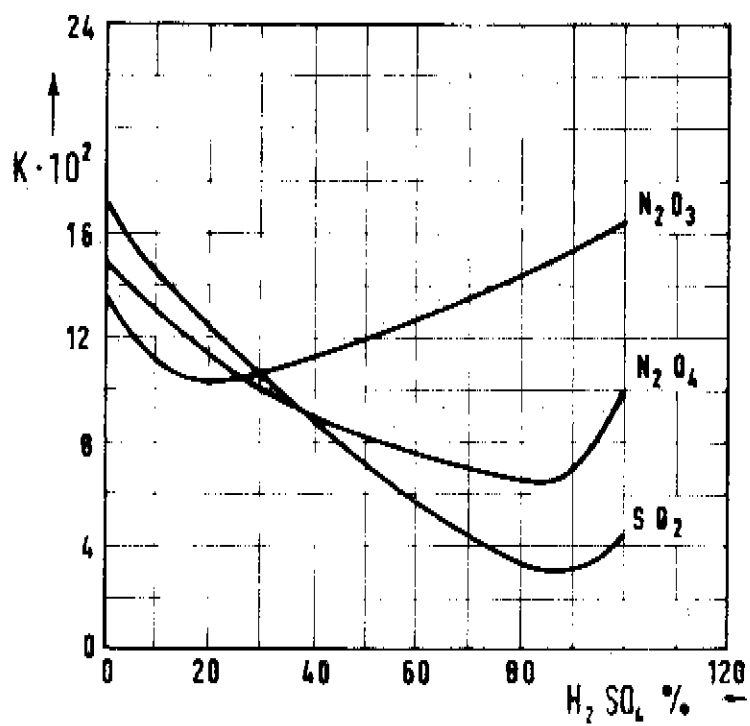


FIGURE 3

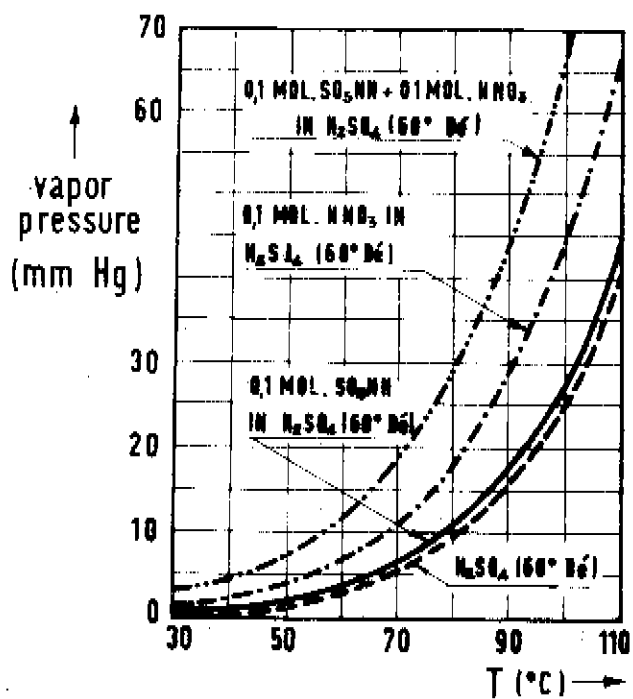


FIGURE 4

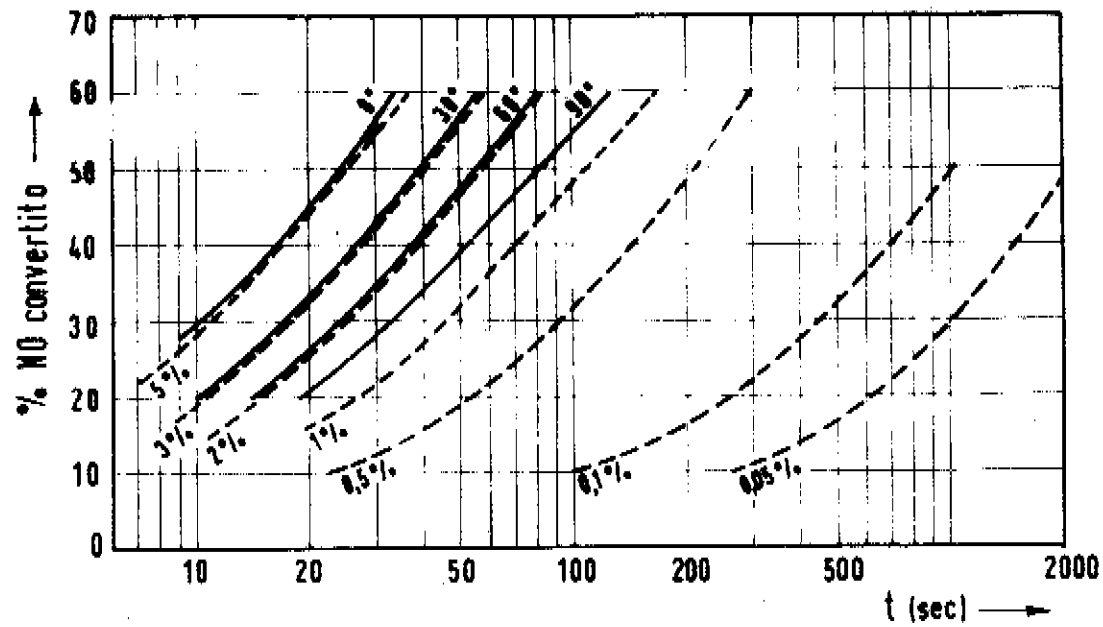


FIGURE 5

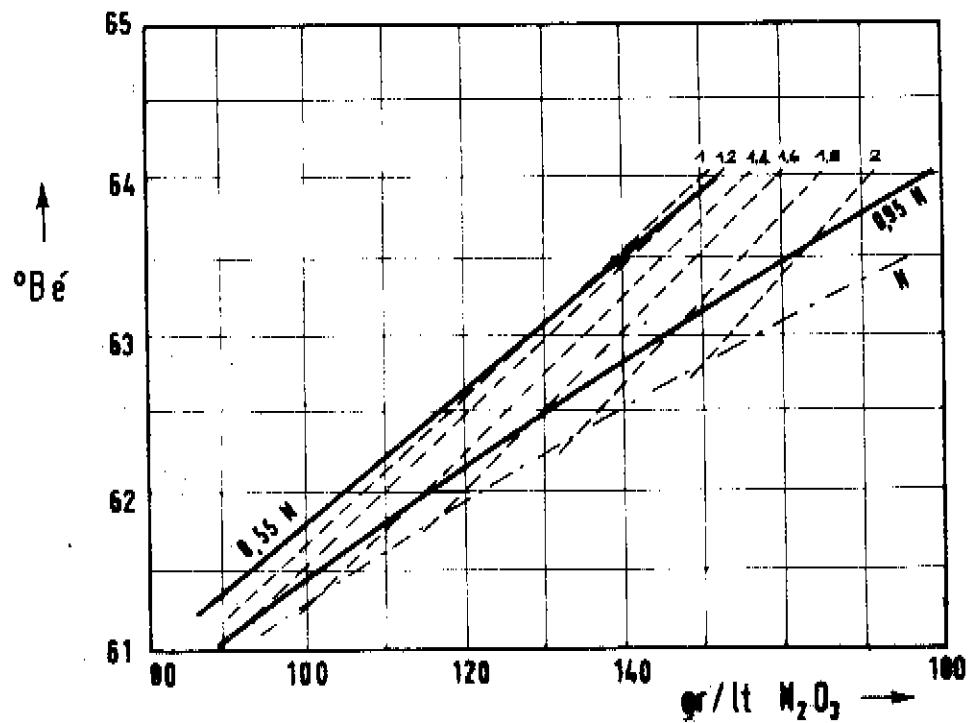


FIGURE 7

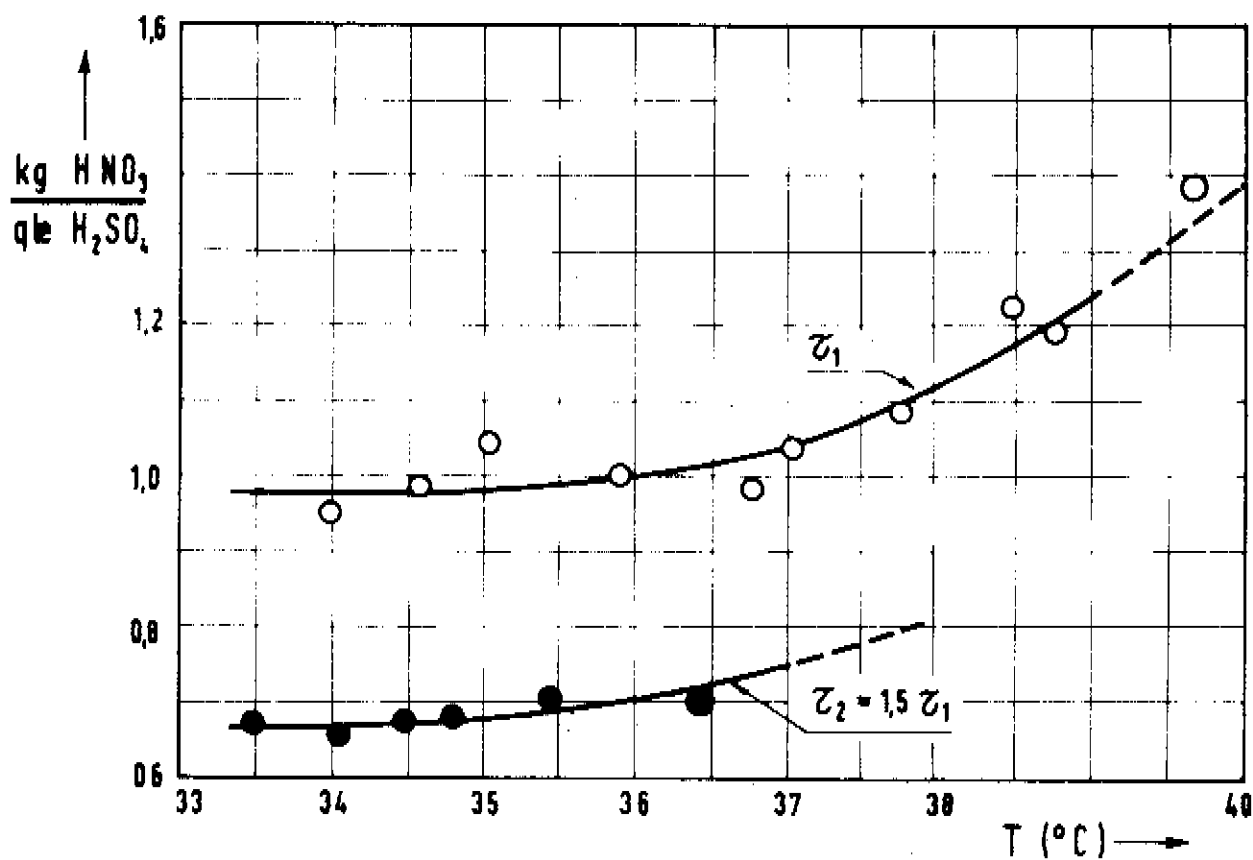


FIGURE 8

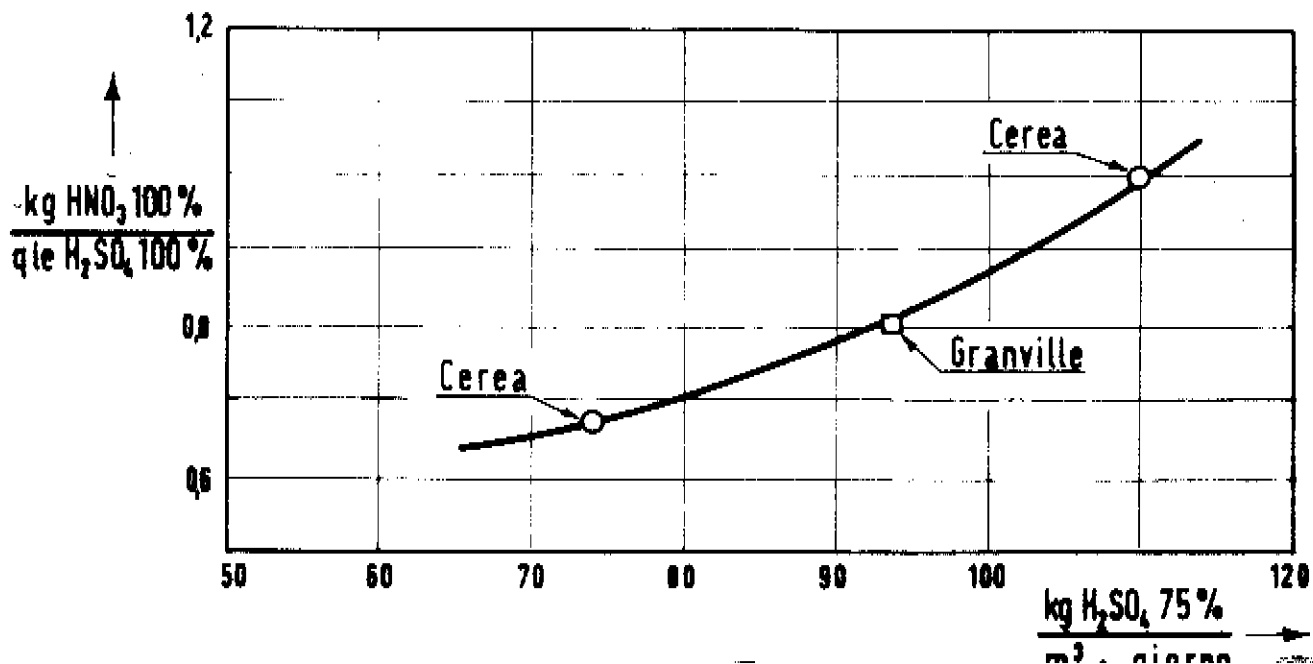
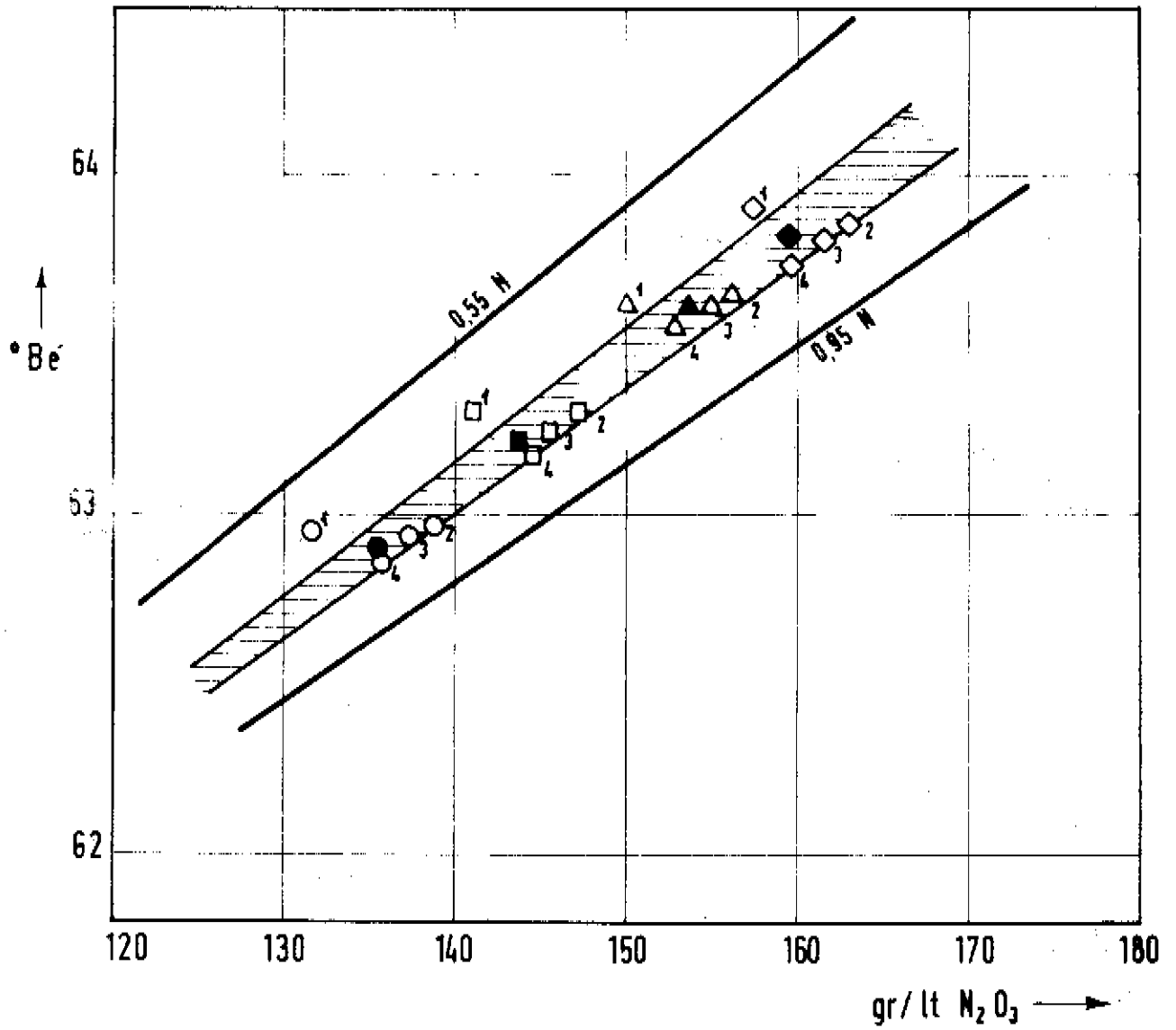


FIGURE 6



DISCUSSION

MR. MENIN (Fabbrica Perfosfati Cerea, Italy): Our intention in presenting this paper was to describe progress in the knowledge of the reaction dynamics enabling the conditions for optimum yield to be individualised in sulphuric acid works using processes involving nitrogen oxides. We indicate a development of the process in conditions of optimum yield and a suitable design for a plant to produce sulphuric acid competitively with the contact process, when raw materials are pyrites or blends and when all the acid is used for fertiliser production. This is why we investigated the theoretical conditions of optimum yield and compared them with experimental values gathered in relation to all operating variables in a 45 tpd sulphuric acid plant, the flow sheet of which is shown in figure 1. We are dealing here with a classical plant with a Glover tower, 4 reaction towers in ordinary steel and 2 PVC Gay-Lussac towers. All the towers are filled with Raschig rings.

In a paper presented to the 10th congress of the Italian Chemical Society, we showed the validity of the Kachkaroff theory as developed by Salsas-Serra. In our work, we have considered this theory solely as a hypothesis, and we compared the results which can be obtained with those given by experimental measurement. According to the Kachkaroff-Salsas-Serra theory, the reaction kinetics of sulphuric acid formation - the reaction quoted as no. 6 in the paper results from the type where XN_2O_3 is the molar concentration of N_2O_3 in liquid phase, YSO_2 the molar concentration of SO_2 in gaseous phase, k the constant of the speed of reaction modified by the theoretical constant of absorption of SO_2 in liquid phase. The intervention of the differential equation of the initial moment up to the retention time T , where T is the ratio between the volume of the reactors and the speed of the gases leads immediately to three conclusions;

- the proportion of converted SO_2 is constant.
- the capacity of the apparatus is proportional to the initial value of the concentration of SO_2 in the gases.
- the optimum value of the molar concentration of N_2O_3 in the liquid phase for a 99% conversion of SO_2 is 0.06, i.e. nearly 150 g of N_2O_3 per litre of nitrose.

Using the measurement of Szego and Lombardi for the absorption of SO_2 , N_2O_3 and N_2O_4 in sulphuric acid, and taking account of the reactions by which oxides of nitrogen are absorbed - reactions quoted as nos. 2 and 3 in the paper - one arrives at a fourth result. The optimum NO/NO_2 ratio in the gases entering the Gay-Lussac towers must be as close as possible to unity. Excess water is lost in the flue, while excess NO_2 , easily absorbed by reaction no. 3, increases the vapour tension of the nitrose in a remarkable manner, as can be seen from figure 3.

Apart from this, we examined the influence of temperature on one of the most important phases of the whole process, i.e. the reoxidation of NO by the reaction to $2NO + O_2 \rightarrow 2NO_2$, where the kinetic constant decreases with increasing temperature, as one can see from figure 4 in which the curves are parametric for temperature and initial concentration of NO . The analysis of conditions of optimum yield from the kinetic point of view has been pursued by studying the fluidynamic conditions in the reaction towers and in the Gay-Lussac towers, with the object of verifying the plant design.

In this way we were able to show the importance of nitrose recycle in the reactors, either for plant operating stability or for increasing the kinetic constant of the NO oxidation reaction. Throughout the fairly wide

range of operating conditions in which we worked the plant, we observed a more than satisfactory operating stability when the conditions of nitrosity and density of the acid in the reactors was kept within the limits fixed by Salsas-Serra shown in figure 5.

In figure 6, a particular case of figure 5, we show the shaded area where the average conditions of the nitrose in the reactor must be maintained to fall within the conditions of optimum yield of the plant. And there again, we recorded the conditions relative to each reactor. The measurements made on the plant on the influence of temperature, retention time and N_2O_3 concentration in the nitrose enable us to obtain experimental conditions for optimum yield which show a very great coincidence with the theoretical conditions obtained by developing the initial working hypothesis, i.e. the formula which I used before.

In figure 7 one can see the nitric acid consumption in relation to gas temperature at the tail of the plant and in relation to retention time, while figure 8 shows the consumption of the oxidising agent in relation to specific capacity for sulphuric acid plants using intensive processes involving oxides of nitrogen.

What I have said so far constitutes the theoretical and technical aspect of a plant which, with regard to its operating simplicity and, particularly, its very low cost of installation and maintenance, represents a really economic system for the fertiliser industry for the production of sulphuric acid up to a capacity of about 100 tpd, if one must use sulphurous ores such as pyrites or blendes.

MR. E. JADOT (Société de Prayon, Belgium): I am not very familiar with sulphuric acid plants using nitrogen oxides. My company abandoned the use of this process about twenty years ago and, at that time, it was a question of the traditional lead chambers.

In his paper, the author shows that he has a deep theoretical knowledge of the chemical phenomena occurring in such a plant, and that he has known how to use this knowledge to obtain the best operation of these plants. He derives three main practical conclusions, and it might be best if I recall them again before putting certain questions. Firstly, the need for a careful control of the operating conditions to ensure stable working and to avoid corrosion of the apparatus; secondly, optimum operation depends mainly on the acid recycle in the towers and on the efficiency with which it is cooled; and thirdly, nitric acid consumption is strictly a function of temperature and retention time. For a gas of fixed composition entering the system, it varies directly with the specific capacity of the plant.

Sulphuric acid plants using nitrogen oxides are said to be competitive with plants using the direct catalytic oxidation of sulphurous anhydride up to a certain capacity and providing a particular quality of product acid is not required. I should like to ask the author if the former type of plant does not require more experience or knowhow from the operating personnel than the latter type of plant

Secondly, in the technical literature there has often been mention of a process for the enrichment of the oxygen content of roaster gases with the object of increasing the production and/or the yield of existing contact sulphuric acid plants. In certain industrial regions, oxygen distribution networks have been established. If the possibility existed for enriching

the oxygen content of the gases of an intensive sulphuric acid plant, could this be used to achieve a significant increase in capacity or to make operation more flexible?

Thirdly, can the author say whether there are any plants using nitrogen oxides which are fed with gases obtained by burning sulphur? If such plants exist, are they competitive for the same volume of production with plants using the contact process designed to use gases from sulphur burning?

MR. MENIN: I must first emphasize that, whilst the old lead chamber plants which used the same process, i.e. the process with nitrogen oxides, had a specific capacity of about 10 kg. sulphuric acid per cubic m of chamber per day, in the intensive plants using nitrogen oxides the specific capacity is ten times higher. Moreover, instead of using lead in the intensive process, ordinary steel is used. For this reason, I think your company did well when it abandoned the lead chamber process twenty years ago.

The first question related to the need for more careful control and regulation by comparison with the contact process. I can reply by simply saying that there are only two workers in the whole sulphuric acid plant - one in the pyrites roaster and the other in the plant itself - and the intervention of the second worker is not very frequent.

With regard to figure 6, I have already stated that one has operating stability when the average operating conditions of the reactors are maintained in the shaded area. The two variables are density and N_2O_3 concentration in the nitrose and their measurement is very rapid and, if desired, automatic. To vary density and nitrosity, one has only to regulate two valves, one for water and the other for nitric acid, and hence one can appreciate why it can be done automatically. We are now in the course of developing the system.

The second question concerned the use of oxygen-enriched air or oxygen itself. For example, if one uses less air in the pyrites roaster one increases the initial SO_2 concentration of the gases entering the Glover tower and, as one can see from the relevant equation, one increases the capacity of the apparatus. This is the first of the conclusions which I mentioned before. The oxygen required for reoxidising the NO can be added after the first reactor and, consequently, one can obtain an increase of the capacity of the apparatus and the possibility of controlling the NO/ NO_2 ratio at the entry of the Gay-Lussac towers, thus enabling nitric acid consumption to be reduced. But although this is technically possible, it is necessary to pay for the oxygen which must be available, and this is the reason why many projects have not materialised.

With regard to the question as to whether there are plants using nitrogen oxides from sulphur burning plants, I can say that there were some, but generally when sulphur is the raw material, there is no need to wash and dry the gas and the contact process becomes more simple and therefore more appropriate. I should repeat, therefore, that nitrogen oxide plants are really competitive only when pyrites or blends are the raw material.

MR. O. JENSEN (A/S Dansk Svovlsyre - og Superphosphat Fabrik, Denmark): The absorption and oxidation of the SO_2 is a combination of an absorption and a chemical process and has not the same dependence on temperature as a pure absorption process.

According to experts, the diffusion speed of the N_2O_3 , or shall I say $NOHSO_4$, to the surface of the acid is the deciding factor for the reaction velocity. Therefore it is an advantage to work with a rather high temperature, shall we say 90-100° in the production zone of the system, as the diffusion speed increases with the temperature. The importance of a low temperature in the Gay-Lussac system is obvious, but could you not achieve a higher productivity by increasing the temperature in the Glover and the first production tower?

I should like to know which construction materials you have used for the first two towers and the gas pipes around them.

MR. MENIN: With regard to the influence of temperature on the whole process, the Kacharoff theory, which we have demonstrated with experimental results, states that the slowest reaction of the process is the NO reoxidation reaction, i.e. when SO_2 is absorbed in the liquid phase. The reaction for the formation of sulphuric acid is very rapid. In their liquid phase, these reactions liberate NO which must be reoxidised before the recycle, i.e. NO and NO_2 are absorbed in equal molar quantities by the sulphuric acid in the last sections of the apparatus, i.e. in the third and fourth reactors and, particularly, in the Gay-Lussac tower. If the longest phase of the process is the NO reoxidation, it is necessary to reduce the gas temperature more than one might think. This is due to the reaction of the NO reoxidation, where the kinetic content is greater at lower temperatures. This is why we need to maintain the process temperature as low as possible.

On the other hand, however, the acid arriving in the Gay-Lussac tower is acid coming from the Glover tower, where the denitration must occur, i.e. where all the nitrogen oxides in the acid must be released. On the one hand there is the need to strip the acid and, on the other, the need to make an absorption. Thus if you reduce the acid temperature entering the Gay-Lussac tower you can obtain a good gas absorption but, on the other hand, the acid from the Gay-Lussac tower entering the Glover tower reduces the temperature in the Glover tower and, in this case, the stripping is not very good in the Glover tower.

With regard to the third question, I confirm that we use only iron.

MR. J. BROCARD (Ugine Kuhlmann, France): The author states that his plant has a capacity of about 45 tpd H_2SO_4 and that a plant of 100 tpd would cost two or three times less the investment required for an equivalent plant using the contact process. Does this figure of 100 tpd constitute a limit or ceiling for the process for technical or constructional reasons, or could one design a plant of greater capacity? In the affirmative case, would the investment advantage remain the same in relation to the contact process, or would it disappear? You have emphasised, rightly in my opinion, the reduction of the co-efficient of oxidation of NO to NO_2 as a function of temperature, and this shows the importance of the cooling of the acid. We all know from experience that acid produced from pyrites, despite all purification, tends to produce deposits or scaling in the coolers. I should therefore like to ask what type of cooler is used in order to overcome this disadvantage.

MR. MENIN: I think that if the plant capacity is increased beyond 100 tpd, for example to 300-400 tpd, the incidence of the cost of installation, or the gas scrubbing and drying section of the plant using the contact process, becomes progressively less than in the case of a 100 tpd plant. Consequently, the ratio of 2.5 which I quote becomes almost unity for 300-400 tpd. At such capacities, I prefer the contact process.

With regard to the cooler, our plant uses pyrites and has been operating for ten years. We have never cleaned the coolers, and we have not found any scaling inside them. We use water cascade coolers.