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MODELLING OF ABSORPTION EFFICIENCY
IN NITRIC ACID MANUFACTURE

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SUMMARY

In order to optimize our several nitric acid plants and to evaluate designs for improvements and new plants, Norsk Hydro a.s has developed an absorption model for estimation of nitrogen oxide emission.

Unlike other models published in recent years, our approach has been to develop a mechanistic model for the upper low concentration part, which is responsible for less than 20% of the total absorption, but comprises more than 70% of the absorber height. It is shown that the degree of oxidation is constant throughout this part of the absorber, the value depending on design and operational parameters. The correction of the model for the lower, high concentration part of the absorber (where the model is invalid) has been made empirically.

Values of nitrogen oxide emission estimated by the model have proved to be in excellent agreement with the actual performance of all our plants, including packed as well as sieve plate absorbers, operating at pressures ranging from 1 to 9 bars.

Some examples are given to show model predictions of how load, pressure, temperature, absorption volume and excess of oxygen affect the emission of nitrogen oxides.

INTRODUCTION

Norsk Hydro is the largest producer of nitrogen compound fertilizers in the Nordic countries, having a total nitric acid production in excess of 4000 t HNO_3/day. The production facilities comprise a number of plants of different design, ranging from atmospheric absorption in packed bed towers via medium pressure to high pressure (9 bar abs) absorption in sieve plate absorbers.

Like most other nitric acid producers Norsk Hydro has been confronted with strict regulations on nitrogen oxide emissions, requiring extensive optimization and improvements on old plants and also replacements by new plants.

Although there are numerous publications dealing with reaction mechanisms and models for nitrogen oxide absorption, we found a lack of data applicable for design, revamping or optimization of nitric acid absorption plants. We therefore found it appropriate to develop a mathematical absorption model which

would meet our requirements for discriminating between alternative designs and contractors, and for predicting the effect of operational and constructional changes in our plants.

SCOPE OF THE MODEL

Most models for nitric acid absorption towers published in recent years have made an attempt to use the same set of mechanisms to describe the complete absorption system. Most of these models apply a static approach assuming equilibrium conditions to prevail, and in general give large deviations when used for predicting emissions [1, 2, 3, 4, 5, 6, 7].

Considering a reliable prediction of emission to be the most important goal for a nitric acid absorption model, we have chosen to use a completely different approach: first to develop a mechanistic model giving the best possible description of the upper, low concentration part of the absorber, and secondly to develop an empirical model for the lower, high concentration part. Although this lower part accounts for 80-90% of the produced acid, it includes only 10-30% of the total absorption volume of a modern high efficiency absorption plant. Some uncertainty in the model for this part therefore has only minor effect on the estimation of the total absorption efficiency.

CHEMICAL AND PHYSICAL ASSUMPTIONS

In developing the mechanistic model covering the upper, low concentration part of the absorption column, it is assumed that the gas and liquid mass transfer resistances can be neglected, and that temperature, pressure and volumetric flow can be considered constant throughout this part of the column. The absorption process may then be described by the well known reaction mechanisms:

$$2NO + O_2 \rightarrow 2NO_2 \tag{1}$$

$$2NO_2 \rightleftharpoons N_2O_4 \tag{2}$$

$$N_2O_4 + H_2O \rightarrow HNO_3 + HNO_2 \tag{3}$$

$$2HNO_2 \rightleftharpoons N_2O_3 + H_2O \tag{4}$$

$$N_2O_3 \rightleftharpoons NO + NO_2 \tag{5}$$

At the moderate temperatures and NO_2/NO ratios prevailing in this part of the column, reaction (1) can be considered irreversible. The reactions (2) and (5) are fast and will attain equilibrium. At the prevailing low gas concentrations the fractions of dimers are low, and calculatory errors in replacing the 4-valent nitrous-N by nitrogen dioxide can be neglected. As the acid concentration is less than 30%, reaction (3) may also be considered irreversible. Reaction (4) is moderately fast compared to (1) and (3), and the concentration of nitrous acid will exceed the equilibrium in the liquid. The reaction can nevertheless be considered fast and irreversible for the purpose of the stoichiometry of this model.

Thus the absorption rate will be limited by the rate of reactions (1) and (3), with the individual rate expressions in terms of partial pressures:

$$- \frac{d}{dt} (p_{NO}) = k_1 \cdot p_{NO}^2 \cdot p_{O_2} \tag{6}$$

$$- \frac{d}{dt} (p_{NO_2}) = k' \cdot a' \cdot p_{N_2O_4} = k_2 \cdot a' \cdot p_{NO_2}^2 \tag{7}$$

where k_1 and k_2 are reaction rate constants, and a the interfacial absorption area.

Combining the rate expressions (6) and (7) with the stoichiometry of eq. (1) to (5), and introducing p_N for the total partial nitrous-N pressure, and the degree of oxidation: $\mathcal{X} = p_{NO_2}/p_N$, the rate expressions for a flow system become:

$$- \frac{d}{d(H/u)} (p_{NO_2}) = p_N^2 \cdot \left[\frac{3}{4} a \cdot k_2 \cdot \mathcal{X}^2 - k_1 \cdot p_{O_2} \cdot (1-\mathcal{X})^2 \right] \tag{8}$$

$$- \frac{d}{d(H/u)} (p_{NO}) = p_N^2 \cdot \left[k_1 \cdot p_{O_2} \cdot (1-\mathcal{X})^2 - \frac{1}{4} a \cdot k_2 \cdot \mathcal{X}^2 \right] \tag{9}$$

$$- \frac{d}{d(H/u)} (p_N) = p_N^2 \cdot \frac{1}{2} a \cdot k_2 \cdot \mathcal{X}^2 \tag{10}$$

where u = actual gas flow/unit cross-sectional area (linear gas velocity)

H = height of absorption column

DEGREE OF OXIDATION

Dividing eq. (8) by eq. (10) yields:

$$\frac{dp_{NO_2}}{dp_N} = \frac{3}{2} - \frac{2k_1 \cdot p_{O_2}}{a \cdot k_2} \cdot \left(\frac{1-\mathcal{X}^2}{\mathcal{X}} \right) \tag{11}$$

Analyzing this equation, one will find that when the gas passes through the column, the degree of oxidation will asymptotically approach a constant value $\mathcal{X}^*$, given by the equation:

$$\left(\frac{3}{2} - \mathcal{X}^* \right) \cdot \left(\frac{\mathcal{X}^*}{1-\mathcal{X}^*} \right)^2 = \frac{2k_1 \cdot p_{O_2}}{a \cdot k_2} = \alpha \tag{12}$$

This steady state degree of oxidation will thus be a function of α only, with the given relation to absorption surface,

oxygen content, pressure and temperature.

Measurements of $\mathcal{X}$ in commercial packed as well as sieve plate absorption towers confirm that such steady state degree of oxidation $\mathcal{X}^*$ exists in the major part of the absorber, i.e. from the region where approximately 80% absorption is achieved and to the gas outlet. In this region also the oxygen content is practically constant.

The relation between the steady state of oxidation and α is shown in Fig. 1. This graph can be used for determining α from a measured $\mathcal{X}^*$ in an absorber under given conditions, and further to predict how α and $\mathcal{X}^*$ will change when operating conditions are altered.

To estimate α and thereby $\mathcal{X}^*$ directly, we have used the activation energies given by Bodenstein [8] and Hoftyzer and Kwanten [9] to compensate for the temperature coefficients of k_1 and k_2, and recommend the following relation:

$$\alpha = \frac{p_{O_2}}{a \cdot T} \cdot 10^{(9.565 - \frac{1581}{T})} \tag{13}$$

ABSORPTION SURFACES

In estimating the average interfacial absorption surface per unit volume we have modified the relation given by Calderbank [10] for sieve plate towers and by Dankwerts [11] for packed towers:

$$a = \frac{h_L \cdot 307 \cdot u^{0.9}}{h_p \cdot n^{0.125} \cdot d_p^{0.458}} \qquad , m^2/m^3 \tag{14}$$

$$a = a_t \cdot z \cdot \left[1 - 10^{-\frac{8.5 \cdot u_L^{0.4} \cdot p^{0.1}}{a_t^{0.35}}} \right] \qquad , m^2/m^3 \tag{15}$$

The symbols are explained in the symbol list enclosed.

MECHANISTIC MODEL FOR THE UPPER PART OF ABSORBER

As it is shown that the actual degree of oxidation is independent of the partial pressure of total nitrous-N and equals $\mathcal{X}^*$, eq. (10) can be rearranged and integrated:

$$-\frac{dp_N}{p_N^2} = \frac{1}{2u} \cdot a \cdot k_2 \cdot \mathcal{X}^{*2} \cdot dH \tag{16}$$

$$\frac{1}{p_N} - \frac{1}{p_N^o} = \frac{1}{2} \cdot a \cdot k_2 \cdot \mathcal{X}^{*2} \cdot p \cdot \frac{H}{u} \tag{17}$$

To replace the partial pressures of nitrogen oxides by mol fraction $y_N = p_N/P$, eq. (17) may be multiplied by the total pressure P:

$$\frac{1}{y_N} - \frac{1}{y_N^o} = \frac{1}{2} \cdot a \cdot k_2 \cdot x^{*2} \cdot p \cdot \frac{H}{u} \qquad (18)$$

According to eq. (18) a plot of $1/y_N$ as a function of absorber height H should yield a straight line intersecting the ordinate axis at the inverse nitrogen oxide inlet mol fraction $1/y_N^o$

EMPIRICAL ADJUSTMENT FOR LOWER PART OF ABSORBER

When plotting real measured values of $1/y_N$ against H for a commercial absorption tower, however, we will obtain plots as shown in Figure 2. For the low concentration part the plot will asymptotically approach a straight line, but this line will not intercept the ordinate axis at a positive value $1/y_N^o$, but at a <u>negative value</u> $-\Upsilon^*$.

The plot clearly indicates that, as expected, the model does not apply for the lower, high concentration part of the absorber, and that the overall rate of absorption in this part is much lower than predicted by the model. The reasons for this are obvious: At high concentrations the rate of absorption is limited by mass and heat transfer resistances, and also by equilibrium, rendering the assumptions of irreversibility false. Further, most of the tetravalent nitrous-N is dimerized, and eq. (7) will therefore be invalid.

- The deviation of absorber height between eq. (18) and the measured values represents, however, less than 30% of the total height of modern high efficiency absorbers. Some uncertainty in estimating this deviation ("inefficient height") therefore has minor importance for the applicability.

Plotting measured values from our different plants the same way as in Fig. 2 indicates that the interception between the asymptote and the ordinate all give approximately the same value of $-\Upsilon^*$ ($\pm$ 10%), independent of load, pressure or temperature, but the value increases with rising strength of the produced acid. Eq. (18) should thus be changed to:

$$\frac{1}{y_N} + \Upsilon^* = \frac{1}{2} a \cdot k_2 \cdot x^{*2} \cdot p \cdot \frac{H}{u} \qquad (19)$$

where we recommend the following value for Υ^* :

$$\Upsilon^* = 900 + 30 \cdot 10^{\left(\frac{0.1}{0.7-w}\right)} \qquad (20)$$

w = weight fraction of nitric acid in product.

FINAL MODEL

To develop eq. (19) further for practical use the value of k_2 is adjusted according to measured values and the temperature dependence as given in [9] is introduced. Further, the linear gas velocity u is replaced by using the total molar tail gas flow G and the cross-sectional area A. The recom-

mended formula for determining the nitric oxide emission then becomes:

$$\frac{1}{y_N} = \frac{a \cdot A \cdot H}{G} \; p^2 \cdot \chi^{*2} \cdot 10^{(2233/T-9.285)} - 900 - 30 \cdot 10^{(\frac{0.1}{0.7-w})} \quad (21)$$

where χ^* is given by eq. (12) and (13), and the absorption interface area, a, by eq. (14) or (15) for packed and sieve plate absorbers, respectively.

Fig. 3 shows a plot of eq. (21) together with measured values of $1/y_N$ under varying operating conditions in different plants. These plants comprise packed as well as sieve plate absorbers, and operating pressures ranging from 3 to 9 bars.

The correspondence between measured and calculated values seems to be rather satisfactory.

A similar mechanistic model for absorption of nitrogen oxides in alkaline, acid urea and oxidizing solutions has also been developed. In that model also the kinetics of N_2O_3 absorption has been included.

OPTIMIZATION APPLICATIONS

Finally we will show a few examples of how this model can be used for optimization of operational and design parameters for a given sieve plate absorber operating at pressures 4-10 bar.

Fig. 4 demonstrates how the emission of nitrogen oxides depends on the number of plates (and absorber height).

Fig. 5 demonstrates the effects of production load on nitrogen oxide emission.

Fig. 6 demonstrates the nitrogen oxide emission dependence on temperature.

Fig. 7 and 8 demonstrate how absorption loss and tail gas nitrogen oxide concentration, respectively, depend on oxygen content in the tail gas. Production load of HNO_3 is constant.

CLOSING REMARKS

The model described is rather simple, but has shown a remarkable agreement with the actual performance of our nitric acid plants. It has therefore been a valuable tool in our efforts towards optimizing and improving our old plants, as well as for evaluating new plants offered.

It is therefore our hope and intention with this paper that the model can also be of value to other nitric acid producers in a similar situation.

SYMBOLS

A	cross section of absorption tower	(m^2)
a	average interfacial area of tower	(m^2/m^3)
a_t	interfacial area of packing	(m^2/m^3)
dp	diameter of holes on sieve plates	(m)
G	molar tail gas flow	$(kmol/s)$
H	height of absorption tower	(m)
h_p	average plate distance	(m)
h_L	static liquid seal	(m)
k_1	reaction rate constant (oxidation)	$(1/bar^2 \cdot s)$
k_2	reaction rate constant (absorption)	$(m/bar \cdot s)$
n	numbers of holes per sieve plate area	$(1/m^2)$
P	total pressure	(bar)
p_x	partial pressure of species x	(bar)
T	temperature (outlet of absorber)	$(^{\circ}K)$
t	time	(s)
u	linear gas velocity	(m/s)
u_L	linear liquid velocity	(m/s)
w	weight fraction of produced acid	$(-)$
y_N	mole fraction of nitrogen oxides	$(-)$
z	average fraction of packing in tower	$(-)$
α_*	parameter function	$(-)$
γ	empirical function	$(-)$
$\varkappa$	degree of oxidation	$(-)$
$\varkappa^*$	steady state degree of oxidation	$(-)$

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FIG. 1   NITRIC ACID PRODUCTION

STEADY STATE DEGREE OF OXIDATION
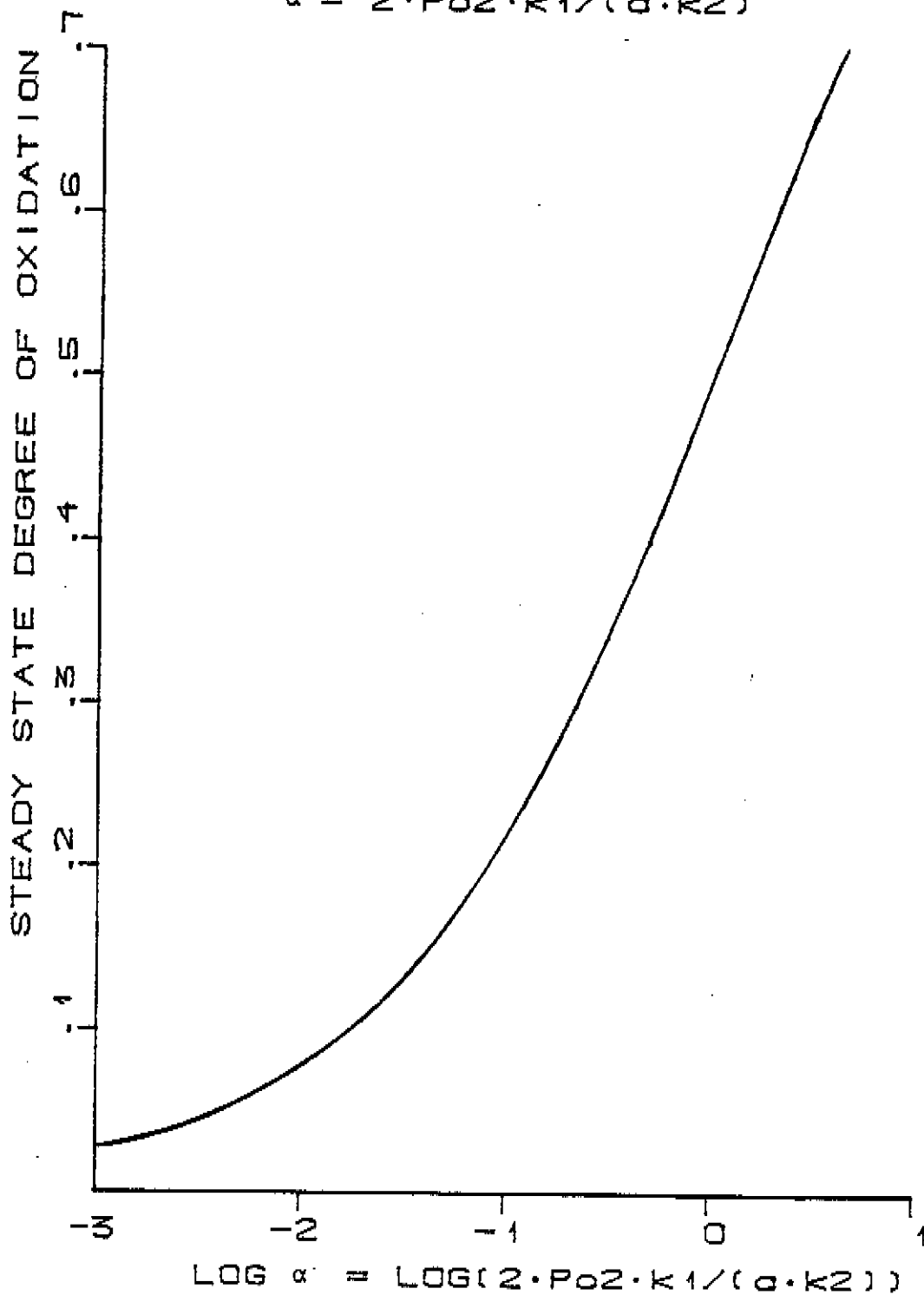AS DEPENDING ON
$\alpha = 2 \cdot P_{o2} \cdot k_1 / (a \cdot k_2)$

LOG α = LOG($2 \cdot P_{o2} \cdot k_1 / (a \cdot k_2)$)

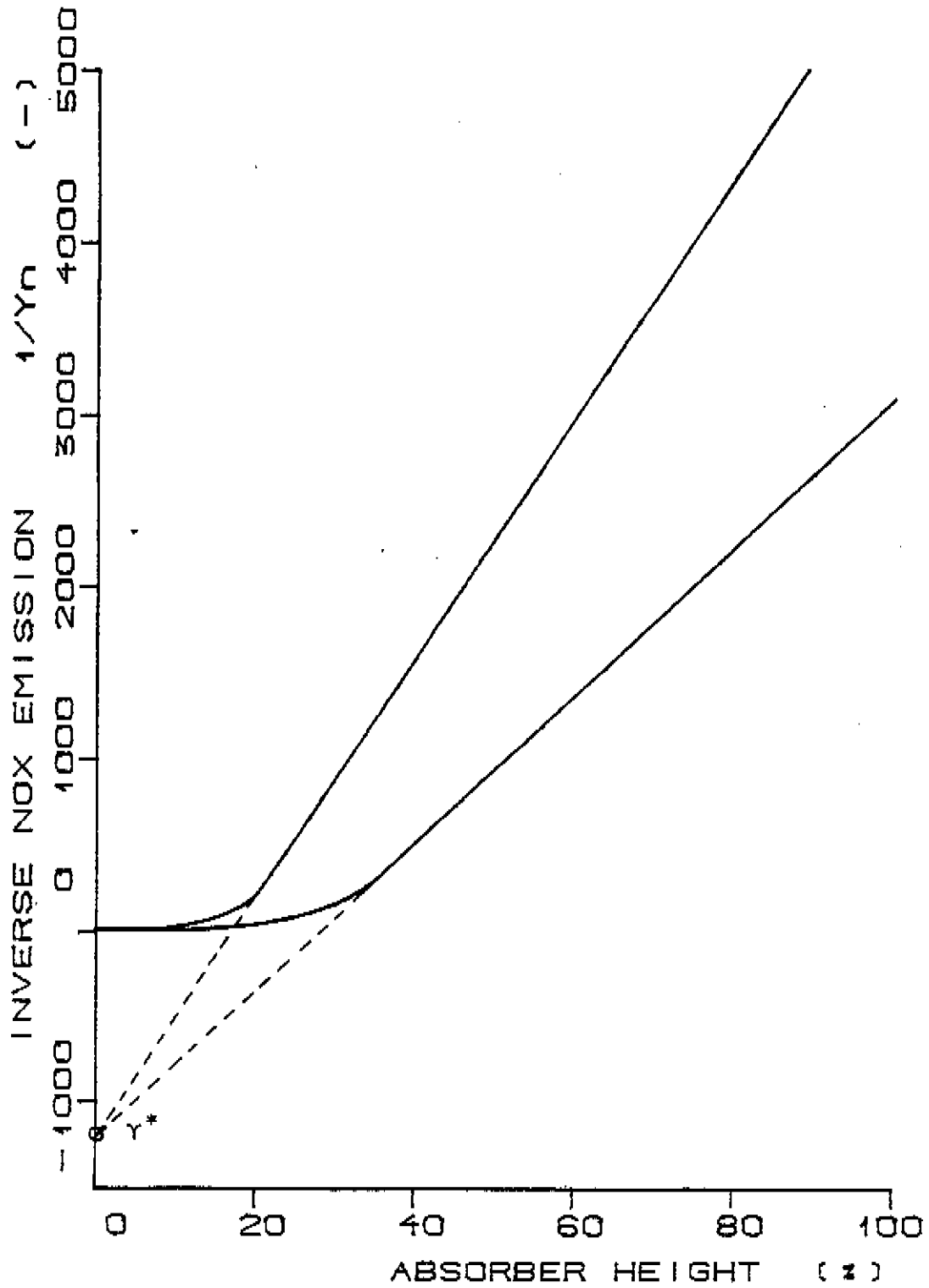# FIG. 2   NITRIC ACID PRODUCTION

INVERSE NOX EMISSION VS. ABSORBER HEIGHT

FIG. 3   NITRIC ACID PRODUCTION

MEASURED AND CALCULATED VALUES
OF INVERSE NOX CONCENTRATION
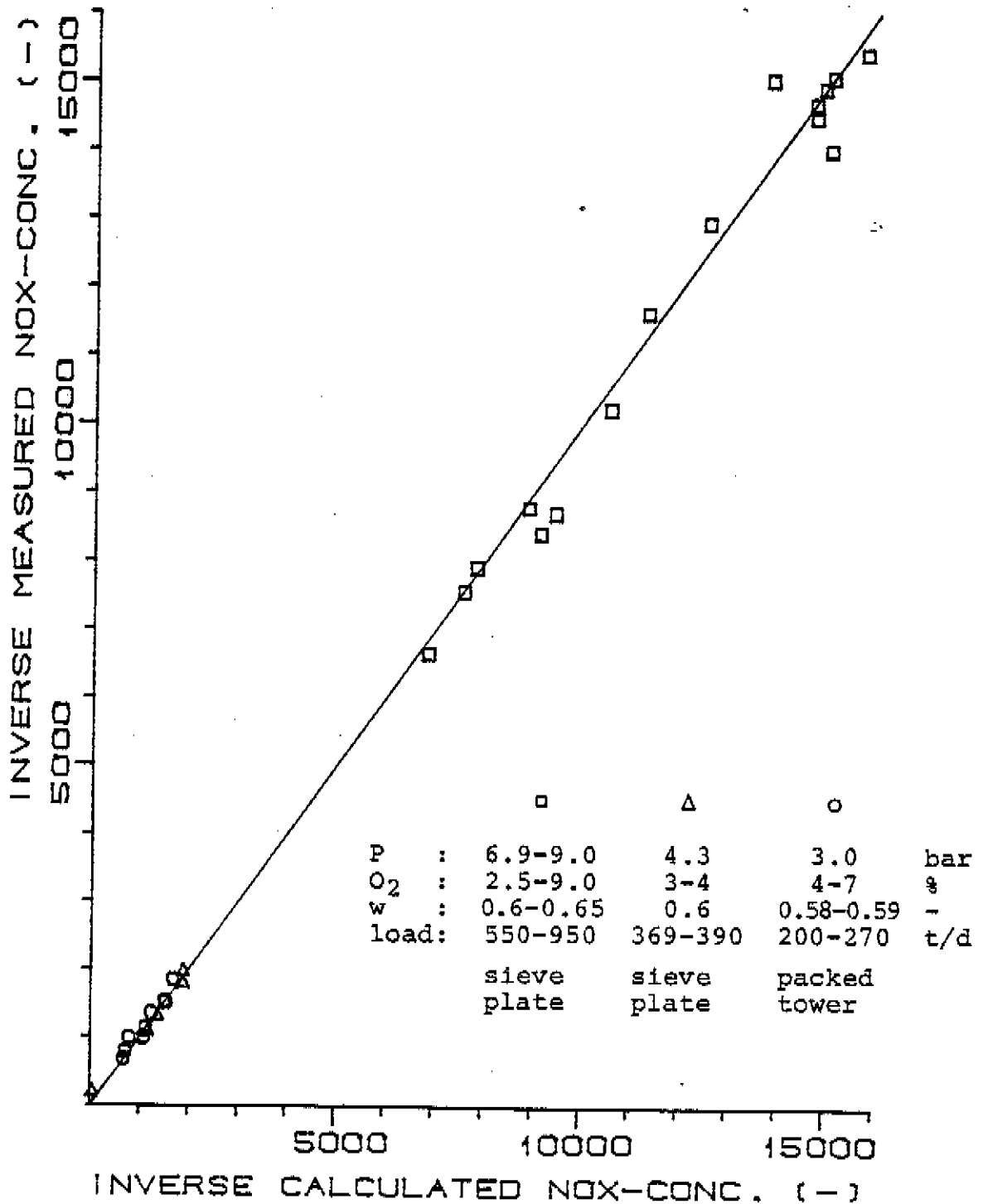IN DIFFERENT NORSK HYDRO PLANTS

INVERSE MEASURED NOX-CONC. (−)

15000

10000

5000

		□	Δ	○	
P	:	6.9-9.0	4.3	3.0	bar
O$_2$	:	2.5-9.0	3-4	4-7	%
w	:	0.6-0.65	0.6	0.58-0.59	−
load:		550-950	369-390	200-270	t/d
		sieve	sieve	packed	
		plate	plate	tower	

5000   10000   15000

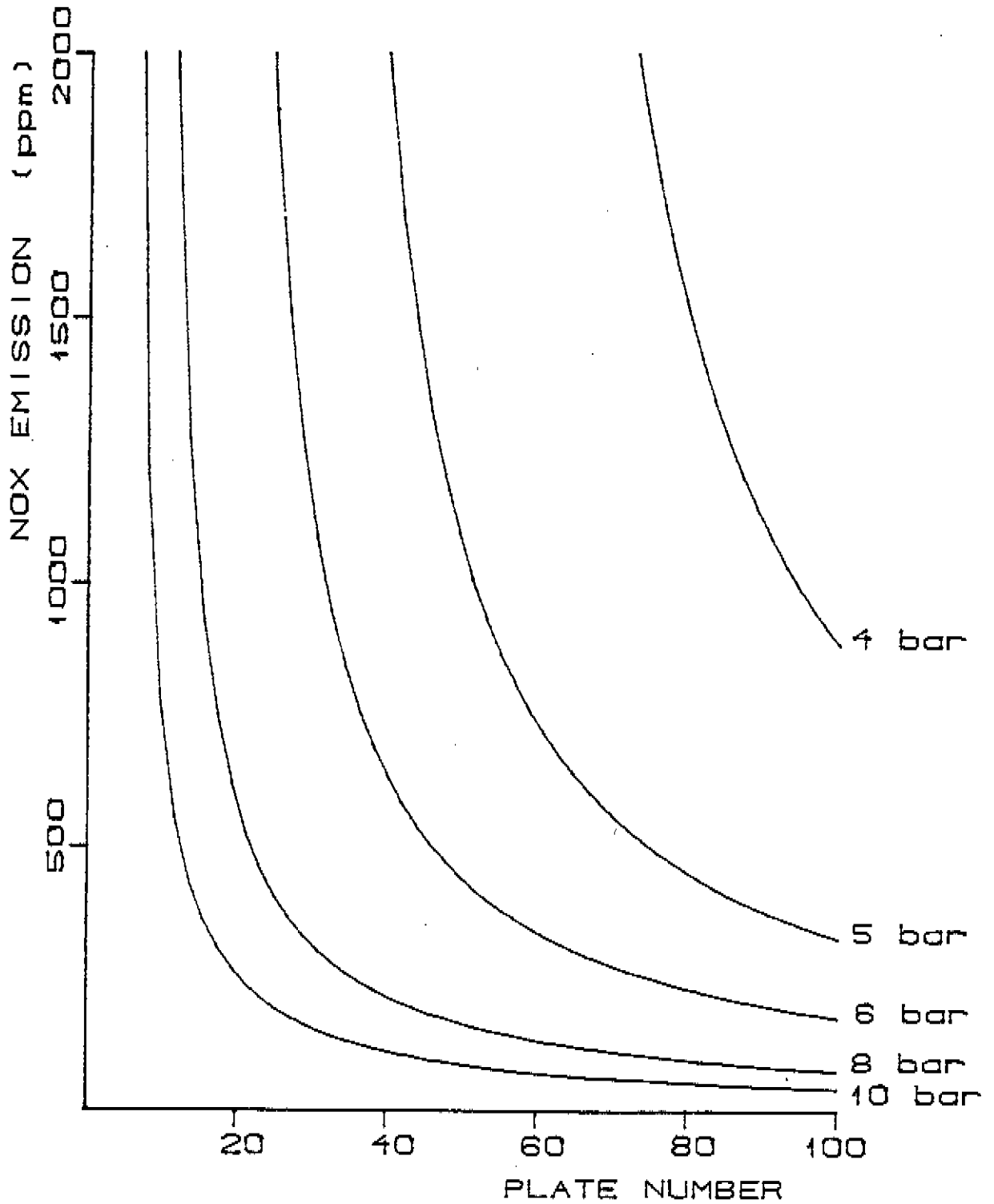INVERSE CALCULATED NOX-CONC. (−)

FIG. 4   NITRIC ACID PRODUCTION

EMISSION VS. PLATE NUMBER
IN GIVEN ABSORBER
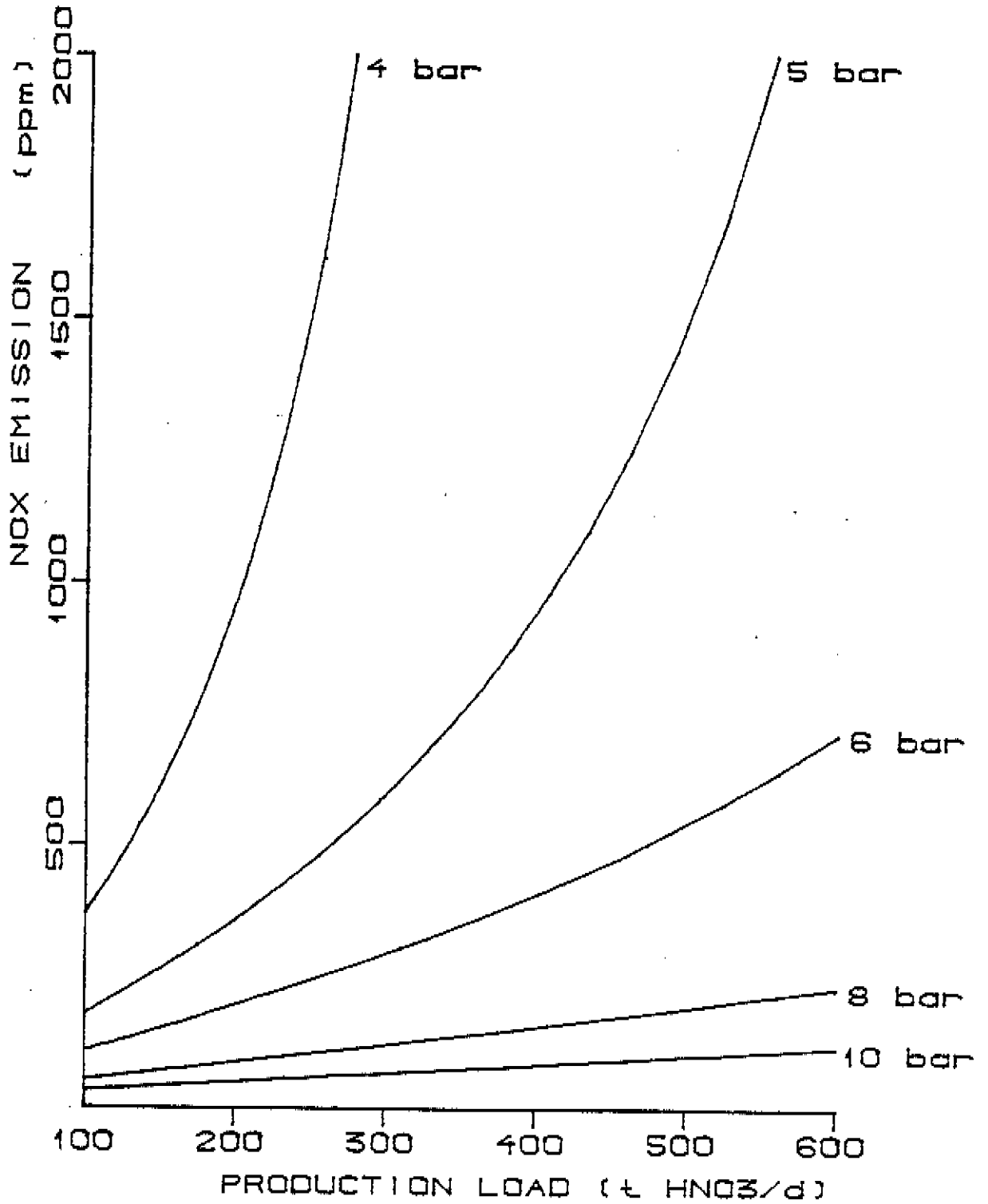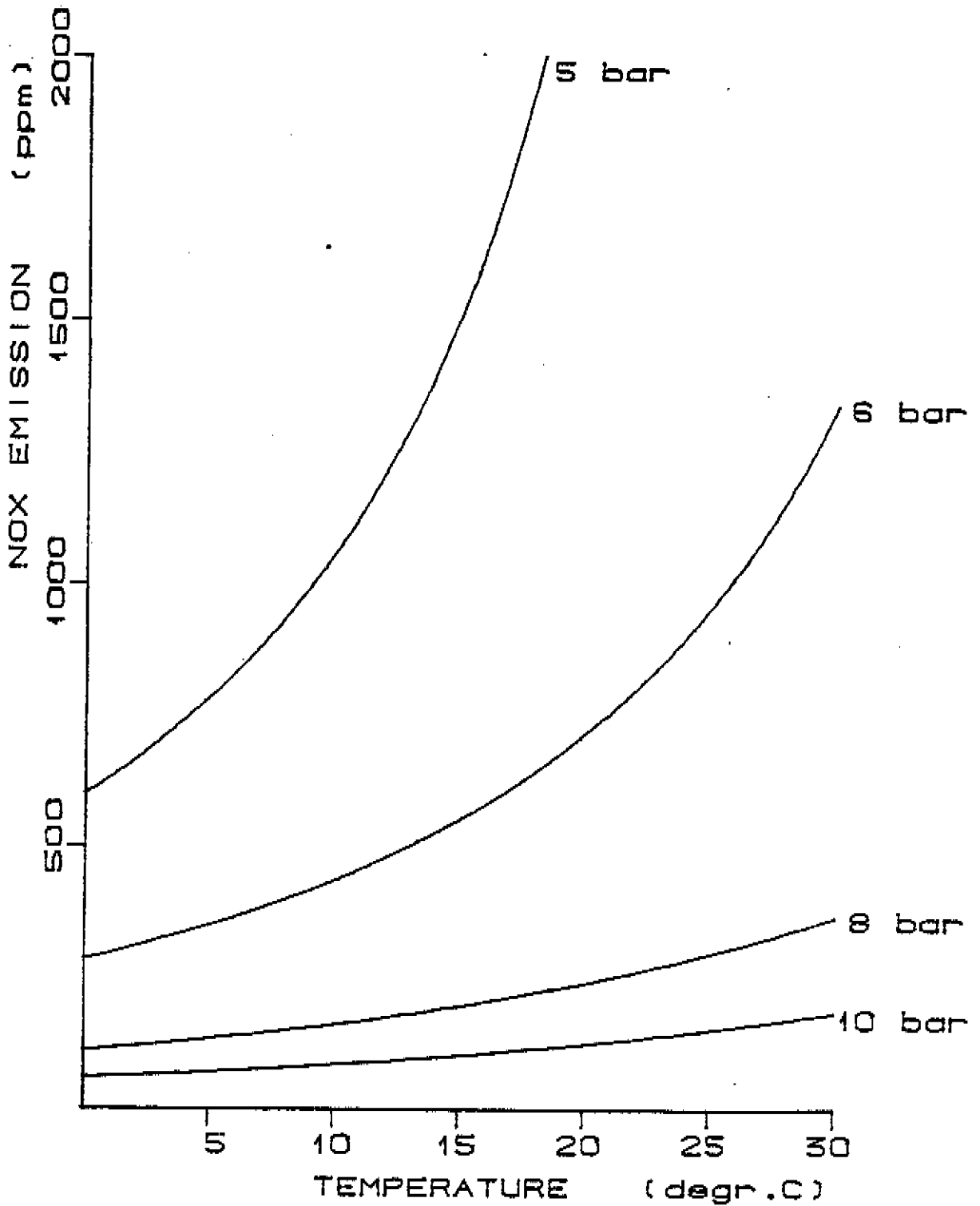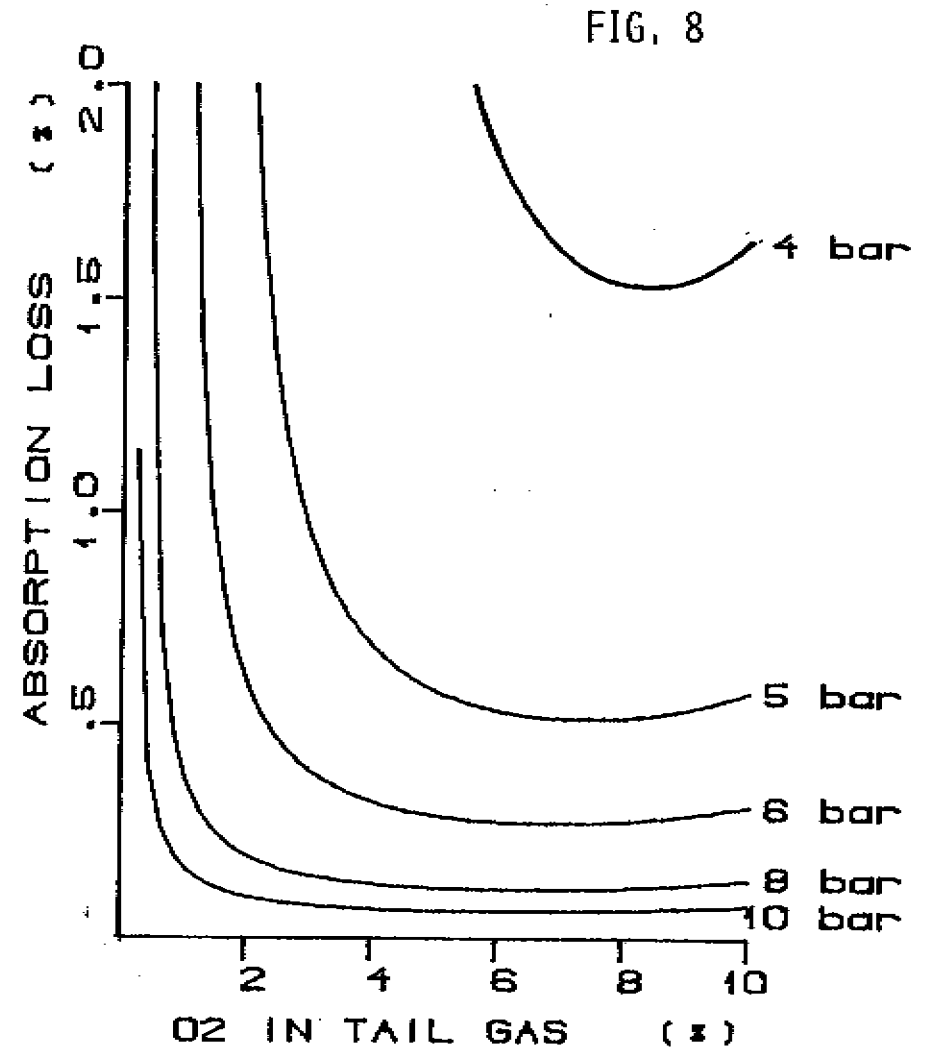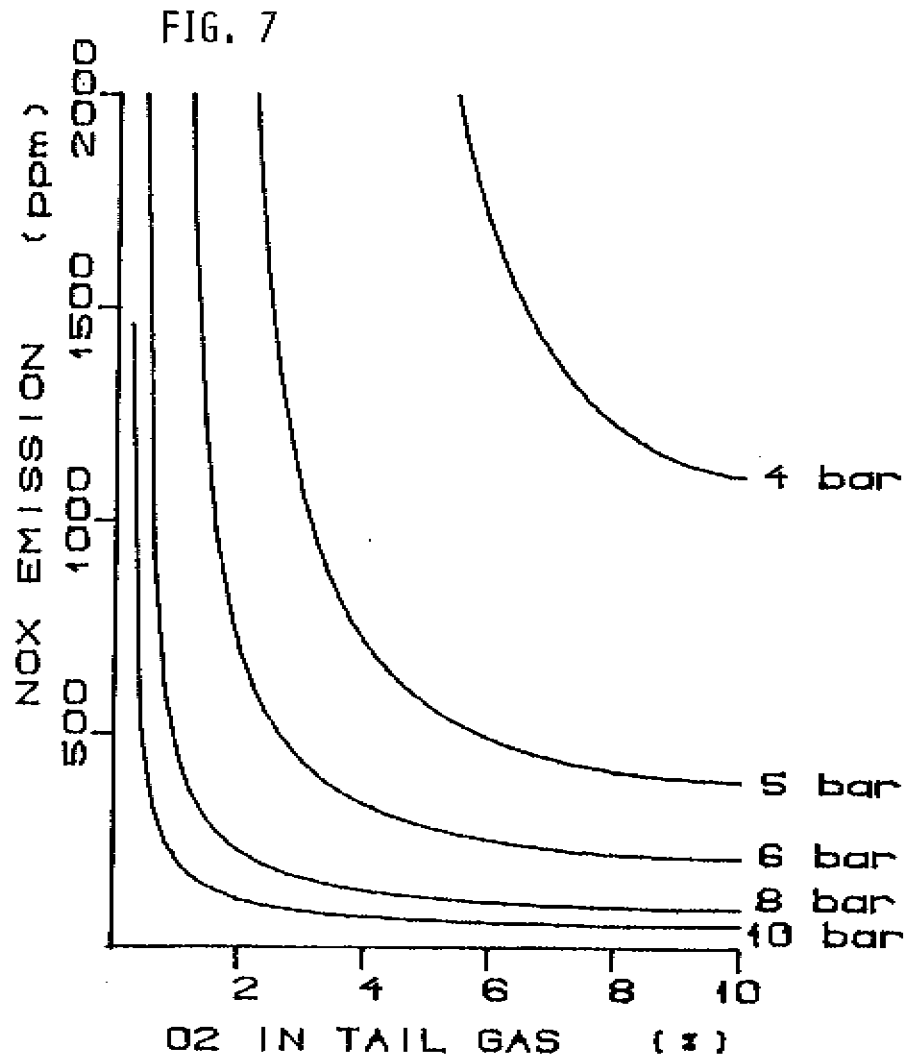
FIG. 5   NITRIC ACID PRODUCTION

EMISSION VS. PRODUCTION LOAD
IN GIVEN ABSORBER

FIG. 6   NITRIC ACID PRODUCTION

EMISSION VS. TEMPERATURE
IN GIVEN ABSORBER

NITRIC ACID PRODUCTION

EMISSION VS. O2 IN TAIL GAS
IN GIVEN ABSORBER

FIG. 7

NOX EMISSION (ppm)

4 bar

5 bar

6 bar

8 bar

10 bar

O2 IN TAIL GAS (%)

FIG. 8

ABSORPTION LOSS (%)

4 bar

5 bar

6 bar

8 bar

10 bar

O2 IN TAIL GAS (%)

TA/80/19   Modelling of absorption efficiency in nitric acid manufacture by
           G. Kongshaug, G.Th. Mejdell, Norsk Hydro, Norway

DISCUSSION : (Rapporteur J. Eimers, Uhde GmbH, Germany)

Q - Mr. J. Eimers, Uhde GmbH, Germany

           It is sometimes stated that especially at lower concentrations the
           resistances are important and it can take hours before equilibrium
           will be reached. What is your opinion?

A -   For low concentrations, this will be true, in our cases equilibrium
           will be reached quickly.