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

BASF PROCESS FOR THE CATALYTIC PURIFICATION
OF NITRIC PLANT TAIL GAS

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In the 1960's, BASF AG started laboratory investigations aimed at reducing the nitrogen oxides, present in the tail gas from nitric acid plants, selectively, ie. without significant consumption of oxygen, to nitrogen by a catalytic process using NH_3 as the reducing agent. Amongst the oxides of V, Mo and W (tested as catalysts), V_2O_5 proved to be particularly active.

In the interim, the process has become accepted to the extent that in Western Europe 7 nitric acid plants are employing this purification process. 5 further plants are to be fitted with this system in the near future. The process can be installed in existing older plant, so as to reduce emission. The required reaction temperatures are from 230° to 350°C . The space velocities depend on the pressure, the temperature, the NO_x content and the degree of oxidation of the nitrogen oxides in the off-gas. In the new "mono-medium-pressure" plants, the reduction of the emission to 200 ppm of NO_x , demanded in certain countries, is easily achievable by means of the process under discussion. This type of plant thus offers an alternative to high-pressure absorption, where emissions

of up to 200 ppm of NO_x can be achieved without catalytic purification.

We report on several years' practical experience with the novel catalytic process for tail gas purification.

1. On reading the relevant technical journals, a reader with awareness of environmental problems will be struck by how many publications are concerned with emissions of nitrogen oxides, their consequences, and the elimination of such emissions. Japan, a country with particularly rigorous environmental protection regulations, is currently the most active in this field. However, Europe has also not been idle, and in particular the conspicuous brown tail gas plumes from nitric acid plants made counter-measures essential. Thus, even in the 1960's BASF in Ludwigshafen were investigating the selective catalytic reduction of nitrogen oxides, even though at that time it was not absolutely essential to employ the method industrially. However, because of the strict regulations which were expected concerning permitted emissions, and because of the slowly growing awareness of environmental problems by the public, the process was at that time developed to a stage where it was ready to be put into use when required.

At the present time, the limits imposed in the Federal Republic of Germany on tail gases from new plants are as follows: medium-pressure plants 1 g of NO/m^3 or ~750 ppm v/v; high-pressure plants 0.7 g of NO/m^3 or ~500 ppm v/v. In practice, however, the approving authorities demand far lower emission values and also require that the tail gas should be colorless. Furthermore, subsequent improvement of previously approved older plants may be demanded. In addition to the ability to reduce the emission of nitrogen oxides

in such cases by, for example, alkaline absorption or more extensive acid absorption, a catalytic process is now also available.

2. The catalytic processes for the treatment of nitrogen oxides can be classified into selective catalytic reduction and non-selective catalytic combustion.

The term "selective" means that the fuel - in the present case ammonia - reacts only with the nitrogen oxides to give nitrogen, with no significant side-reaction with the oxygen present.

2.1. The basis of the catalytic combustion is that a liquid or gaseous fuel is added to the tail gas of the HNO_3 plant, which still contains 2 - 3% of O_2 , at a high temperature - namely the start temperature of the fuel - and that the reactions between the fuel, oxygen and nitrogen oxides take place over a noble metal catalyst. Catalytic combustion may be carried out by an oxidative method or by a reductive method.

2.1.1. In the oxidative method, only a part of the oxygen is consumed; this means that a less than stoichiometric amount of fuel is employed and the conditions remain oxidizing, with about 1 - 1.5% of O_2 being left. The reaction of the fuel, for example methane, with the oxygen heats the preheated off-gas to above 600°C ; this additional energy correspondingly provides more compression energy in the expansion turbine. A colorless or virtually colorless off-gas is formed, since, with rising temperature, more and more NO_2 decomposes into $\text{NO} + \text{O}_2$, and above 640°C only NO (which

is colorless) is stable. Under these conditions, the NO hardly undergoes reaction, and evidently a low NO_x concentration is not achievable by this method.

2.1.2. In the reductive method, an excess - of up to 30%, based on oxygen present - of fuel is added to the preheated tail gas. Here, the oxygen is consumed preferentially and only afterwards is the NO attacked. If methane, in the form of natural gas, is employed as the fuel, the stack gas contains CO, a few thousand ppm v/v of uncombusted hydrocarbons, and, in addition, NH_3 and other components. In this process, the high temperatures can damage the catalyst and hence the latter is arranged in 2 or more beds (depending on the O_2 concentration in the off-gas), with intermediate cooling. Disadvantages of this process are the unsolved problem of secondary emissions, and the high fuel consumption, which can reach $1,300 \text{ m}^3/\text{h}$ of natural gas for a 120 tonnes of N/day plant. In the Federal Republic of Germany, this method of destroying nitrogen oxides is ruled out because the legal limit of emission of unconverted hydrocarbons is 200 mg of C/m^3 . This value corresponds to 375 ppm v/v of methane; in practice, the method just discussed gives values which are more than ten times higher.

2.2. In the early 1960's, the patent literature disclosed processes for the selective removal of nitrogen oxides from oxygen-containing gas mixtures, using NH_3 as the fuel and noble metals (palladium, rhodium, ruthenium or platinum), or iron, cobalt or nickel, as catalysts.

This literature contained indications, also confirmed by us, that when using supported platinum metal catalysts the activity decreases more rapidly at relatively high contents of NO_2 in the tailgas; at the same time, the color of the catalyst becomes lighter. However, relatively high NO_2 concentrations in the emissions from HNO_3 plants must certainly be expected. For the base metal catalysts described elsewhere (Fe, Co and Ni on Al_2O_3 , kieselguhr and $\text{Al}_2\text{O}_3/\text{SiO}_2$ mixed carriers), the Examples did not state the catalyst life; furthermore, mainly NO -containing gases were used and water vapor contents, such as are found in the conventionally encountered tail gases, were left out of account in the Examples.

In our search for other catalysts, we particularly encountered the metal oxides of sub-groups 5 and 6 of the periodic table; amongst these, it was particularly V_2O_5 on an inert carrier, but also tungsten oxide and molybdenum oxide, which gave good results. It is true that NH_3 is an expensive reducing agent. Since, however, oxygen only participates to a very slight degree in the reaction, and the nitrogen oxides react with an equimolar amount of NH_3 , the amounts of NH_3 required are low. Of course, it is a precondition that the acid absorption should already have been carried out so efficiently that only relatively small amounts of nitrogen oxides remain to be destroyed.

3. The laboratory investigations which were commenced in the first half of the 1960's were carried

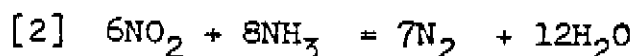
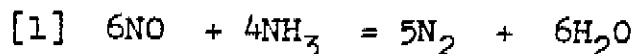
out with many different catalysts which had been produced in the BASF catalyst factory.

3.1. The laboratory experiments were carried out in a glass apparatus, containing 100 ml of catalyst.

The gases required were added through orifice meters and were then mixed, the mixture was preheated, and, finally, NH_3 was metered in a short distance upstream of the catalyst tube. The gases could be moistened by means of a stock of water at a thermostatically controlled temperature. The temperature of the gas mixture was measured at the entry to and exit from the catalyst bed; the nitrogen oxides were determined by means of a photometer and accompanying I_2O_5 tube, or by means of a chemiluminescence detector. NH_3 was determined photometrically after absorbing the gases in sulfuric acid.

3.2. Amongst the catalysts tested, V_2O_5 on an alumina carrier appeared particularly active and we shall therefore here report, first of all, some results obtained with this catalyst, in a laboratory apparatus and under atmospheric pressure.

(1) The literature gives the following equations for the selective destruction of nitrogen oxides (Figure 1):



Equation [3] is a combination of equations [1] and [2].

We have found that the reaction according to equation [3]

takes place preferentially. Excess NO present reacts further with an equimolar amount of NH_3 in accordance with equation [4]. In the absence of O_2 , the reaction according to equation [1] takes place extremely sluggishly in the temperature range which is of interest in industrial operation; at the same time, the V_2O_5 is reduced to lower oxidation levels. The oxygen which the reaction requires is however always present in the off-gas from an HNO_3 plant.

(2) Side-reactions, in which NH_3 reacts with the O_2 present in the off-gas, with formation of N_2 , N_2O or NO , are of no significance in the temperature range investigated, namely $240^\circ\text{C} - 330^\circ\text{C}$. Formation of NO is only to be expected from about 350°C upwards.

(3) The activity of the catalyst increases linearly over the temperature range of from about 200°C to about 280°C , and approaches a maximum at about 350°C . The degree of conversion of course depends on the space velocity. For a given volume of catalyst, the external geometrical surface of the catalyst extrudates has a marked effect on the activity.

(4) The requisite space velocity for reducing the nitrogen oxides concentration to a certain final value depends on the initial nitrogen oxides concentration and also on the temperature, the degree of oxidation of the nitrogen oxides, and the pressure (see below).

(5) CO_2 and N_2O have no effect on the reaction and steam only has a slight effect. An increased O_2 content (for example 20%) also does not interfere.

(6) In the temperature range investigated, namely above 230°C , a homogeneous gas reaction will also occur in an empty tube, though the conversion is very poor.

(7) Our own investigations, and data in the literature, have shown that the alkali-containing sulfuric acid catalyst has only a low activity and is unsuitable for selective catalytic reduction.

(8) We have no experience of sustained operation of the process at lower temperatures ($<230^{\circ}\text{C}$). At lower temperatures, and when using an excess of NH_3 , the catalyst tends to turn green, and lose its activity.

(9) Catalysts based on MoO_3 and WO_3 have a somewhat lower activity than the conventional V_2O_5 catalyst. With Pd-containing catalysts, formation of NO occurs at temperatures as low as 250°C ; Cr(III) oxide catalysts tend to cause formation of N_2O .

In 1964, BASF filed a patent relating to the selective destruction of nitrogen oxides with ammonia over a V_2O_5 catalyst.

4. A pilot-plant reactor was installed in the bypass of a pressure column of the Ludwigshafen nitric acid plant, so as to be able to carry out controlled measurements on the catalyst even under pressure. The gas can be brought to the desired temperatures by means of an upstream heat exchanger, and the pressures (≤ 7.3 bar) and gas throughputs can be varied by valve settings.

Pure NO can be metered-in by means of a membrane compressor, and fully oxidized gas can be taken off downstream of the oxidation tower and be fed to the part-stream of off-gas upstream of the pilot-plant reactor. Accordingly, various NO_x concentrations, including relatively high concentrations, with various degrees of oxidation, can be set up and investigated. The catalyst is accommodated in 2 fixed beds, one below the other. This arrangement also makes it possible to test catalyst combinations.

A few Figures will show the various measurements obtained in the pilot-plant experiments. Figure 2 shows how, with increasing temperature, the NH₃ breakthrough diminishes for the same conversion, and the reaction proceeds more rapidly. Figure 3 shows the dependence on pressure; with increasing pressure, the conversion takes place more rapidly, with less NH₃ breakthrough. Figure 4 shows the effect of the degree of oxidation on the reaction. The degree of oxidation of the unpurified tail gas is plotted on the left-hand leg of the triangle and the degree of oxidation of the purified tail gas on the right-hand leg of the triangle. The bottom leg shows the NO_x concentration in the purified tail gas. At 50% degree of oxidation in the feed gas, the degree of oxidation of the purified tail gas is also 50%. If the degree of oxidation of the unpurified gas is above 50%, the degree of oxidation of the purified gas is higher still; conversely, if the degree of oxidation of the unpurified gas is below 50%,

the degree of oxidation of the purified gas is lower still. These findings, together with a quantitative determination of the nitrogen oxides which have reacted, indicate that the reaction takes place preferably with a mixture of $\text{NO} + \text{NO}_2$ in the molar ratio of 1 : 1.

Figure 5 shows the conversion of nitrogen oxides in a gas mixture, under specific conditions, as a function of the residence time, and also indicates the NH_3 breakthrough. The shape of the curve shows that a rapid initial reaction is followed by a slow secondary or parallel reaction.

5. The process has been in operation in an industrial plant in Ludwigshafen since January 1975, the plant capacity being 270 tonnes of HNO_3 /day. With tail gas concentrations of, normally, 450 - 800 ppm v/v (in extreme cases up to 1,100 ppm v/v) we obtain final values of between 50 and 150 ppm v/v of NO_x . The NO_2 content is 20 - 50 ppm v/v and hence below the limit of visibility. The concentration of NH_3 which breaks through is 5 - 20 ppm v/v. We have hitherto not observed a diminution of catalyst activity. Figure 6 shows a flow chart for HNO_3 absorption with catalytic tail gas purification. The gaseous NH_3 is fed in regulated amounts to the mixing apparatus. If the temperature falls below a certain minimum value, the NH_3 regulating valve shuts so as to prevent breakthrough of liquid NH_3 . The NH_3 valve also shuts if the compressor is switched off. If the gas temperature downstream of the expansion turbine drops below a certain

minimum temperature, an alarm is triggered and the valve is shut. The temperatures are 270 - 280°C upstream of the turbine and 80 - 90°C downstream of the turbine. After charging the reactor with the catalyst, and fitting the mixing apparatus, the measured pressure loss over the mixing zone and the catalyst bed was found to be 1.5 m of water column. The temperature rise in the gas, which, depending on the degree of oxidation, is 10 - 12°C for conversion of 1,000 ppm of nitrogen oxides, compensates this pressure loss in respect of energy recovery in the expansion turbine. Careful admixture of the small amounts of NH_3 to the tail gas stream appears to be an important factor in the process. Apart from the filter screen, upstream of the turbine, which was present even before the selective catalytic process was fitted up, no additional catalyst dust removing device was installed. The reactor, which is of the radial flow type, is shown in Figure 7. Figure 8 shows NO_x - NH_3 breakthrough curves for this unit. The intensity with which the catalyst is charged into the reaction vessel, and/or vibrated therein, is an important factor in respect of the pressure drop in the unit. Figure 9 shows the coefficient of resistance as a function of the Reynolds number for 3 different bulk densities γ_i ; it follows that the pressure drops $\frac{\Delta p}{H}$ can differ considerably for one and the same Reynolds number.

5.1. The nitrogen oxides concentration upstream and downstream of the reactor is checked from time to time

by means of a chemiluminescence detector. The gas is passed, hot and undiluted, through an insulated line into the analysis chamber; relatively high flow rates, necessitating a bleed upstream of the detector, are required to avoid substantial post-oxidation. It is advantageous to heat the lines through which the gas passes, since deposits may form in cold gas-sampling lines. The chemiluminescence equipment is checked, and calibrated, by means of NO and NO₂ calibrating bottles.

The NH₃ in the residual gas in practical operation is monitored by continuous pH measurement, for which the residual gas is absorbed in deionized water. Below pH 8 (at a defined tail gas:water ratio) this method is very sensitive. If the concentration of the acid constituents, NO_x, HNO₃ and CO₂, which the off-gas carries together with NH₃, is reasonably constant, a calibration curve relating the pH to the NH₃ concentration can be drawn up. The position of the calibration curves changes somewhat with changing concentration of the acid constituents in the gas. Above pH 8, the method is no longer sufficiently sensitive, because large changes in NH₃ concentration produce only slight changes in pH. The pH measurement is calibrated by also absorbing the NH₃ in dilute H₂SO₄ and carrying out a photometric determination with Nessler's reagent.

The formation of deposits in pipes and on walls as a consequence of crystallization phenomena is governed - as are all crystallizations from the vapor phase (ie. desublimations) - by the Hertz-Knudsen

equation

$$j = \frac{\alpha \cdot (p - p_s)}{\sqrt{2 \pi M R T}}$$

- j = mass flow density (condensation rate) [mole/cm².sec]
 p = partial pressure of the component to be deposited,
 for example NH₄NO₃
 p_s = saturation vapor pressure of the component to be
 deposited
 M = molecular weight of the component to be deposited
 T = absolute temperature [K]
 R = gas constant, namely 8.31×10^7 erg. K⁻¹ . mole⁻¹
 α = "condensation coefficient", in general <1 and
 determined by the kinetics of the deposition reac-
 tion.

Since nucleation and crystal growth depend on the saturation ratio $\frac{p}{p_s}$ or on the supersaturation $p - p_s$, sufficiently high temperatures, accompanied by a rise in the saturation vapor pressure of NH₄NO₃, counteract crystallization and prevent deposits. Existing deposits can also be removed by injecting water or blowing in steam, because this produces a partial vapor pressure of water which exceeds the saturation vapor pressure of a saturated NH₄NO₃ solution. Only <56°C is the formation of NH₄NO₂ deposits to be expected.

Data on the vapor pressure of ammonium nitrate are to be found in J. Chem. Eng. Data 7 [2] (1962), 227-28 and also in Proc. Fert. Soc. No. 110 (1969).

5.2. Under what conditions can the selective process

be employed? Because of the low pressure loss and the small temperature rise caused by the reaction the process is in principle suitable for old plant, because the process parameters are only changed slightly.

A precondition is that the tail gas temperatures should be sufficiently high (from about 230°C to a maximum of 350°C). At tail gas concentrations of, for example, 1,500 ppm v/v NO_x or more it is necessary to test whether combining more extensive acid absorption with the selective process might not be more economical.

For new HNO_3 plant where the capacity is not excessive (for example for 300 tonnes of HNO_3 /day), a mono-medium pressure unit employing about 5 bar absorption pressure in combination with catalytic purification of the off-gas appears to be the most economical. This type of plant not only conforms to official requirements, but also requires somewhat lower investment than medium-high pressure plants (10 bar absorption pressure) of comparable capacity, without catalytic purification. It is true that the N-yield is about 0.7% lower than in a medium-high pressure plant, but on the other hand the export of steam is higher by about 1 tonne/tonne of N. Furthermore, operation is simpler, in that the nitrous gas compressor is not needed.

Summarizing, it is today possible to achieve concentrations of ≤ 200 ppm v/v of NO_x in the tail gas, the latter also being colorless. Selective catalytic reduction is one of the possible methods. It is

increasing in importance, and has proved successful in industrial operation.

The captions of the Figures have not been translated since they are explained in the text.

Figure 1

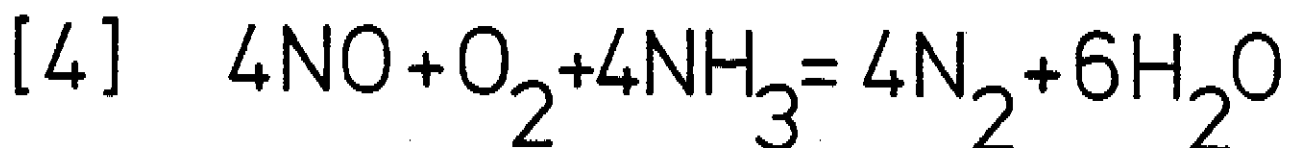
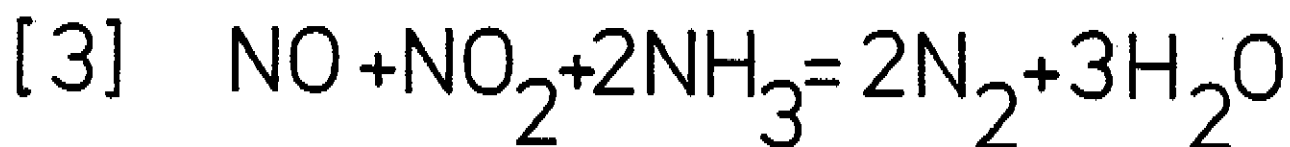


Figure 2

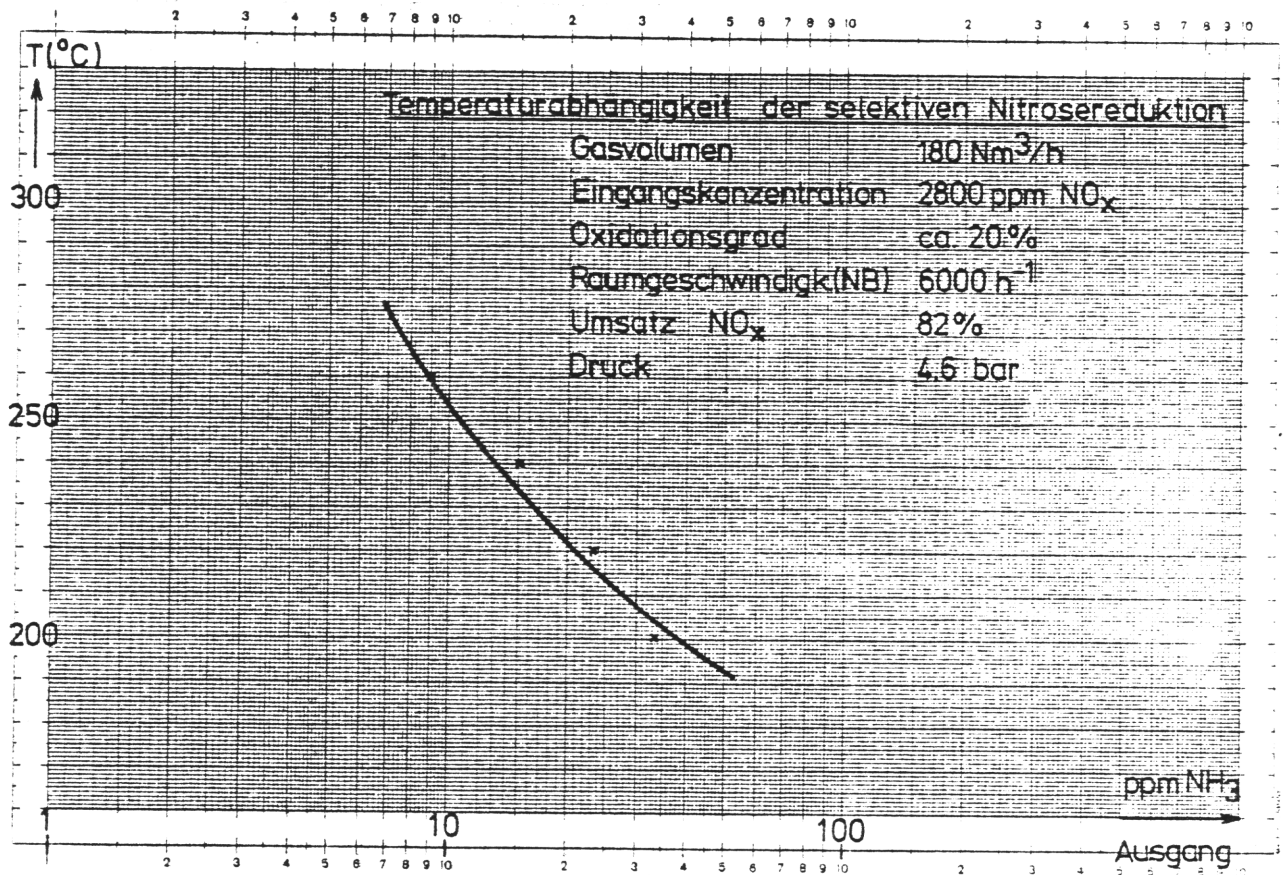


Figure 3

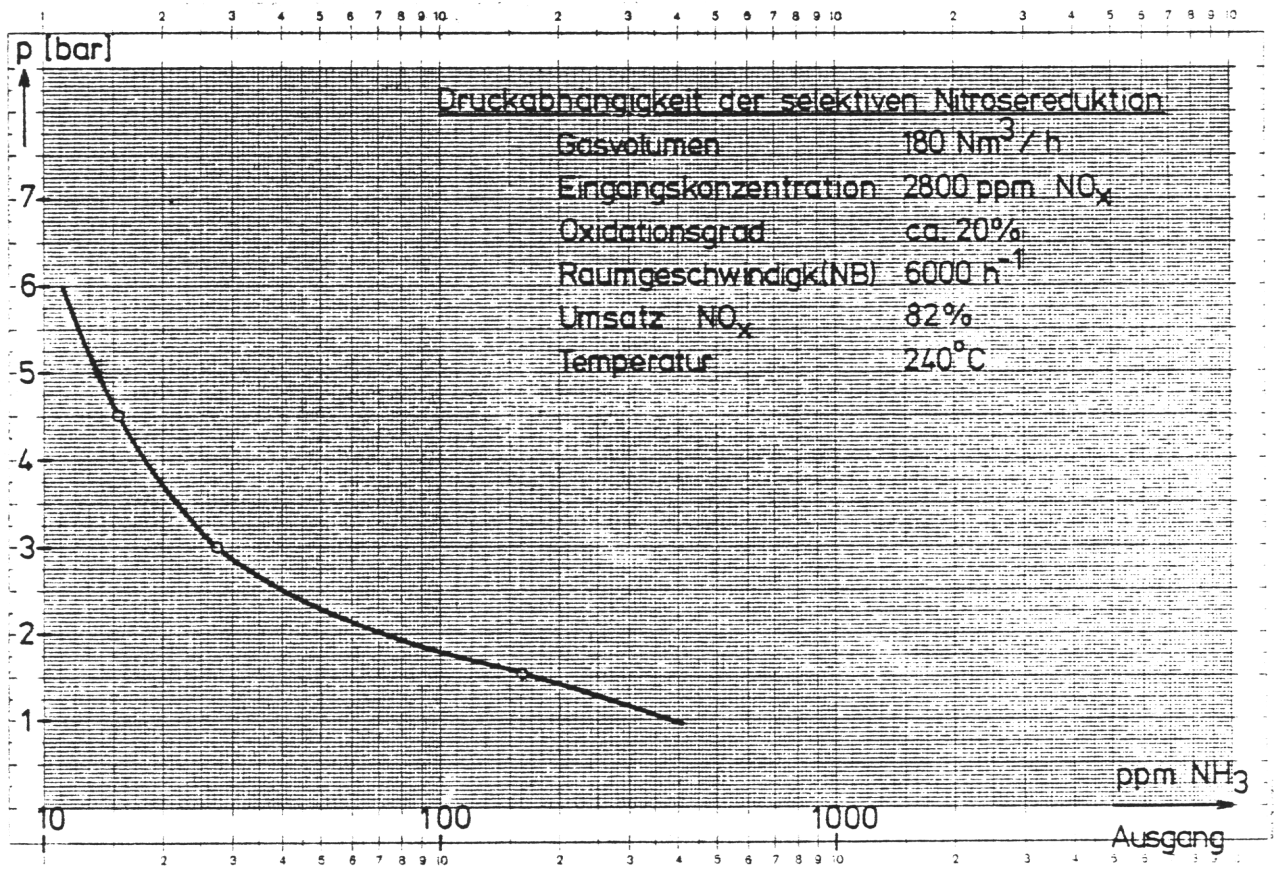


Figure 4

Einfluss des Oxidationsgrads

ungereinigtes Eingangsgas:
 Konzentration 1200 ppm NO_x
 Raumgeschwindigkeit 17500-35000 m³ (NB)
 Temperatur 215°C
 Druck 71 bar

gereinigtes Abgas:
 Konzentration 16 ppm NH₃

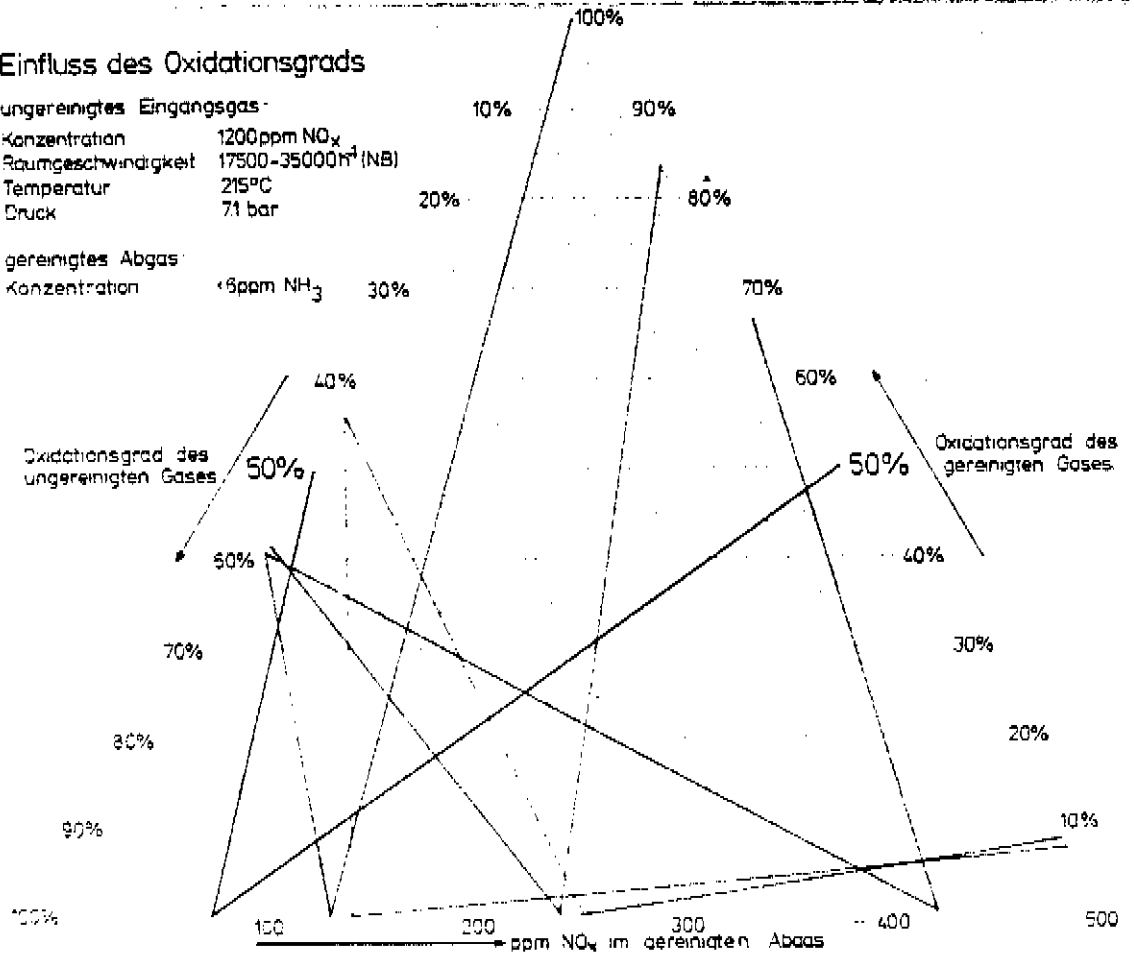


Figure 5

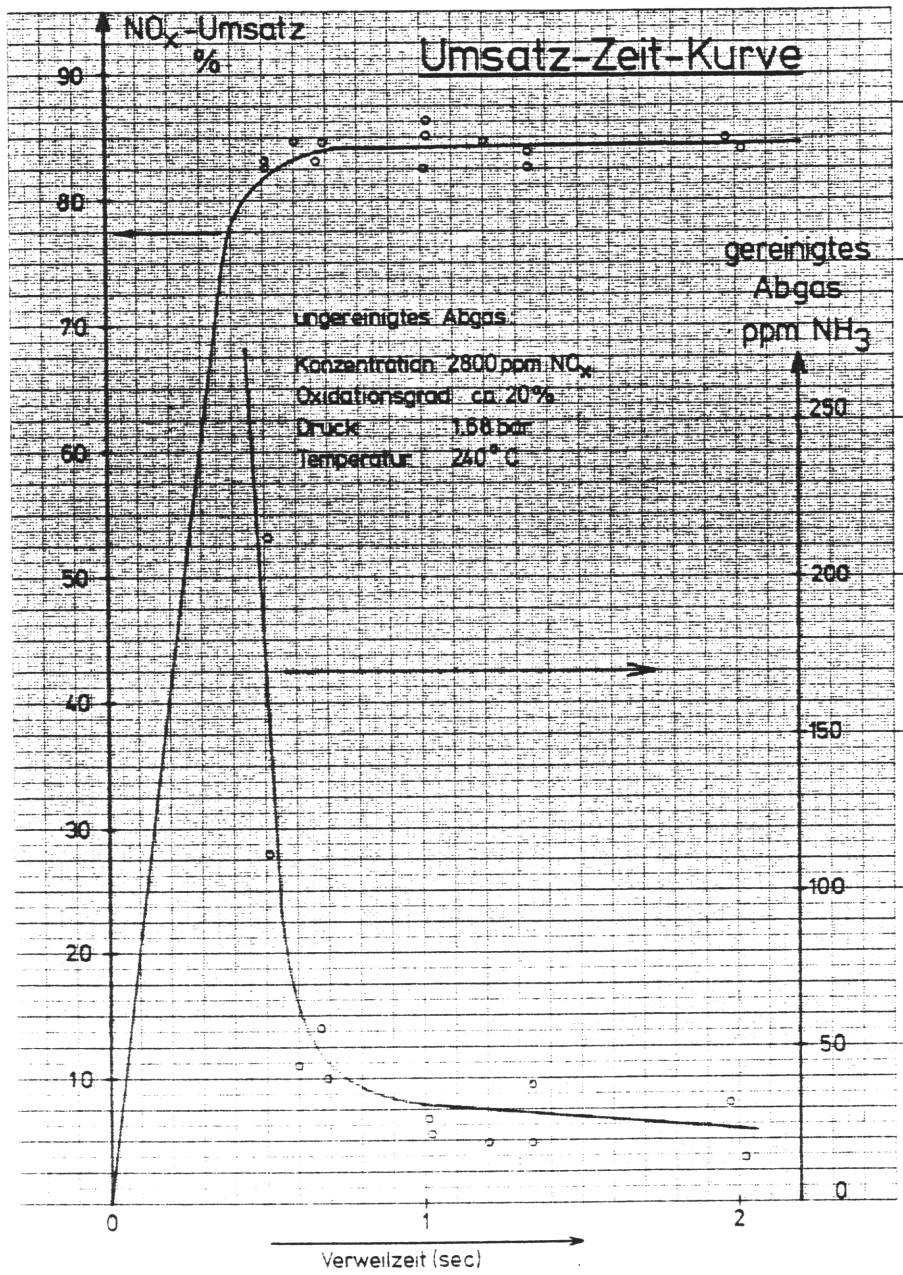


Figure 6

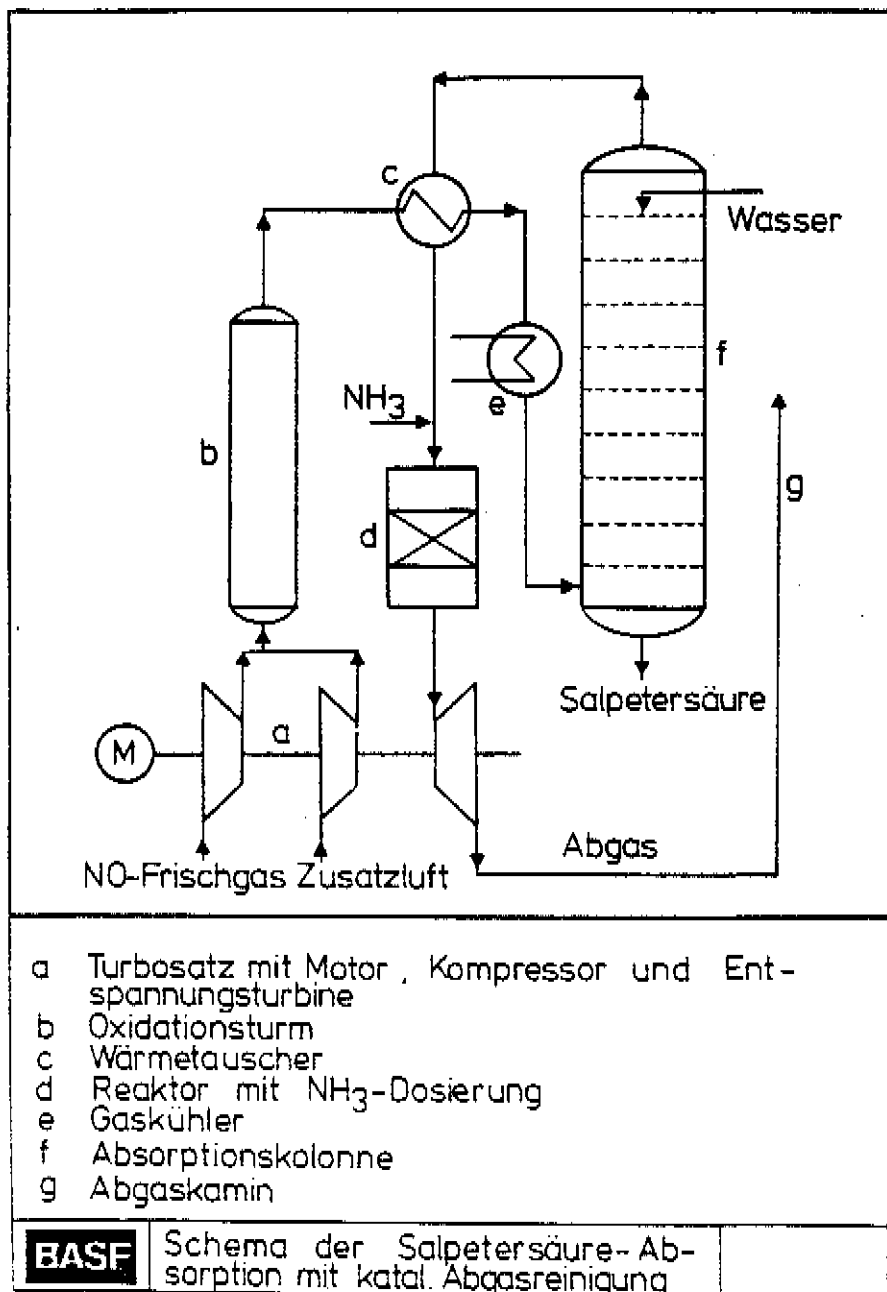


Figure 7

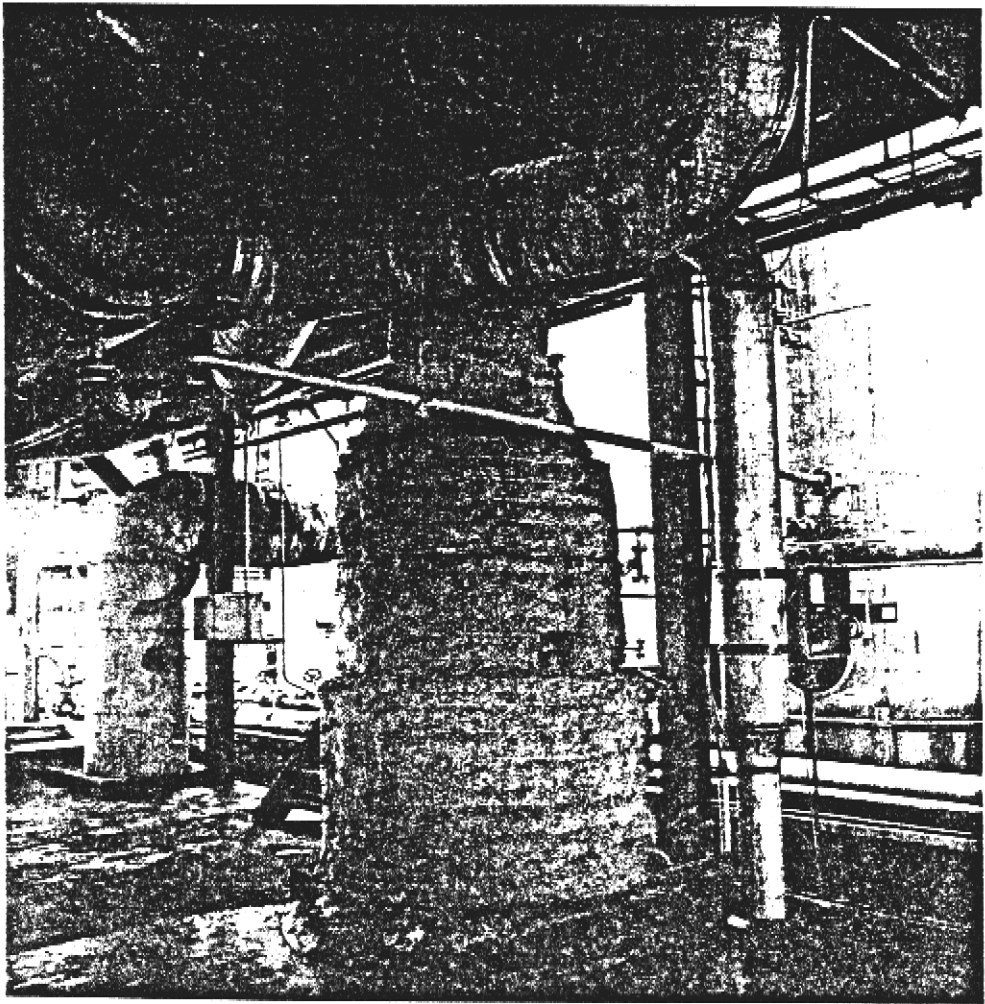


Figure 8

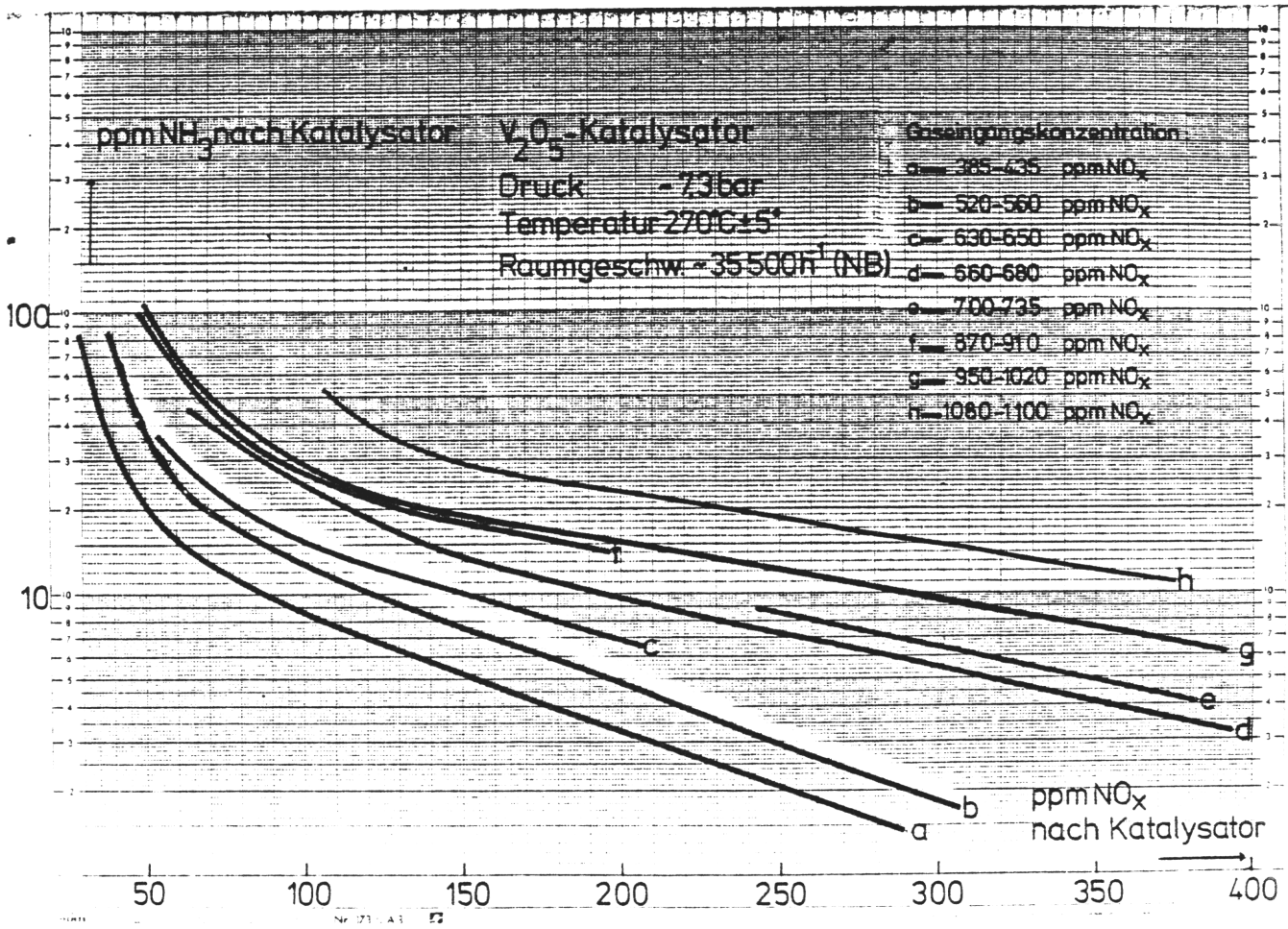
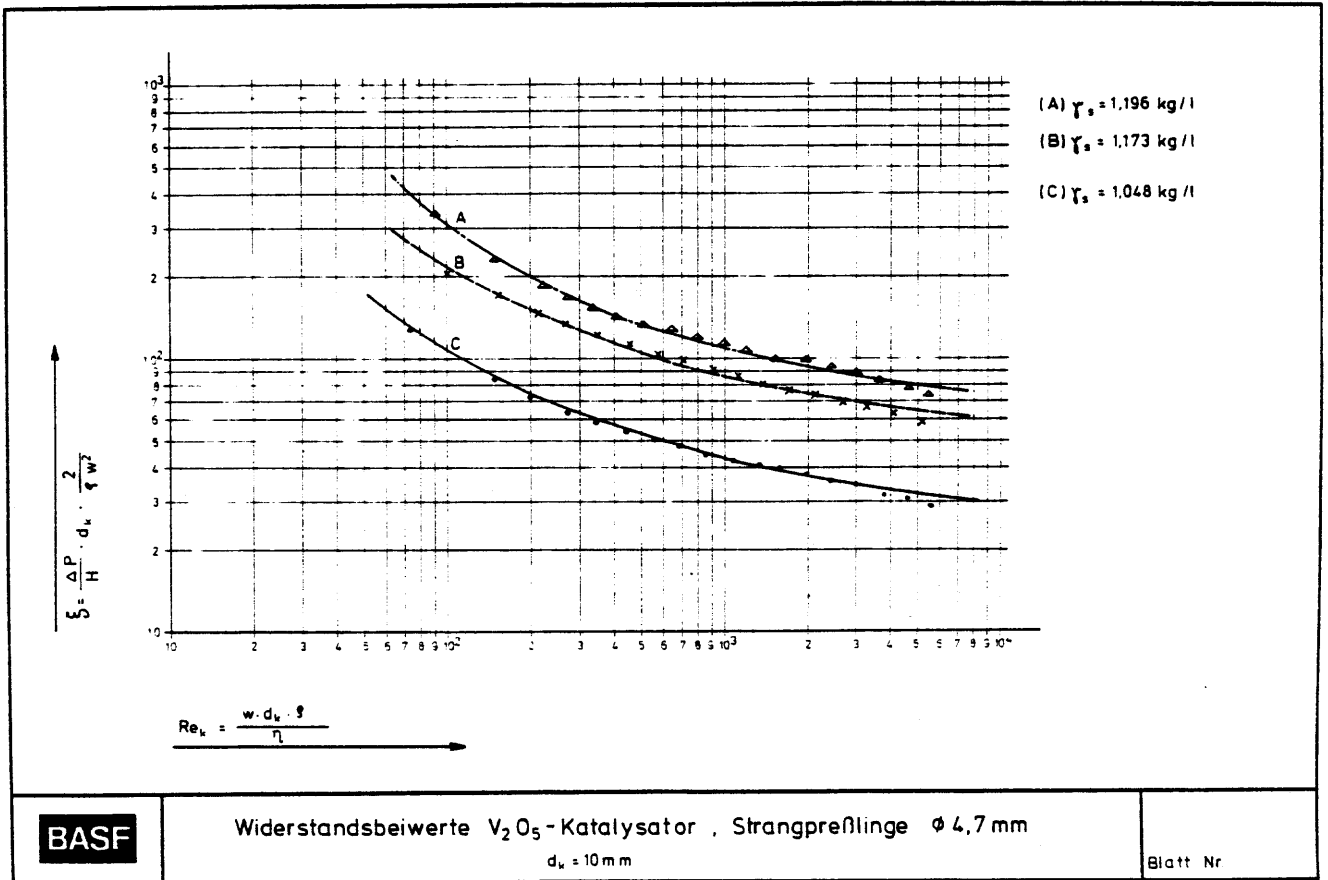


Figure 9



BASF

Widerstandsbeiwerte V₂O₅-Katalysator, Strangpreßlinge ϕ 4,7 mm
 d_k = 10 mm

Blatt Nr

TA/80/18 BASF experience of the catalytic purification of exhaust gases in nitric acid plants by H. Dittmar, BASF, Germany

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

Q - Mr. B.K. JAIN, F.A.I., India

What is the expected life of U_2O_5 -catalyst?

A - As the first catalyst charge was at the beginning of 1975, and as the catalyst is still working faultlessly, we can state that the minimum life is 6 years. We expect a longer life. We do not know about influences of higher or lower temperatures than $270^\circ C$ on the catalyst life.

Q - Mr. M. BERNHEIM, Lonza S.A., Switzerland

In your paper you gave a very good description of all technical aspects of the problem. But what about the economics? What are additional costs per ton HNO_3 for introducing the catalytic treatment (cleaning from 1,200 ppm to 200 ppm at 300 tpd HNO_3)?

A - The variable costs depend essentially on the NH_3 consumption. In a 300 tpd plant with ab. $41,300 m^3$ (S.T.P.) waste gas/h the ammonia consumption used for the reduction from 1200 to 200 ppm is $41 m^3/h NH_3$ or 31.6 kg/h. The costs of catalyst and reactor including mixer and control instruments, depend upon the quantity of catalyst required. This will be determined in a pilot plant and depends on the NO_x -concentration in the treated and in the untreated waste gas, the degree of oxidation, pressure and temperature as well as on the quantity of waste gas.

Installation of a reactor upstream the waste gas turbine will reduce the pressure P_1 to the extent of the pressure loss caused by this reactor but, on the other hand, the increase in temperature in the catalyst bed causes an increase of the temperature T_1 ; so that both effects at least partly cancel each other out with respect to the energy supplied to the turbine.

Q - Mr. J. LIPSCH, Stamicarbon, Netherlands

In your paper you stated that the most economical plant for reasonable capacities would be a monopressure plant operating at 5 bar in the absorption section. This would comply with the legal emission limits. Do you mean here the German legal limits? If so, what would be the most economical plant if you have to meet the EPA-limits of 200 ppm NO_x ?

A - In general, it can be assumed that in most countries the 200 ppm NO_x is required by law. We believe that in the plant capacity range of about 300 tpd HNO_3 the mono medium pressure plant with selective gas treatment is more economic than a medium high pressure plant without gas purification.

Q - Mr. P. BALDWIN, Cremer & Warner, United Kingdom

On the figure 2 on page 18-10 the curve is drawn concave. Why is it not a straight line or convex to follow the points as determined?

A - The curve is drawn concave in figure 2 in order to show the difficulty in obtaining a complete NH_3 conversion at such low NH_3 -concentrations. It should not be forgotten that in NH_3 combustion at $800-900^\circ C$ certain

small quantities of NH_3 pass the pt grids unreacted.

Q - Mr. J. OLIVARES, E.R.T., Spain

As we know, there are in Europe several nitric acid plants employing medium pressure processes ($3-4 \text{ kg/cm}^2$), which operate very efficiently and economically, but which have environmental problems. Almost all of these plants have an energy recuperation system based on an expander turbine that covers ab. 15-30% of the total power requirements of the air turbo compressor.

Q - What is the range of applicability of the BASF non-noble catalysts to this type of plants in terms of:

- ammonia consumption
- pressure drop
- spacial velocity (h^{-1})
- risk of ammonium nitrate-nitrite in expander turbine?

A - The ammonia consumption is equimolar to the reacted NO_x . The pressure drop in the reactor in our Ludwigshafen plant including mixing equipment is about 1.5 m of water column.

The spacial velocity depends upon operational conditions such as:

- NO_x content in impure and in pure waste gas
- degree of oxidation of the nitrose
- operating pressure
- temperature

Taking the extreme values into consideration, the spacial velocities are from 3,000 to 70,000 h^{-1} (under standard temperature and pressure conditions for the gas).

The maintenance of certain temperatures prevents deposits from forming in the waste gas turbine. These temperatures are obtained - under thermodynamical considerations - from the NH_4NO_3 vapour pressure curve. This means that, at higher NH_3 -concentrations, the waste gas temperature must also be higher. The exact temperatures can only be given from case to case after the NH_3 -concentration (in the pilot plant reactor) has been measured.

Formation of deposits in the waste gas stack depends not only on the exit temperature of the waste gas from the turbine and the NH_4NO_3 -concentration but also on the velocity in the tube, the outside temperature and the insulation of the stack.

Q - Mr. F.G. MEMBRILLERA, S.A. Cros, Spain

Is your catalytic purification process able to work at a temperature of about 450°C in a commercial unit?

A - The catalyst is not employed in plants with waste gas temperature of 450°C .

Q - Mr. R. van HARDEVELD, D.S.M., Netherlands

Can you give some data on catalyst stability and life if possible also as a function of operating temperature.

A - The catalyst support is alpha- Al_2O_3 , a hard material as you know. We have not found pressure loss to increase due to mechanical damage in 6-year operation (at ab. 270°C). The operating temperature is from 220° to 350°C .

Q - Mr. FERNANDEZ RODRIGUEZ, Technicas Reunidas, Spain

In your paper you mention a V_2O_5 -catalyst. I would like to know more about this catalyst, e.g., support, specific surface area, etc...

A - The statement that the catalyst support is alpha- Al_2O_3 permits conclusions to be drawn as to the active surface. The change in the valency of V in the V_2O_5 is known. At lower temperatures the catalyst tends to change to green which corresponds to a lower valency state. This means in other words that oxygen from the V_2O_5 lattice participates on the reaction.