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## LONG-TERM EXPERIENCE WITH CATALYTIC REDUCTION OF NO<sub>x</sub>

J. Vlasák and J. Scharf

Lovochemie a.s., Czech Republic

### RESUME

*On produit l'acide nitrique depuis 1954 à Lovochemie. Cinq unités de production relativement petites avec combustion atmosphérique et absorption à moyenne pression ont une capacité totale de 800 t/j ; la dernière avec système aquipression (3,5 bar) a une capacité de 270 t/j. Cette unité a été équipée avec la technologie Kavag de réduction catalytique non sélective de NO<sub>x</sub> utilisant le catalyseur Pt sur support métallique. La performance de cette technologie est très bonne, le rendement de la réduction atteignant 95-100 %. Les résultats sur le long terme et leur dépendance des conditions de production et la qualité de régénération du catalyseur ont été résumés. Le passage comme agent de réduction au gaz naturel à la place de gaz de ville est en préparation pour l'année 1996.*

*Les unités d'acide nitrique fonctionnant avec combustion atmosphérique marchent avec réduction sélective de NO<sub>x</sub> depuis 1980. Le plan et l'équipement sont d'origine tchèque. La technologie a fonctionné d'une manière fiable avec un rendement de 95 %, la concentration maximum de NO<sub>x</sub> dans les gaz de sortie étant de 200 ppm. Tous les gaz en aval de la turbine d'expansion sont entraînés en un seul courant divisé ensuite en deux lignes séparées. La solution a quelques avantages mais aussi des inconvénients. De nombreuses expériences sur les conditions de procédé, le réglage et le contrôle ont été acquises au cours des 15 dernières années.*

*A Lovochemie, l'importance des conditions de marche des unités d'acide nitrique et, surtout, des concentrations en substances dangereuses, a été reconnue. A titre d'exemple, dans la communication, le problème du maintien du plus bas niveau possible de NO<sub>x</sub> dans l'unité en considérant les conditions réelles des unités les plus anciennes sera discuté.*



### 1. INTRODUCTION

Lovochemie a.s. is the biggest fertiliser manufacturer in the Czech Republic. The tradition is based on the production of sulphuric acid and superphosphate that began in 1903, and on the manufacture of nitric acid and nitrogen fertilisers that started in 1954. Advantageous location of the company's plant as far as the road and railway transport is concerned, and particularly company's own port on Elbe river creating direct connection with Hamburg in Germany, form good conditions for both manufacture and trade. These advantages are further augmented by the fact that the company is located in fertile Elbe valley as well as by favourable distance from other producers of fertilisers.

The company does not operate its own ammonia plant, and buys the main ammonia supplies from Chemopetrol Litvinov situated 50 km from company's facilities.

### 2. DECREASE OF NO<sub>x</sub> EMISSIONS FROM THE MANUFACTURE OF NITRIC ACID

The production of fertilisers is based on the manufacture of nitric acid. There are 5 production units with atmospheric oxidation of ammonia and with 3.5 bar absorption process, and one equipressure 3.5 bar unit in Company facilities. The total production capacity amounts to an average of 1,050 tons/day. These plants are 37-42 years old. I would like to explain how we fulfill the required limits of emissions with these plants. These limits are as strict as those being in force in European Union in relation to new plants. The BAT handbook gives 4.2 kg/ton of 100% HNO<sub>3</sub> for existing plants and 1.6 kg/ton of 100% HNO<sub>3</sub> for new plants. The limit in force for Lovochemie a.s. is 2.1 kg/t of 100% HNO<sub>3</sub> which is 200 ppmv. Ppmv units are given in the diagrams because they better correspond with traditional documents and development.

In the former socialist planned economy, the concept of manufacture in Lovochemie was based particularly on quantity, but the quality of production, environmental protection and working conditions lagged to some extent behind. Despite this policy, the technicians in charge of design and manufacture tried to introduce, from the very beginning, new technical solutions that together with the intensification of the manufacture

contributed also to the decrease of emissions. As each increase of the production of fertilisers in the company depended on the performance of nitric acid plants, all technical improvements were immediately utilised for the increase of fertiliser production, and environmental parameters were controlled by technological conditions. The concept, design and realisation of both types of nitric acid plants had their own specific characteristics and solutions, and they were developed in a specific way.

The equipressure unit (Figure 1) is of exclusively domestic origin comprising both design and manufacture of individual pieces of equipment with only one exception which is the non-selective catalytic reduction of  $\text{NO}_x$  (NSCR) with Pd-Pt catalyst on metallic carrier which was supplied by Kawag of Hasselroth (Federal Republic of Germany). This equipressure plant produces excess of energy. The heat generated by ammonia oxidation produces steam in a boiler which then drives a turbo-generator producing electricity. The energy released by exothermic reaction in the NSCR reactor is utilised in a gas turbine driving an air compressor. The excess of energy is used in a turbo-generator forming a part of the turbo-set. The results of emissions are given in Figures 2 and 3.

The operation of NSCR was trouble-free from the very beginning but as far as technology is concerned, the reduction process grappled a number of both objective and subjective problems.

1. The catalyst is very sensitive to the precision and quality of workmanship, to the positioning of metallic carrier and to the depositing of precious metal. This was found already during the tests of new or regenerated catalyst. This quality was achieved by German companies, lately by ENVITOREC.
2. From the beginning, city gas was used as reduction medium that should contain 54% of  $\text{H}_2$  on average. When the concentration of hydrogen dropped, not only the efficiency of reduction decreased but it resulted also in a significant increase of the consumption of city gas because another constituent of the city gas - methane practically does not react under given temperatures.
3. The reduction process is to a large extent influenced by free oxygen in the final gas. Lower  $\text{O}_2$  content adversely affects the efficiency of absorption while higher content adversely affects the course of the reduction proper. This is related also to the parameters of the absorption system of the plant that despite two upgradings shows low specific absorption volume. The lower content of oxygen causes a lower degree of the oxidation of nitrogen oxides and lower efficiency of absorption. This is combined, particularly in summer months, with the effect of the temperature of cooling water which results in a lower efficiency of circulation cooling towers. Despite these problems in the operation of the plant, required emission limits are being observed.

The other part of the nitric acid plant uses atmospheric oxidation and 3.5 bar absorption (Figure 4). Originally all the units were equipped with absorption towers of SBA system. Exit concentration of  $\text{NO}_x$  was considerably high (0.45 vol. %). That is why the absorption system has been gradually improved. In the 1960's another absorption towers with foam regime or oxidation-absorption towers with perforated plates were added to existing absorption systems.

As the exit concentration of  $\text{NO}_x$  was too high (2500-3000 ppmv) even after these modifications, a team comprising experts from the company, from Chemoprojekt Prague and from the Czechoslovak Academy of Sciences began to prepare a final solution of the problem of  $\text{NO}_x$  in early 1970's. There were several possible solutions - final alkaline absorption, a combination of enlarged absorption with physical absorption, non-selective catalytic reduction, and selective reduction (SCR). Pilot plant operated under real working conditions revealed considerable problems connected with alkaline absorption, particularly the large size of the equipment, and a low degree of the oxidation of gases as well as a problematic processing of the solutions produced. SCR technology was then chosen because of its simplicity, feasibility and operation independent of the manufacture of nitric acid. In the course of realisation all the alternatives were tested both in laboratory and in a pilot plant. The selective reduction proper was also selected from a number of possible solutions. When evaluating platinum, chromium and vanadium catalysts,  $\text{V}_2\text{O}_5$  deposited on alumina proved to be the best of all, and Russian catalyst AVK10 containing 10% of  $\text{V}_2\text{O}_5$  was found as the best of a number of vanadium catalysts. When designing the equipment the alternative based on selective reduction unit on the pressure side of each manufacturing unit was abandoned, and it was decided to built the equipment in the form of two lines separated from the manufacturing unit and located beyond expansion turbines. In such an arrangement the selective reduction can work quite independently. Based on the results of pilot project, and due to safety reasons, a new stack was built for SCR. The equipment is of domestic provenance protected by a number of patents. It applies particularly to the reactor that due to specific design is characterised by large area in small space. The results of emissions are given in Figures 5 and 6.

The equipment worked trouble-free from the very beginning, there were only mechanical problems with fans. The sixteen years of operation enables us to arrive at the following conclusions:

1. The independent operation of SCR was found very soon as illusory. The inhabitants in the region as well as competent authorities got very quickly used to the fact that the permanently criticised and ridiculed red smoke over the plant disappeared, and that  $\text{NO}_x$  can be released directly into atmosphere from the old stack just for few minutes in case the production plants are cut off. If there is a defect in SCR the nitric acid plants must be shut down.
2. From the very beginning of the operation a high degree of efficiency was achieved that even surpassed the expectations. This enabled us to decrease the  $\text{NH}_3/\text{NO}_x$  ratio from original 1.05 to 0.95 which positively affected the consumption of ammonia. The original catalyst had two layers -  $\text{V}_2\text{O}_5$  and  $\text{Fe}_2\text{O}_3$  with  $\text{Cr}_2\text{O}_3$ . The role of the lower layer was to degrade the surplus of ammonia. Lower  $\text{NH}_3/\text{NO}_x$  ratio and problematic service life of this layer resulted in its gradual removal. The way of operation can be modified according to the main criterion which can be either a maximum efficiency of the equipment or an economical operation within the emission limits set by competent authorities. During the starting years the first alternative was chosen because the consumption of ammonia, i.e. commercial results could be planned but in recent years the economy of manufacture seems to be decisive of course with required emission limits strictly observed.
3. The chosen technical solution is very flexible from the standpoint of technology, which applies particularly to the control of exit concentrations of  $\text{NH}_3$  and  $\text{NO}_x$ , with the proviso that the measuring system is perfect.
4. The efficiency of reduction is significantly influenced by the type of catalyst. Here we were lucky because the supplied Russian catalyst AVK 10 worked with excellent efficiency and we could say that the older it was the better. After 14 years of operation it was replaced by the same type in one line, and the original one still works in the other. The long service life of the catalyst makes the disposal of spent catalyst easier. We suppose to accept the offer of a Czech company that has offered to process the catalyst at reasonable price.
5. Very important information relates to the safety of operation. The first data indicated a possible forming of the deposits of ammonium salts, particularly nitrates and nitrites inside the equipment, piping and stack. As already mentioned, we even erected a new stack equipped with water inlet at the top for flushing internal space of the stack. In case of defect, the stream of gas coming from absorption unit is automatically separated from SCR and switched into the old stack. It was found very quickly that, when technological parameters, particularly the temperature at reactor outlet, are observed, no deposits were formed. The stack was flushed with water several times but only traces of  $\text{NO}_3^-$  were found at the bottom of the stack. The water inlet was later replaced by saturated steam.

### 3. WORKING CONDITIONS AND ENVIRONMENT

The nitric acid plants are so arranged that all the personnel running the oxidation of ammonia and turbo-compressors have their workplace in a common hall 130 m long. The absorption staff had to spend the time with absorption equipment located in open air or they can use small cubicles. The quality of area in which all the people operated can be seen from Figures 7 - 10.

Up to 1973 the measurement of  $\text{NO}_x$  concentration in the workplace was done only from time to time but since 1976 the concentrations have been measured systematically once a month. More frequent measurement is considered as unnecessary because the values measured are stabilised and considered as safe.

During 1975-76 the process control was gradually transferred to two control rooms in a burning plant, and one in absorption plant. The reason was not only to improve working condition but also to reduce the staff. The control rooms were equipped with classic analog instrumentation but due to the instruments and experience available at that time, some instruments and particularly control elements used for start-up and shut down remained in the production hall. Because of this, the service staff could check the parameters of the process in an air-conditioned control room with considerably lower  $\text{NO}_x$  concentrations, and leave it just for checking the equipment during start-up or shut down procedures.

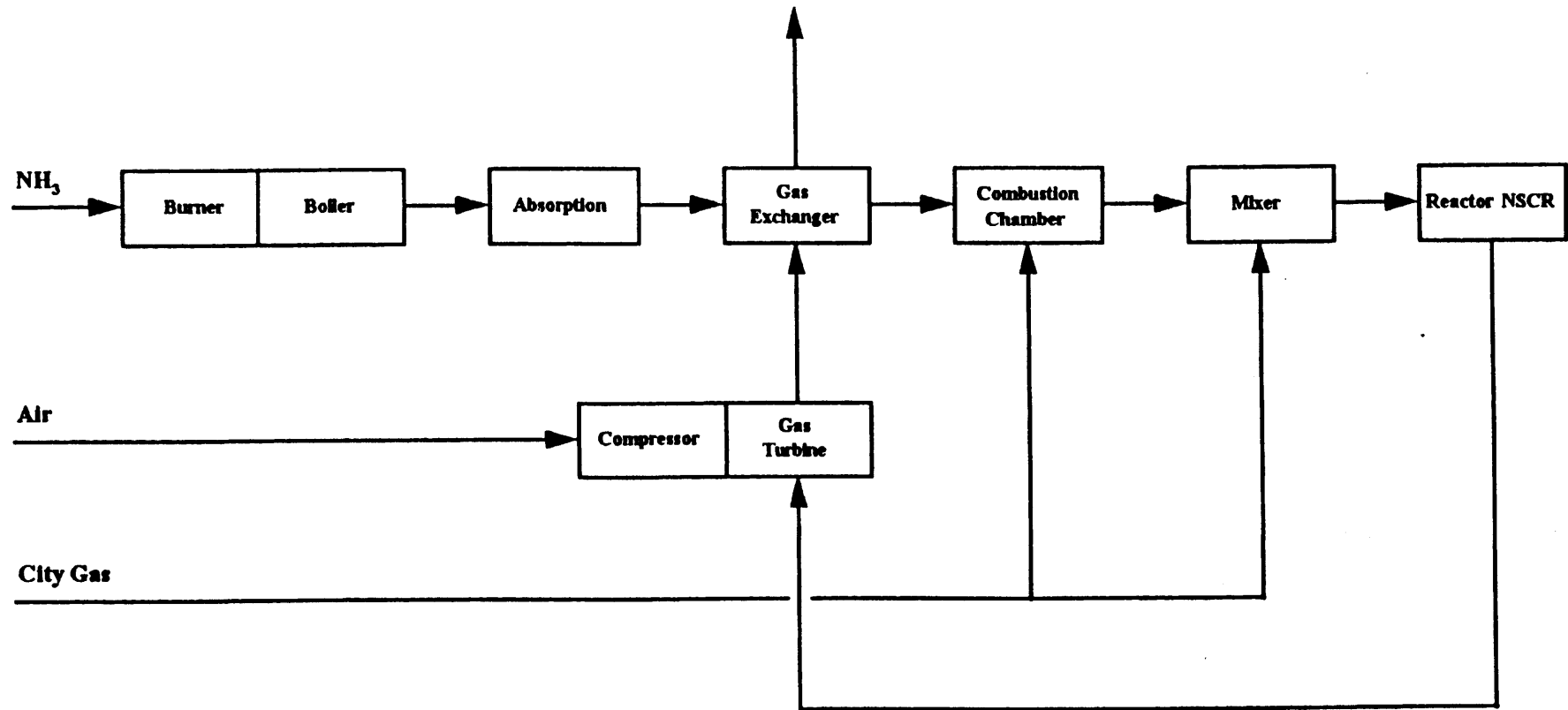
We can summarise the experience obtained so far as follows:

1. The air-conditioned control rooms considerably reduced the exposition of the staff not only to  $\text{NO}_x$  but particularly in summer months they create better working conditions. Contrary to it, though it was not scientifically approved, frequent changes between lower temperatures in the control rooms and higher ones in burning plant have adverse effect on the sickness rate of the staff.
2. A long-term development confirms that the exposition of the personnel working directly in production halls cannot be significantly reduced, and certain improvement can be reached only by:
  - A total reconstruction of the control rooms particularly as far as the measurement and control elements are concerned. Measuring system should be complemented with modern instruments, and a new control system involving start-up and shut down procedures should have to be built.
  - A modernisation of a number of apparatuses, e.g. ammonia burners, fans for ammonia-air mixture, acid pumps, etc. When evaluating a system comprising 15 burners, 7 boilers, 32 absorption towers, 110 pumps, etc., it is necessary to decide whether it is more economical or not, after 40 years of operation, to build a brand new plant despite high capital expenditures.
3. When we compare the plants with atmospheric oxidation with this based on pressure oxidation having more sophisticated control system and technology, it can be seen that a significant reduction of  $\text{NO}_x$  concentration in working environment cannot be expected. That is why we consider the limits set by Czech authorities - 10 mg  $\text{NO}_x$  per  $\text{m}^3$  on average, and max. concentration of 20 mg  $\text{NO}_x$  per  $\text{m}^3$  as reasonable ones.

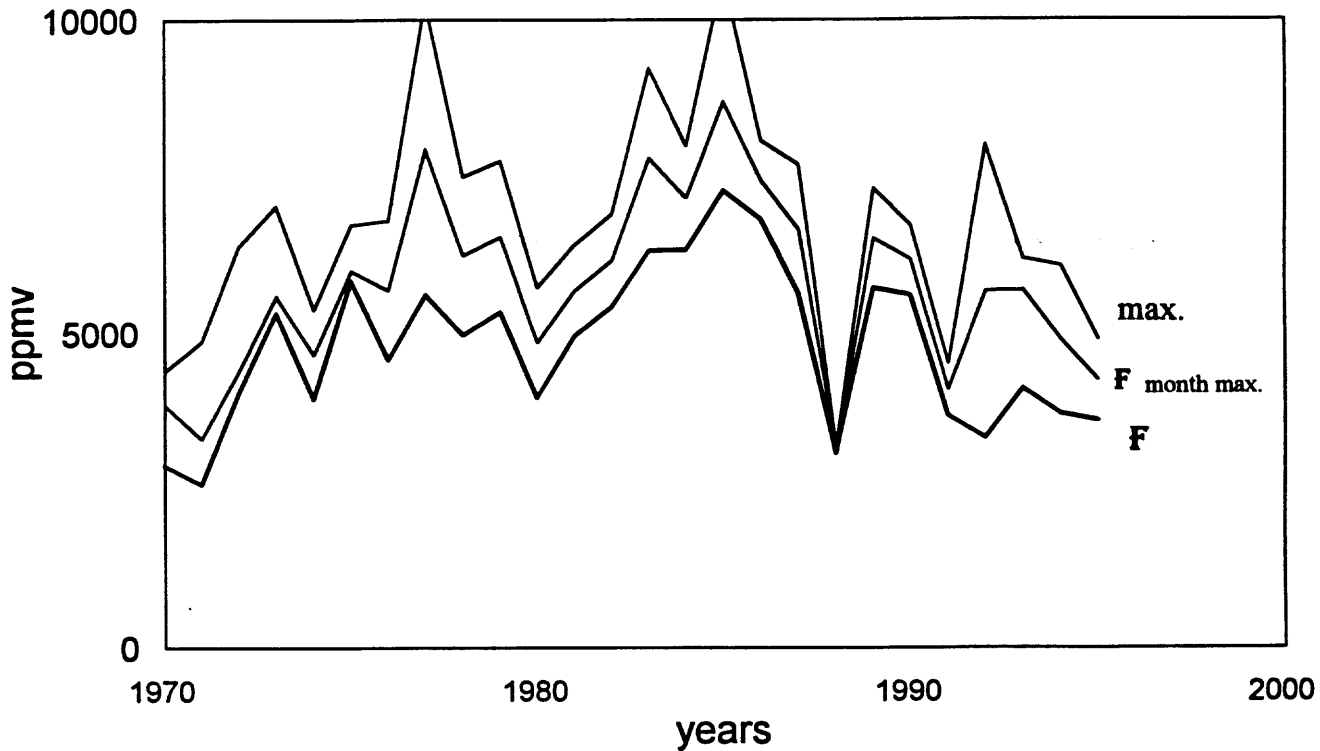
**The future** of SCR and NSCR is divided into two stages. The first one includes the replacement of metallic NSCR catalyst by ceramic catalyst in summer 1996, when city gas will be no more available in the region, and natural gas will be used as fuel. As far as the second stage is concerned, we believe that new nitric acid plant will be built soon, which may make the catalytic reduction superfluous.

The economy of company's main products which are fertilisers, particularly of the newly built CAN plant, depends to some extent also on the solution of nitric acid manufacture. We also expect an improvement of the quality of working conditions and environment. Nevertheless our long-term experience confirms that, even before the new plant is built, satisfactory parameters of both exit gases and working environment can be achieved with this old long-term operated equipment.

**FIGURE 1. NITRIC ACID WITH NSCR**



**FIG.2**  
CONCENTRATION OF NO<sub>x</sub> FROM ABSORPTION  
HNO<sub>3</sub> WITH NSCR



**FIG.3**  
CONCENTRATION OF NO<sub>x</sub> FROM NSCR

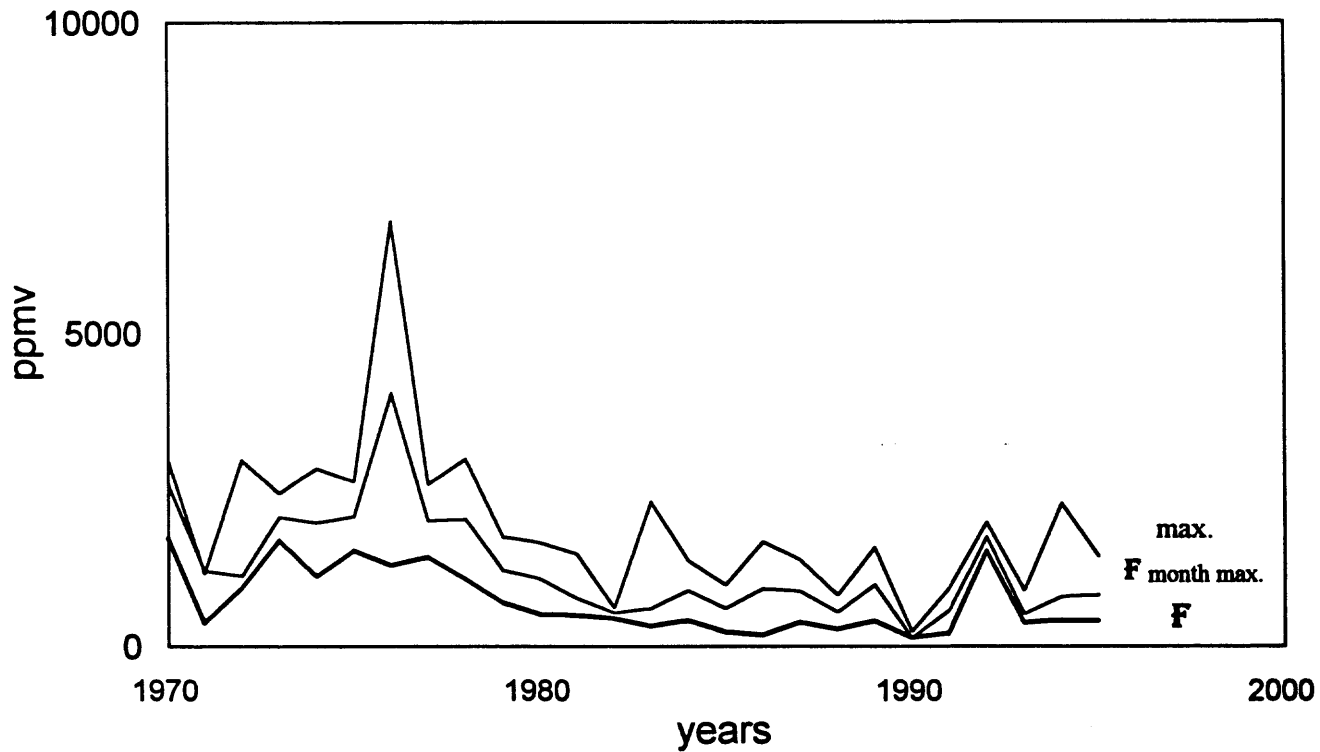
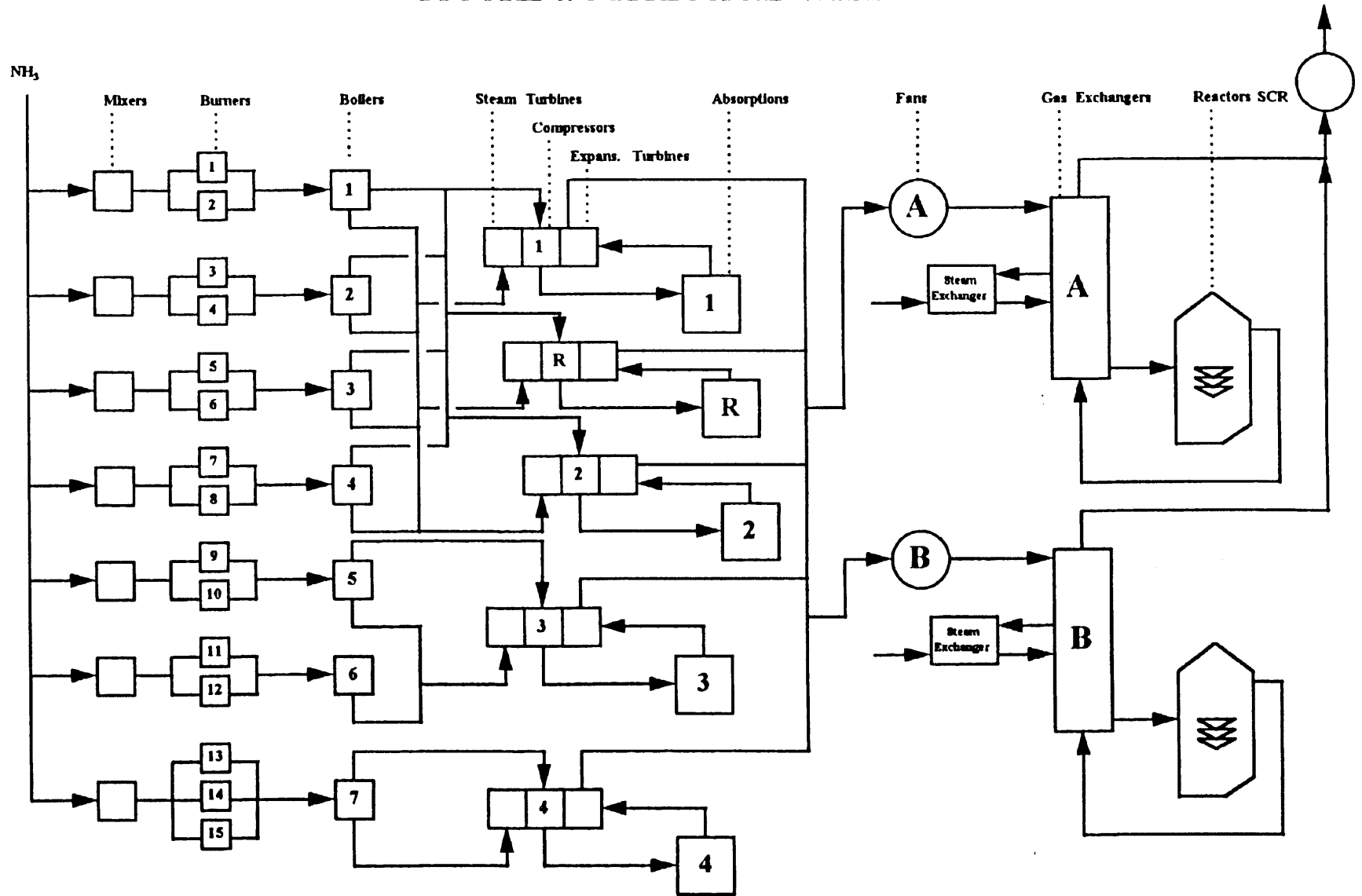
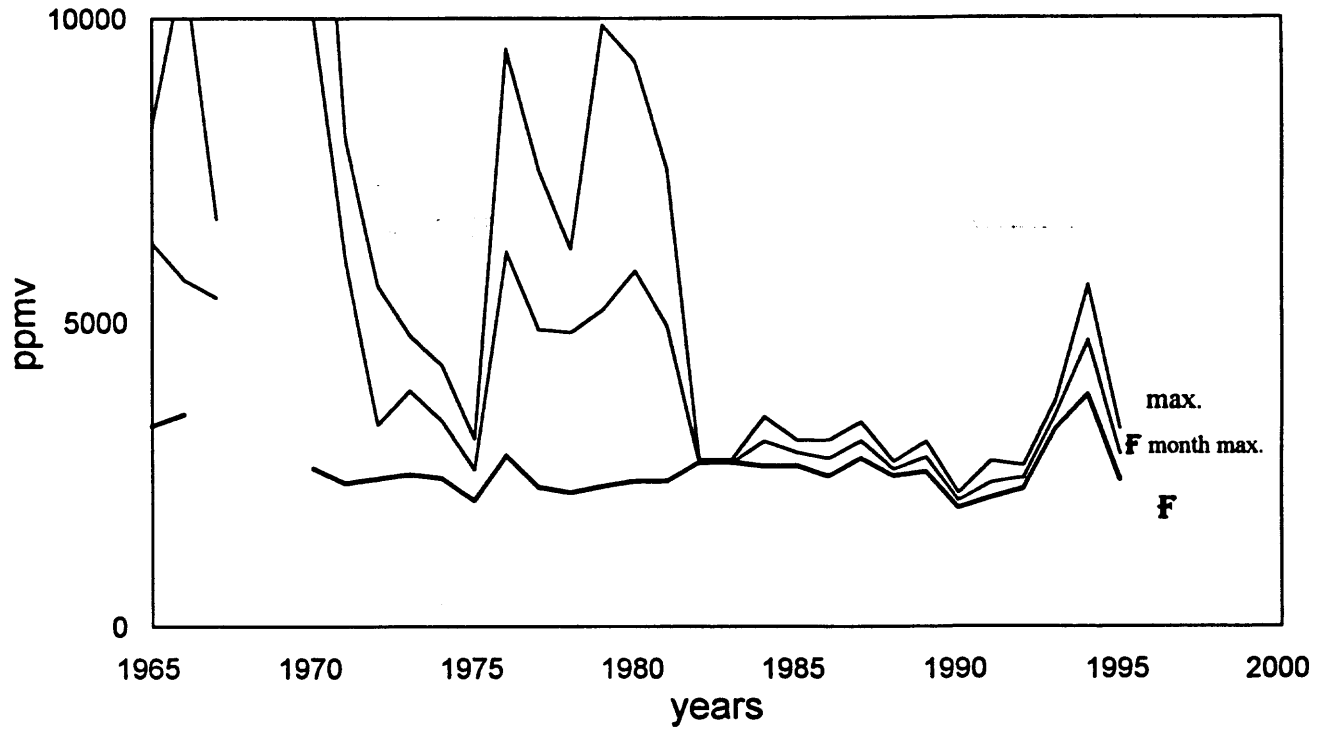


FIGURE 4. NITRIC ACID WITH SCR

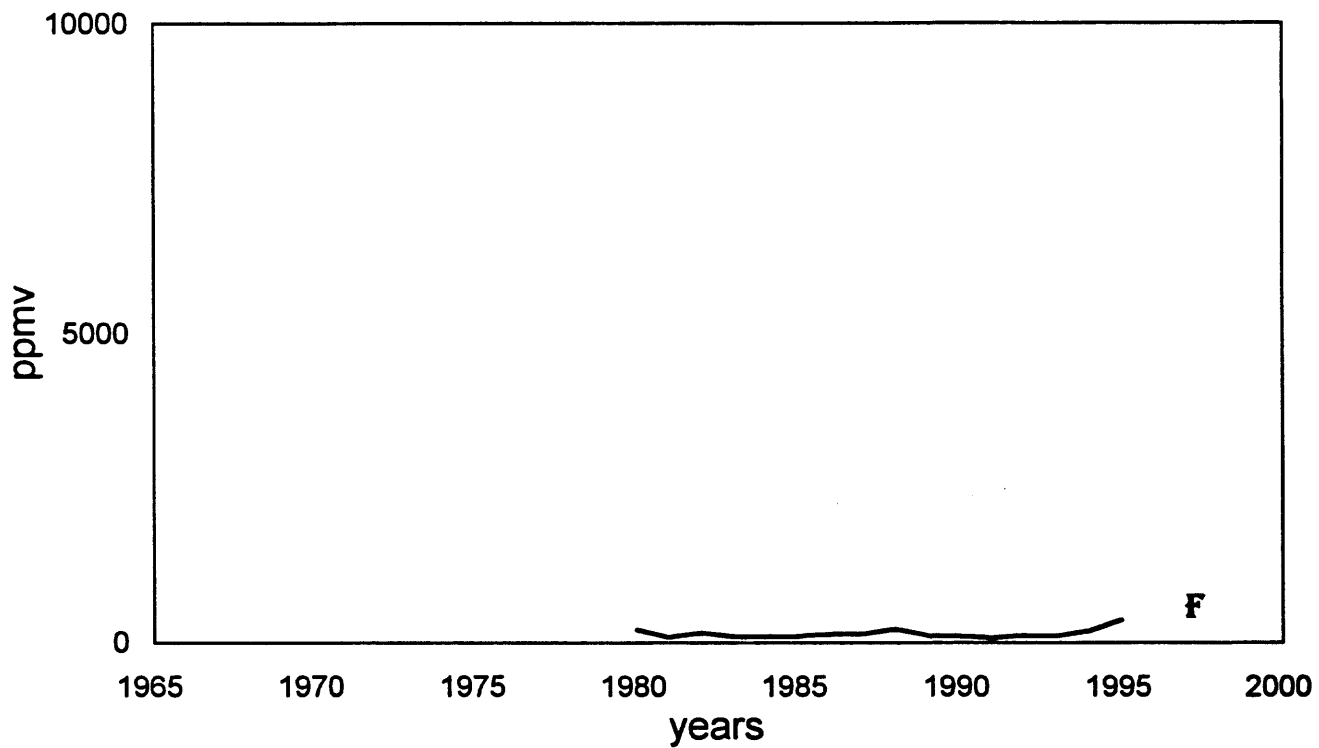




**FIG.5**  
CONCENTRATION OF NO<sub>x</sub> FROM ABSORPTION  
HNO<sub>3</sub> WITH SCR



**FIG.6**  
CONCENTRATION OF NO<sub>x</sub> FROM SCR



OCCUPATIONAL EXPOSURE LIMIT VALUE for NO<sub>x</sub>  
THE HALL OF OXIDATION AND COMPRESSOR CONTROL ROOM - OXIDATION OF NH<sub>3</sub>

FIG.7

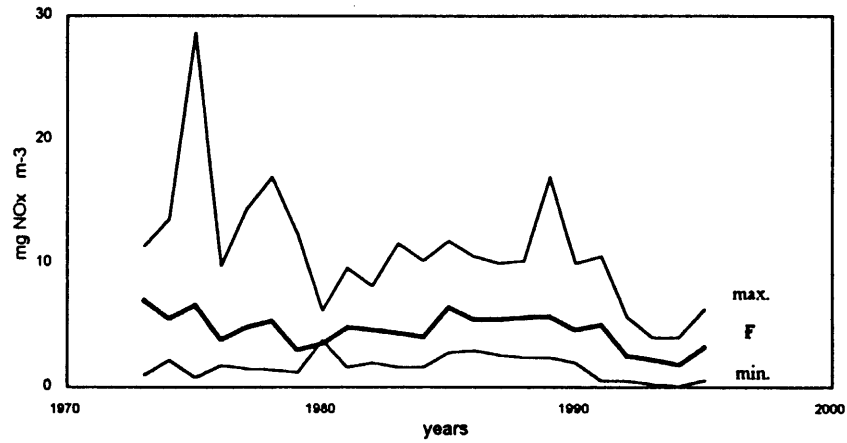
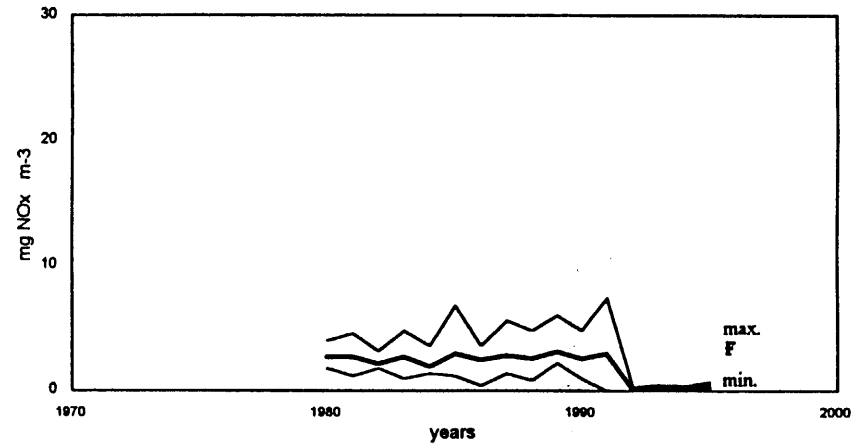
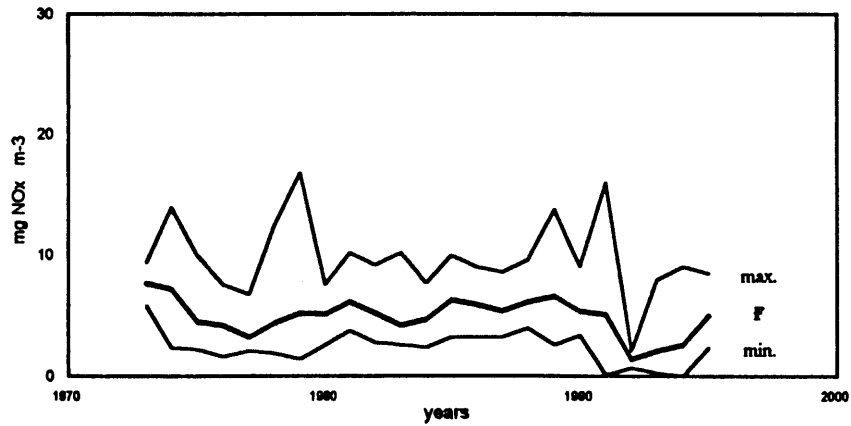


FIG.8



ABSORPTION

FIG.9



CONTROL ROOM - ABSORPTION

FIG.10

