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A CONTROL SYSTEM FOR NITROGEN OXIDES POLLUTION ABATEMENT BY SCR (SELECTIVE CATALYTIC REDUCTION)

P. Belli(*), S. Bittanti(*), P. Bolzern(*), M. Campi(°), A. De Marco(•), A. Ferretti(*), S. Malloggi(†) W. Prandoni(•)

(*) *Dipartimento di Elettronica e Informazione, Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 Milano, Italy*
(°) *Dipartimento di Elettronica per l'Automazione, Università di Brescia, Via Branze 38, 25125 Brescia, Italy*
(•) *ENEL-CRA , Via Volta 1, 20093 Cologno Monzese MI, Italy*
(†) *ENEL-CRT, Via A. Pisano 120, 56122 Pisa, Italy*

Abstract: This paper deals with the control of nitrogen oxides emission in thermal power plants by the use of the so-called Selective Catalytic Reduction (SCR) technology. A model of the process based on first principles and suitable constitutive equations has been developed. The corresponding simulator points out that the effect of inlet ammonia concentration on outlet nitrogen oxides concentration is adequately described by a low order linear model in all typical operating conditions. Such a model is used to design a control system capable of maintaining the pollutant emissions under a prescribed threshold, while reducing the ammonia slip at the reactor outlet. The proposed controller is verified through several simulation tests.

Keywords: Power plant modelling; Power plant control; Catalytic reduction, Nitrogen oxides control.

1. INTRODUCTION

The emission of nitrogen oxides due to the operation of thermal power plants has been increasingly controlled in the last few years. Together with sulphur oxides, nitrogen oxides (NO_x) are not only harmful since they cause the acid rain, but also because their reaction with volatile organic compounds increases the level of ozone (see e.g. Boer et al., 1990). About 95% of the molar concentration of nitrogen oxides is due to nitrogen monoxide (NO).

Many techniques have been developed for NO_x abatement (see Bosch and Janssen, 1987). They can be basically divided into two groups. Primary techniques (or combustion control) are based on low NO_x burners, stage combustion, reburning technology, and gas recirculation. These methods control the NO_x generation and possibly destruction at combustion level. Secondary techniques are based on flue gas treatment. Of course, one can combine both primary and secondary techniques in order to increase efficiency and decrease costs.

In this paper we consider a secondary technique based on the so called Selective Catalytic Reduction (SCR), where ammonia is injected in order to reduce the nitrogen oxides in the flue gas to nitrogen. In order for this reaction to take place, it is necessary to resort to a catalytic reactor.

The control problem consists of minimizing the NO_x concentration at the reactor outlet while keeping the outlet concentration of ammonia below a given threshold. The control system is demanded to reject the effect of several disturbances arising from plant operation. They include variation in the flow rate, temperature, and nitrogen oxides concentration of the flue gas.

The paper is organized as follows. A list of symbols is introduced in Sect. 2. The reactor is concisely described in Sect. 3, where a model based on a set of partial differential equations is also proposed. The dynamic of the reactor is analyzed in Sect. 4. By neglecting the storage terms related to diffusion and transport of NO and NH_3, it is possible to work out an approximate linear ODE model (Sect. 5) which is then used to design a suitable controller (Sect 6).

2. LIST OF SYMBOLS

$C_{NH3}(x,z,t)$ concentration of ammonia in the gas phase in the porous medium.
$C_{NO}(x,z,t)$ concentration of nitrogen monoxide in the gas phase in the porous medium.
$C_{NH3,b}(z,t)$ concentration of ammonia in the gas phase in the channel.
$C_{NO,b}(z,t)$ concentration of nitrogen monoxide in the gas phase in the channel.
$\vartheta(x,z,t)$ fractional coverage of the surface with ammonia.
$C_{NO,i}$ concentration of nitrogen monoxide at the inlet.
$C_{NO,o}$ concentration of nitrogen monoxide at the outlet.
w_g total mass flow rate in the channel.
w_{NH3} ammonia mass flow rate injected.
$h_{d,NH3}$ gas-solid mass transfer coefficient of NH_3.
$h_{d,NO}$ gas-solid mass transfer coefficient of NO.
D_{NH3} effective intraporous diffusivity of NH_3.
D_{NO} effective intraporous diffusivity of NO.
K_A NH_3 absorption constant.
K_D NH_3 desorption constant.
K_R intrinsic kinetic rate constant.
Φ absorption capacity of the catalyst.
ω perimeter of the channel.
A_g area of the channel section.
ρ_g density of flue gas.

3. REACTOR MODEL

The metal oxide catalysts are widespreadly adopted. They are typically composed of a ceramic material containing titanium oxide, supporting vanadium oxides with possible addition of other metal oxides. The reactor is generally composed of a ceramic monolith of rectangular section (e.g. 15 x 15 cm.) with length that typically ranges in between 30÷100 cm. Each monolith is usually crossed by several square channels (side 3÷7 mm) along which the flue gases flow (Boer et al., 1990). The reactor is arranged in different structures with monoliths in parallel and possibly in series.
The catalyst is selective, in the sense that it mainly activates the nitrogen oxide reduction. Such a selectivity is maximized in a suitable range of temperature, i.e. between 300-400 °C. If the catalytic reactor is placed along the flue gas path after the economizer, the suitable temperature range is reached in most of the plants, in the loading manoeuvre from the minimum load ("control load") to the nominal load.
The papers published about the dynamics of NO_x abatement with SCR techniques are very few. The dynamics of the reactor arises from the storage of NH_3 on the porous catalyst surface; this phenomenon is clearly described in (Anderson et al., 1994), where also kinetic correlations are shown. However, the storage of NH_3 is distributed in the catalyst in a way strongly dependent on the diffusion of NH_3 and NO in the porous medium, and this phenomenon should also be taken into account in the model.
The global reaction involving NO and NH_3 is:

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O$$

Both gases NO and NH_3 diffuse into the porous structure of the catalyst; on the catalytic surface NH_3 is strongly absorbed, whereas the absorption of NO can be neglected. The chemical absorption mechanism can be described by the Langmuir model of isothermal absorption (see Inomata et al., 1980, 1982). Accordingly, the mass net flux of NH_3 from the porous medium to its surface is given by:

$$v_{AD} = K_A C_{NH3}(1-\vartheta) - K_D \vartheta$$

In the operating condition of this reactor, the oxygen is always at a high concentration level within the catalyst, so that the reaction mechanism of the absorbed NH_3 and gaseous NO can be described by taking into account only the concentration of NO. As proposed in (Inomata et al., 1980, 1982), the dilute gas conditions of NO and NH_3 allow one to use the Eley-Rideal mechanism of reaction. Then the mass flux of NO reacting on the catalyst surface is given by:

$$v_R = K_R C_{NO} \vartheta$$

This molar flux of NO is equal to a corresponding molar consumption term of absorbed NH_3.
Finally a mass conservation equation of NH_3 on the catalytic surface is to be included:

$$\Phi \frac{\partial \vartheta}{\partial t} = K_A C_{NH3}(1-\vartheta) - K_D \vartheta - K_R C_{NO} \vartheta \qquad (1)$$

The reactor is modeled as a single channel surrounded by the catalyst (Fig. 1). The diffusion of NH_3 and NO in the catalytic medium, taking also into account the already mentioned consumption and generation terms, is described by the following equations (Inomata et al., 1992):

$$\frac{\partial C_{NH3}}{\partial t} = \frac{\partial}{\partial x}\left(D_{NH3} \frac{\partial C_{NH3}}{\partial x} \right) - K_A C_{NH3}(1-\vartheta) - K_D \vartheta \qquad (2.a)$$

$$\frac{\partial C_{NO}}{\partial t} = \frac{\partial}{\partial x}\left(D_{NO} \frac{\partial C_{NO}}{\partial x} \right) - K_R C_{NO} \vartheta \qquad (2.b)$$

It is assumed that in the middle section of the catalytic wall the fluxes of NH_3 and NO are null, whereas at the boundary between the wall and the catalytic channel the fluxes are given by:

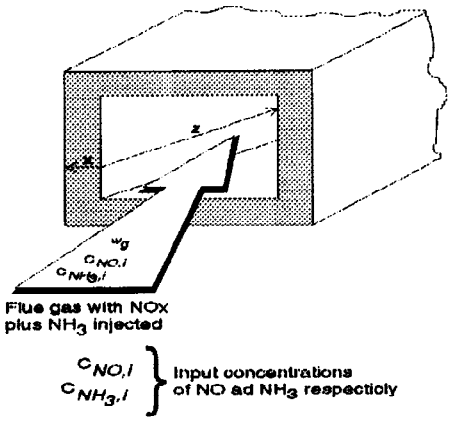

Fig.1. Geometry of the channel (□) and catalytic porous medium (▨).

$$-D_{NH3}\left(\frac{\partial C_{NH3}}{\partial x}\right)_{x=0} = h_{d,NH3}\left[C_{NH3,b}(z,t) - C_{NH3}(0,z,t)\right] \tag{3.a}$$

$$-D_{NO}\left(\frac{\partial C_{NO}}{\partial x}\right)_{x=0} = h_{d,NO}\left[C_{NO,b}(z,t) - C_{NO}(0,z,t)\right] \tag{3.b}$$

The mass conservation equations of NH_3 and NO in the channel are considered taking into account only the storage terms, the convective terms and their fluxes towards the catalyst; however the hydrodynamic variables (total mass flow rate and pressure) are assumed uniform with respect to z. This results in:

$$A_g \frac{\partial C_{NH3,b}}{\partial t} = -w_g \frac{\partial}{\partial z}\left(\frac{C_{NH3,b}}{\rho_g}\right) + h_{d,NH3}\omega\left[C_{NH3,b} - C_{NH3}(0,t)\right] \tag{4.a}$$

$$A_g \frac{\partial C_{NO,b}}{\partial t} = -w_g \frac{\partial}{\partial z}\left(\frac{C_{NO,b}}{\rho_g}\right) + h_{d,NO}\omega\left[C_{NO,b} - C_{NO}(0,t)\right] \tag{4.b}$$

All parameters appearing in eqs. (1)-(4) are determined via constitutive equations related to the following phenomena:

i) absorption and desorption of NH_3 and reaction of NO with absorbed NH_3 (Anderson et al., 1994);
ii) diffusion of NH_3 and NO in the porous catalyst (Tronconi et al., 1991);
iii) mass transfer of NO and NH_3 between the channel and the catalyst (neglecting any entrance effect in the channel) (Tronconi and Forzatti, 1992).

As for these constitutive equations, see also (Belli and Ferretti, 1995).

Obviously, the kinetic constants are strongly dependent on the catalyst temperature, so that a suitable one dimensional model of the temperature field in the channel and the surrounding catalyst has been developed. This model considers the storage of energy both in the channel and in the catalyst, the transfer of thermal energy between flue gases in the channel and the catalyst, and, of course, the convective term in the channel.

In conclusion the proposed model is constituted by a set of nonlinear partial differential equations given by (1)-(4) and by the energy equations in the catalyst and in the channel.

4. SIMULATION

The numerical method used in the solution of the partial differential equation is a finite difference method based on a suitable integration grid. More precisely, the reactor is cut into n_s slices along z, and each slice is divided into n_c cells along the x-direction. Integration along z gives a set of equations which can be solved in cascade according to the flow of flue gases along the channel. The equations of each slice are integrated along the x coordinate and with respect to time, using a fully implicit method. With this procedure the final (nonlinear) algebraic equations are solved with the Newton-Raphson method, using an efficient algorithm for the associated Jacobian matrix (see the details in Belli and Ferretti, 1995). The dimension of the integration grid has been optimized, with a thicker grid in proximity of the channel.

First, the dynamic behaviour of the reactor has been studied in a number of limit cases, related to different types of phenomena:

i) no NH_3 and only NO diffusion;
ii) no NO and NH_3 absorption;
iii) no injection of NO and NH_3 but the catalyst is initially loaded with absorbed NH_3 (desorption).

The simulation results (see Belli and Ferretti, 1995) show that the corresponding time scales range from fractions of second (i) to hundreds of seconds (ii) to thousands of seconds (iii).

The dynamics of the diffusion of NO and NH_3 could be neglected, but the concentration field related to diffusion is important in order to describe the absorption of NH_3 and the reaction of NO.

Furthermore, a set of simulations associated with typical operating conditions of the SCR reactor has been performed. The diagrams of NO concentration at the outlet in response to step variations of NH_3 and NO concentrations at the input are reported in Figs. 2 and 3, respectively. These responses have been obtained starting from three steady state conditions, that are typical in the operation of the SCR:

1) Boiler load: 100%, $C_{NO,i}$=100%, $C_{NH3,i}$=90%;
2) Boiler load: 70%, $C_{NO,i}$=70%, $C_{NH3,i}$=60%;
3) Boiler load: 40%, $C_{NO,i}$=40%, $C_{NH3,i}$=30%.

One can notice that the time constants are of the order of one hundred seconds and that the transients are only slightly dependent on the operation point. On the contrary, further simulations pointed out that the transients change if the steady state difference in the molar concentrations of NH_3 and NO at the inlet varies; in particular the dynamics becomes very slow if the steady state condition is reached with a molar ratio of NH_3 and NO close to 1, but this is an abnormal condition in SCR operation.

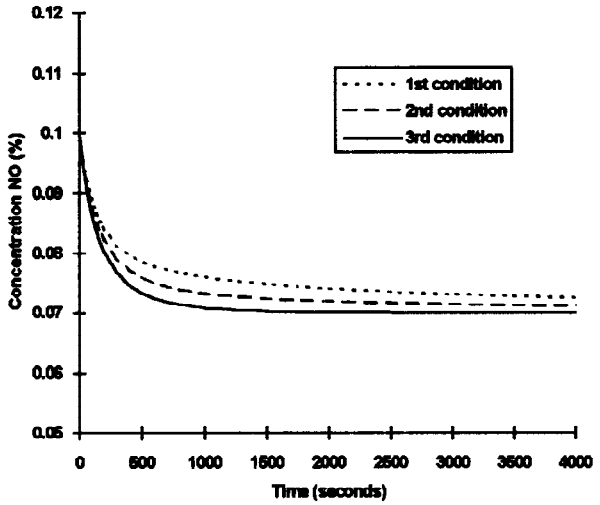

Fig.2. Time response to a step variation of $C_{NH3,i}$

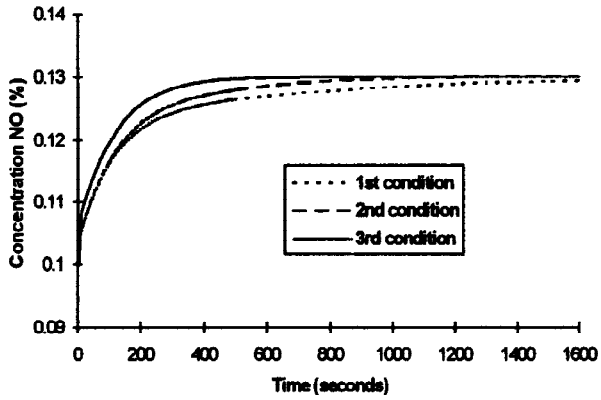

Fig.3. Time response to a step variation of $C_{NO,i}$

5. FROM NONLINEAR TO LINEAR

The model introduced above is a distributed parameter nonlinear one. A considerable simplification can be achieved by passing to an approximate model of ordinary differential equations (ODE), through the following steps:

- the set of PDE's originally introduced (Sect. 3) is replaced by a set of nonlinear ODE's as done for simulation purposes, in Sect. 4;
- these nonlinear ODE's are linearized;
- the storage terms related to diffusion and transport of NO and NH_3 are neglected due to their short time scale, (see Sect. 4);
- the storage terms of ammonia are retained as state variables and the order n of the system is equal to the number of cells in the catalyst (about 100÷200).

The resulting model is most useful to study the influence of the injected ammonia on the NO outlet concentration. The associated transfer function $F(s)$ has the following main features:

- the number of zeros is equal to $n-1$;
- the zeros ($-1/\tau_{zj}$) and the poles ($-1/\tau_{pi}$) are all negative and real;
- the gain is -1.

Interestingly enough, this transfer function exhibits a peculiar pole-zero cancellation effect, in the sense that many zeros and poles are so close to each other that a simplified transfer function of moderate order (n'=4÷5) provides a satisfactory fit.

6. CONTROL

6.1. General control scheme, constraints and disturbances

To the best knowledge of the authors, this is the first paper dealing with the problem of designing suitable control strategies for a SCR plant. Based on the experience of the Italian Electric Board (ENEL) a suitable control scheme is proposed including:

i) feedforward steady state compensation of the disturbance constituted by variations of the total NO mass flow rate in the flue gases at the reactor inlet;

ii) feedback action based on NO concentration at the reactor outlet;

iii) derivative compensation of fast disturbances of NO mass flow rate.

The level of NO concentration that can be reached at the reactor outlet is limited by the constraint on NH_3 concentration in the emitted flue gases (ammonia slip). In any condition, such a concentration must be lower than 5 ppm (Boer et al., 1990). However, the existing laws on pollutant emission compel values of NO concentration high enough to avoid excessive ammonia slip.

For safety reasons, the set point of NO concentration must be lower than the value of NO concentration imposed by the law, so as to accommodate for disturbances, always present in the operation of the plant.

Since the SCR is operated above the control load of the plant, it can be assumed that the main disturbances of NO in the flue gases are due to load variation.

Load variations due to the operator (load following or economic dispatching) can be very large but are generally slow. Load variations due to secondary frequency control (load frequency control) are generally slow and with small amplitude (±5%). Load variations due to primary frequency control can be both large and fast, but the amplitude of the variation is in relation with the electric network size. Of course, in a large electric network the probability of a fast and large variation is very rare (isolated grid).

6.2. Model of the overall process for control design

The design of the SCR control system is based on the process linearization determined in Section 5. In particular, the transfer function $F(s)$ from the inlet NH_3 concentration $C_{NH3,i}$ to the outlet NO concentration $C_{NO,o}$ has been approximated as

$$F(s) \cong \frac{-1}{1+s\tau_p}$$

with τ_p=80÷115 s, depending on steady conditions.
Moreover, the relationship between $C_{NH3,i}$ and w_{NH3} is given by:

$$C_{NH3,i}=K_1 w_{NH3}/w_g$$

where K_1 is a suitable constant.
As for the transfer function from the flue-gas mass flow-rate to the outlet NO concentration, it can be approximated by the lead function:

$$F_w(s) = k_w \frac{s\tau_w}{1+s\tau_w}$$

with τ_w roughly equal to τ_p
The model has been completed with a suitable description of the actuators for ammonia injection and the sensors for measurements of NO concentration. Particular attention must be deserved to the delay τ_d in the NO transport from the flue output to the measurement site. This delay usually ranges from 5 to 10 seconds. In some retrofitted plant, due to space constraints, this delay can be much higher.

6.3. Control system

The structure of the control system has been suggested by the considerations made in Sections 6.1-6.2. In Fig. 4 the diagram of the process with the control system is shown (hatted symbols denote measurements while the overbar indicates reference values).
The required value of NH_3 concentration in the stream entering the SCR is obtained as the sum of the following signals:

- u_1 is the feedforward action based on the desired value of NO concentration at the outlet and the actual value of NO concentration at the inlet of the SCR;
- u_2 is the feedback action based on the measured value of NO concentration at the outlet;
- u_3 is a dynamic compensation based on the required (by the turbine-boiler control system) value of air mass flow rate $\overline{w}_g$, which is almost equal to the actual flue gas mass flow rate w_g.

The last compensation is useful especially if there are fast and large variations of load of flue gas mass flow rate. The derivative action compensates via the required NH_3 concentration the derivative action of w_g on the outlet NO concentration.

6.4. Simulation results

The control system has been tested against the load disturbances previously discussed. It appears that small amplitude disturbances are effectively rejected. Then the control system has been tested against:
i) a ramp with a maximum rate of 5% per minute and load variation from the control load to the maximum load;
ii) a ramp with rate of 90% per minute, with a load variation of 15% of the maximum load (isolated grid or grid of small size).
The performance of the control system has been evaluated by looking at the peak of NO concentration at the outlet, which in normal operating conditions must not exceed an admissible level. Of course, the chosen value of the set-point is a compromise between the cost of NH_3 and the possible overcoming of the admissible limits in the presence of disturbances. The diagrams of Figs. 5-6 show the results of the simulation with disturbances i) and ii) and the control system with and without the derivative action.

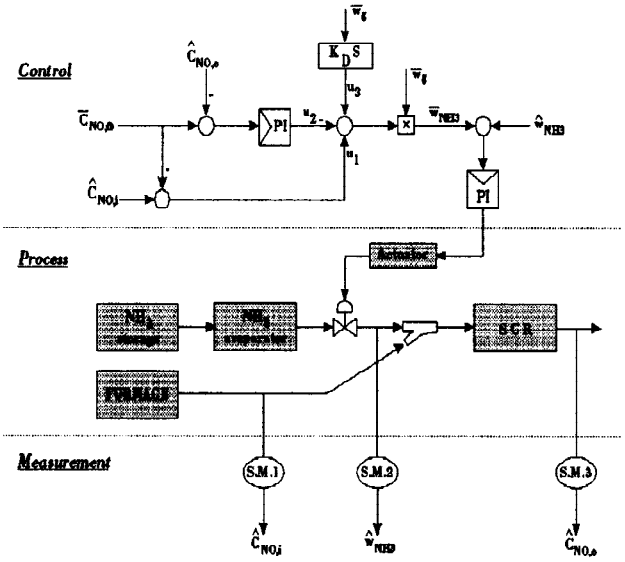

Fig.4. The proposed control scheme

The derivative action is not essential for the disturbance of i) type; however also in this case its use is advantageous because the set-point can be set at a higher level.
It is possible to show that only limited improvements can be achieved by the use of gain scheduling of the main PI regulator, because the dynamics of the system is lightly dependent on the load steady state value.
As the time delay τ_d becomes higher, the performance of the control system becomes poorer. In that case, it would be necessary to reduce the value of the NO set point in order to meet the requirements of the NO concentration at the outlet, with a consequent increase in the ammonia consumption. Then, a more sophisticated control system has been designed using the Smith predictor to compensate for the dead time delay.
A large value of the dead time delay (τ_d=30 s) has been considered in order to show possible improvements attainable by the use of the Smith predictor. The simulation results pointed out a slight improvement, perhaps not paying the increase of complexity and the decrease of robustness of this structure.

7. CONCLUSIONS

In this work, the dynamics of a SCR reactor has been investigated in some depth. Eventually, the analysis has led to a reduced order linear model that closely captures the behaviour of the outlet NO concentration in response to the control variable (inlet NH_3 concentration) and to the most significant process disturbances. Based on this model, a closed-loop control scheme has been proposed in order to keep the outlet concentrations of NO and NH_3 below prescribed thresholds. The simulation tests point out that both the feedforward static compensation of the NO content in the flue gas and the derivative compensation of flow rate disturbances are quite effective.

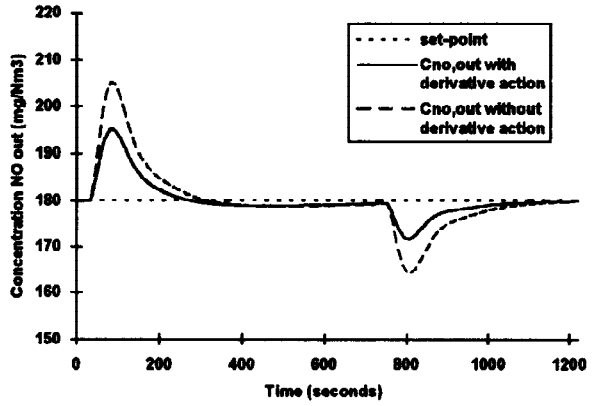

Fig.5. Time response to disturbance i)

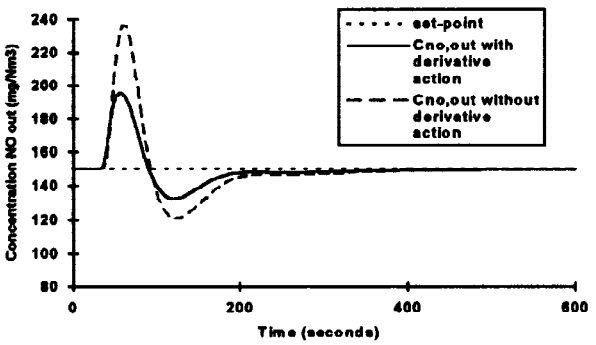

Fig.6. Time response to disturbance ii)

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