Modeling of NOx Selective Catalytic Reduction in Pulverised Coal Power Plants

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EDF has equipped its coal-fired power plants with nitrogen oxide emissions (NO_x) reduction processes in order to ensure the regulatory pollutant emissions.

A common control technique for limiting NO_x emissions is the Selective Catalytic Reduction (SCR) of NO_x by NH_3 in presence of a catalyst. This process is the most developed and most widely used for flue gas treatment for the control of NO_x emissions due to its efficiency, selectivity and economics. .

Nevertheless, SCR management has to integrate some constraints such as deactivation by poisoning or ash-plugging that limits the lifetime of catalysts.

EDF R&D has therefore developed an in-house SCR model describing, on one hand, the physicochemical processes occurring in the monolithic reactors and on the other hand, the catalyst deactivation due to poisoning. This modeling is used as a basis for optimizing the control and maintenance of SCR processes in EDF's coal-fired power plants. This paper provides results of NOx emission and ammonia slip which are compared to power plant measurements.

1. Introduction

Many flue gas denitrification techniques exist on the market. They are divided into three main categories:
- primary destruction by staging of air, fuel or re-combustion (reburning);
- the selective non-catalytic reduction (SNCR);
- the selective catalytic reduction (SCR).

For existing boilers, the first method is very capitalistic since it requires the replacement of burners and the modification of their position in the boiler. The second method, SNCR, is suitable when NOx are not in high content in flue gas. For high NOx contents, high rates of reduction are required which makes SCR the most suitable and simplest option to implement (Wendt et al. (2001), Dvořák et al. (2010)).

In order to meet European regulations in 2015 on atmospheric emissions of pollutants, EDF has installed denitrification and desulphurization systems on its existing power plants. An economic comparison of the processes, leaded EDF to equip two of its power stations (Le Havre and Cordemais) with SCR denitrification. It corresponds to the reduction of nitrogen oxides (NOx) by ammonia (NH_3) in presence of a catalyst.

This paper presents an overview of SCR principle and the approach followed for its modeling. This paper presents the main results of the model that are validated with

industrial data collected during overall tests on EDF's coal-fired power stations. The modeling of catalyst ageing is also considered.

2. SCR modeling and model validation

The catalytic materials used can be made up of various natures such as titanium oxides, zeolites or activated carbon. EDF chose to equip its units with SCR catalyst modules made up of metallic oxides TiO_2 (substrate) which includes active sites of V_2O_5 in its porous structure. WO_3 is used as a dope to promote the reactions between NOx and NH_3. The objectives of the model are to predict the NOx emission and to find out an optimal strategy in aged SCR monoliths replacement.

2.1 Detailed chemical scheme

The description of the chemical reactions is developed through elaborated kinetic diagrams which detail the catalyst elementary reactions. This process of reaction of vanadium is detailed by Topsoe et al. (1995) in Figure 1. The ammonia (NH_3) is fixed on Brönsted acid sites of the type V^{5+}-OH. These sites are activated by adjacent groups of the type V^{5+}=O. NH_3 fixing is coupled with the partial or total transfer of an atom of hydrogen of NH_3 which reduces the sites V^{5+}-OH into V^{4+}-OH sites. Activated NH_3 then reacts with a molecule of NO. The resulting intermediary V^{5+}-O-... $+H_3N$-N=O quickly breaks up by releasing N_2 and H_2O. The key stage is the existence of an intermediate species which break up selectively into nitrogen and water molecules. This model is precise enough to allow a fine description of the catalytic mechanisms, but it has only been established today in laboratory conditions which are different from our industrial case.
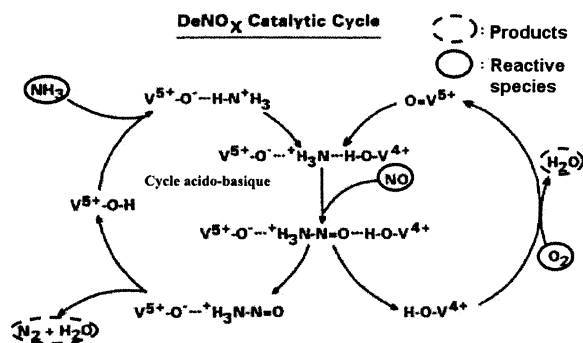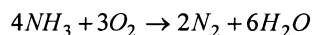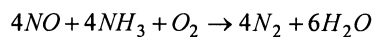

Figure 1: Detailed chemical mechanism, Topsoe et al. (1995).
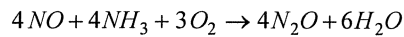
2.2 Reduced chemical scheme

The adopted approach is a reduced chemical scheme considering the following reactions:

$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$ Destruction of NH_3 thanks to O_2

$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$ NO destruction (global reaction)

$$4NO + 4NH_3 + 3O_2 \rightarrow 4N_2O + 6H_2O \qquad \text{N}_2\text{O destruction}$$

$$3N_2O + 2NH_3 \rightarrow 4N_2 + 3H_2O \qquad \text{N}_2\text{O destruction}$$

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \qquad \text{NO formation}$$
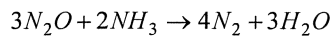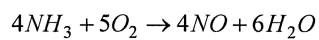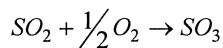
$$SO_2 + \frac{1}{2}O_2 \rightarrow SO_3 \qquad \text{SO}_2 \text{ oxidation into SO}_3$$

Several assumptions were made in order to solve the problem:

1. The main assumption is the flue gas homogeneity at the inlet of the SCR reactor. This is expressed by:

    a) a uniform distribution of flow: catalyst channels are all supposed to receive the same flow rate, so no clogging nor fouling with dust are supposed to occur in some catalyst channels;

    b) an homogeneous concentration of species such as NO and NH_3 on the catalyst section,

    c) a uniform flue gas temperature on the catalytic section and the process is supposed to be isothermal. The last assumption is correct even if the global chemical process is exothermic: the concentrations of species involved in the reactions are low enough to not to induce a significant temperature rise.

2. NO_2 reduction by NH_3 is not taken into account (NO_2 represents very few percents of the total NOx).

3. Monoliths and flue gas are at the same temperature.

4. Each layer is made up of the same type of catalyst.
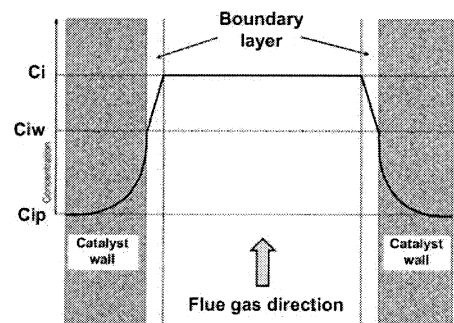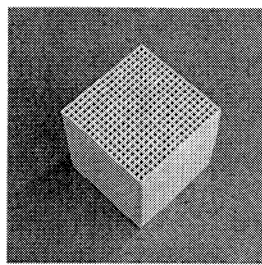
2.3 Physical model

Figure 2: Examples of catalyst monolith (left) and monolith elementary channel (right)

Each catalyst channel is modeled as a plug flow reactor with limitation in transversal diffusion. SCR reactions occur inside the porous volume of the catalyst channel, which is limited by the walls, and not only by their total surface. Thus, to estimate the conversion rate of the chemical species, it is necessary to take into account the following phenomena (see Figure 2, right):

- External diffusion limitations, i.e. the presence of a boundary layer in gas phase side.
- Internal diffusion limitations, i.e. the migration of the species inside the porous media.

External transfer: In order to model the external transfer inside the catalyst channel, the equation of Beeckman and Hegedus (1991) giving the evolution of the species concentration along the channel is used:

$$-u\frac{dC_i}{dx} = k_{m,i}A_e\left(C_i - C_{iw}\right) \tag{1}$$

Where C_i is the bulk concentration of specie i at position x of the plug flow reactor, u is the flow velocity in the catalyst channel, C_{iw} is the concentration of the specie i at the wall surface of the reactor, A_e is the total area of the catalyst channel inlet. The mass transfer coefficient $k_{m,i}$ is given by Hawthorn correlation (Wendt et al., 2001):

$$k_{m,i} = \frac{D_i \cdot Sh}{d_h}\left(1 + 0,095\frac{d_h}{l}Re \cdot Sc_i\right)^{0,45} \tag{2}$$

Where D_i is the diffusion coefficient of specie i and d_h and l are respectively the hydraulic diameter and the length of the catalyst channel. Re, Sh and Sc_i are respectively the Reynlods, Sherwood and Schmidt numbers.

Internal transfer: The coupling between chemical reactions and internal diffusion within catalyst can be expressed by the equation given by Wendt et al. (2001):

$$D_{e,i}\frac{d^2C_i}{dy^2} = S_{cata}R_{s,i} \tag{3}$$

Where $D_{e,i}$ is the diffusion coefficient of specie i inside the catalyst material. y is the wall normal distance in porous media, C_i is the specie concentration in porous media of catalyst reactor; S_{cata} is the material surface of catalyst channel. $R_{s,i}$ is the chemical source term of specie i given by reduced chemical scheme given in paragraph 2.2.

The boundary condition at the gas / solid interface is:

$$k_{m,i}\left(C_i - C_{iw}\right) = D_{e,i}\left(\frac{dC_i}{dy}\right)_{wall} \tag{4}$$

Concerning the catalyst ageing, the different factors causing this phenomenon are:

Poisoning: it is the principal cause of the loss of catalyst activity, and it is mainly a chemical mechanism. The substances present in the coal used in the boilers, such as alkaline, alkaline-earth ones, arsenic, chlorine, fluorine or mercury, are found in the flue gas. They fix on the active sites of catalyst which limits the diffusion of the reagents within the pores of catalyst, but they also limit the reactions of denitrification. In order to mitigate this deactivation, the active phase or the support of catalyst is improved. For example, the addition of MoO_3 on catalyst makes it possible to fix As_2O_3 more easily than V_2O_5 and thus leaves free the active sites.

Sintering: it is the modification of the crystalline structure of catalyst, caused by too high temperatures.

Clogging: the clogging or the fouling of the channels by ash, oxides of calcium or other particles present in the flue gas pleads to mechanical deactivations of catalyst. The substances present in the flue gas will come to fix on the catalyst surface and to block the active sites and the pores. The fine particles tend to be fixed on the walls, in particular when they have a rough surface, while the large particles can have a cleaning effect. The deposit of dust is done mainly at the entry and the exit of the channels, in zones of recirculation of the flue gas.

2.4 Results

For confidentiality reasons, this paper only shows results expressed relatively to industrial data at the exit of the catalyst (Figure 3).

Among the three analyzed cases, the quantity of output NOx is perfectly modeled in one case but appeared to be underestimated by the model in the two other cases. Indeed, the current model of the SCR is in a new state of development, without clogging (nor poisoning), whereas measurements were carried out after a few operating hours of the SCR. The current model is thus too optimistic compared to the actual values.

Indeed, the installations of SCR being still too recent, it is currently not possible to quantify the rate of plugging nor of fouling of the channels of each layer in a dynamic way. The literature makes it possible to note that it can reach up to 20%.
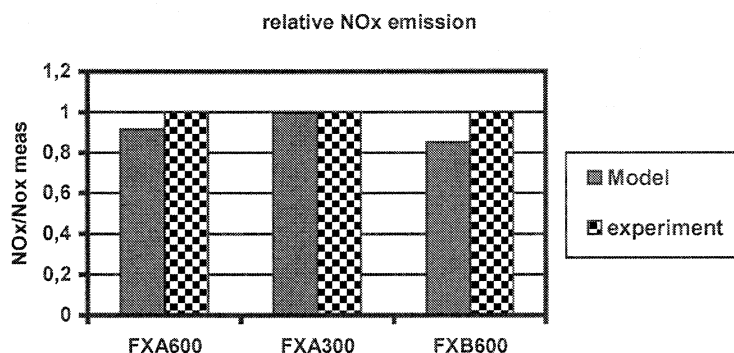

Figure 3: Comparison of model results and power plant measurements for output NOx (measurement values are set to unity).

To predict catalyst deactivation due to ageing, EDF strategy for catalyst layers management was followed. This strategy consists in running initially the SCR installation with two catalyst layers adding a third layer after several thousands of hours and then changing periodically the most deactivated layers. An EDF power station of 600 MW in 2007 is taken as a reference. The Figure 4 shows a satisfying modeling of ageing since the NH_3 slip increases with time e.g. with deactivation. The periodical reductions of NH_3 slip are due to the replacement of deactivated layers by regenerated or new ones.
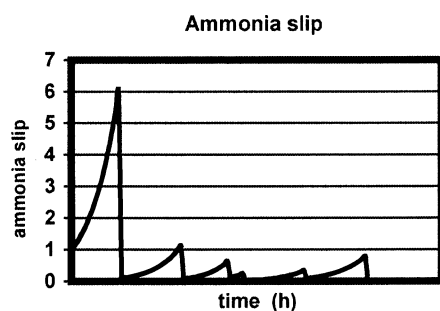
Figure 4: Ammonia slip over time relatively to operation starting time value of NH₃.

The assumption of flue gas homogeneity (velocity, concentration and temperature) should have an impact on NH_3 slip prediction. These phenomena are taken into account in ongoing work.

3. Conclusion

The purpose of this modeling is to be integrated in a complete simulation of the advanced coal-fired power plant, starting from combustion until desulphurization and eventual CO_2 capture, while passing by the SCR and the dust extractor.

The model gave results close to reality, for a new catalyst. More precise results could be obtained with data input of more complete and more precise SCR. However, the model of ageing could be improved when a law of clogging of the channels can be given thanks to an experience feedback, and when additional tests make it possible to obtain realistic coefficients of deactivation. Moreover, the model was used so as to consider the poisons and their action in a bulk way on the unit of the reactions. Thus, more pushed characterization of catalysts would make it possible to uncouple the physical phenomena from poisoning related to each reagent and according to poisons present in the flue gas.

References

Beeckman J.W. and Hegedus L.L., 1991, Design of Monolith Catalysts for Power Plant NOx Emissions, Ind. Eng. Chem. Res. 30, 969-978.

Dvořák R., Chlápek P., Hanák L., Jedlička F. and Stehlík P., 2010, Catalytic Filtration of Flue Gases Polluted by NOx, Chemical Engineering Transactions, 21, 799-804 DOI: 10.3303/CET1021134.

Topsoe N.-Y., Dumesic J.H and. Topsoe H., 1995, Vanadia/Titania Catalysts for Selective Catalytic Reduction of Nitric Oxide by Ammonia, J. of Catalysis, Vol. 151, 241-252.

Wendt J., Linak W., Groff P. and Srivastava R., 2001, Hybrid SNCR-SCR Technologies for NOx Control: Modelling and Experiment, AIChe Journal vol. 47, 11: 2603-2617.