Modeling of NO_x reduction from exhaust gas by SCR

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Abstract:

Due to the introduction in 2016 the new standards for emissions of nitrogen oxides (NO_x), examine the possibility of using the technology of selective catalytic reduction (SCR) as a supplement to the primary methods. The use of a catalyst as an additional module purifying exhaust gas from NO_x allows prolonged operation time of coal-fired plants after 2016.
Reduction of nitrogen oxides occurs by injecting reagent (ammonia, ammonia water) in the flue gas duct in front of the catalyst. NO_x conversion is realized on catalytic surface inside SCR reactor in lower temperature than in selective non-catalytic reduction.
This paper is based on numerical model of NOx reduction from the exhaust gas by the SCR system in coal-fired power plant. The intrinsic surface of the channels of catalyst (length of catalytic surface: 0.35 m, 0.7 m and 1.05 m) was modeled using Ansys Fluent code. Different models of turbulence was used to calculate flow of mixture of flue gases and ammonia (*k-ε, k-ω, SST k-ω* and *transition SST*). Was examined which model is the best for modeling SCR catalyst in compare to measurements made in coal-fired power plant.

Keywords:

CFD model, De-NO_x, selective catalytic reduction, SCR

1. Introduction

1.1. Emission conditions for coal power plants

The coal combustion plants contribute to the industrial emission of gaseous pollutants (such as SO_2, NO_x), particulate pollutants and waste water into the environment. Due to the care of the environment and public health, EU introduced standards to limit the emissions of substances detrimental. The content of nitrogen oxides (NO_x) and sulfur dioxide are determined by the Directives and national regulations on environmental protection. The most important document in the next few years is the Directive 2010/75/EU (IED) of the European Parliament and of the Council of 24 November 2010. Previously, industrial emissions was controlled by several separate directives, including LCP Directive (on limitation of emissions from large combustion plants), IPPC (integrated pollution prevention and control) and the Waste Incineration Directive and reduce emissions of volatile organic compounds.[1][2]

The Polish energy sector is required to comply with emission levels, which have been shown in the Table 1, consistent with the current regulation of the Minister of the Environment with the installation of flue gas cleaning [2]. In the case of NO_x reduction methods are used related to conducting primary fuel combustion process in a way that minimizes the formation of these pollutants (combustion in fluidized bed boilers, low-emission burners, fuel and air staging systems – OFA and SOFA). However, from 1 January 2016 the level of nitrogen oxide emissions will be further reduce, which may involve the need to retrofit the coal blocks (inter alia boilers: OP-650, AP-1650, BB-1150) including the use of secondary NO_x reduction methods, especially the selective catalytic reduction (SCR).

Table 1. NO_x emission limits for energy facilities burning hard coal and lignite in Poland [2]

Nominal thermal input [MW]	Emission limits of NO_x [mg/m^3_n]	
	New power plants	Existing installations
50 ÷ 100	300	300
50 ÷ 100 (pulverized lignite-fired blocks)	400	450
100 ÷ 300	200	200
> 300	150	200
> 300 (pulverized lignite-fired blocks)	200	200

1.2. Selective catalytic reduction

Applying the SCR system reduces the activation energy for the process of nitrogen oxides reduction involving reagent (NH_3, NH_4OH). The catalyst installation is usually constructed with a monolith honeycomb, a grid of elongated channels or stainless steel plates arranged parallel to each other. Placing on the porous surface of catalyzing elements (vanadium, tungsten-vanadium or platinum) decreases demanded temperature of the reduction process to value t = 300 ÷ 400°C. The reagent injection occurs in advance in the flue gases duct, which is provided with a series of turning vanes and straightener. This allows to achieve the optimal distribution of NO_x and NH_3 molecules in the exhaust stream in front of the SCR reactor. Reactions of reduction occur in SCR reactor according to equations (1÷4) [3,4]:

$$6NO + 4NH_3 \rightarrow 5N_2 + 6H_2O \qquad \Delta H = -300{,}8 \text{ kJ/mol NO} \qquad (1)$$

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \qquad \Delta H = -406{,}1 \text{ kJ/mol NO} \qquad (2)$$

$$6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O \qquad \Delta H = -453{,}0 \text{ kJ/mol } NO_2 \qquad (3)$$

$$2NO_2 + 4NH_3 + O_2 \rightarrow 3N_2 + 6H_2O \qquad \Delta H = -663{,}5 \text{ kJ/mol } NO_2 \qquad (4)$$

ΔH – negative value indicates the exothermic process

As a result of the work of selective catalytic reduction, receives a much reduced level of nitrogen oxides and the formation of neutral molecules for the environment – N_2 and H_2O. This process is considered as the Best Available Technology - BAT, which is one of the best techniques for cleaning the flue gases, without waste. In order to maintain an optimal level of NO_x conversion, in presence of NH_3, is the provision of a suitable temperature and injection of the appropriate amount of reagent into the exhaust stream in front of catalyst. Otherwise there is the possibility of slip throughout the SCR reactor of unreacted ammonia with the flue gases. [5,6]

2. Numerical model of SCR reactor

The purpose of CFD simulations here is to determine the effect of the catalytic-tubes length and various numbers of catalytic layers (0.35 m = 1 layer, 2x0.35 m = 2 layers, 3x0.35 m = 3 layers) on NO_x reduction. Similar modeling was presented in [16], where was presented the influence of another dimension of tubes of SCR-DeNO_x reactor (pitch and wall thickness).

Additionally were taken into account the different models describing flow inside SCR-tubes. The numerical calculations were carried out by several models of phenomena transport, including the chemical reactions. The use of non-laminar models is based on the value of the Reynolds number, which is greater than 2300. For the parameters listed in Table 2 and catalytic channel's diameter of 8.2 mm the Reynolds number equals 3718, therefore, this flow can be define as transition between laminar and turbulent. For calculations a few turbulence models were chosen: *k-ε, k-ω, SST k-ω* and *transition SST* for comparison of the results. The modeling of the reaction of nitrogen oxide

reduction was based on Laminar Finite-Rate with enabled options: diffusion energy source, full multicomponent diffusion, thermal diffusion and for wall surface reaction – Heat of surface. [7,8]

Table 2. Boundary conditions for flue gases at inlet of modelled channels [6]

Temperature [K]	Velocity of exhaust gas [m/s]	Density of exhaust gas [kg/m^3]	Mass fraction in flue gases [%]					
			N_2	O_2	CO_2	H_2O	NO	NH_3
602	13	0.6	71.366	3.6	21	4	0.022	0.012

2.1. Models of turbulence flow

The construction of a mathematical model for the selective catalytic reduction gives the opportunity to perform numerical simulation of flow and chemical reactions occurring on the inner walls of channels in catalyst. Mapping of the flue gas mixture with a reagent, which flows through the SCR's channel, entails the need to use the alternative models requiring computational grids with fewer nodes. The addition of modeling the chemical reactions, taking place on the intrinsic walls of the channel, requires the use of significant computing power.

The design of SCR reactor was based on the three-dimensional description of the flow of the mixture of flue gases with ammonia and kinetic chemical reaction of the NO_x reduction occurring in the catalyst in accordance with equation (2). Transport phenomena in 3D is obtained from the solution of equations of momentum conservation and energy, determined composition of the gas mixture and the mass balance. To speed up calculations and reduce the consumption of resources was decided to extract a single channel of catalyst to modeling NO_x reduction process.

Ansys Fluent was used as modeling environment, which allows the use of several variants of computational of turbulence, while taking account of the exhaust gas flow and chemical reactions on the inner walls of the reactor. The most common approach is to solve Navier-Stokes equations averaged in time (RANS equations – Reynolds-Averaged Navier-Stokes). Navier-Stokes equation is nonlinear, therefore, each averaging process produces the additional unknowns that need to be in some way linked to average values, and at this stage there appear the turbulence modeling.[7]

The proposal to take into account the flow disturbances consisted in the introduction of two new variables, i.e.: turbulent kinetic energy (k) and energy dissipation (ε). These variables submit to the turbulent viscosity (μ_t), whose task is to include the increase in viscosity due to additional flow fluctuations. This model of transport was used in [17] to modeling turbulent flow in the SCR-DeNO_x system installed in flue gas duct of 350 MW coal-fired boiler. The transport equations for the model *Realizable k-ε* (standard wall function used in simulations) is described by [7]:

$$\frac{\partial}{\partial t}(\rho k)+\frac{\partial}{\partial x_j}\left(\rho k u_j\right)=\frac{\partial}{\partial x_j}\left[\left(\mu+\frac{\mu_t}{\sigma_k}\right)\frac{\partial k}{\partial x_j}\right]+G_k+G_b-\rho\varepsilon-Y_M+S_k$$

and

$$\frac{\partial}{\partial t}(\rho\varepsilon)+\frac{\partial}{\partial x_j}\left(\rho\varepsilon u_j\right) =\frac{\partial}{\partial x_j}\left[\left(\mu+\frac{\mu_t}{\sigma_\varepsilon}\right)\frac{\partial \varepsilon}{\partial x_j}\right] +\rho C_1 S\varepsilon-\rho C_2\frac{\varepsilon^2}{k+\sqrt{\nu\varepsilon}}+C_{1\varepsilon}\frac{\varepsilon}{k}C_{3\varepsilon}G_b+S_\varepsilon$$

where

$$C_1=\max\left[0.43,\frac{\eta}{\eta+5}\right],\ \eta=S\frac{k}{\varepsilon},\ S=\sqrt{2S_{ij}S_{ij}}$$

The turbulence model *k-ω*, which is based on the Wilcox's *k-ω* model, takes into account the effect of low Reynolds number, compressibility and expansion of the flow stress. However, the weakness of this model is the sensitivity in achieved solutions for parameter *k* in the outer layers of the shear, therefore is not widely used model. For this modeling were enabled options: shear flow corrections and production limiter. Excepting the additional of turbulence kinetic energy equation *k*, model takes into account the frequency of turbulence (*ω*) [7]:

$$\frac{\partial}{\partial t}(\rho k)+\frac{\partial}{\partial x_i}(\rho k u_i)=\frac{\partial}{\partial x_j}\left(\Gamma_k\frac{\partial k}{\partial x_j}\right)+G_k-Y_k+S_k$$

$$\frac{\partial}{\partial t}(\rho \omega)+\frac{\partial}{\partial x_i}(\rho \omega u_i)=\frac{\partial}{\partial x_j}\left(\Gamma_\omega\frac{\partial \omega}{\partial x_j}\right)+G_\omega-Y_\omega+S_\omega$$

The turbulence model *SST k-ω* was created after the earlier analysis of models *k-ε* and *k-ω*. This was done because it was observed that the first model is better in simulation of the turbulence in the free flow and near the shear layers. In addition, has a low sensitivity for the value of the inlet conditions characterized by turbulence. This feature is important because in practice calculations of these values are given only approximate. The *k-ω* model is doing well with modeling of turbulent flow, however, in contrast to the *k-ε* model, is sensitive to the values which describe the turbulence. It was decided to combine both models, thus creating the *SST k-ω*. The use of this combination allowed to deal with the difficulties of solving problems where the high pressure gradients exist (*k-ε*), and where the flows with significant turbulence intensity occur (*k-ω*). The option production limiter was enabled for this modeling. The transport equations for this model look like [7]:

$$\frac{\partial}{\partial t}(\rho k)+\frac{\partial}{\partial x_i}(\rho k u_i)=\frac{\partial}{\partial x_j}\left(\Gamma_k\frac{\partial k}{\partial x_j}\right)+G_k-Y_k+S_k$$

$$\frac{\partial}{\partial t}(\rho \omega)+\frac{\partial}{\partial x_j}\left(\rho \omega u_j\right)=\frac{\partial}{\partial x_j}\left(\Gamma_\omega\frac{\partial \omega}{\partial x_j}\right)+G_\omega-Y_\omega+D_\omega+S_\omega$$

There was another model of turbulence used to calculation. The *Transition SST* model is based on a combination of *SST k-ω* model with two more equations. Considered are equations for intermittency and for the transition onset criteria, in respect of momentum-thickness Reynolds number. The empirical correlation of Langtry and Menter, used in Ansys Fluent, has been performed to cover standard by-pass transition as well as fluid in the environment with low turbulence. In this simulation were used options: production Kato-Launder and production limiter. The transport equation for this model and defined transition sources are below [7]:

$$\frac{\partial(\rho\gamma)}{\partial t}+\frac{\partial\left(\rho U_j\gamma\right)}{\partial x_j}=P_{\gamma 1}-E_{\gamma 1}+P_{\gamma 2}-E_{\gamma 2}+\frac{\partial}{\partial x_j}\left[\left(\mu+\frac{\mu_t}{\sigma_\gamma}\right)\frac{\partial\gamma}{\partial x_j}\right]$$

$$\begin{aligned} P_{\gamma 1} &= C_{a1}F_{length}\rho S[\gamma F_{onset}]^{c_{\gamma 3}} \\ E_{\gamma 1} &= C_{e1}P_{\gamma 1}\gamma \end{aligned}$$

2.2. Model of chemical reaction

Laminar Finite-Rate is based on the calculation of the rate of chemical reaction kinetics using the Arrhenius equation and assumptions of the average concentration of the substance and the average temperature in the each cell of model. The model of kinetic reaction for NO_x reduction by ammonia over V_2O_5/TiO_2 catalysts were presented in many papers [e.g. 9,12,13,14,15].

The chemical reaction site are the inner walls in modeled channel, and therefore, it was important to apply the appropriate computational grid density in the boundary layer in place of the reduction reaction. The Arrhenius equation is the formula which takes into account the effect of temperature on the reaction rate of the process. To enter the model must be known the kinetic factors of chemical reaction such as activation energy E_r and pre-exponent factor A_r that determine the rate of reduction of nitrogen oxides $k_{f,r}$ [7,9]:

$$k_{f,r}=A_r T^{\beta_r} e^{-E_r/RT}$$

Where: A_r - pre-exponent factor, T - temperature, E_r - activation energy, R - universal gas constant = 8314 J/kmol-K, β_r - temperature exponent.

For the purposes of this analysis, the reaction (2) was taken into account, which is one of the most important for the reduction in SCR. Was adopted the vanadium (V) oxide catalyst based on TiO_2, which is quite common in commercial installations. This catalyst was used to analyze the reduction reaction of nitrogen oxides by Wong and Nobe [10], while the kinetic parameters were collected and presented by Marangozis [11]. For the catalyst with 10% coverage of V_2O_5/TiO_2 the reaction rate were determined for NH_3=0, NO=1, and O_2=0.25. Modeling the NO_x reduction in the presence of said catalyst lowers the activation energy to E_r=4.4673e+07 with the pre-exponent factor A_r=150. [11] For all simulations the fly ash deposition and its effect on the flow field were neglected.

2.3. Geometrical model

Commercial SCR reactors for coal-fired power plants are usually composed of several modules arranged in layers. The module consists of a monolith such as honeycomb-type with elongated channels or ribbed plates, made of sheet steel. The selection of suitably small dimensions of the channels increases the surface area of the catalyst. However, when choosing the size of the channels should be guided by the type of burned fuel. If the unit used for combustion the gas or liquid fuel, can be used channels having a diameter less than 6 mm. Combustion of solid fuels is connected with emission of fly ash, therefore in order to prevent clogging of the catalytic-channels, in front of the SCR reactor is necessary to use an electrostatic filters or diameter of the tubes more than 7 mm. Consequently the optimal size of channels depends on the type of power plant. [6,8]

During the construction of a numerical model, were taken into account previous analyzes reduction of nitrogen oxides from flue gas using a catalyst [8], therefore separated only one channel with the diameter of 8.2 mm, which is the one of many channels composed on the SCR reactor. Prepared several variants of channels reducing NO, namely a single channels with catalytic lengths: 0.35 m, 0.7 m and 1.05 m, as well as models which composed of two and three consecutive channels with a length of 0.35 m each. The modeling results for multilayer catalyst systems are compared with single-layer models with the same total length of catalyst channels. The geometric model, before and after the catalytic-layer, has got the channel with length 0.30 m without the process of NO reduction. In meshing, for near-wall layer, was used inflation method with smooth transition, which leading to low values of parameter Y+ in the boundary layer.

3. Selected results of numerical modeling

After the calculations in the Ansys Fluent, analyzed the impact of the chosen variant of turbulence model on the process of reduction of nitrogen oxide which occurs on the inner walls of the channel inside SCR. The same the composition of flue gas and its parameters were previously analyzed by

modeling Ebsilon®Professional NO reduction in [6,8], where there was a slight increase of temperature flue gases at outlet of the SCR reactor (increase about 3-4 K). Similar conditions was included in modeling of this process in Ansys. The level of NO_x reduction was also alike in [6].

3.1. NO reduction along modeled channels

A change in a mass fraction of nitrogen oxide in cross section along the modeled channel was presented in the Fig. 1-5. There we can see the channels with 350/700/1050 mm length of catalyst surface and channels with 2 and 3 catalyst layers, each 350 mm. In variants with 2 and 3 layers, between them there is a non-catalytic channel with 300 mm length. Only the *k-ε* model was problem with calculate NO reduction.

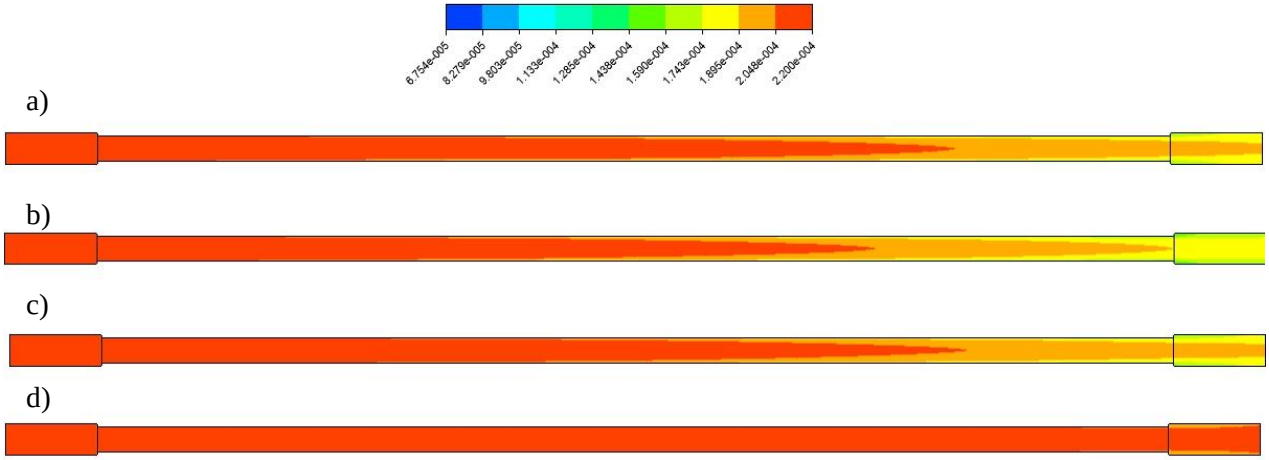

Fig. 1. Visualization of the NO mass fraction in cross section along the channel (350 mm) for: a) SST, b) SST k-ω, c) k-ω, d) k-ε

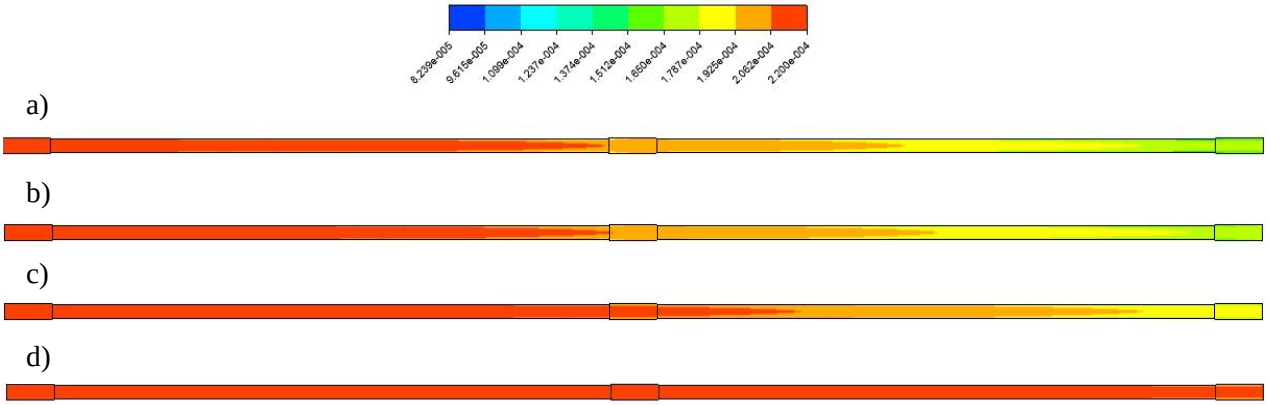

Fig. 2. Visualization of the NO mass fraction in cross section along the channel (2 layers x 350 mm) for: a) SST, b) SST k-ω, c) k-ω, d) k-ε

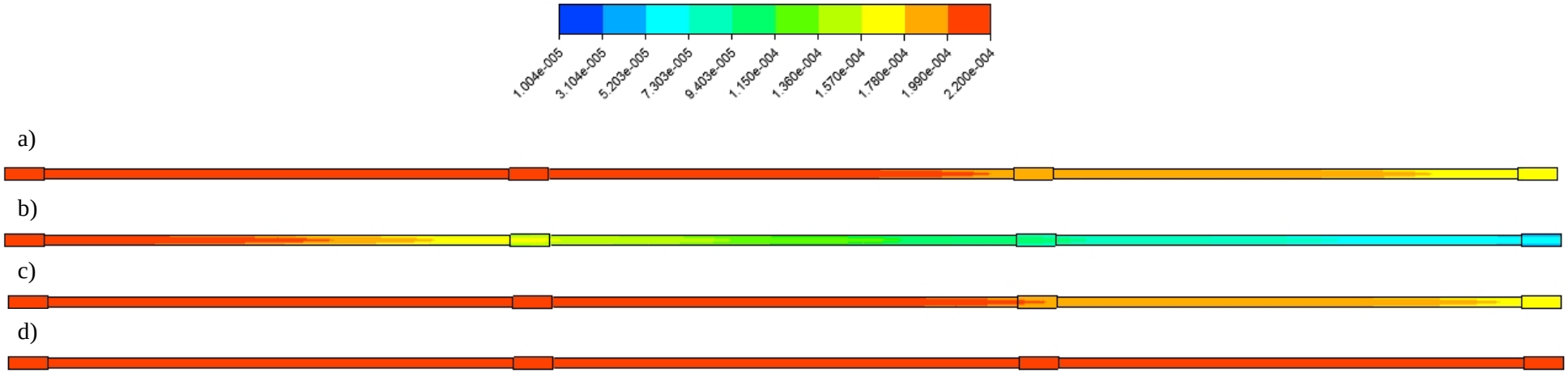

Fig. 3. Visualization of the NO mass fraction in cross section along the channel (3 layers x 350 mm) for: a) SST, b) SST k-ω, c) k-ω, d) k-ε

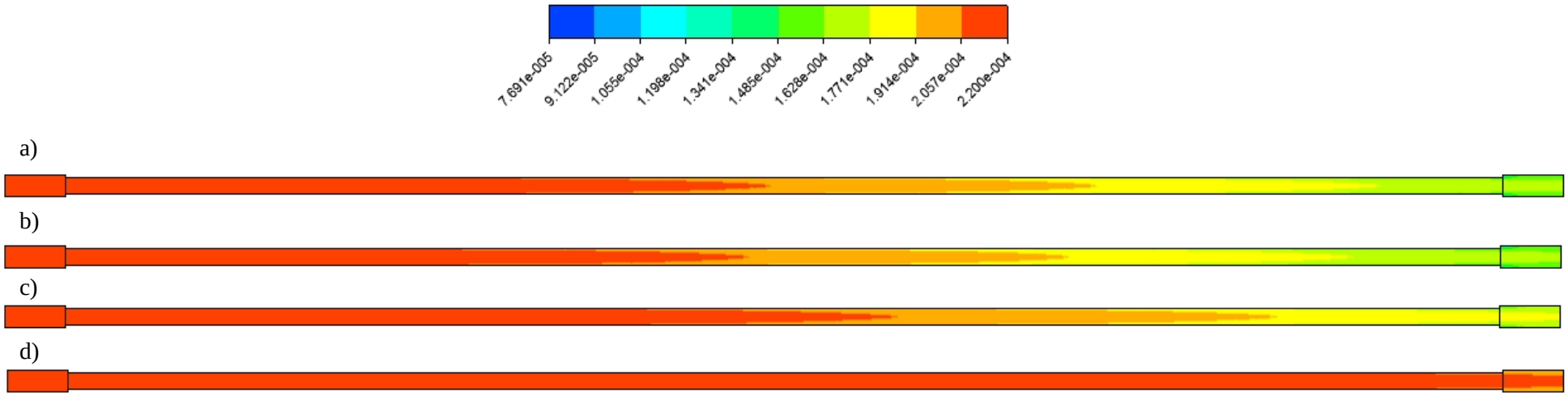

Fig. 4. Visualization of the NO mass fraction in cross section along the channel (700 mm) for: a) SST, b) SST k-ω, c) k-ω, d) k-ε

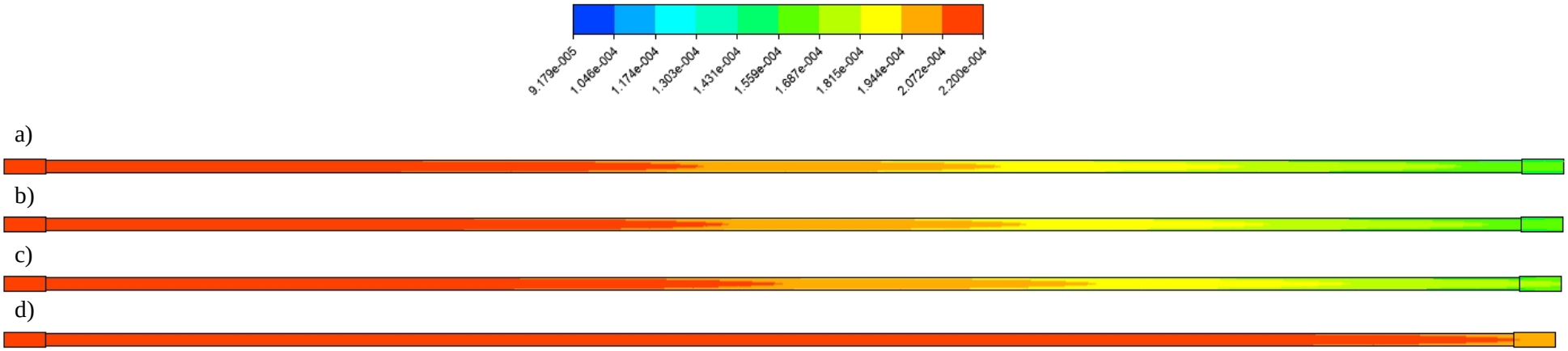

Fig. 5. Visualization of the NO mass fraction in cross section along the channel (1050 mm) for: a) SST, b) SST k-ω, c) k-ω, d) k-ε

To compare results for 700 mm and 1050 mm length channels with 2 and 3 layers channels was made graph Fig. 6. and Fig. 7.

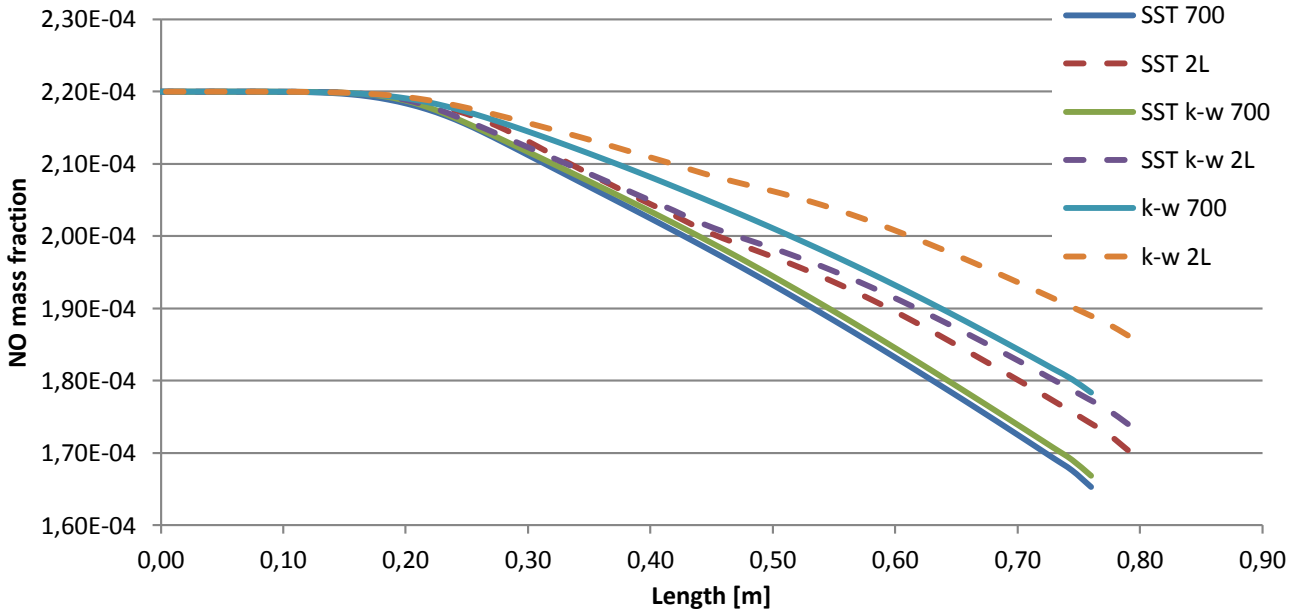

Fig. 6. Comparing results of NO-reduction for 700 mm and 2 layers channels for turbulence models: SST, SST k-ω and k-ω

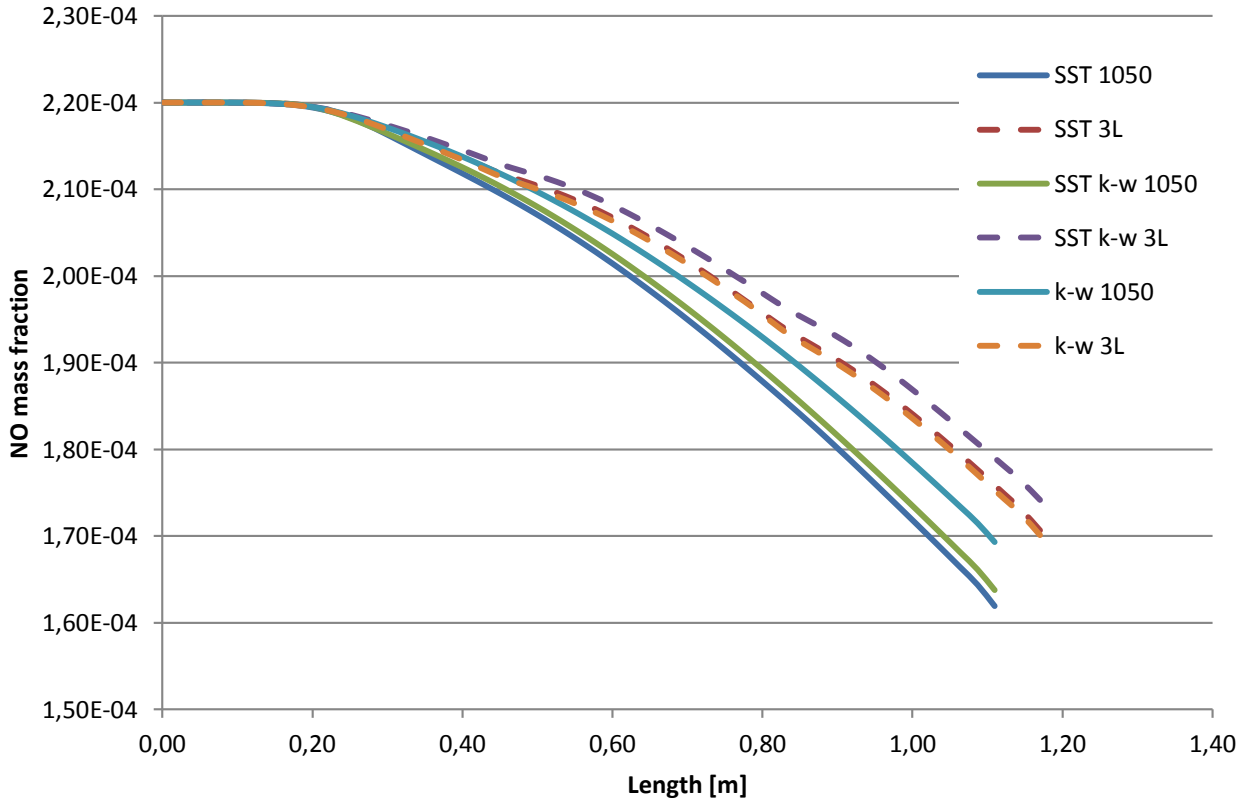

Fig. 7. Comparing results of NO-reduction for 1050 mm and 3 layers channels for turbulence models: SST, SST k-ω and k-ω

As shown in the Fig. 6 and 7, the longitudinal channels have a greater decrease in the mass fraction of NO along the channel. The catalyst composed of layers has got a little less efficiency, but this disparity could be relevant for large coal-fired power plants.

3.2. Selected results for temperature of NO reduction in channels

Increasing the exhaust gas temperature is the result of an exotherm of reduction of nitrogen oxides (chapter 1.2). This depends mainly on the intensity of the reaction and the concentration of NO in the exhaust gas. This modeling shows that the temperature at the outlet of the channels is greater than the inlet temperature for a few degrees in each models.

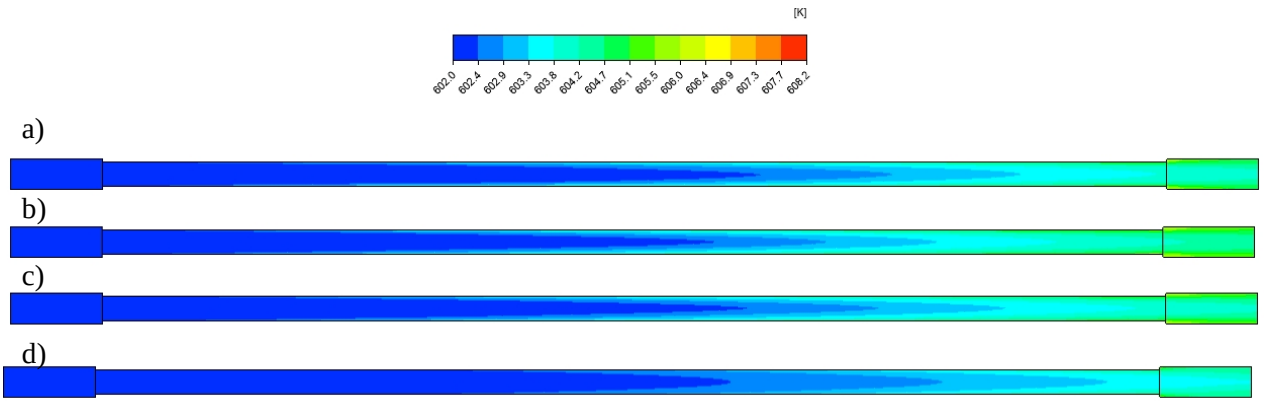

Fig. 8. Visualizations of temperature in cross section along the channel 350 mm for: a) SST, b) SST k-ω, c) k-ω, d) k-ε

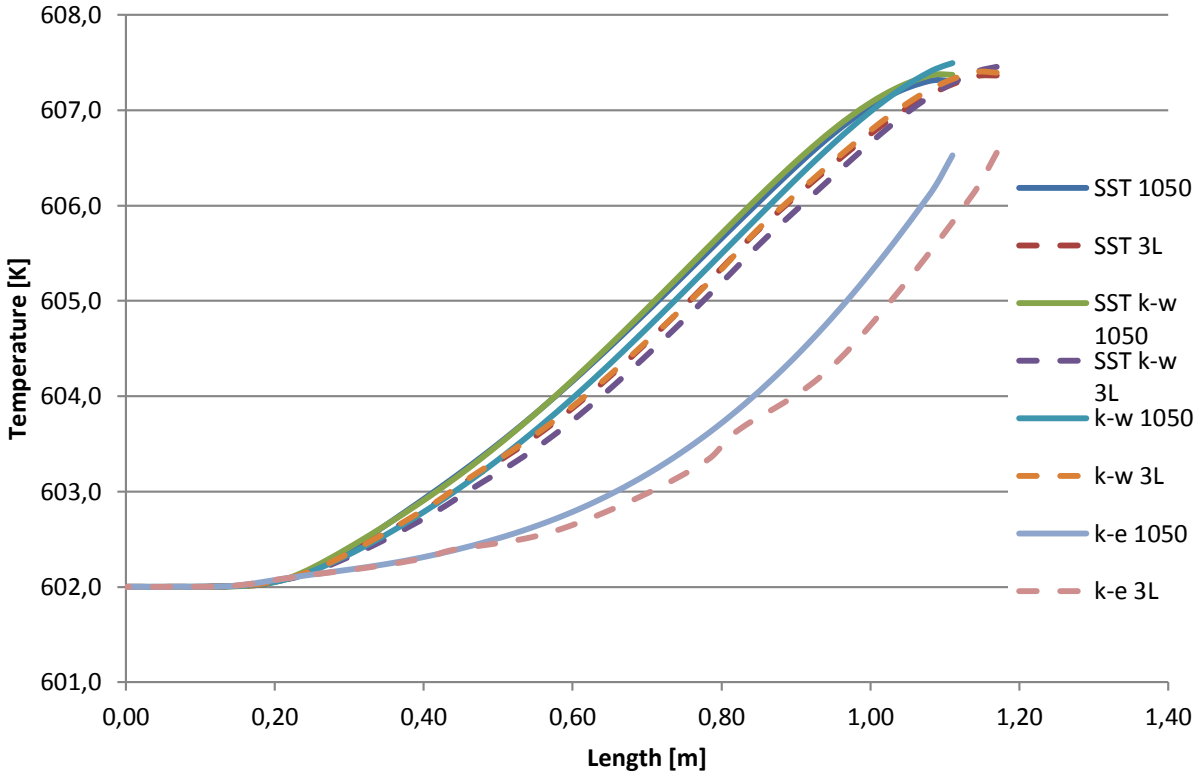

Fig. 9. The temperature distribution along the channels (1050 mm and 3-layers) for different turbulence models

4. Conclusions

This paper presents the method of modeling the reduction of nitrogen oxide from flue gas stream through the SCR catalyst based on V_2O_5/TiO_2 10%. Were modeled different variants of a single channel with the catalyzing denitrification process on inner wall of SCR reactor. To carry out the numerical modeling, the parameters of flue gases were taken for 900 MW coal-fired power plant.

To compared the effects of selected models of turbulent flow, on the reduction of nitrogen oxides, the assumptions have been made for the geometry of catalytic channels (chapter 2.3) and the kinetics of chemical reactions (chapter 2.2). For simulation were taken turbulence models: *k-ε, k-ω, SST k-ω* and *transition SST*.

It should be noted that the turbulence model *k-ε,* in cause of their nature, cannot adequately reproduce the chemical reaction of NO reduction. The better solution were presented by models *SST* and *SST k-ω*, which show much more accurate modeling of flow combined with a chemical reaction located on the inner walls of the channel.

Reduction of nitrogen oxides is more efficiently in the elongated channels (700 mm and 1050 mm) than in catalyst with few layers (2 x 350 mm and 3 x 350 mm). However, the use of catalysts composed of layered modules is easier to replacement and regeneration in further operation time.

The temperature of the exhaust gas flowing through the channel as shown in Fig. 9. also shows the inaccuracy *k-ε* turbulence model. At the end of channel the temperature should be stabilized as in the models *SST* and *k-ω*.

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