CFD Model of SNCR with Shifting Effect of CO

Tomáš Blejchař[*], Jana Jablonská[**], Zbyszek Szeliga[**],
Ondřej Zavila[**], Jaroslav Konvička[**],
Paweł Regucki[***], Renata Krzyżyńska[***]
[*]IT4Innovations – National Supercomputing Center,
VŠB – Technical University of Ostrava, Czech Republic
[**]VŠB – Technical University of Ostrava, Czech Republic
[***]Wrocław University of Science and Technology, Poland

1. Introduction

The retrofitting of large coal fired boilers with NO_x control systems has been concluded in Western Europe many years ago. Since the selective catalytic reduction process (SCR) was considered as the best available technology (BAT) in the eighties and nineties, most of the boilers are equipped with SCR now (Dąbrowski at al. 2013).

The SNCR process has been considerably improved during the last years for small and medium sized boilers burning municipal and industrial waste, biomass, sludge, etc. These types of boilers are generally designed in such a way that the first flue gas pass is free of heat exchangers so that the injection and distribution of the reagent into the optimum temperature window can easily be realized. Since, for these applications, NO_x limits of 100 mg/Nm³ and lower can now be achieved and maintained at all operating conditions, the SNCR process represents today the 'Best Available Technology' (BAT). Therefore more and more owners of waste-to-energy plants replace their existing SCR NO_x control system by SNCR technology because of the low operating costs at comparable performance.

The kinetic behavior of the deNO$_x$ process is very complex and there are not many studies providing experimental information from laboratory–scale combustors operating with this process. Tayyeb at al. presented an experimental investigation concerned with an assessment of additives such as CO and H$_2$ on urea deNO$_x$ over a temperature range of 850–1200°C. They observed that both of the additives have significant influence on the process performance with H$_2$ being observed to be more profound on the NO$_x$ reduction performance. A shift of 215°C was observed in peak reduction temperature with the addition of CO in flue gas up to 1000 ppm, where as the kinetic modeling suggested 150°C. The discrepancy was due to the plateau of about 100°C noticed during the experimental observations without injection of any additive. The addition of H$_2$ had a significant influence on the process performance and a downwarded shift of 275°C in the peak reduction temperature was observed although with an impaired efficiency (Tayyeb at al. 2008). Zhou at al. confirmed that CO can lower the SNCR reaction temperature, narrow the temperature region and reduce the maximum NO$_x$ removal efficiency. The higher the CO volume fraction is, the more obvious changes will be (Zhou at al. 2015).

Since emission limits and operating costs are still increasing, it is necessary to use modern methods, such as CFD simulation, to help efficiently manage the deNOx process. At present, there are SNCR models, but they are so simplified that they do not affect a range of influences, such as the temperature window shifts depending on the CO concentration at the injection area. By including these phenomena, and by expanding the CFD simulation of these effects, far more accurate simulations can be achieved. This is necessary to estimate the efficiency of SNCR technology and the subsequent design of the injection nozzles and their location. During last years CFD models of SNCR have been improved and modified with respect to current computer performance. Nowadays, researchers focuses on extending the original 9- step kinetics mechanism of SNCR (Modliński 2015, Musa at al. 2013).
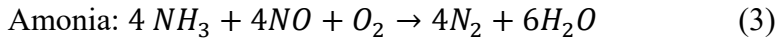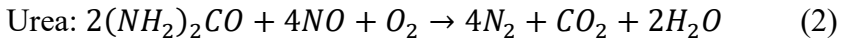
The main objective of this paper is the modification of original 9-step kinetics mechanism of SNCR in such a way that it is able to predict the effect of CO and modification of the kinetics mechanism of SNCR model for practical application in CFD codes.

2. Elementary Chemistry of SNCR Technology

Selective Non-Catalytic Reduction (SNCR) technology is based on injection of reductant in aquageous solution (Urea solution, Ammonia water) or in gaseous form (Ammonia) into hot flue gas downstream of main combustion zone where nitrogen oxides NO_x are reduced by amine radical NH_2- to molecular nitrogen N_2 and water vapour H_2O. A dominant chemical reaction is very simple and defined by the following chemical formula (Kohl at al. 1997, Von der Heide 2008):

$$NH_2^- + NO \rightarrow N_2 + H_2O \tag{1}$$
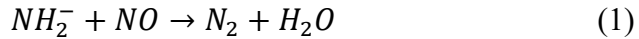
Basically, both urea solution and ammonia water are usually used for the NO_x reduction in combustion plants at the present. The SNCR process can be described by the following chemical net reaction (Kohl at al. 1997, Von der Heide 2008):

$$\text{Urea: } 2(NH_2)_2CO + 4NO + O_2 \rightarrow 4N_2 + CO_2 + 2H_2O \tag{2}$$

$$\text{Amonia: } 4\,NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O \tag{3}$$

Depending on the application both reductants have specific advantages and disadvantages. For an optimum NO_x reduction with a minimum NH_3 slip it is "only" necessary to evenly distribute and thoroughly mix the reductant in the flue gases within the appropriate temperature window in which a NO_x reduction is possible. The optimum temperature range to achieve a high NO_x reduction together with a minimum consumption of reductant and a low ammonia slip is rather narrow and mainly depends on the flue gas composition.

The main problem of SNCR method is a relatively narrow temperature window (870-1050°C). For coal-fired boilers the optimum temperature lies between ca 960 and 1020°C, which is so called "temperature window", what is presented in Fig. 1.

Above this temperature range ammonia is oxidised to an increasing extent and, e.g. nitrogen oxides are formed. At lower temperatures the reaction rate is slowed down, causing an ammonia slip, which may result in the formation of ammonia salts like ammonium sulphate and ammonium bisulphate and may lead to secondary problems, downstream the flue gas path. Therefore, the ammonia slip should be kept at a minimum. The objective of all NO_x control technologies is to reach

a high NO_x reduction with a minimum consumption of reagent while the ammonia slip must be kept low at the same time. This only can be achieved with an even distribution of the reagents in the flue gas at the right temperature. In the following part of this article we will focus on effect of CO and exact specification of shift of the temperature window.
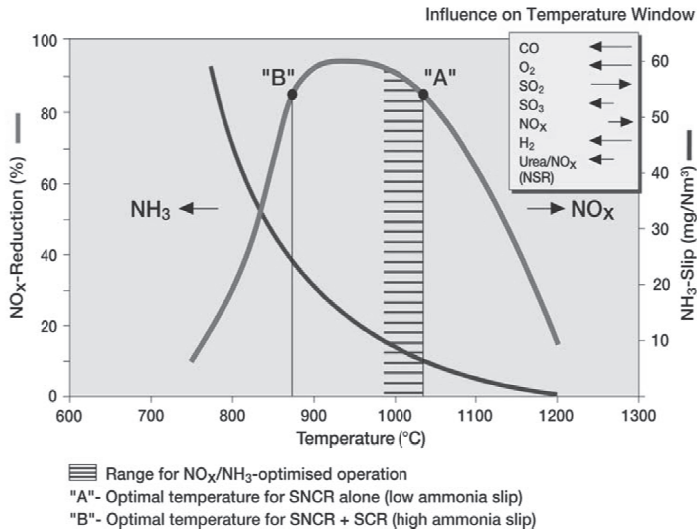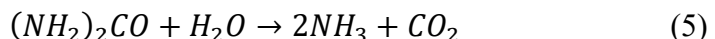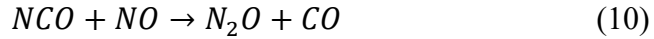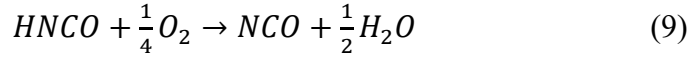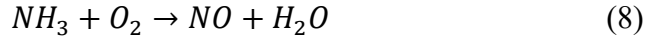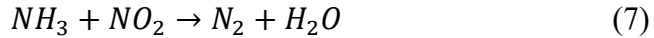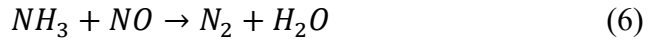

Fig. 1. NO_x reduction as a function of temperature and composition of flue gas (Von der Heide 2008)
Rys. 1. Redukcja NO_x w funkcji temperatury i składu spalin (Von der Heide 2008)

3. SNCR Chemical Kinetics Model

Proposed model of SNCR technology with urea solution, as a reagent, is based on nine-step kinetic mechanism proposed by Brouwer (Brouwer at al. 1996). The origin nine-step mechanism was modified to exclude the radical NH_2^- due to removal of problematic non-stable transitional material. This model also includes two-way mechanism for breakdown of urea into ammonia NH_3 and radical HNCO.

$$(NH_2)_2CO \rightarrow NH_3 + HNCO \qquad (4)$$

$$(NH_2)_2CO + H_2O \rightarrow 2NH_3 + CO_2 \qquad (5)$$

$$NH_3 + NO \rightarrow N_2 + H_2O \tag{6}$$

$$NH_3 + NO_2 \rightarrow N_2 + H_2O \tag{7}$$

$$NH_3 + O_2 \rightarrow NO + H_2O \tag{8}$$

$$HNCO + \frac{1}{4}O_2 \rightarrow NCO + \frac{1}{2}H_2O \tag{9}$$

$$NCO + NO \rightarrow N_2O + CO \tag{10}$$

$$N_2O \rightarrow N_2 + \frac{1}{2}O_2 \tag{11}$$

$$CO + \frac{1}{2}O_2 \rightarrow CO_2 \tag{12}$$

Chemical reactions included in CFD algorithm are usually based on the Arrhenius equation, which describes the reaction rate:

$$k = A \cdot e^{\frac{-E}{R \cdot T}} \cdot T^{\beta} \left[\left(\frac{mol}{m^3} \right)^{1-n} \cdot \frac{K^{-\beta}}{s} \right] \tag{13}$$

where:

k – reaction rate, A – pre-exponential factor, E – activation energy, R – universal gas constant, T – temperature, β – temperature exponent, n – the sum of the number of reaction orders. The Table 1 lists the kinetic parameters of the individual equations.

Table 1. Kinetic parameters of SNCR model
Tabela 1. Parametry kinetyczne modelu SNCR

Reaction	A $\left[\left(\frac{mol}{m^3} \right)^{1-n} \cdot \frac{K^{-\beta}}{s} \right]$	β [1]	E $\left[\frac{J}{mol} \right]$	n [1]
(4)	1.27E+04	0	65048	1; [(NH$_2$)$_2$CO][1]
(5)	6.13E+04	0	87819	2; [(NH$_2$)$_2$CO][1]; [H$_2$O][1]
(6)	4.20 E+02	5,3	315937	2; [NH$_3$][1]; [NO][1]
(7)	4.20E+02	5.3	349937	2; [NH$_3$][1]; [NO$_2$][1]
(8)	3.50E-03·	7.65	544487	2; [NH$_3$][1]; [O$_2$][1]

Table 1. cont.
Tabela 1. cd.

Reaction	A $\left[\left(\frac{mol}{m^3}\right)^{1-n} \cdot \frac{K^{-\beta}}{s}\right]$	β [1]	E $\left[\frac{J}{mol}\right]$	n [1]
(9)	6.24E+09	0.85	284637	1.25; $[HNCO]^1$; $[O_2]^1$
(10)	1.00E+07	0	-1632	2; $[NCO]^1$; $[NO]^1$
(11)	6.90E+12	-2.5	151075	1; $[N_2O]^1$
(12)	1.26E+06	0	167742	1.75; $[CO]^1$; $[O_2]^{0.25}$; $[H_2O]^{0.5}$

## 4. Influence of CO – Temperature Shift

The influence of CO on the SNCR process indicates that the presence of CO shifts the selectivity, by increasing the rate of NH_2^- formation and the rate of NH_3 oxidation, to NO. Higher CO level shifts the optimal temperature for NO reduction to lower temperatures due to enhanced chemical rates in presence of CO. The shift in the selectivity is accomplished by two mechanisms:

- increasing local temperature,
- increasing net production of OH radical.

The first effect is due to exothermicity of the main CO burnout reaction (14), while the second effects is due to chain branching that results from the H produced in this reaction (Kohl at al. 1997):

$$CO + OH \rightarrow CO_2 + H \tag{14}$$

$$H + O_2 \rightarrow O + OH \tag{15}$$

$$O + H_2O \rightarrow OH + OH \tag{16}$$

Presence of CO in injection area products radical OH·, which leads to high concentration of NH_2^-· radical (see eq. 17-18).

$$NH_3 + OH \leftrightarrow NH_2 + H_2O \tag{17}$$

$$NH_3 + O \leftrightarrow NH_2 + OH \tag{18}$$
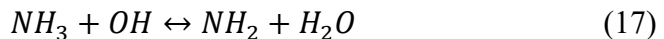
Higher concentration of CO in injection zone leads to shift the temperature window towards lower temperatures (Fig. 2) and/or increase the efficiency of NO_x reduction.

The contribution of CO oxidation to the local temperature is accounted for in the model. Empirical adjustment to the rates is used to account for the effect of CO without including details radical chemistry. The empirical adjustment is applied in the form of shift in effective temperature to account for the radical chemistry effects of CO as follows.
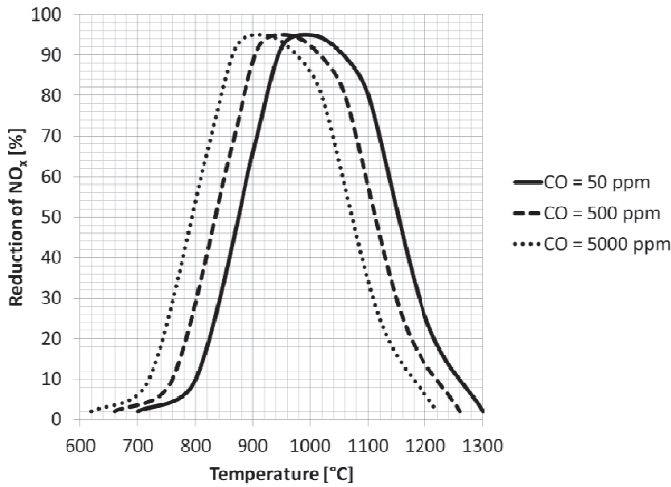
Fig. 2. Temperature shift as a function of CO concentration
Rys. 2. Przesunięcia temperatury w funkcji stężenia CO

Brouwer proposed a modification of reactions rate for reactions (6-9) as follows (Brouwer at al. 1996):

$$k = A \cdot e^{\frac{-E}{R \cdot (T + S_{CO})}} \cdot (T + S_{CO})^{\beta} \tag{19}$$

S_{CO} is the shift in the temperature required to achive the same NO reduction and reagent decomposition compared to the case without CO.

$$S_{CO} = 17.5 \ln(X_{CO}) + 173 \tag{20}$$

where:
X_{CO} – volume fraction of CO.

Application of modified rate of reaction is not possible to set in CFD code ANSYS CFX. Analysis of equations (19) and (20) shows that the equation (19) can be simplified as follows and term $X_{CO}{}^{\gamma}$ describes CO shift in simplified form.

$$k = A \cdot X_{CO}{}^{\gamma} \cdot e^{\frac{-E}{R \cdot T}} \cdot T^{\beta} \left[\left(\frac{mol}{m^3} \right)^{1-n} \cdot \frac{K^{-\beta}}{s} \right] \qquad (21)$$

Kinetic parameters of SNCR model with CO shift are presented in table 2.

Table 2. Kinetics parameters of SNCR model with CO shift
Tabela 2. Parametry kinetyczne modelu SNCR z przesunięciem CO

| Reaction	A $\left[\left(\frac{mol}{m^3} \right)^{1-n} \cdot \frac{K^{-\beta}}{s} \right]$	β [1]	γ [1]	E $\left[\frac{J}{mol} \right]$	n [1]
(6)	8.63E+04	5.27	0.58	311822	2; $[NH_3]^1$; $[NO]^1$
(7)	1.39E+05	5.27	0.63	345403	2; $[NH_3]^1$; $[NO_2]^1$
(8)	2.63E+01	7.61	0.97	537456	2; $[NH_3]^1$; $[O_2]^1$
(9)	3.88E+11	0.84	0.46	281090	1.25; $[HNCO]^1$; $[O_2]^1$

5. CFD Model of SNCR Technology

Proposed kinetics model of SNCR was checked by the comparison with several experimental data, which are available in studies. Reduction of NO_x depending on temperature of flue gas and reduction of NO_x depending on stochiometric ratio β was confronted with experimental results, which are generally validated.

The constant improvement of computer resources is providing a continuous increase of the use of computational fluids dynamics in various branches of engineering. Nowadays they are supplied not only to optimise aerodynamic equipment, but also to simulate typical industrial processes, such as SNCR. The main advantage of CFD codes is their capability to describe complex processes in detail (detail simulation of reagent injection in combustion chamber), thus avoiding the simplifying assumption required to solve the lumped-parameters model.

The simplified kinetics model was tested by means of CFD simulation of simply real-size reactor, showed in Fig. 3, in typical industrial condition, such as real composition of flue gas, spraying of reagent etc.

The simulation of SNCR process was realized as solution with constant residence time. Residence time specifies the time of all chemical compounds interaction. A lot of conditions of simulation and experimental research data were the same. The mathematical background of multi-phase flow with chemical reaction is discussed in several books, which basically deal with numerical simulation of the turbulent fluid flow.
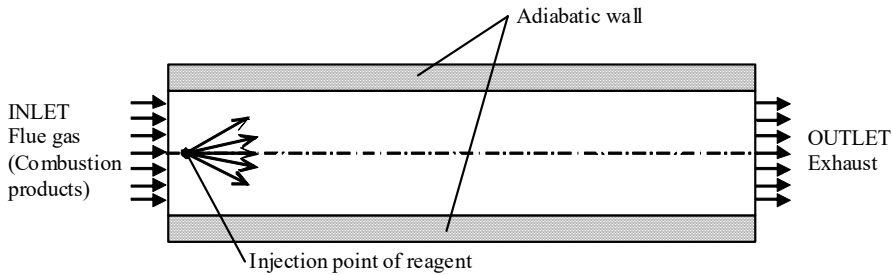
Fig. 3. Basic design of test reactor
**Rys. 3.** Schemat reaktora badawczego

At first there was investigated the influence of coupling the CFD with the simplified kinetics model previously discussed. The effect of turbulence was modelled using standard k-ε approaches. The classical approach to model of turbulent flows is based on single point averages of the Navier-Stokes equations. These are commonly called Reynolds Averaged Navier-Stokes Equations (RANS). The most simple model for turbulent flow is k-ε one. Even though it certainly is the best compromise for engineering design using RANS approach.

6. Results of CFD simulation

The results obtained with the simplified kinetics model of test reactor CFD simulation are presented in Fig. 4.

Analyzing the figure one can see that, in spite of the severe limitations of this kinetics model, it is able to reproduce the main trends evidenced experimentally. In particular, it is worthwhile to mention that in the low temperature range the prediction of the CFD model is equal to the experimental data. Moreover, one can see that in the high temperature

region the CFD model predicts lower NO reduction in good agreement with experimental measurements. This is an important point since it means that the CFD model is able to identify correctly the transition from the region where chemical kinetics reaction controls from the one where mixing become controlling.
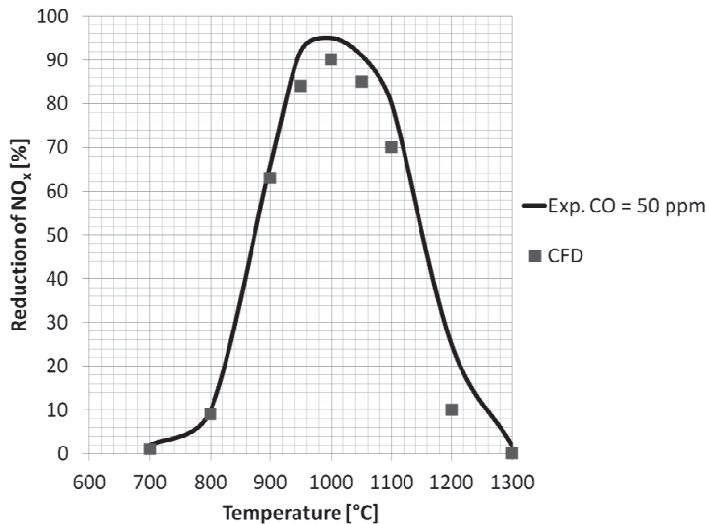

Fig. 4. Comparison of NO_x reduction - temperature window given by experimental data and simplified kinetics CFD model with concentration of CO = 50 ppm
Rys.4. Redukcja NO_x w funkcji temperatury. Wyniki eksperymentalne i z modelu kinetycznego CFD dla stężenia CO = 50 ppm

However, this also means on one side that reduced kinetics model provide roughly the same characteristics time for reaction, and on the other side that the influence of mixing has to be mainly ascribed to macroscopic phenomena. In spite of some quantitative discrepancies among the model predictions are evident, it is also evident that the main quantitative features (maximal reduction of NO located around 970-1020°C) are well reproduced by the simplified kinetics model.

Next, CFD simulations for a modified model, involving the influence of CO, were calculated. CO shift was simulated for lower and higher concentration of CO = 20 and 200 ppm respectively. Figures 5 and 6 illustrate the CO temperature shift.
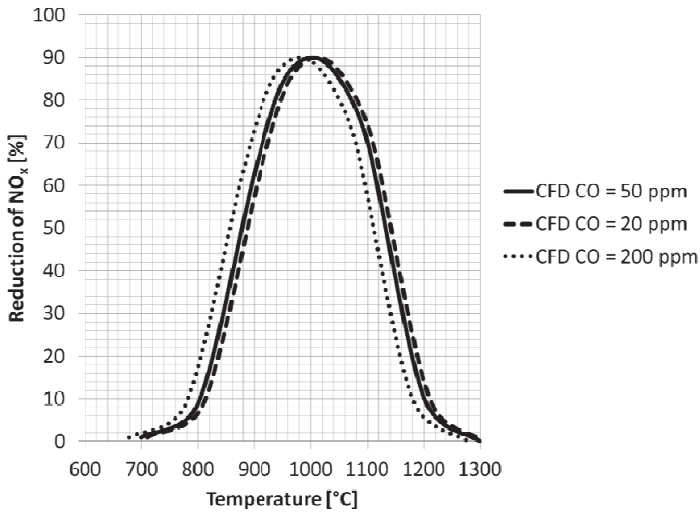
Fig. 5. CO temperature shift calculated by CFD simulation with modified mechanism
Rys. 5. Przesunięcie temperaturowe dla różnych stężeń CO obliczone za pomocą symulacji CFD ze zmodyfikowanym mechanizmem
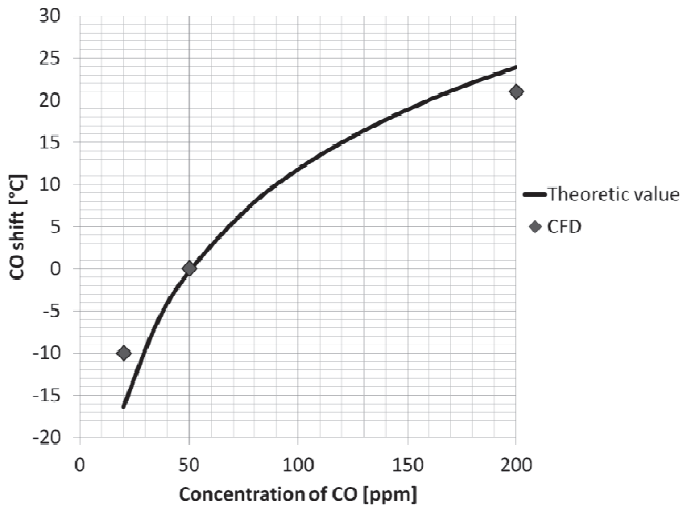
Fig. 6. Comparision of CO temperature shift calculated with empirical adjustment (19), (20) and CFD model with modified mechanism
Rys. 6. Przesunięcie temperaturowe CO obliczone na podstawie założeń empirycznych (19), (20) i modelu CFD ze zmodyfikowanym mechanizmem

7. Conclusions

Over many years of experiences in continuous operation in various combustion plants, the SNCR process has proven to be a reliable and economical solution for NO_x reduction fulfilling the required NO_x limits. In the discussed power plants all guarantees were satisfied and in many cases exceeded by far. From the process point of view, it is practically of no relevance whether urea solution, ammonia water or a mixture of both is used as reagent. If a plant is engineered, installed and operated appropriately, neither media is expected to have an impact on the availability of the overall plant.

Furthermore, all technological measures like optimizing the combustion and flue gas recirculation should be taken if they are technically feasible as well as commercially justified. New boilers could be designed in such a way that they meet the requirement of SNCR, which is basically an extension of the space in the area of the injection levels. The invest cost would be negligible in comparison to the cost of the whole boiler. The application of the SNCR technology for large power boilers still leaves open questions and not all problems are solved yet. However, the situation was not much different five years ago for waste incinerators. Today NO_x levels < 100 mg/Nm³ are state of the art.

Still increasing pressure to reduce NO_x and increase the efficiency of the SNCR method (small ammonia slip) cause intensive optimization of SNCR technology, which cannot be done without modern methods such as CFD simulations. The proposed CFD model of SNCR technology with CO temperature shift could be used for optimisation of SNCR technology at the stage of the basic and detailed design.

References

Brouwer, J., Heap, M. P., Pershing, D. W., Smith, P. J., (1996). *Model for Prediction of Selective Non-Catalytic Reduction of Nitrogen Oxides by Ammonia, Urea, and Cyanuric Acid with Mixing Limitations in the Presence of CO*. Reaction Engineering International. Presented at the 26th International Symposium on Combusion, July, 1996, Naples, Italy.

Von der Heide, B., (2008). *Ist das SNCR-Verfahren noch Stand der Technik*. Thomé-Kosmiensky, Mi-chael Beckmann (Hrsg.): Energie aus Abfall – Band 4. Neuruppin: TK Verlag Karl Thomé-Kozmiensky, 275-293, ISBN 978-3-935317-32-0

Dąbrowski, J. at al., (2013). Laboratory Studies on the Effectiveness of NOx Reduction by Selective Catalytic Reduction SCR Method. *Rocznik Ochrona Srodowiska*, *15*, 301-313.

Kohl, A., Nielsen, R., (1997). *Gas Purification.* Fifth Edition, Gulf Publishing Company, Houston, Texas, ISBN 0-88415-220-0

Modliński, N., (2015). Numerical simulation of SNCR (selective non-catalytic reduction) process in coal fired grate boiler. *Energy*, *92*, 67-76.

Musa, A.A.B at al. (2013). Numerical simulation on improving NO_x reduction efficiency of SNCR by regulating the 3-D temperature field in a furnace. *Advanced Materials Research*, *807-809*, 1505-1513.

Tayyeb Javed, M. at al. (2008). Experimental and modeling study of the effect of CO and H_2 on the urea $DeNO_x$ process in a 150 kW laboratory reactor. *Chemosphere*, *70*, 1059-1067.

Zhou, H.E. at al. (2015). Solve CO inhibition of SNCR reaction by additive MMT. *Journal of Zhejiang University (Engineering Science)*, 49(12), 2237-2243.

Modelowanie procesów SNCR uwzględnieniem efektu przesunięcia w zakresie CO

Streszczenie

Artykuł przedstawia wyniki symulacji procesów SNCR z wykorzystaniem obliczeń CFD z uwzględnieniem przesunięcia temperaturowego związanego z obecnością CO oraz parametrów kinetycznych przedstawionych w tekście reakcji chemicznych. Wpływ CO na proces SNCR opisuje empiryczna korekta parametrów kinetyki reakcji chemicznych. Wyniki symulacji CFD porównano z wynikami pomiarów eksperymentalnych. Chociaż proponowany kinetyczny model technologii SNCR jest uproszczony, to jest w stanie opisać redukcję NO_x, z uwzględnieniem wielu parametrów technologii SNCR, z dobrą precyzją. Opisany model może być wykorzystany na etapie projektowania instalacji SNCR uwzględniając m.in. miejsca iniekcji i układ lanc.

Abstract

The paper deals with CFD simulation of SNCR technology with implemented CO temperature shift. The influence of CO on the SNCR process is described by empirical adjustment of kinetics parameters of chemical reactions. Results of CFD simulation were compared with results of experimental measurements. Although the proposed kinetics model of SNCR technology is simplified, it is able to describe reduction of NO_x and other phenomena of SNCR with good precision. The model can be used to verify of injection levels and injection lances arrangement at design phase.

Słowa kluczowe:
technologia SNCR, roztwór mocznika, tlenki azotu NO_x, usuwanie NO_x

Keywords:
SNCR technology, Urea solution, NO_x nitrogen oxides, NO_x removal