Laboratory Studies on the Effectiveness of NOx Reduction by Selective Catalytic Reduction SCR Method

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1. Introduction

Thermal treatment of municipal and industrial waste is one of the methods of disposal of such waste. However, these processes generate considerable amounts of air pollutants, including nitrogen oxides [2, 4, 7, 13]. The secondary methods of reduction of nitrogen oxides generated during combustion include: non-selective catalytic reduction (NCR) and selective catalytic reduction (SCR) [3, 5, 12, 14]. In each of methods the aim is to break the bonds of nitrogen oxides and release free nitrogen. In the NCR process hydrogen, carbon monoxide, methane or other hydrocarbons may be used as reducing agents. Process catalysts are transition metal oxides and noble metals, especially the platinum, affixed to different carriers. In his work, T. Paryjczak [9] mentions that the main disadvantage of these processes is that apart from main goal – reduction of nitrogen oxides, also other, harmful nitrogen compounds such as nitrous oxide, ammonia and hydrogen cyanide are generated. Furthermore, reducing agents used in the method exhibit much higher affinity to oxygen than to nitrogen oxides, so the NCR method can only be used when the concentration of oxygen in the exhaust gases is low; also it is necessary to apply considerable excess of reducing agents.

SCR methods are used more often. The most common is the method of introduction of ammonia NH_3 after a particulate filter, which leads to a specific chemical reactions. In this method NO_x reduction

without catalysts requires high temperatures, i.e. 1123–1273K. These reactions may also take place at lower temperature, but it requires application of catalysts. Such technologies, based on the use of oxides in the catalyst system, especially WO_3, V_2O_5 and TiO_2 are now widely used. The node of NO_x reduction in the system of exhaust gases treatment is in the form of a column. Inside the column catalysts are placed on baffles fixed on certain levels of the column. There gas streams containing ammonia and NO_x combine. After passing through the catalyst, as a result of chemical reactions, nitrogen oxides in the exhaust gases are converted into nitrogen N_2 and water steam. The temperature at which the process is carried out is within the range of 573–723K [5, 12].

This paper presents the results of laboratory investigations on the effectiveness of NO_x reduction by selective catalytic reduction. Tests were carried out using an installation designed in the Department of Water and Sludge Technology and Waste Utilization of Koszalin University of Technology.

2. Description of the test installation

Installation for experimental studies on the removal of nitrogen oxides NO_x using selective catalytic reduction method is shown in Photograph 1 and as a diagram in Figure 1 The installation is composed of three basic nodes: preparation and dosage an absorption (reducing) solution liquid, reactor for the catalytic reduction of nitrogen oxides and nitrogen oxides concentration measurement. In the method of selective catalytic reduction ammonia, NH_3 is used as a reducing agent [8]. However, according to the data sheet, 25% aqueous ammonia solution is classified as hazardous, because this reagent is a very toxic and corrosive substance. Additionally, there is a risk of explosion (mixture with air containing 15 to 27% of ammonia is explosive) or formation of toxic gases with many substances, including carbon dioxide, oxygen. Therefore for investigations 32.5% aqueous solution of urea, obtained from technically pure urea and demineralized water was used as absorption liquid. It is a non-toxic substance and safe for the environment and only the storage of the solution at a temperature above 30°C may cause its disintegration with generation ammonia. The urea solution is successfully applicable to the selective catalytic reduction as a reducing agent.
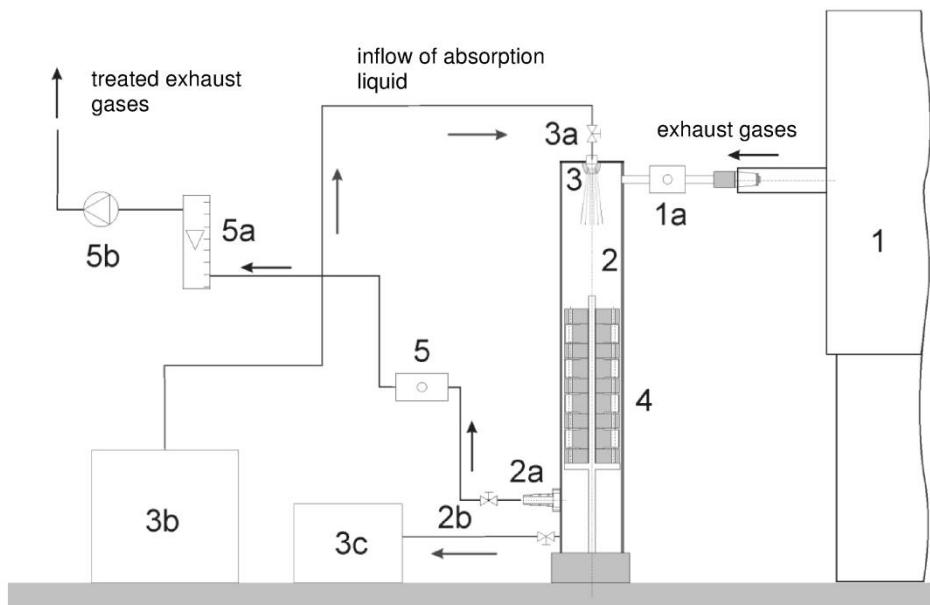
Photo 1. Installation for experimental studies on the removal of NO$_x$ using SCR method; in the middle baffles with catalyst
Zdjęcie 1. Instalacja laboratoryjna do badania procesu usuwania NO$_x$ metodą selektywnej redukcji katalitycznej; obok układ katalizatorów

The injection of urea solution were made by sprayer (3) covering with solution fog the entire cross section of flue gas channel in spray scrubber (2). In the scrubber reaction of nitrogen oxides in exhaust gases arising during the combustion process in laboratory pipe incinerator (1) with adsorption liquid. Exhaust gases are cooled to the desired temperature, measured by thermocouple EMT-50-K with NiCr-NiAl thermoelement in the exhaust gas temperature measurement system (1a) (SCR process proceeds optimally at a temperature of exhaust gases in the range 423–673K [6, 14]). The volume flow of the sprayed absorption liquid was regulated using valve (3a) in the tank (3b). Post process product flowed gravitationally into a tank (3c).

The direction of flow of adsorption liquid and exhaust gases streams was co-current. Urea solution is injected into the hot flue gases (where it evaporates) before the catalyst. Scrubber is equipped wth channel form filled with a catalyst. The catalyst system (4) was made of six ceramic elements placed vertically, along with vertical downward flow of

exhaust gases. Layer of catalyst (vanadium oxide V_2O_5 was used during investigations) was placed on ceramic elements.

Rys. 1. Schemat stanowiska badawczego do procesu usuwania NO_x metodą selektywnej redukcji katalitycznej; 1 – piec rurowy, 2 – skruber natryskowy, 3 – układ zraszacza cieczy adsorpcyjnej, 4 – układ katalizatorów, 5 – miejsce pomiaru stężeń NO_x przy pomocy sondy analizatora spalin
Fig. 1. Diagram of installation for experimental studies on the removal of NO_x using SCR method; 1 – laboratory pipe incinerator, 2 – spray scrubber, 3 – sprinkler system of adsorption liquid, 4 – catalyst system 5 – NO_x concentration measurement point with the exhaust gas analyzer probe

        The exhaust gases after the reduction of nitrogen oxides outflowing from scrubber by its lower discharge port (2a) through the valve (2b) were analyzed. Determination of concentration of NO_x in flow gases was conducted. At the measuring point (5) gas probe of NO_x analyzer was placed. The flow of gas from the scrubber (2) adjusted was by diaphragm pump (5b) and was measured with a table rotameter (5a).

3. Research methodology

During investigations of NO$_x$ removal with SCR metod following independent parameters (variables) were used:

- L$_{NH3}$, m^3·m^{-2}·s^{-1} – spray density of absorption solution, resulting from the formula L$_{NH3}$ = $\frac{\dot{V}_c}{A}$, m^3·m^{-2}·s^{-1}, where: $\dot{V}_c$ – volume flow of absorption liquid, m^3·s^{-1}, A – sectional area of the absorber, m^2. Measuring of volume flow of absorption liquid (volumetric flow rate of absorption liquid) was controlled by suitable valves in sprinkler and was determined using a graduated cylinder and a timer. The amount of liquid spray is relative to the sectional area of the absorber column and ultimately indicated as the spry density L$_{NH3}$. The laboratory installation for the SCR reduction of NO$_x$ used in the research was equipped only with one scrubber and therefore the spry density of absorbent solution was determined at variable volume flow and constant sectional area of the absorber. Values of L$_{NH3}$ were: 5.90·10^{-5}, 6.77·10^{-5}, 7.64·10^{-5} and 8.45·10^{-5} m^3·m^{-2}·s^{-1}

- $\dot{V}_s$, m^3·s^{-1} – exhaust flow, measured at the discharge port of treated flue gas in spray scrubber Values of this parameter were: 1.20·10^{-5}, 2.80·10^{-5}, 6.10·10^{-5} m^3·s^{-1}.

- T$_s$, K – exhaust gas temperature measured at the inflow port of the exhaust into spry scrubber. Value of this parameter were changed within the range: 433.15–573.15K.

However, dependent (output) parameter in this study was the effectiveness of NO$_x$ removal η$_{NOx}$, %, calculated according to formula $\eta_{NOx} = \frac{c_{NOx}^0 - c_{NOx}}{c_{NOx}^0} \cdot 100\%$, where: c_{NOx}^0, c_{NOx} are respectively concentrations of NO$_x$ in exhaust inflowing into the scrubber and outflowing from it.

Research on exhaust treatment was conducted under the following constant parameters of the process of combustion: temperature in the combustion zone of incinerator T = 1373.15 K, the air excess coefficient λ = 1.8, material mass index m = 1.2 kg·m^{-3}. Sample were incinerated in a PRC 20 HM furnace. It is a laboratory one zone pipe incinerator with horizontal heating installation, with a maximum continuous operating temperature 1473K. The incineration process was conducted in the air,

which was fed to the incinerator by diaphragm pump with table rotameter ROS-06. Its air flow measurement rate was in the range 0.5–8.5 $dm^3 \cdot min^{-1}$.

Constant values of above mentioned parameters were determined on the basis of previous studies of incineration of different fuels (including waste, sewage sludge and coal dust, using the same installation) and analyzes of the impact of changes of these parameters on concentration of NO_x in the exhaust gases [including 10, 11]. For example, coal incineration tests were carried out within a range of combustion temperature 873.15–1443.15K and with sufficient amount of air in the incineration zone (air excess coefficient was 1.3–1.8). In addition, sample mass was changed – the material mass index was: 1.2–3.6 $kg \cdot m^{-3}$. The increase of combustion temperature and air flow supplied to the incinerator caused increase of the concentration of nitrogen oxides in the exhaust gases. It was finally observed (at temperature in the combustion zone of the incinerator T = 1373.15K, air excess coefficient λ = 1.8 and fuel mass index m = 1.2 $kg \cdot m^{-3}$) that the average concentration of NO_x was c_{NOx}^0 = 160 $mg \cdot m^{-3}$. At such concentration of NO_x in the exhaust gas inflowing to the absorber, laboratory investigations on the process of reduction were carried out.

4. Results and analysis

Table 1 shows aggregated results of the laboratory tests on impact of spray density of absorption solution, temperature and exhaust gas flow on the efficiency of NO_x removal by SCR, along with their descriptive statistics. Their graphic interpretation as plotted average values of these parameters is shown in Figure 2.

Results obtained were compiled using the nonlinear estimation of quasi-Newton using STATISTICA 10 application. Examination of the relationships between the independent and the dependent variables was accomplished using approximation method of a central point developed by of prof. T. Piecuch [1]. The final approximation equation describing the process is as follows:

$$\eta_{NOX}(L_{NH3}, v_s, T_s) = -745.04 + 970552.00 \cdot L_{NH3} + $$
$$+ \exp(3.43 - 1.03 \cdot 10^{-5} \cdot \dot{V}_s) - 2.88 \cdot 10^{-3} \cdot T_s^2 + 2.92 \cdot T_s \qquad (2)$$

where:

η_{NOX} – effectiveness of NO$_x$ removal NO$_x$, %,
L_{NH3} – spray density of absorption solution, m^3·m^{-2}·s^{-1},
$\dot{V}_s$ – exhaust flow, m^3·s^{-1},
T_s – exhaust gas temperature, K.

The developed equation is valid for the following ranges of parameters variability:

$L_{NH3} \in 5.9 \cdot 10^{-5}$–$8.45 \cdot 10^{-5}$ m^3·m^{-2}·s^{-1};
$\dot{V}_s \in 1.2 \cdot 10^{-5}$–$6.1 \cdot 10^{-5}$ m^3·s^{-1};
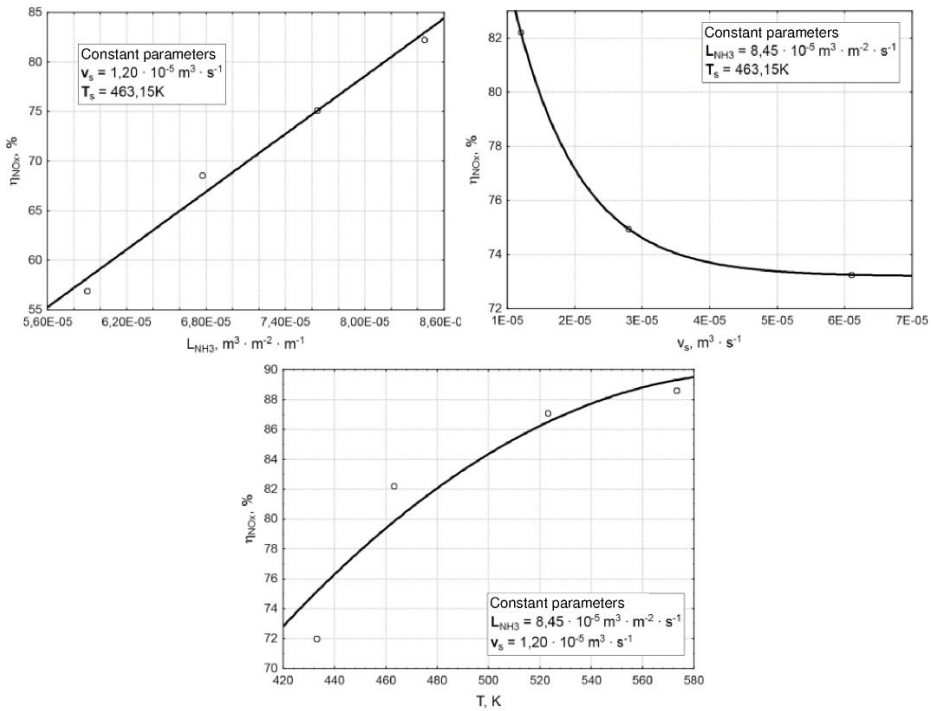$T_s \in 433.15$–573.15K.

Fig. 2. Imapact of spray density of absorption solution, temperature and exhaust gas flow on the efficiency of NO$_x$ removal by SCR
Rys. 2. Wpływ zmian gęstości zraszania roztworem absorpcyjnym, temperatury i przepływu spalin, na skuteczność usuwania NO$_x$ metodą selektywnej redukcji katalitycznej

Table. 1. Descriptive statistics of variable parameters influencing NO_x removal by SCR
Tabela. 1. Statystyka opisowa parametrów zmiennych wpływających na proces redukcji NO_x metodą SCR

Parameter		N of valid	η_{NOx}, % – effectiveness of NO_x removal						
			Average	Median	Min.	Max.	Variance	Standard deviation	Variability index
L_{NH3}, $m^3 \cdot m^{-2} \cdot s^{-1}$	$5.90 \cdot 10^{-5}$		56.87	56.56	55.00	59.37	2.01	1.42	2.50
	$6.77 \cdot 10^{-5}$		68.56	67.81	66.25	71.25	3.42	1.85	2.70
	$7.64 \cdot 10^{-5}$		75.06	75.00	72.50	77.50	2.82	1.67	2.24
	$8.45 \cdot 10^{-5}$		82.17	82.50	80.00	84.37	2.01	1.42	1.72
T_s, K	433.15	22	78.59	78.12	75.00	82.50	8.50	2.92	3.71
	463.15		82.21	82.50	80.00	84.37	1.95	1.40	1.70
	523.15		87.09	87.50	84.37	89.37	2.39	1.56	1.78
	573.15		88.43	88.12	85.00	92.50	4.66	2.16	2.44
$\dot{V}_s$, $m^3 \cdot s^{-1}$	$1.20 \cdot 10^{-5}$		82.21	82.50	80.00	84.37	1.95	1.40	1.70
	$2.80 \cdot 10^{-5}$		74.93	75.00	73.75	76.87	1.11	1.05	1.40
	$6.10 \cdot 10^{-5}$		73.25	73.75	71.25	75.00	1.34	1.15	1.58

The equation was verified by obtaining the relationship between the measured and calculated NO$_x$ reduction efficiency by investigated method. Coefficient of conducted multiple regression was R = 0.969. Graphical representation of the results of the verification are shown in Figure 3.
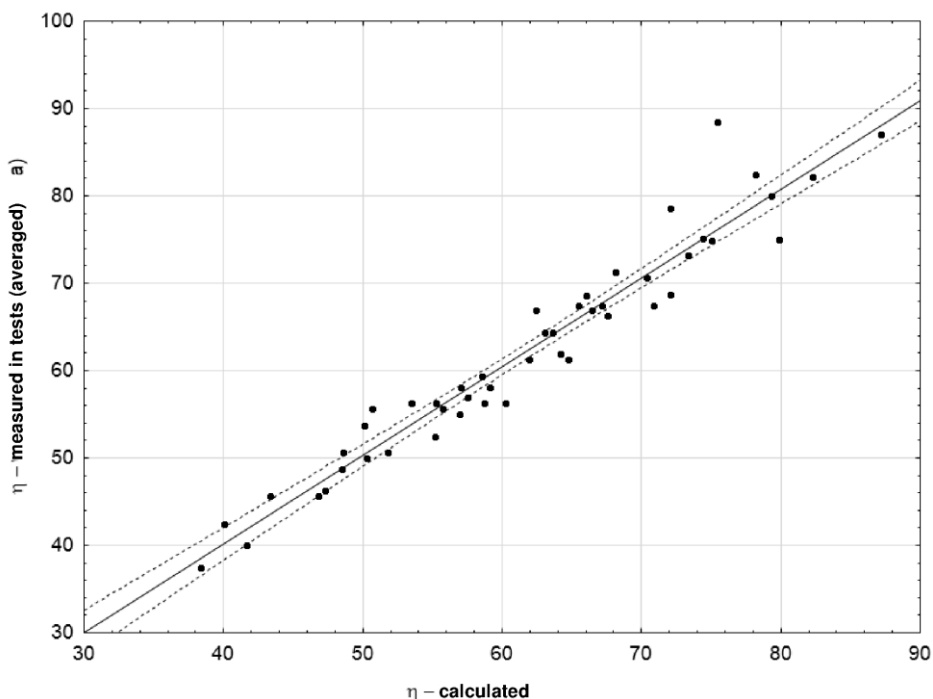

Fig. 3. Comparison of the measured and calculated NO$_x$ reduction efficiency by laboratory SCR method
Rys. 3. Porównanie zmierzonej i obliczonej skuteczności redukcji tlenków azotu laboratoryjną metodą SCR

Analysis of the results of the influence of changes of the spray density of absorption solution on the NO$_x$ removal efficiency by examined method showed that effectiveness of reduction of nitrogen oxides increases along with increase of spray density with aqueous ammonia. Linear characteristic of curve describing this relationship within examine range of parameters changes is important, and shows that further increase of spray density will cause a further increase in NO$_x$ reduction efficiency.

Comparatively low efficiency of the process within the tested range of spray densities of aqueous ammonia, at constant flow and exhaust temperature was observed. Its value was about 57% at lowest value of examined variable parameter L_{NH3} and only 82% at the highest value of this parameter. This may be caused by still too low absorption liquid flow (aqueous ammonia solution) through the scrubber.

The second considered parameter significantly affecting the NO_x reduction efficiency was the exhaust flow, which variability was tested at a constant temperature of exhaust gases and a constant spray density of solution absorption. The analysis of results shown in Figure 2 shows that the increase of gas phase flow in the installation causes degradation of removal efficiency of nitrogen oxides in the exhaust gas, which is obvious. Increase of exhaust gas flow through the installation causes a reduction of the contact time of the gas phase with the absorption liquid droplets. Shape of the curve in Figure 2 shows that further decrease of the flow rate of exhaust gas through the spray scrubber is not expected to significantly affect the value of the NO_x reduction efficiency, but also increase of the gas flow rate exceeding examined range will not deteriorate the achievable NO_x removal efficiency of the installation.

Results of investigations on the influence of the exhaust gas temperature on the NO_x removal efficiency prove that increase of temperature within the tested range (433.15–573.15K) causes about 14% increase of NO_x reduction efficiency to the highest value of about 88%. Shape of the course of examined parameter change suggests that further increase of exhaust gas temperature will not result in a significant increase of NO_x reduction.

Studies on impact of changes in the exhaust gas temperature was carried out at a constant, maximum in examined range, spry density of absorbent solution and at a constant flow of exhaust gases, which value was the lowest of tested in the study. Therefore, reached value of more than 88% of NO_x removal efficiency is the highest value that could be obtained by changing the assumed variables in investigations SCR method of NO_x removal.

3. Conclusions

1. Obtained NO$_x$ removal efficiency over 88% is the highest value that could be obtained by changing assumed independent variables in the system of SCR of NO$_x$. Also SCR method with application of urea aqueous solution and catalyst (vanadium oxide V$_2$O$_5$) proved to be efficient.
2. The most important parameter influencing SCR of NO$_x$, among tested, seems to be spray density of absorber solution.
3. Process of reduction of NO$_x$ using SCR metod in the presented installation may be described by analytical-empirical equation.

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Laboratoryjne badania nad skutecznością redukcji tlenków azotu metodą selektywnej redukcji katalitycznej

Streszczenie

W pracy przedstawiono wyniki badań laboratoryjnych nad skutecznością redukcji tlenków azotu metodą selektywnej redukcji katalitycznej. Badania realizowane były przy użyciu instalacji zaprojektowanych w Kadrze Techniki Wodno-Mułowej i Utylizacji Odpadów Politechniki Koszalińskiej. Instalacja ta składała się z trzech podstawowych węzłów: przygotowania i dozowania roztworu cieczy absorpcyjnej (redukującej), reaktora do katalitycznej redukcji tlenków azotu oraz układu pomiarowego stężeń tlenków azotu. Do badań, jako ciecz absorpcyjną zdecydowano się zastosować 32,5% wodny roztwór mocznika.

Jako parametry niezależne (zmienne) przyjęto: gęstość zraszania roztworem absorpcyjnym L_{NH3}, $m^3 \cdot m^{-2} \cdot s^{-1}$, przepływ spalin mierzony w punkcie wylotu oczyszczonych gazów spalinowych ze skrubera natryskowego $\dot{V}_s$, $m^3 \cdot s^{-1}$ oraz temperatura spalin, T_s, K. Natomiast parametrem zależnym (wynikowym) w tych badaniach była skuteczność usuwania tlenków azotu η_{NOx}, %.

W pracy pokazano zbiorcze wyniki badań laboratoryjnych wpływu zmian gęstości zraszania roztworem absorpcyjnym, temperatury i przepływu spalin, na skuteczność usuwania NO_x metodą selektywnej redukcji katalitycznej, wraz z ich statystyką opisową, na podstawie której wykreślono graficzną interpretację uśrednionych wielkości tych parametru.

Otrzymane wyniki opracowano metodą estymacji nieliniowej quasi-Newtona z zastosowaniem aplikacji STATISTICA 10. Badanie związków po-

między zmiennymi niezależnymi a zmienną zależną dokonano stosując aproksymację metodą punktu centralnego opracowana przez prof. T. Piecucha. Ostatecznie opracowano równanie aproksymacyjne opisujące ten proces. Równanie poddano weryfikacji poprzez uzyskanie zależności między zmierzoną i obliczoną skutecznością redukcji tlenków azotu badana metodą. Współczynnik przeprowadzonej regresji wielorakiej wyniósł R = 0,969.

Analiza wyników badań wpływu zmian gęstości zraszania roztworem absorpcyjnym na skuteczność usuwania NO$_x$ badaną metodą wykazała, że skuteczność redukcji tlenków azotu jest tym większa, im większa jest gęstość zraszania roztworem wody amoniakalnej. Istotna jest liniowa charakterystyka krzywej przebiegu tej zależności w badanym przedziale zmian, pokazująca, że dalsze zwiększanie gęstości zraszania będzie powodowało dalszy wzrost skuteczności redukcji NO$_x$. Zaobserwowano stosunkowo niską skuteczność procesu w badanym zakresie gęstości zraszania wodą amoniakalną przy stałym przepływie i temperaturze spalin, wynoszącą około 57% przy najmniejszej wartości badanego parametru zmiennego L$_{NH3}$ i tylko 82% przy maksymalnej wartości tego parametru.

Wzrost przepływu fazy gazowej w układzie powodował pogorszenie skuteczności usuwania tlenków azotu w spalinach. Dodatkowe obniżenie prędkości przepływu gazów spalinowych przez skruber natryskowy nie wpływał w istotny sposób na wartość skuteczności redukcji NO$_x$, ale też zwiększanie przepływu spalin ponad wartość badaną nie pogarszał skuteczności usuwania NO$_x$ osiągalnej w układzie.

Jak wskazują wyniki badań wpływu temperatury gazów spalinowych na skuteczność usuwania z nich tlenków azotu, wzrost temperatury w badanym zakresie (433,15–573,15K) powodował około 14% zwiększenie skuteczności redukcji NO$_x$ do maksymalnej wartości około 88%. Charakter przebiegu zmian badanego parametru pozwala sądzić, że dalsze zwiększanie temperatury spalin nie spowoduje znacznego wzrostu stopnia redukcji NO$_x$.

Osiągnięta wartość ponad 88% skuteczności usuwania NO$_x$ jest wartością największą, jaką można było uzyskać zmieniając założone parametry zmienne w układzie badania selektywnej metody redukcji katalitycznej NO$_x$.