

APPLICABILITY OF SECONDARY DENITRIFICATION MEASURES ON A FLUIDIZED BED BOILER

JITKA JENÍKOVÁ*, KRISTÝNA MICHALIKOVÁ, FRANTIŠEK HRDLIČKA,
JAN HRDLIČKA, LUKÁŠ PILAŘ, MATĚJ VODIČKA, PAVEL SKOPEC

Czech Technical University in Prague, Faculty of Mechanical Engineering, Department of Energy Engineering, Technická 4, Prague 6, Dejvice, 160 00, Czech Republic

* corresponding author: jitka.jenikova@fs.cvut.cz

ABSTRACT. This article compares the performance of selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR) applied on the same pilot unit, a 500 kW fluidized bed boiler burning Czech lignite. A correlation of the denitrification efficiency and the normalized stoichiometric ratio (NSR) is investigated. The fundamental principle of the SCR and SNCR is similar with the same reaction scheme. The difference is in the use of the catalyst that lowers the activation energy of the key reaction. As a result, the reduction is performed at lower temperatures during the SCR method. During experiments, the NSR was up to 1.6 for the SCR method. For the SNCR method, which has a higher reducing agent consumption, the maximum denitrification efficiency was reached for NSR of about 2.5. The efficiency of both secondary methods was investigated. The denitrification efficiency during experiments exceeded 98 % for the SCR method, and the SNCR method, together with the primary measures, reached an efficiency of 58 %.

KEYWORDS: SCR, SNCR, fluidized bed boiler, denitrification, deNO_x, coal.

1. INTRODUCTION

Many countries rely on and will have to rely on the combustion of fossil fuels for electricity and heat production over the next few years. The combustion of fossil fuels is associated with the production of pollutants that must be minimized in order to operate the technology with low environmental impacts. Nitrogen oxides can be identified among typical pollutants and are responsible for acid gas deposition, ozone depletion, and health effects on humans. In the field of pollutant reduction, the most important regulation is given by the BAT (Best Available Techniques) Reference Document for Large Combustion Plants (LCP) [1] that describes the primary and secondary measures to reduce the release of nitrogen oxides (so-called denitrification) from combustion plants to the atmosphere. These measures, which are usable for fluidized bed boilers, are summarized in Table 1 with the corresponding general NO_x reduction rates efficiencies.

This article is focused on the experimental investigation of secondary denitrification measures in a bubbling fluidized bed boiler using Czech lignite as a fuel. Reachable denitrification levels are analysed using the SCR and SNCR technologies. The mitigation of nitrogen oxides is important for more than just meeting the BAT and emission standards. Regarding upcoming trends of lowering CO₂ emissions from energy conversion, combustion systems using fossil fuels can be extended by CCS/U technologies, most typically post-combustion systems or oxy-fuel combustion. The reduction in NO_x production is crucial for those

Primary measures	NO _x reduction rate [%]
Low excess air firing	10–44
Air staging	10–77
Flue-gas recirculation (FGR)	20–60
Reduction of the combustion air temperature	20–30
Secondary measures	
Selective catalytic reduction (SCR)	80–95
Selective non-catalytic reduction (SNCR)	30–50

TABLE 1. NO_x reduction rates of primary and secondary measures [1].

technologies as well, since a high purity of CO₂ and low levels of acid-forming gases (like nitrogen oxides) are required.

2. NITROGEN OXIDES

2.1. FORMATION OF NO_x EMISSIONS

There are three known mechanisms of nitrogen oxides formation in combustion processes [2–4]:

- thermal NO_x – oxidation of molecular nitrogen from the oxidant at high temperatures, known as the Zeldovich mechanism,
- fuel NO_x – oxidation of chemically bound nitrogen in solid fuels,

- prompt NO_x – reactions of molecular nitrogen with hydrocarbon radicals with subsequent oxidation of intermediate products in high-temperature reducing flame zones, known as the Fenimore mechanism.

NO_x from conventional coal combustion typically consists of nitric oxide (NO) and nitrogen dioxide (NO₂), where NO is the most dominant with a share of about 90 % and more. The dominating formation mechanisms depend on the type of combustor. In the high-temperature systems, e.g. pulverized coal combustion, Zeldovich and Fenimore mechanisms are more dominant, while fuel-N oxidation dominates in fluidized beds. The fuel-N mechanism is only weakly dependent on the combustion temperature, and there is a proportional correlation with oxygen stoichiometry [5–8]. In addition to NO and NO₂, a significant nitrous oxide production (N₂O) can also be observed. N₂O is not part of NO_x emission limits and the measures for its reduction are not part of BAT, it is a gas of importance due to its high GWP potential [9]. The measured N₂O emissions from coal combustion systems (except fluidized bed) as the ratio of N₂O/NO_x emissions are typically less than 2 percent [4]. For coal-fired fluidized bed combustors, N₂O emissions are within the range of 17 to 48 % of overall NO_x emissions [4]. N₂O is produced in fluidized bed boilers due to its dependence on the bed temperature. A higher temperature leads to lower N₂O emissions, which is the reverse of the bed temperature dependence of NO formation [10]. The amount of conversion of fuel-bound nitrogen to NO and N₂O is considered to be roughly constant as shown by de las Obras-Loscertales et al. [11].

2.2. DENITRIFICATION METHODS

Denitrification is a general term for a NO_x limitation. Technologies for NO_x reduction can be categorized into primary measures that consist of modifying the operating parameters of combustion, leading to a suppression of the formation mechanisms, and secondary measures. Secondary measures represent flue gas treatment leading to the reduction of NO_x already formed. Those technologies can be used independently or in combinations.

2.2.1. PRIMARY MEASURES

The primary measures are typically most effective for the Zeldovich and Fenimore mechanisms, and they are focused on reducing the oxygen available in the combustion zone and reducing the peak temperatures. Primary measures technologies include air or fuel staging, low NO_x burners, and flue gas recirculation systems.

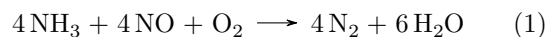
When solid fuels are burned in fluidized bed boilers, the relevant measures to reduce the NO_x production are those that focus on fuel-N-originating NO_x. As explained in Section 2.1, the fuel-NO_x mechanism is mostly dependent on the concentration of oxygen in the primary combustion zone. Therefore, the most effective measures aim only at lowering the

stoichiometry of the primary air and not at lowering the combustion temperature, since the fluidized bed temperature is inevitably too low for the thermal and prompt mechanism to occur. In particular, the only primary measure, which is not an inherent part of the fluidized bed combustion control process, is the staged injection of combustion air. It is used to achieve the required combustion parameters, such as sub-stoichiometric conditions in the dense bed (which decrease the NO_x formation), simultaneous combustion of the unburned CO in the freeboard section, and increase of the freeboard temperature for efficient injection of the reducing agent. When secondary air is used to burn unburned CO, no more nitrogen oxides are formed in the freeboard section [3, 12–16]. Air staging has been shown to be an effective primary measure for NO_x reduction in a fluidized bed boiler; for example, Lupiáñez et al. [13] observed a 40 % reduction in NO_x for a 20 % secondary air ratio as compared to NO_x without air staging. However, air staging shows insufficient NO_x reduction rates to meet the emission limits defined in the LCP directive, and secondary measures have to be applied.

2.2.2. SECONDARY MEASURES

Secondary measures, also called post-combustion methods, represent a group of chemical processes in which already formed nitrogen oxides are decomposed into molecular nitrogen and water vapor using a reducing agent. Typical reducing agents are ammonia and urea solutions. Selective non-catalytic reduction and selective catalytic reduction are the basic secondary methods. Other processes developed to date, such as simultaneous denitrification and desulphurization methods or wet scrubbing, have not been applied on a larger scale [7, 17, 18].

SNCR The selective non-catalytic reduction is a method that reduces nitrogen oxides in the absence of a catalyst. The process is based on the following reaction [18]:



To achieve a sufficient NO to N₂ conversion, the reaction temperature of 900 °C is required according to the calculation of the Gibbs energy. The typical temperature window for SNCR in industrial applications is between 850 and 1100 °C. When the reducing agent is injected into the low temperature region, the nitrogen oxides do not react with the NH₂ radical due to the low reaction rate and unreacted ammonia leaves the combustor with the flue gas. As a result, the concentration of ammonia in the flue gas increases and it may also be adsorbed on fly ash particles. On the other hand, when the reducing agent is injected above the high boundary of the temperature range, the NH₂ radical preferentially begins to react with

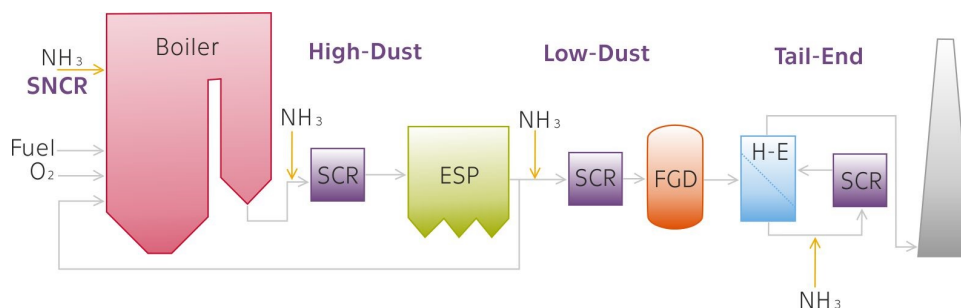


FIGURE 1. Possible locations of secondary denitrification measures.

oxygen, resulting in an increase in NO_x concentration in the flue gas. The efficiency of this method is, therefore, highly dependent on the injection of the reducing agent at the right temperature, which can differ with the used reducing agent. The optimum temperature for the reaction also varies depending on the reducing agent used. For example, for ammonia, it is in the range of 850–1000 °C, and for urea, between 950–1100 °C [4–6, 17].

SCR The fundamental principle of the selective catalytic reduction is similar to that of the non-selective reduction with the same reaction scheme. In this method, a catalyst is used that lowers the activation energy of the key reaction. As a result, the reduction can be performed at lower temperatures, and there is no need to keep the reacting substances for the necessary period of time in the high-temperature region. Depending on the type of catalyst, the temperature window can be 250 °C to 600 °C (for zeolite catalysts) [7], but the most commonly used vanadium pentoxide catalyst in the titanium dioxide carrier has an optimal temperature window of 250–430 °C with an achievable denitrification efficiency of more than 90% [3, 7, 17, 19]. The lower temperature limit is set by the reaction rate and formation and deposition of the ammonium sulphate salt, which may deposit on the catalyst and cause its temporary deactivation. The upper temperature limit is established by physical damage to the catalyst by sintering and by oxidation of NH_3 to NO , thus limiting the NO_x conversion, and by supersaturation of the catalyst that leads to an excess of unreacted ammonia, which escapes along with the combustion gas [4, 18, 20]. The latest V_2O_5 -based SCR catalysts are produced with the addition of tungsten trioxide (WO_3) and molybdenum trioxide (MoO_3), which are added for the expansion of the optimal temperature window and because of their ability to resist catalyst poisoning. These are applied by impregnation on a TiO_2 support that has a good resistance to sulfur oxides. This support is coated on the ceramic skeleton of the catalyst body. Vanadium catalysts work the best at temperatures of about 350 °C [5]. At lower temperatures, their efficiency decreases rapidly and at higher temperatures, corrosion problems arise [2, 7, 19]. The catalyst can be placed at different locations along the flue gas con-

duit as shown in Figure 1, and the placement depends on its type and material. It is not appropriate to place the catalyst in the high dust region for the fluidized bed combustion while using the dry additive desulfurization method because of the high abrasion properties of the present particles.

3. EXPERIMENTAL SET-UP

3.1. EXPERIMENTAL FACILITY

The experimental boiler is located in the CTU laboratories in Prague. This pilot unit is a fluidized bed boiler with a thermal output of 500 kW, and its scheme is shown in Figure 2.

Fluidization is achieved by primary air together with recirculated flue gas passing through the distributor, which consists of 36 nozzles. The distributor is described in detail in [21] and the boiler in [22]. The combustion chamber has a cylindrical cross section. In the freeboard area, there are 6 thermocouples placed along the height. The secondary air is supplied to the freeboard section by four evenly placed distributors on a perimeter, and each distributor can provide a secondary air inlet at 4 different heights. The heat exchanger is located in the second descending draft of the boiler. The flue gases are sampled downstream of the boiler prior to the cyclone particle separator, and its composition is continuously analysed. In particular, the volumetric fractions of the following components are measured: O_2 using a paramagnetic sensor; SO_2 , NO_x , CO_2 and CO using NDIR analysers. The boiler can also be operated in oxy-fuel mode. The off gas was also sampled downstream of the de NO_x unit and analysed using the multicomponent FT-IR analyser.

The SNCR reducing agent distribution line basically consists of two main components: a probe with a spray nozzle and a system for transporting the reducing agent to the spray system. The probe is cooled by water to prevent the reducing agent from boiling before it is sprayed. Compressed air is introduced in front of the nozzle orifice to improve the atomization of the supplied reducing agent. It is possible to place the probe in various inspection holes in the combustion space of the boiler and thus change the height of the injection of the reducing agent. For the experiments, secondary air inlets at a height of

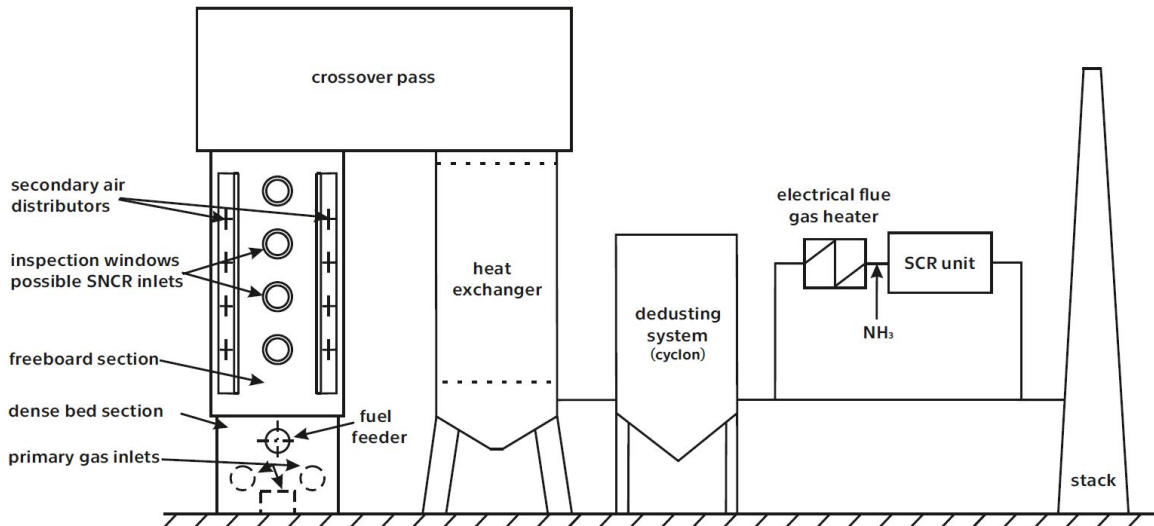


FIGURE 2. Fluidized bed boiler scheme.

Properties “As received”			Properties “Dry ash free”				
LHV [MJ/kg]	Water [wt. %]	Ash [wt. %]	C [wt. %]	H [wt. %]	O [wt. %]	N [wt. %]	S [wt. %]
18.5	25.0	9.3	72.3	6.3	19.0	1.1	1.3

TABLE 2. Proximate and ultimate analysis of the fuel

550 mm above the fluidized bed were used to achieve the optimal temperature window.

The catalyst for the SCR method has dimensions of 160 mm × 160 mm × 1260 mm. The reduction of NO_x in the flue gas is carried out by means of ammonia, which is dosed into the flue gas stream before the reactor itself. The technology is connected to the output of a cyclone separator from the fluidized bed boiler. Dedusted flue gases at a temperature of 150–180 °C are heated in an electric heater to the required temperature of 250–300 °C. The amount of flue gas that passes through the reactor at a speed of 4.5 m/s through the catalyst is approximately 150 Nm³/hour. It is necessary to inject the ammonia gas into the flue gas for the reaction on the catalyst surface. The stoichiometric amount of ammonia is approximately 0.012–0.016 kg/h. The catalyst itself is a honeycomb-type based on vanadium pentoxide (V₂O₅) with the addition of tungsten trioxide (WO₃) and molybdenum trioxide (MoO₃). Doping is applied by impregnation of the TiO₂ supporting body and is used to improve the mechanical stability and chemical resistance of the catalyst, which is related to the widening of the optimal temperature window.

3.2. FUEL AND REDUCING AGENTS

Lignite from the coal basin of North Bohemia was used as fuel for the experiments. Its proximate and ultimate analysis is shown in Table 2. The size of the coal particles was less than 10 mm. Pure ammonia was used as the SCR reducing agent and AdBlue (a

chemically highly pure aqueous solution of synthetic urea – 32.5 % wt. urea) was used for the SNCR.

3.3. METHODS

The normalized stoichiometric ratio is the proportion of the molar ratio of the reducing agent and nitrogen oxides at the beginning of the denitrification process. The range of variables measured was as follows. A detailed description of the variables is given in Table 2, where the O₂ concentrations are related to 6 % vol. of O₂ in dry flue gas.

For the SNCR method:

- NSR values from 0.55 to 3.47,
- application of primary measures (flue gas recirculation and air staging),
- temperature for reducing agent injection from 880 to 950 °C,
- the average time in one setting was 45 min.

For the SCR method:

- NSR values from 0.29 to 1.6,
- application of primary measures (flue gas recirculation),
- catalyst temperatures from 259 to 299 °C,
- the average time in one setting was 74 min.

Individual states were set maintaining a constant temperature while the injection of the reducing agent was gradually changed. The urea solution was chosen

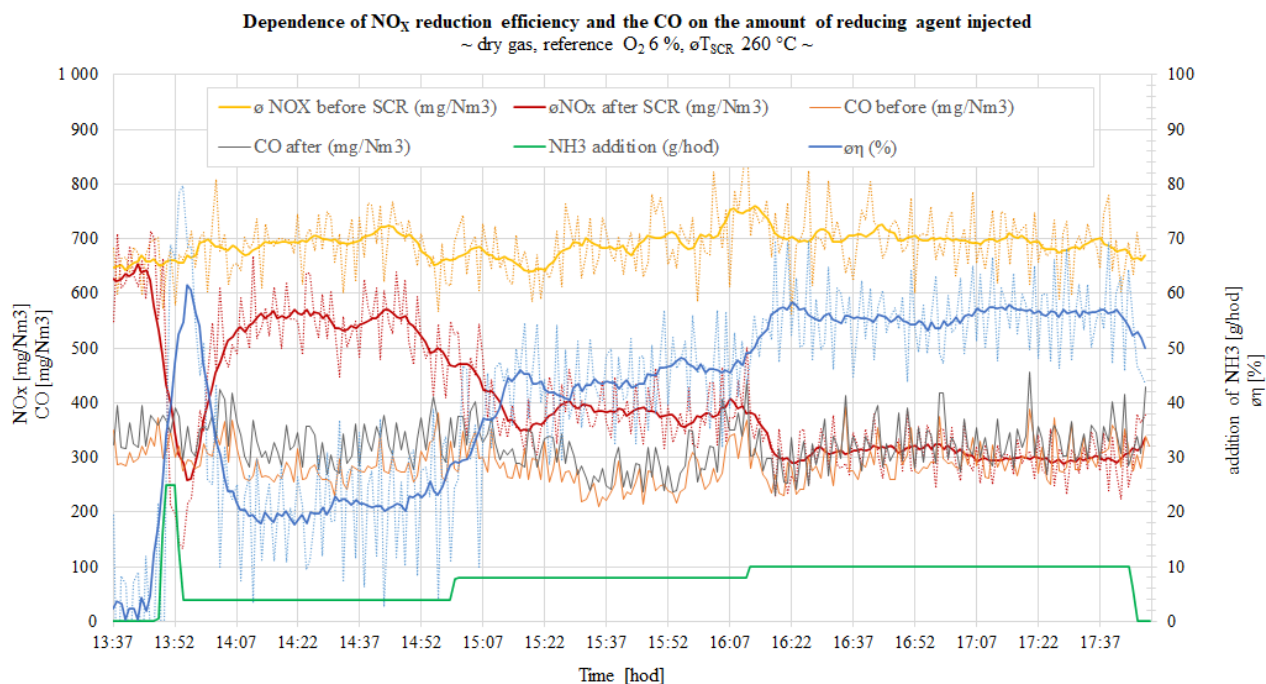


FIGURE 3. Summarization of the experimental results for SCR and SNCR.

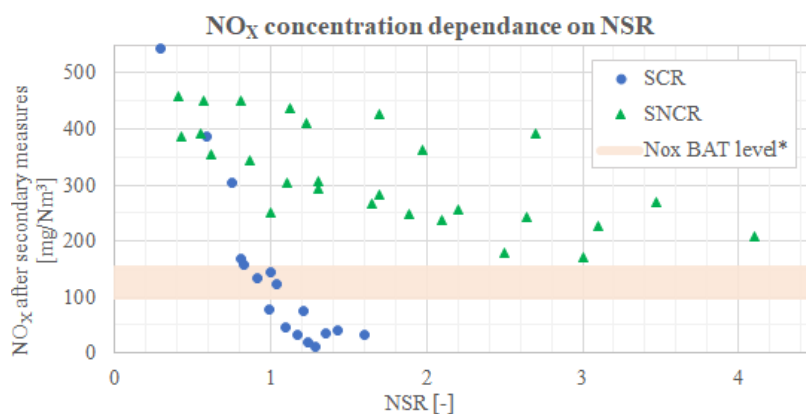


FIGURE 4. Achievable NO_x level for SCR and SNCR methods in NSR for the same BFB boiler.

*BAT-AELs (mg/Nm³) for NO_x emissions from combustion of black and/or brown coal into the atmosphere for the new combustion plants with the total rated thermal output < 100 MWth of 100–150 mg/m³ [23].

for the SNCR due to the properties of ammonia, which has very strict storage rules, and therefore is not used in large industrial plants for the SNCR method. Nevertheless, the fundamental reaction scheme for SCR and SNCR and both used reagents remains similar. Furthermore, the experiments performed are closer to the practical results due to the size of the experimental boiler.

4. RESULTS AND DISCUSSION

Measured data are presented in Table 3 and Figure 4. More detailed data with their variations are listed in Appendix.

The CO emissions were also measured, however, no significant correlation between CO and NO_x was observed as can be seen in Figure 3.

4.1. REDUCING AGENT EXCESS

As shown in Figure 4, there is a significant difference between the excess of reducing agent needed to achieve the same NO_x reduction efficiency for the SCR and SNCR denitrification methods. As can be seen from Figure 4, the experiments confirmed that for SCR, a lower excess of the reducing agent is needed to reach the same NO_x level after the secondary denitrification method because the catalyst reduces the activation energy of the chemical process.

According to [24], the reducing agent stoichiometry for SNCR has the optimum values between 1.5–2.5. Experiments showed the highest efficiency values when using NSR around 2.5, but it is always necessary to monitor the ammonia slip in the flue gas, which is subject to the BAT-associated emission level. According to BAT, the level of NH₃ emissions into the air from

Meas- urement no.	Tempe- rature [°C]	NO _x before SNCR	NO _x after SNCR	NO _x conversion	NSR	NH ₃ slip	
		[mg/Nm ³]	[mg/Nm ³]	[%]	[mol/mol]	[mg/Nm ³]	
1			250	22.1	1.00		
2	959	321	238	26.0	2.10		
3			228	29.0	3.10		
4			209	35.1	4.10		
5				392	14.7	0.55	
6	883	459	303	34.1	1.10	not measured	
7			267	41.9	1.65		
8			257	43.9	2.20		
9			242	47.2	2.64		
10	886	408	356	12.9	0.62		
11			293	28.2	1.30		
12			249	39.0	1.89		
13			179	56.3	2.50		
14			170	58.4	3.00		
15	868	424	388	8.7	0.43		0.3
16			343	19.2	0.87		0.2
17			306	28.0	1.30		0.1
18			284	33.0	1.70		0.2
19			269	36.7	3.47		0.4
20	948	461	450	2.3	0.57	0.0	
21			437	5.2	1.12	0.0	
22			426	7.7	1.70	0.0	
23			393	14.7	2.70	0.8	
24				458	8.0	0.41	0.1
25	925	498	450	9.5	0.81	0.0	
26			410	17.7	1.23	0.0	
27			364	26.9	1.97	0.3	
Meas- urement no.	Tempe- rature [°C]	NO _x before SCR	NO _x after SCR	NO _x conversion	NSR	NH ₃ slip	
		[mg/Nm ³]	[mg/Nm ³]	[%]	[mol/mol]	[mg/Nm ³]	
1	260	692	544	21.0	0.29	0	
2		705	386	45.0	0.59	0	
3		698	305	56.0	0.75	0	
4		593	132	77.6	0.91	0	
5		533	31	94.1	1.17	0.1	
6		613	12	98.0	1.29	0.9	
7	290	518	168	67.4	0.81	0.2	
8		519	158	71.1	0.83	0.3	
9		504	79	85.2	0.99	0.2	
10		528	124	76.7	1.04	0.2	
11		487	47	90.4	1.09	0.2	
12		477	18	96.2	1.28	0.3	
13		486	36	93.0	1.35	0.0	
14	300	520	144	72.4	1.00	0.1	
15		531	75	85.9	1.21	0.1	
16		519	40	92.3	1.43	0.1	
17		539	31	94.1	1.60	0.1	

TABLE 3. Summarization of the experimental results for SCR and SNCR.

the use of SCR and/or SNCR is $< 3\text{--}10\text{ mg/m}_N^3$ [1]. In the case of plants that burn biomass and operate at variable loads, the upper end of the BAT-AEL range is 15 mg/m_N^3 [1]. Some of the unreacted ammonia is converted to ammonia salts and bound to fly ash, which then exhibits an unwanted odour and could become unapplicable in future use. In addition, leachable ammonia salts can restrict its application as well. Stricter requirements are therefore required by fly ash buyers who use it in the construction industry. Therefore, large combustion sources require values as low as 7 mg/m_N^3 for NH_3 in the flue gas after ESP, although ammonia can be smelled already at values of 5 mg/m_N^3 . For these reasons, the feeding of higher amounts of the reducing agent and thus a higher NSR is not desirable.

The NO_x reduction efficiency of more than 90% can be reached with the NSR greater than 1.1 for the SCR method. Further increase in the reducing agent feed is not desirable because the catalyst would be supersaturated and excess unreacted ammonia would escape along with the flue gas, causing the above-mentioned problems with the ash utilisation. In general, the SCNR method requires higher doses of the reducing agent for the same NO_x level required in the flue gas.

4.2. SCR AND SNCR EFFICIENCY

The NO_x reduction efficiency varied between 2% and 58% for the SNCR method and between 21% and 98% for the SCR method. The lower value corresponds to the lowest injection rate of the reducing agent for both methods. For the SNCR method, the best results were achieved for temperatures between 880 and 890 °C and NSR between 2.2 and 3.0 when efficiency reached 44 to 58%. For the SCR method, efficiencies higher than 90% were reached for all catalyst temperatures, while the NSR's were between 1.1 and 1.6. The results agree with the BAT conclusions as stated in Section 1. From Table 2, it can be seen that the primary measures reduce the input NO_x concentrations for the SNCR method to values between 321 and 498 mg/Nm^3 . The primary measures on this boiler are used mainly to increase the temperature in the freeboard section and thus to ensure that the optimum temperatures for NO_x reduction are reached. The SCR method was tested with flue gas recirculation (in order not to lower NO_x emission but to keep the combustion process stable) and the initial NO_x concentrations ranged between 477 and 705 mg/Nm^3 . The nitrogen emissions concentrations after the denitrification measures were between 170 and 458 mg/Nm^3 for the SNCR method and between 12 and 544 mg/Nm^3 for the SCR method (the highest value is for an insufficiently low NSR of 0.3).

4.3. SCR AND SNCR EFFICIENCY

CORRELATION WITH TEMPERATURE

There is a clear effect of temperature on the SNCR method at the feeding point of the reducing agent. In Figure 5, it can be seen that higher efficiencies are achieved at temperatures up to about 900 °C, and with increasing temperature, the efficiency decreases at the same NSRs. This corresponds to the theoretical knowledge as mentioned in Section 2.2.2, where the optimal temperature window for urea is said to be between 850 and 1000 °C.

In contrast, in the case of the SCR method, the correlation with temperature is minimal and the efficiency basically depends only on the NSR, as shown in Figure 6.

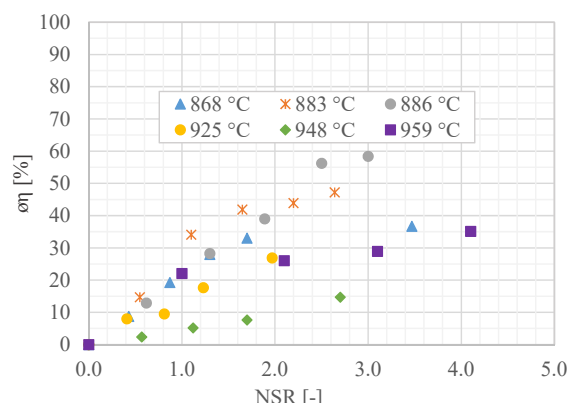


FIGURE 5. Correlation of SNCR efficiency and temperature.

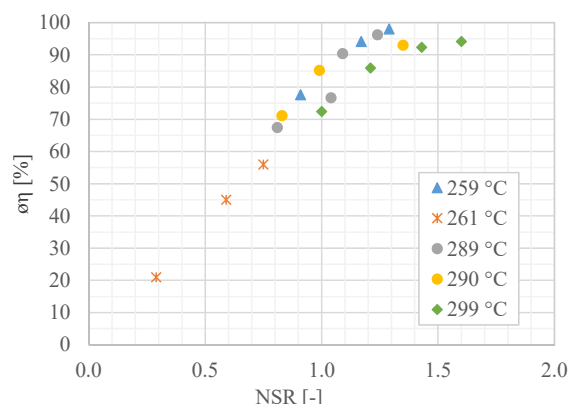


FIGURE 6. Correlation of SCR efficiency and temperature.

4.4. SCR AND SNCR COMPARISON FOR THE SAME NO_x INPUT CONCENTRATIONS

A specific comparison was made for the same NO_x input concentrations. The inlet nitrogen oxides concentration was kept at 500 mg/Nm^3 , and no primary measures were used with the purpose of lowering nitrogen oxides levels. Different NSRs were used and the trend of NO_x reduction according to the NSR can be seen in Figure 7.

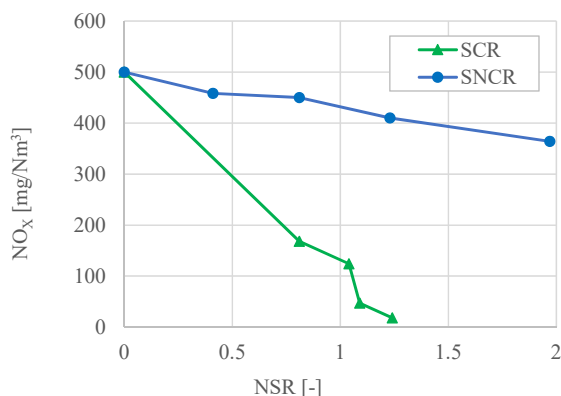


FIGURE 7. Comparison of the SCR and SNCR methods used within the same BFB boiler.

The maximum NSR for the SNCR method was 1.97. From other experimental results, we can assume that with a greater injection of the reducing agent and a lower temperature of the fluidized bed, lower nitrogen emissions could be achieved. In general, from the results it can be seen that a lower excess of the reducing agent is needed for the SCR method. The decision of whether to use the SCR or SNCR denitrification method depends on the final required level of nitrogen oxides and on the consideration of investment and operating costs.

5. CONCLUSIONS

The experimental results show the denitrification possibilities applied on the fluidized bed boiler with a thermal output of 500 kW. The size of the experimental equipment is the biggest benefit of performed experiments. The combustion of various fuel types and the generation of emissions have already been investigated, but those are mainly experimental reactors with a diameter of 100–150 mm and laboratory-made flue gas mixtures [16, 25]. Initial NO_x concentrations in the experimental boiler with lignite combustion range from 321 mg/Nm³ to 705 mg/Nm³.

The correlation of the denitrification efficiency and the NSR was investigated. It has been found that the SCR needs a lower NSR than the SNCR method to reach the same efficiency. The lower need for the reducing agent corresponds to the higher efficiency of the method because the catalyst reduces the activation energy of the reaction. In particular, NSR up to 1.6 was used for the SCR method. With higher NSRs, the ammonia slip could become too high and the ash could be degraded in the practical use of High-Dust catalysts. In contrast, the SNCR method has a higher reducing agent consumption and the best denitrification results were achieved for NSR around 2.5.

For the efficiency of both denitrification methods, the results are as follows. The SNCR method, together with primary measures (flue gas recirculation and air staging), reaches the efficiency of 58% and the efficiency of the SCR method exceeds 98%.

ACKNOWLEDGEMENTS

This work was supported by the project from Research Center for Low-Carbon Energy Technologies, CZ.02.1.01/0.0/0.0/16_019/0000753 which is gratefully acknowledged.

LIST OF SYMBOLS

BAT	best available techniques
CTU	Czech Technical University
FT-IR	Fourier transform infrared spectroscopy
LCP	large combustion plants
MoO ₃	molybdenum trioxide
NDIR	non-dispersive infrared
NH ₃	ammonia
NSR	normalized stoichiometric ratio
NO	nitric oxide
NO _x	oxide emissions
NO ₂	nitrogen dioxide
N ₂ O	nitrous oxide
SCR	selective catalytic reduction
SNCR	selective non-catalytic reduction
TiO ₂	titanium dioxide
V ₂ O ₅	vanadium pentoxide
WO ₃	tungsten trioxide

REFERENCES

- [1] T. Lecomte, J. Ferrería de la Fuente, F. Neuwahl, et al. *Best Available Techniques (BAT) reference document for large combustion plants*. EUR 28836 EN. Publications Office of the European Union, 2017. <https://doi.org/10.2760/949>.
- [2] J. Vejvoda, P. Machač, P. Buryan. *Technologie ochrany ovzduší a čištění odpadních plynů*. University of Chemistry and Technology, 2003. ISBN 80-708-0517-X.
- [3] F. Normann, K. Andersson, B. Leckner, F. Johnsson. Emission control of nitrogen oxides in the oxy-fuel process. *Progress in Energy and Combustion Science* **35**(5):385–397, 2009. <https://doi.org/10.1016/j.pecs.2009.04.002>.
- [4] C. T. Bowman. Control of combustion-generated nitrogen oxide emissions: Technology driven by regulation. *Symposium (International) on Combustion* **24**(1):859–878, 1992. [https://doi.org/10.1016/S0082-0784\(06\)80104-9](https://doi.org/10.1016/S0082-0784(06)80104-9).
- [5] J. Hemerka, P. Vybíral. *Ochrana ovzduší*. Czech Technical University in Prague, 2010. ISBN 978-80-01-04646-3.
- [6] P. Machač, E. Baraj. A simplified simulation of the reaction mechanism of NO_x formation and non-catalytic reduction. *Combustion Science and Technology* **190**(6):967–982, 2018. <https://doi.org/10.1080/00102202.2017.1418335>.
- [7] P. Forzatti. Present status and perspectives in de-NO_x SCR catalysis. *Applied Catalysis A: General* **222**(1-2):221–236, 2001. [https://doi.org/10.1016/S0926-860X\(01\)00832-8](https://doi.org/10.1016/S0926-860X(01)00832-8).

- [8] K. El Sheikh, M. J. H. Khan, M. Diana Hamid, et al. Advances in reduction of NO_x and N_2O_1 emission formation in an oxy-fired fluidized bed boiler. *Chinese Journal of Chemical Engineering* **27**(2):426–443, 2019. <https://doi.org/10.1016/j.cjche.2018.06.033>.
- [9] IPCC, 2007. *Climate Change 2007: Synthesis Report. Contribution of Working Groups I, II and III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change [Core Writing Team and Pachauri, R.K. and Reisinger, A. (eds.)]*. IPCC, Geneva, Switzerland, 2007. ISBN 92-9169-122-4.
- [10] L. E. Aamand, B. Leckner, S. Andersson. Formation of nitrous oxide in circulating fluidized-bed boilers. *Energy & Fuels* **5**(6):815–823, 1991. <https://doi.org/10.1021/ef00030a008>.
- [11] M. de las Obras-Loscertales, T. Mendiara, A. Rufas, et al. NO and N_2O emissions in oxy-fuel combustion of coal in a bubbling fluidized bed combustor. *Fuel* **150**:146–153, 2015. <https://doi.org/10.1016/j.fuel.2015.02.023>.
- [12] M. Vodička, J. Hrdlička, P. Skopec. Experimental study of the NO_x reduction through the staged oxygen supply in the oxy-fuel combustion in a 30kW_{th} bubbling fluidized bed. *Fuel* **286**:119343, 2021. <https://doi.org/10.1016/j.fuel.2020.119343>.
- [13] C. Lupiáñez, L. I. Díez, L. M. Romeo. Influence of gas-staging on pollutant emissions from fluidized bed oxy-firing. *Chemical Engineering Journal* **256**:380–389, 2014. <https://doi.org/10.1016/j.cej.2014.07.011>.
- [14] M. de las Obras-Loscertales, A. Rufas, L. de Diego, et al. Effects of temperature and flue gas recycle on the SO_2 and NO_x emissions in an oxy-fuel fluidized bed combustor. *Energy Procedia* **37**:1275–1282, 2013. <https://doi.org/10.1016/j.egypro.2013.06.002>.
- [15] T. Czakiert, Z. Bis, W. Muskala, W. Nowak. Fuel conversion from oxy-fuel combustion in a circulating fluidized bed. *Fuel Processing Technology* **87**(6):531–538, 2006. <https://doi.org/10.1016/j.fuproc.2005.12.003>.
- [16] W. Moroń, W. Rybak. NO_x and SO_2 emissions of coals, biomass and their blends under different oxy-fuel atmospheres. *Atmospheric Environment* **116**:65–71, 2015. <https://doi.org/10.1016/j.atmosenv.2015.06.013>.
- [17] X. Cheng, X. T. Bi. A review of recent advances in selective catalytic NO_x reduction reactor technologies. *Particology* **16**:1–18, 2014. <https://doi.org/10.1016/j.partic.2014.01.006>.
- [18] F. Gholami, M. Tomas, Z. Gholami, M. Vakili. Technologies for the nitrogen oxides reduction from flue gas: A review. *Science of The Total Environment* **714**:136712, 2020. <https://doi.org/10.1016/j.scitotenv.2020.136712>.
- [19] Y. GAO, T. LUAN, T. LÜ, et al. Performance of $\text{V}_2\text{O}_5\text{--WO}_3\text{--MoO}_3/\text{TiO}_2$ catalyst for selective catalytic reduction of NO_x by NH_3 . *Chinese Journal of Chemical Engineering* **21**(1):1–7, 2013. [https://doi.org/10.1016/S1004-9541\(13\)60434-6](https://doi.org/10.1016/S1004-9541(13)60434-6).
- [20] L. Olsson, H. Sjövall, R. J. Blint. A kinetic model for ammonia selective catalytic reduction over Cu-ZSM-5 . *Applied Catalysis B: Environmental* **81**(3-4):203–217, 2008. <https://doi.org/10.1016/j.apcatb.2007.12.011>.
- [21] J. Hrdlicka, P. Skopec, F. Hrdlicka. Trough air distributor for a bubbling fluidized bed boiler with isobaric nozzles. In *Proceedings of the 22nd International Conference on Fluidized Bed Conversion*, vol. 1. Turku, Finland, 2015. ISBN 978-952-12-3222-0.
- [22] P. Skopec, J. Hrdlička, J. Opatřil, J. Štefanica. NO_x emissions from bubbling fluidized bed combustion of lignite coal. *Acta Polytechnica* **55**(4):275–281, 2015. <https://doi.org/10.14311/AP.2015.55.0275>.
- [23] Provdádcí rozhodnutí komise (EU) 2021/2326. *Úřední věstník Evropské unie* **L 469**:1–81, 2021. <https://eur-lex.europa.eu/legal-content/CS/TXT/PDF/?uri=CELEX:32021D2326&from=EN>.
- [24] M. Mladenović, M. Paprika, A. Marinković. Denitrification techniques for biomass combustion. *Renewable and Sustainable Energy Reviews* **82**:3350–3364, 2018. <https://doi.org/10.1016/j.rser.2017.10.054>.
- [25] Y. Hu, S. Naito, N. Kobayashi, M. Hasatani. CO_2 , NO_x and SO_2 emissions from the combustion of coal with high oxygen concentration gases. *Fuel* **79**(15):1925–1932, 2000. [https://doi.org/10.1016/S0016-2361\(00\)00047-8](https://doi.org/10.1016/S0016-2361(00)00047-8).

A. APPENDIX

SNCR							
Meas- urement no.	Tempe- rature [°C]	NO _x before SNCR [mg/Nm ³]	NO _x after SNCR [mg/Nm ³]	NO _x conversion [%]	NSR [mol/mol]	O ₂ [%]	NH ₃ slip [mg/Nm ³]
1			250 ± 12	22.1 ± 2.3	1.00	5.0 ± 0.2	
2			238 ± 9	26.0 ± 1.0	2.10	6.5 ± 0.7	
3	959 ± 5	321 ± 31	228 ± 14	29.0 ± 0.8	3.10	7.1 ± 0.2	
4			209 ± 9	35.1 ± 1.7	4.10	6.6 ± 0.2	
5			392 ± 33	14.7 ± 7.2	0.55	6.9 ± 0.6	
6			303 ± 14	34.1 ± 3.0	1.10	5.9 ± 0.3	
7	883 ± 10	459 ± 29	267 ± 15	41.9 ± 3.3	1.65	5.7 ± 0.3	
8			257 ± 14	43.9 ± 3.4	2.20	5.7 ± 0.3	
9			242 ± 10	47.2 ± 2.3	2.64	5.9 ± 0.3	
10			356 ± 25	12.9 ± 3.3	0.62	5.3 ± 0.4	
11			293 ± 29	28.2 ± 3.6	1.30	4.6 ± 0.4	
12	886 ± 8	408 ± 22	249 ± 23	39.0 ± 3.1	1.89	4.5 ± 0.4	
13			179 ± 37	56.3 ± 3.9	2.50	4.7 ± 0.7	
14			170 ± 11	58.4 ± 0.6	3.00	3.6 ± 0.3	
15			388 ± 25	8.7 ± 3.6	0.43	6.5 ± 0.8	0.3 ± 0.1
16			343 ± 19	19.2 ± 1.7	0.87	5.8 ± 0.5	0.2 ± 0.1
17	868 ± 20	424 ± 33	306 ± 15	28.0 ± 1.1	1.30	5.5 ± 0.6	0.1 ± 0.1
18			284 ± 13	33.0 ± 1.2	1.70	5.1 ± 0.4	0.2 ± 0.1
19			269 ± 22	36.7 ± 2.0	3.47	5.5 ± 0.5	0.4 ± 0.2
20			450 ± 22	2.3 ± 3.4	0.57	6.4 ± 0.5	0.0 ± 0.1
21			437 ± 38	5.2 ± 1.2	1.12	5.4 ± 1.8	0.0
22	948 ± 29	461 ± 7	426 ± 27	7.7 ± 2.1	1.70	4.3 ± 0.3	0.0
23			393 ± 12	14.7 ± 0.8	2.70	4.4 ± 0.4	0.8 ± 0.3
24			458 ± 12	8.0 ± 2.6	0.41	7.0 ± 0.3	0.1 ± 0.1
25			450 ± 8	9.5 ± 1.5	0.81	7.2 ± 0.3	0.0
26	925 ± 11	498 ± 8	410 ± 12	17.7 ± 2.6	1.23	7.2 ± 0.2	0.0
27			364 ± 43	26.9 ± 8.8	1.97	7.3 ± 0.8	0.3 ± 0.2

TABLE 4. Experimental results for SNCR.

SCR							
Meas- urement no.	Tempe- rature [°C]	NO _x before SCR [mg/Nm ³]	NO _x after SCR [mg/Nm ³]	NO _x conversion [%]	NSR [mol/mol]	O ₂ [%]	NH ₃ slip [mg/Nm ³]
1	260 ± 2	692 ± 74	544 ± 58	21.0 ± 9.9	0.29 ± 0.02	10.1 ± 0.5	0
2		705 ± 60	386 ± 46	45.0 ± 7.3	0.59 ± 0.03	10.5 ± 0.9	0
3		698 ± 50	305 ± 38	56.0 ± 6.5	0.75 ± 0.03	10.6 ± 0.7	0
4		593 ± 54	132 ± 20	77.6 ± 3.0	0.91 ± 0.07	9.8 ± 0.7	0
5		533 ± 70	31 ± 15	94.1 ± 2.5	1.17 ± 0.12	9.7 ± 0.8	0.1 ± 0.2
6		613 ± 73	12 ± 4	98.0 ± 0.9	1.29 ± 0.09	10.5 ± 0.9	0.9 ± 0.2
7	290 ± 1	518 ± 40	168 ± 24	67.4 ± 4.3	0.81 ± 0.06	9.8 ± 0.6	0.2 ± 0.1
8		519 ± 19	158 ± 11	71.1 ± 1.8	0.83 ± 0.04	9.5 ± 0.5	0.3 ± 0.1
9		504 ± 19	79 ± 9	85.2 ± 1.7	0.99 ± 0.05	9.3 ± 0.5	0.2 ± 0.1
10		528 ± 45	124 ± 24	76.7 ± 3.6	1.04 ± 0.15	10.7 ± 1.4	0.2 ± 0.1
11		487 ± 28	47 ± 9	90.4 ± 1.9	1.09 ± 0.06	8.4 ± 0.4	0.2 ± 0.1
12		477 ± 46	18 ± 7	96.2 ± 1.4	1.28 ± 0.10	8.4 ± 0.6	0.3 ± 0.1
13		486 ± 18	36 ± 8	93.0 ± 1.6	1.35 ± 0.05	9.0 ± 0.5	0.0 ± 0.1
14	300 ± 1	520 ± 37	144 ± 17	0.4 ± 2.4	1.00 ± 0.06	9.2 ± 0.5	0.1 ± 0.1
15		531 ± 15	75 ± 5	85.9 ± 1.0	1.21 ± 0.06	9.4 ± 0.2	0.1 ± 0.1
16		519 ± 15	40 ± 7	92.3 ± 1.2	1.43 ± 0.07	9.3 ± 0.4	0.1 ± 0.1
17		539 ± 30	31 ± 6	94.1 ± 1.2	1.60 ± 0.09	9.5 ± 0.4	0.1 ± 0.1

TABLE 5. Experimental results for SCR.