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Selective Non-catalytic Reduction (SNCR) and its Efficiency with Respect to Various Combustion Parameters

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Nitrogen oxides, which are formed for example during the combustion process in coal power plants, have negative impact on the environment. It is one of the main components of greenhouse gases and together with sulfur oxides cause acid rains. When reducing the formation and discharge of nitrogen oxides, it is possible to proceed several technological processes. One of the methods that is used in practice for reducing these pollutants, is selective non-catalytic reduction (SNCR). Increasingly stringent emission limits forcing businesses to invest in a system for removing NO_x. SNCR method is one of the cheapest, but sufficiently effective alternative to achieve these levels.

This contribution describes the experimental tests of injecting a reducing agent into the flue gas stream. In this case a reducing agent (with the trade name Satamin) consisting of an aqueous urea solution and an additives. The tests were performed in the boiler K14 at the power plant in Ostrava - Třebovice, CZ. The aim of the tests was to reduce NO_x emissions achieved by primary measures (e.g., adjusting the pressure of the boiler unit, low NO_x pulverised coal burners, change media for grinding mill circuits) so that the flue gas at the outlet reaches approximately 190 mg/m_N³, because NO_x emission limit specified by legislation is established to 200 mg/m_N³.

Efficiency SNCR was determined based on the conversion rate of Satamin and the associated reduction of primary NO_x to a final value measured at a chimney. The contribution shows and compares the impact of various factors (the concentration of CO in the flue gas stream, the primary value of NO_x , the temperature in the combustion chamber, etc.) that affect, positively or negatively, the reaction process of Satamin and NO_x according to the equations (Dvořák, et al., 2010):

$$4NO + 2(NH_2)_2CO + 2H_2O + O_2 \rightarrow 4N_2 + 6H_2O + 2CO_2$$
(1)

$$6 NO_2 + 4 (NH_2)_2 CO + 4 H_2 O \rightarrow 7 N_2 + 12 H_2 O + 4 CO_2$$
(2)

1. Introduction

Selective non-catalytic reduction (SNCR) is one of the denitrification methods, which belongs to the secondary measures. Operation costs of SNCR are lower than SCR and also efficiency is very different. Average efficiency for SCR is about 92 % (with fixed bed catalytic reactor), however for SNCR is mostly about 55 % (European IPPC Bureau, 2014). It depends on boiler condition and significantly on temperature at level of dosing reducing agents (e.g. ammonia and urea). Suitable range of temperature is called temperature window. Reduction by applying urea is usually done in ranging from 950 °C to 1,050 °C (European IPPC Bureau, 2014).

Urea reacts with NO_x contained in flue gas. The most amount of NO_x is represented by nitric oxide (NO), however other oxide, as nitrogen dioxide (NO₂) or nitrous oxide (N₂O), take only few percent of NO_x (Dvořák, et al., 2010). Desired reactions between NO_x and urea solution is Eq(1) and Eq(2) (Dvořák et al., 2010). If temperature in dosing zones reaches out of temperature window undesired reactions Eq(3), Eq(4), Eq(5) proceed (Kanniche et al., 2011). Urea doesn't react when temperature is below range and causes ammonia slip. Over the range reductant burns and the amount of NO_x increases.

$$4NO + 4NH_3 + 3O_2 \to 4N_2O + 6H_2O \tag{3}$$

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$$4NH_3 + 5H_2O \to 4NO + 6H_2O \tag{4}$$

$$4NH_3 + 3O_2 \to N_2 + 6H_2O \tag{5}$$

Limit of NO_x emission for coal power plants stipulated by Czech legislation is 200 mg/m_N³ (Czech Government Regulation 352/2002 Sb.). In the present it doesn't define any limit of ammonia slip. Acceptable value of ammonia slip was determined under 5 mg/m_N³.

2. Boiler unit and combustion process

Measurements were carried out in the boiler K14, which is part of the production block of power plant Třebovice. It is a steam coal boiler (hard coal) with a dry bottom furnace. Steam boiler capacity is 110 t/h to 220 t/h. The outlet temperature and pressure is 535 °C and 10.89 MPa.

2.1 Description of boiler unit

Coal dust is prepared in two grinding mill circuits (GMC) for burning. Milling circuits are independent on each other. Boiler system consists of 18 burners (Figure 1) - 12 pulverised-coal burners (numbers 1-12), 2 start-up and stabilising burners and 4 waste-vapour burners (A - D). Pulverised-coal burners are located at the corners of the boiler unit in three levels. Waste-vapour burners lead into the boiler waste vapours (preheated air containing particles dedusted in cyclones), which are dosed between the middle and upper level of the pulverised-coal burner (see Figure 1). Stability of the flame is checked by 8 pyrometers disposed between the upper and middle levels of burners. Additional air is delivered into the fireplace. These are called over fire air - OFA, which is important in terms of NO_x reduction.



Figure 1: Placement of burners and SNCR method in boiler unit

2.2 Description of flue gas cleaning

Part of the gas cleaning system except SNCR technology is also electrostatic precipitator and DeSOx technology to eliminate emissions of SO₂, which is implemented by dosing sorbent into the flue gas. In the combustion chamber (at a height of 18.3 m) is the flue gas temperature measured using the AGAM system (acoustic gas temperature measurement) with six sensors. Measuring emissions of NH₃ slip is implemented by a diode laser spectrometer (LDS 6). As emissions are measured before entry into the chimney, ammonia can be partially dissociated on the filter in the form of salts. Despite the value of NH₃ slip is one indicator of the effectiveness of SNCR technology.

The reducing agent may be dosed into one of two zones, which are at a height of 18 m and 24.3 m above the furnace. There are six nozzles in each layer (three on the right and left side of the boiler). The reduction mixture, consisting of demineralised water and satamin (40 % an aqueous urea solution), is in the nozzle to enlarge the interphase interfaces broken atomising air to fine drops. At the ends of the nozzles special angled nozzles are installed, which with their design regulate drops trajectory. Thanks to this change, the reducing agent gets in lower flue gas temperature and achieves better conversion of chemical reaction.

Switching between zones is automated based on steam output or the temperature in the combustion chamber. Limits for switching to individual layers are described in Table 1. The level switches when the current value of the output or the temperature exceeds the limit. In the transition area reduction takes place from both levels. During the tests only switching zones according to temperature was used. The final adjustment will be made in optimising the operation.

Table 1: Switching output and temperature

Steam boiler output	Temperature AGAM	Number of dosing level
145 t/h	1,000 °C	2
120 t/h	950 °C	1

2.3 Estimated curve dosing the reducing agent

Dosage of satamin is not linear. At low and high outputs are the consumptions the highest (see Figure 2). When the capacity is low, it is more difficult to maintain the stability of the flame inside the boiler, which causes uneven NO_x production in time. The main factors affecting convergence of satamin and nitrogen oxides is the oxygen concentration and temperature in the combustion chamber. Increasing the concentration of oxygen in the combustion process negatively affects the formation of primary NO_x, which must be further reduced.



Figure 2: Dosing of satamin for different steam output

3. Past tests

In the tests several measurements at low and high output were conducted, and when operating at marginal temperature between zones (i.e. 1,000 °C). The assessment was based on data recorded every minute.

3.1 Comparison of injection levels at low power

At steam output of 130 t/h, the temperature was measured by the AGAM system in the temperature range 950 $^{\circ}$ C – 1,010 $^{\circ}$ C. The flue gas temperature depends significantly on the steam boiler output, fuel efficiency and the number of currently operating GMC and partly on the number of pulverised-coal burners.

The following information shows the measurement at capacity of 130 t/h. In the first case (Figure 3(b)) are shut down burners no. 3 and 6. The average low heat value of the fuel is 22.3 MJ/kg and the temperature is around the value of 955 °C. The reducing agent is dosed to the zone 1. In another test bottom burners no. 1, 3 and 4 were shut down, whereby the temperature in the boiler increased. Its value is around the value of 1,008 °C and the low heat value is 20.6 MJ/kg. Thanks to increased temperature, the reducing agent is dosed to the second zone. The values of measured parameters are described in Figure 3(a).



Figure 3: Steam boiler output of 130 t/h (a) Zone 2 (b) Zone 1

Both zones meet the requirements on emission limits, but neither of them is ideal for the conditions. In the case of dosing into zone 1 the consumption of satamin is considerably higher and uneven due to transient NOx emissions. In zone 2 amonia slip is significant, even if the amount of dispensed satamin is more stable and lower than in first one. The parameter values are summarised in Table 2.

Zone	Temperature	NH₃ slip	Satamin	NOx	CO	O ₂
1	955 °C	0.01 mg/m _N ³	205.4 kg/h	169.6 mg/n	า _N 3 27.69 m	ng/m _N ³ 4.83 %
2	1,008 °C	3.11 mg/m _N ³	168.5 kg/h	170.6 mg/n	า _N ³ 54.64 m	ng/m _N ³ 4.03 %

3.2 Test of the steam capacity of 200 t/h

Steam output of 200 t/h is operated with all pulverised-coal burners and usually with both GMC. The temperature ranges from 1,045 °C – 1,110 °C. Nitrogen oxides are reduced by injecting the reducing agent into the level 2. In the performance two separate tests were done with a time delay of eight hours.

The first measurement was carried out with small changes in output and temperature (1,043 °C - 1,087 °C) without significant interference in the combustion process. The quantity of dispensed satamin was stabilised after 12 min at a value 64.47 kg/h (lowest possible flow when valve is opened to 1 %). Under these conditions there was negligible ammonia slip. NO_x emissions were stabilised at 162 mg/ m_N^3 (see Table 3).

Figure 4 corresponds to the second measurement. Despite dosing double amount of the solution into the flue gas NO_x concentration did not decrease, but was slightly higher than in the first case (127 kg/h, 169 mg/m_N³). It can be concluded that the conditions in the boiler are different (i.e. combustion guality or concentration of elements). In the flue gas O₂ concentration increased by 0.4 % compared to the first measurement. At the same time the concentration of CO, which is an indicator of combustion guality, was decreased by 14 mg/mN³. Due to the increased excess air more thermal NO_x is created, more satamin is consumed to its reduction.

During measurement, there were two external intervention into the combustion process, which significantly influenced the reduction of NO_x. Opening the coal feeder because of its cleaning in 16 and 73 minute a large amount of air penetrated into the boiler space, which sharply increased the concentration of CO. Part of the boiler is an oxygen controller, which in case of increasing the CO concentration increases the amount of combustion air. During the huge increase of CO, the O2 will increase, thereby the concentration of primary NOx is increased. After closing feeder and decrease the concentration of CO is gradually reducing the amount of air and after some time, the process stabilises. Manually lowering the oxygen regulator to the level before the external intervention can speed up stabilisation. Exhaust gas oxygen concentration at end of test fell to a value of the first measurement. NO_x emissions were around 151 mg/m_N³. Ammonia slip was not detected. Table 3 shows the average values of the investigated parameters. If the case of CO concentration is due to achieve extreme concentration in the second test the median is given instead of the average value.

Experiment	Temperature	NH₃ slip	Satamin	NOx	CO	O2
1	1,066 °C	0.12 mg/m _N ³	66.1 kg/h	159.8 mg/m _N ³	42.55 mg/m _{N³}	1.85 %
2	1,008 °C	0.00 mg/m _N ³	143.0 kg/h	165.5 mg/m _N ³	35.69 mg/m _N ³	2.01 %



Figure 4: Steam boiler output of 200 t/h

3.3 Automatic switching levels at temperature about 1,000 °C

As mentioned in the introduction, the zones were changed during tests according to the temperature. As the temperature in the boiler depends on many factors, it is not possible to accurately determine the switching performance. It is assumed that the temperature of 1,000 °C will be achieved about output of 140 t/h.

The test was carried out in the range of output of 133 t/h to 149 t/h and at temperatures between 935 °C and 1,049 °C. It is obvious from the large range of temperatures, that dosing zone was changed during the measurements. The test sequence is recorded in Figure 5. The curves showing the satamin dose, concentration of NO_x and ammonia slip value show that even at times when the ammonia slip increases, and the NO_x decreases, the amount of satamin dosed into the flue gas increases. This effect is not desirable and it is caused by wrong setting of the reducing agent which, when power loss is below 138 t/h, adds a huge amount of satamin injected into the flue gas.

The test started in operation of both GMC and without pulverised-coal burners no. 4 and 6. The initial performance of 145 t/h corresponded to the temperature 990 °C. Satamin dosed to level 2. The quantity of satamin decreased at the beginning, because the value of NO_x was kept deep below the limit. At first amplitudes of satamin (in 45 minutes) its value increased of 89 kg/h to 299 kg/h. There are several factors that influenced this increase. Apart from a slight increase in the oxygen concentration in the boiler and the associated increase primary NO_x, steam output decreased to the value of 133 t/h. Satamin reacts with flue gas only partially, and a large part as unreacted goes further into the flue gas cleaning system and through chimney to the atmosphere. The measured ammonia slip reached 6.25 mg/m_N³. Not all amplitudes are related to the capacity. In 89 minute the operating level changed. There was a decrease in NO_x and ammonia slip. Satamin started spraying to a zone with high temperature where it was probably burned and responded to NO_x. Due to growing NO_x, the satamin flow began to rise. In 134 min the temperature exceeded 1,000 °C and operational zone became level 2. Measured parameters began to stabilise.

Intervention in the boiler, in the form of removing GMC 142 in 250 min, firstly caused decrease of NO_x (due to increased concentration of CO) and a subsequent sharp increase in the concentration of these oxides. Subsequently, the burner no. 1 was removed. It was observed from previous measurements on the same device that the shutdown of the burners on the bottom surface favorably influences the concentration of NO_x . Similar situation is during operation at both GMC, when under the same conditions lower values are reached for the primary NO_x than when operating with one GMC or without them.

Another short-term switching levels occurred between 330 and 342 min. Ammonia slip again decreased to a minimum, but due to the high temperature, satamin occurred to combust together with the increase in nitrogen oxides. After switching to zone 2, the values (satamin, NO_x, ammonia slip) returned to the level before switching zones. After replacing the burners (burner shutdown no. 3 and rise burner no. 6) began to decrease gradually. The boiler at the time was run without MLO 142 and without burners no. 1, 3 and 4.



Figure 5: Steam boiler output about 140 t/h

4. Conclusion

SNCR method cannot prevent generation of NO_x (primary measures are used) but allows the nitrogen oxides to reduce to less hazardous substances (H₂O, CO₂, N₂). SNCR efficiency depends on the initial amount of NO_x in the flue gas and other gaseous elements in the boiler. The temperature most significantly affects it at the injection point of the reducing agent. In this case it is an aqueous urea solotion - satamin.

As seen from Figure 3, the effectiveness of the technology in the dosage to the different levels at the same performance varies. Over a suitable temperature window combustion of satamin occurs (Figure 3(b)), while ammonia slip increase at dosage levels below the window temperature (Figure 3(a)).

In case of significant intervention into the combustion process, flame stability and combustion instationary can occur. Not all changes fundamentally affect the creation or reduction of NO_x. The most important criterion, which affects the combustion of the primary quantity of NO_x, is the amount of combustion air. The more air (i.e. oxygen) is fed to the boiler, the more NO_x is formed. It is also obvious from the measurement, that the boiler operates at high powers consumes less reducing agent than at lower performance. One of the reasons is different temperature, respectively dosage at the limit of the temperature window in which the reaction is effective. Another reason is related to the stability of combustion and with false air which enters the boiler through leakages. At high capacity this air is consumed for combustion of fuel and does not significantly affect the NO_x formation. With lower power there is not enough fuel in the boiler, it would react with. In the area of heating boiler a large amount of air will remain, from which thermal NO_x is formed, which will increase the overall formation of primary NO_x.

CO value indicates the quality of combustion. In the case of high concentrations of CO, the combustion is incomplete. When the steam output of 200 t/h (Figure 4) a sharp increase of CO occured twice. In both cases, it was caused by the opening of coal feeder during the boiler control. A large amount of cold air was sucked while opening during the process, which cooled combustion air and deteriorated combustion conditions to increased CO. Once measured CO exceeds the limit, the controller increases the oxygen from air intake above the calculated (stoichiometric) value. This will increase the primary NO_x. After checking and closing feeder, CO value returns to its original level. The reaction rate of the oxygen regulator is slower (several minutes). During regular control, there is a constant increase of oxygen in the combustion process and thus the greater formation of primary NO_x and greater consumption of dosed satamin.

Operation at temperatures of 950 °C to 1,000 °C (output of 133 t/h - 150 t/h) is challenging to determine the appropriate dosage zones for the reducing agent. When dosed to level 2 there is a large ammonia slip, because the flue gas temperature is lower than the optimum for the SNCR (Figure 3(a) and Figure 5). At level 1, the temperature is too high and a portion of the reducing agent is burned, thereby the concentrations of NO_x increase (Figure 3(b) and Figure 5). A big problem was caused by incorrect setting of the controller for dosing a reducing agent, which in case of power loss below 138 t/h increased satamin flow into the boiler, despite nitrogen oxides were decreasing (e.g. Figure 7, 60 min). This caused a significant increase in ammonia slip. Optimising this controller not only based on performance but also by the output or NO_x by ammonia slip, accurate dosing of the reducing agent into the flue gas can be achieved.

Currently, operation optimisation with respect to the primary measures NO_x SNCR is taking place in the K14 boiler, so that the required NO_x values below 200 mg/m_N³ would be kept.

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