UDC:546.17:662.21
DOI:10.7562/SE2022.12.02.02
Research paper
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PRIMARY MEASURES TO REDUCE NOx EMISSIONS AND THE RESULTS OF THEIR IMPLEMENTATION ON THE ENERGY BOILER

Abstract: *The Republic of Macedonia as a signatory to the agreement for the energy community, Treaty Establishing the Energy Community, should fulfill the basic aspects of the European energy legislation, including the LCP Directive. The reduction of nitrogen oxides is one of the conditions that should be fulfilled in accordance with this Directive. This could be carried out using primary and secondary measures. Several methods for carrying out primary measures, along with their specificities and the outcomes of using each, are discussed in the paper.*

Key words: nitrogen oxides, primary measures, reduction.

INTRODUCTION

Signing the Treaty Establishing the Energy Community agreement means fulfilling the basic aspects of the European energy legislation, including the LCP Directive. This directive provides for the desulfurization and elimination of nitrogen oxides in new and existing thermal power plants. This means that reconstruction and modification activities should be undertaken at the existing energy plants in order to meet the limit values. According to the LCP Directive [1], the restrictions after 2016. are: 400 [mg/Nm^3] emissions of sulphur oxides, SOx; 200 [mg/Nm^3] emissions of nitrogen oxides NOx and up to 50 [mg/Nm^3] emissions of particles. In the case of existing buildings, during the reconstruction and revitalization of energy boilers, priority is given to measures which, in addition to reducing the emission and impact on the environment, will also improve their efficiency.

Reduction of nitrogen oxides can be achieved by applying primary and secondary measures. With the secondary measures, binding or reduction of the nitrogen oxides contained in the output gases is carried out in separate plants that are outside the boiler. However, the primary measures of preventing NOx generation are completely concentrated in the furnaces of the boilers. These methods aim to change the operating and design parameters in the combustion process, thereby reducing the formation of nitrogen oxides or transforming those that have already formed in the boiler before they are released.

The current energy crisis may have prolonged and temporarily delayed the implementation of the LCP directive, but this should not reduce the importance of protecting the human environment and clean air, as well as implementing new technologies for cleaner air.

MECHANISM OF FORMATION OF THE NITROGEN OXIDES IN THE STEAM BOILERS FURNACE

The energy boiler is a device that produces steam with a pressure greater than atmospheric, using the chemical energy of fossil fuels (liquid, solid, gas), nuclear energy, electricity, waste heat from industrial-technological processes, aggregates and plants, etc.[2]. The most common heat source for producing steam in steam boilers is the chemical energy of fossil fuels. In fossil fuel steam boilers, first of all, the fuel and oxygen from the air together with the fuel enter into a chemical reaction (combustion), creating combustion products with high heat content.

In a steam boiler furnace, nitrogen oxides can form from the molecular nitrogen in the air used to burn the fuel, as well as from the nitrogen contained in the fuel components in the following three ways [3]:

- by the reaction of nitrogen from the air and oxygen, also from the air, resulting in thermal nitrogen oxides, NOx^T;
- by the reaction of hydrocarbon radicals with molecular nitrogen from the air, resulting in rapid nitrogen oxides, NOx^B;
- by oxidation of nitrogen compounds from the fuel, which produces nitrogen oxides from fuel, NOx^G.

Thermal nitrogen oxide, **NOx^T** is formed as a result of the oxidation of molecular nitrogen and atomic oxygen and the oxidation of atomic nitrogen and molecular oxygen at temperatures higher than 1300°C, according

$$N_2 + O \rightarrow NO + N$$

$$N + O_2 \rightarrow NO + O$$

The first reaction has a major role in the formation of NO^T, but the basic condition is that high-temperature zones (t>1300°C) are formed during combustion in the furnace. In this way, it is possible to increase the concentration of oxygen and nitrogen in the atomic state. Known as the Zeldovich mechanism is the occurrence of

NO^T and it occurs in the flame zone and the zone outside the flame front after the combustion process of the combustible mixture is complete, with an excess of air higher than one. The intensity formation of thermal nitrogen oxide depends primarily on the temperature of the gases and on the time they retain in the high-temperature zones.

Fast nitrogen oxide, **NOx^B**, is the result of reactions of hydrocarbon radicals and molecular nitrogen, such as the following radical-forming reactions:

$$CH + N2 \rightarrow HCN + N$$

$$CH2 + N2 \rightarrow HCN + HN$$

The radicals formed during the above reactions containing nitrogen (HCN, HN, N) enable the formation of nitrogen monoxide in further reactions with oxygen radicals. So, for example, the reaction of atomic nitrogen with the hydroxyl group OH

$$N + OH \rightarrow H + NO$$

In the initial combustion zone of the fuels, these reactions occur very quickly, because the content of combustible substances is high, and the temperatures are higher than 730ºC. The formation of NOx^B, in real conditions ends at temperatures lower than 1200 to 1300°C. The conditions for the formation of NOx^B are influenced by: the local coefficient of excess air in the reaction zone, the temperature, and the rate of flame heating. As the temperature increases, the NOx^B content increases exponentially.

Fuel nitrogen oxide, NO^G, is formed by oxidation of part of the nitrogen contained in the organic mass of the solid and liquid fuels, at temperatures higher than 630°C. In solid fuels, the content of bound nitrogen is the highest, 0,5 to 3,5% of the combustible mass, it is significantly lower in liquid fuels, and in natural gas, there is no bound nitrogen.

Most of the nitrogen (about 75%), during the combustion of solid fuels, passes into a gaseous state and forms combustible nitrogen monoxide. However, a smaller part remains in the composition of various compounds of coke residue and does not participate in the NO^G formation process. In the phase of ignition and combustion of volatile substances, i.e. in the initial part of the flame, the fuel nitrogen oxide is formed. Its achieved content at this stage includes 15 to 20% of the nitrogen contained in the fuel and does not change along the length of the flame, despite the fact that active coal particle combustion continues. It was determined that in the formation zone of fuel nitrogen oxide, its concentration significantly depends on the nitrogen content in the fuel, on the concentration of O_2 and on the temperature in the interval from 680 to 1130°C [3]. With a further increase in the flame temperature, its influence on the formation of fuel nitrogen monoxide decreases, and only the dependence on the concentration of O_2 remains.

According to the mechanism of formation of nitrogen oxides described above, it can be noted that the processes occur and end completely in the zones of active combustion of fossil fuels.

The final concentration of the nitrogen oxides formed in the furnace of steam boilers depends on the conditions in the combustion zone: the concentration of O2, the temperatures and the retention time of the gases in the reaction zones, and the nitrogen content in the fuels.

MEASURES TO REDUCE THE EMISSION OF NITROGEN OXIDES IN STEAM BOILERS

Reducing the emission of nitrogen oxides in the exhaust gases of steam boilers can be done by applying:

- Primary measures, which disrupt the conditions under which NOx formation occurs,
- Secondary measures, with the implementation of additional systems to reduce already formed NOx.

Since the formation processes of nitrogen oxides occur and end in the combustion zone, the primary measures to prevent their formation are completely concentrated in the furnace of the boilers. The primary measures include: lowering the maximum temperature in the furnace, reducing the oxygen concentration in high temperature zones and applying special combustion technologies.

One way to reduce the temperature and oxygen concentration in the combustion zone is shown in Fig. 1, by introducing cooled gases into the furnace [4].

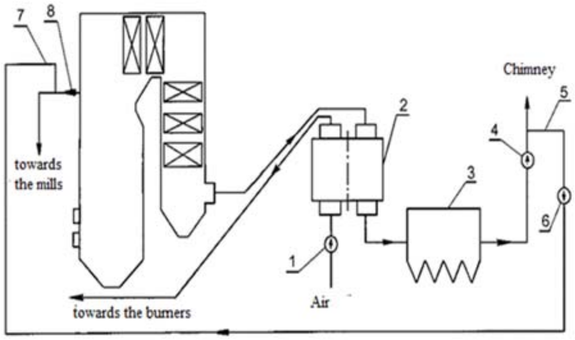

Figure 1. *Principle scheme of a system for bringing part of the cooled gases into the furnace;1.FD fan, 2. Air preheater, 3.Precipitator, 4.ID fan, 5.Recirculation gas extraction, 6.Fan for cold gas recirculation, 7.Cold recirculation gas supply, 8. Duct for gas recirculation from the furnace.*

A method that does not require additional investments, and which achieves a significant reduction in NOx emissions, is control, i.e. reduction of the coefficient of excess air in the furnace. However, this reduction is possible as long as there is no negative impact on the boiler efficiency, that is, an increase in losses due to incomplete fuel combustion (increased amount of combustible substances in the slag and fly ash).

The most efficient way to reduce NOx emission is staged combustion, where fuel and air are injected at several different levels (two or three) to the height of the furnace. At the same time, the formation is limited, and in some cases, a partial reduction of already formed NOx is carried out.

IMPLEMENTATION AND RESULTS

In the boiler, which is taken as a model in this paper, the reduction of nitrogen oxides is carried out by using staged combustion, where the fuel is injected in three levels through the low NOx burners (low nitrogen-emission burners) (fig. 2), introduction the "Over fire air" - tertiary air on two levels - OFA1 and OFA2, (Fig. 3) and reduction of the amount of primary air for temperature regulation of the mills, by introducing some kind of gas recirculation.

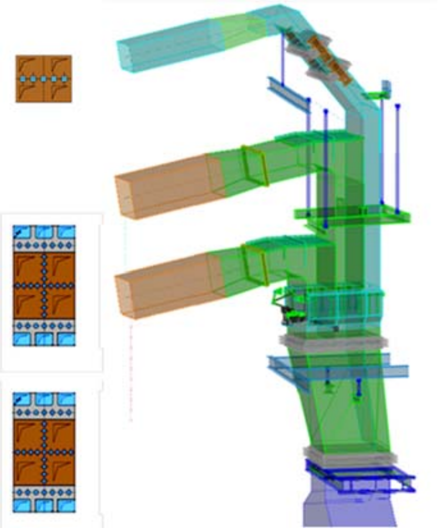

Figure 2. *Low NOx burners and ducts*

Before the implementation of the above-mentioned changes, the concentration of NOx was many times higher than allowed.

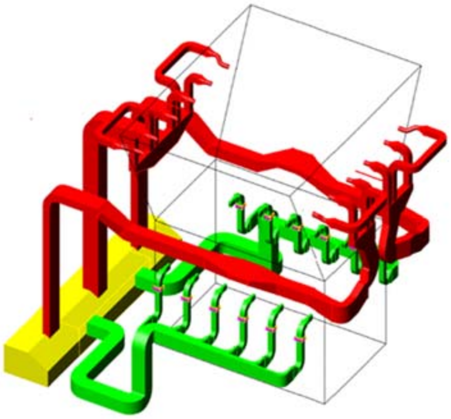

Figure 3. *Tertiary air system OFA 1 and OFA 2 for air mixture*

Figure 4 shows the results of monthly measurements before the application of primary methods for reducing NOx, in the period from 2006 to 2013.

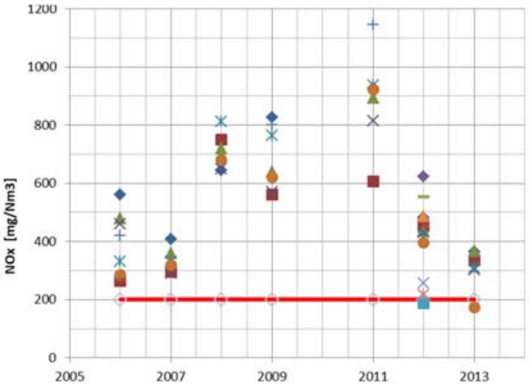

Figure 4. *NOx emission before the implementation of the primary measures for NOx reduction,* monthly *measurements [5].*

Also in Figure 5, it can be seen that in the specified period (before the implementation of primary measures) the maximum values for NOx emissions were in the range of 400 to 1000 [mg/Nm^3].

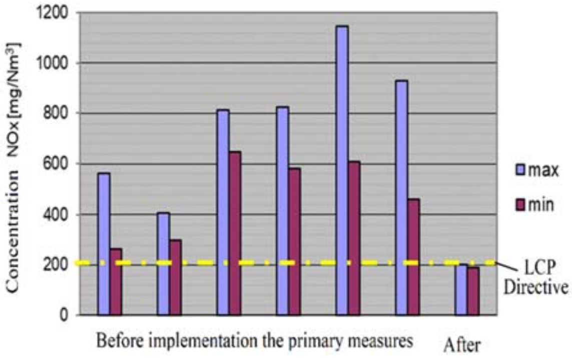

Figure 5. *NOx emission before and after the implementation of the exemplary NOx reduction measures.*

By introducing staged combustion in the boiler, which is taken as a model, the emission of nitrogen oxides is reduced below the limit value according to the directive, i.e. below 200 [mg/Nm^3] (Fig. 5).

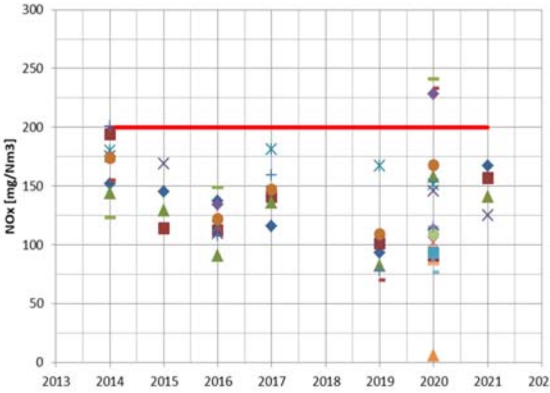

Figure 6. *NOx emission after implementation of the primary measures for NOx reduction, monthly measurements [5].*

By applying primary measures, the organized combustion of the coal dust enables keeping the excess air coefficient lower than 1,2, and at the same time formation of thermal nitrogen oxides is eliminated. Figure 6 shows the monthly measurements after applying primary measures.

CONCLUSION

Following the application of the primary NOx reduction measures on the boiler that were used for the model, NOx emissions were lowered below the Directive's limit value, or below 200 [mg/Nm^3]. Namely, as a result of the measures taken, NOx emissions were decreased on average by nearly four times.

REFERENCES

[1] European Parliament and the Council: *Directive 2001/80/EC on the limitation of emissions of certain pollutants into the air from large combustion plants,* of 23 October 2001.

[2] Л.J.Буреска; Ц. Митревска.; С. Цветковиќ.: *Безбедност при работа на постројки и инсталации под притисок*, МЦСП, 2022, Свети Николе;

[3] Петровски J.Илија: *Парни котли,* Машински факултет , 2004г, Скопје.

[4] L.J. Bureska; V.R Filkoski.i Petrovski J.I.: *Possible action on boilers in TPP Bitola for reduction of NOx emission*, International Symposium ZEMAK 2010, Ohrid .

[5] Технолаб доо.Скопје:*Лабораториски извештаи, месечни за РЕК Битола*, Битола, 2009 до 2022г.

[6] AO ZiO, Kotel parovoñ P-65, TÕS “Bitola”, *Teplovoi ras~et P-88992RR*, Битола, *1994*,

[7] Farmakovski V., Đurić V.:*Parni kotlovi*, I deo, Naućna knjiga, Beograd, 1958.

[8] European Standard *EN 12952-15:2003*.

[9] MWH S.p.A, *Bitola TPP, Macedonia, Technical Audit and Project Review for Rehabilitation and Performance Improvement*, August 2009,Skopje.

[10] TPP Bitola, Unit 3, *Manuel for boiler,* 2013г.

[11] TPP Bitola,BBS: *Tehnical specification of the Modernization of Unit 1,2,3,* 2011g, Skopje.

[12] Хитрин Л.Н.: *Физика горения и взрыва,* МГУ, 1957, Москва.

[13] F. Author, S. Author: *“Title of the book with only first letter capitalized”*, Editor, 2001, New York.

BIOGRAPHY of the first author

Lidija Joleska Bureska was born in Kicevo, Macedonia, in 1969.

She graduated in mechanical engineering and received her Ph.D. degree from the Department for Thermo technic and Thermo energetics at the Faculty of Mechanical Engineering, University of Skopje, “St. Cyril and Methodius”.

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She is currently working as an associate professor at the Faculty of Safety Engineering, International Slavic University "G. R. Derzhavin" St.Nikole and Bitola.

Primarne mere za smanjivanje emisija azotnih oksida u energetskim kotlovima i rezultati njihove primene

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Rezime: *Republika Makedonija kao potpisnica Ugovora o osnivanju energetske zajednica (Treaty Establishing The Energy Community) bi trebalo da odgovori na osnovna načela evropskog zakonodavstva, uključujući i LCP Direktivu. Jedan od uslova koji treba biti ispunjen u skladu sa ovom direktivom je redukcija azotnih oksida. To se može postići primenom primarnih i sekundarnih mera. U radu je predstavljeno nekoliko metoda za izvođenje primarnih mera, kao i njihove specifičnosti i rezultati dobijeni njihovom primenom.*

Ključne reči: azotni oksidi, primarne mere, redukcija.