

REDUCTION OF NO_x BY MEANS OF UREA INJECTION - ROVINARI POWER PLANT CASE

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ABSTRACT: *The paper examines how nitrogen in the fuel is a pollutant. The mechanism of formation of nitrogen oxides is presented: is a function of excess air, coal age (volatile matter content), and function of temperature in the furnace. Some of the methods for reducing the concentration of nitrogen oxides are presented.*

KEY WORDS: emissions, power plant, atmosphere, pollutants.

1. INTRODUCTION

Thermoelectric power plants are a permanent source of pollution of the environment by burning very large amounts of fuel. Following combustion results several categories of pollutants [1]:

- NO_x harmful to the human body: nitrogen oxides (NO_x), sulfur oxides (SO_x), carbon monoxide (CO);
- noxes that affect vegetation: sulfur dioxide (SO₂) and combinations of Cl and H₂;
- NO_x that causes acid rain formation and acts on forests: SO₂, SO₃, NO, NO₂;
- persistent noxious substances in the soil, which accumulate over time and become harmful (heavy metals);
- Pollutants that influence the climate (CO₂ and N₂O) by triggering the greenhouse effect and destroying the ozone layer.

Of the total NO_x generated by combustion, about 95% is in the form of nitrogen monoxide (NO). Eliminated in the atmosphere, NO, in the presence of oxygen in the air and under the influence of ultraviolet rays, turns into NO₂. Sometimes, NO₂ combines with water vapor and forms nitric acid H₂NO₃.

Of the nitrogen oxides, NO has a direct effect on the nervous system. Nitrogen oxides act on

the respiratory system without irritation and therefore are called insidious poisonous.

Nitric acid destroys the tissue of the pulmonary alveoli in any concentration. It also causes corrosion of metals.

Nitrous oxide (N₂O) has a double harmful effect. It contributes 4% to the greenhouse effect and plays an important role in destroying the ozone-protecting group in the atmosphere. N₂O has a catalytic effect in photochemical reactions resulting in active radicals attacking the ozone layer. The phenomenon is also accentuated by the particularly high N₂O lifespan.

2. FORMATION OF NITROGEN OXIDES

The problem of nitrogen oxides is primarily related to their importance in controlling the concentration of free radicals in the troposphere, as precursors involved in the production of ozone and directly or indirectly in the production and deposition of acids [1].

2.1. NO formation of nitrogen in the air

Combustion of solid and liquid fuels in the outbreak forms nitrogen oxides due to the nitrogen in the fuel composition and due to the nitrogen in the air, which is 79% of the total air volume [2].

Nitrogen oxides from the air are divided into thermal nitrogen oxides because they form in the high temperature flame zone due to the oxidation of molecular nitrogen with atomic oxygen and in prominent nitrogen oxides formed in a limited flame area of relative temperature lowered as a result of the interaction of hydrocarbon radicals with the nitrogen molecule. Then the reaction between the atomic nitrogen and the OH radical takes place.

The formation of nitrogen oxides in the flame is dependent on the concentration of nitrogen. In the flame front there are radicals of various substances such as O, H, OH, NO₂, CmHn that are the origin of NO formation. As the training process takes place in a narrow area of the flame front, it is called prompt. Behind the flame front, i.e. in the combustion products, this excess radical concentration decreases by the recombination reaction progressively approaching the equilibrium value [2].

2.2. NO formation of nitrogen in fuel

Nitrogen from the organic carbon is found in its aromatic structure in the form of pyridine, pyrrole or amines. Nitrogen from fuel is found in weight percent of 0.5-2%. Young (bituminous) charcoal has a higher percentage of nitrogen than old coal (anthracite).

One of the causes of nitrogen oxides formation is the volatilization of organic nitrogen in the process of heating the particle. The thermal decomposition process begins at a temperature greater than 500-600K (227-327°C) depending on the degree of carbonation. Young charcoal develops more volatile [3].

The first gaseous components of volatile substances are those with oxygen in their molecule, CO, CO₂ and water vapor. With the increase in temperature, the saturated volatile hydrocarbons C_mH_{2n+2} and C_mH_{2n} unsaturated hydrocarbons, which together with the other volatile substances, form a gas trough around the coal particle in the volatile substances composition; is the time when the first nitrogenous components appear in the volatile substances by breaking the aliphatic and heterocyclic bonds. This breakage occurs at temperatures between 700-1150°C[3].

The liberation of carbon nitrogen from heating does not take place at steady speed. At any point in the coal particle volatilization, the ratio between the volatile release rate and the rate of nitrogen evolution from the fuel is constant.

The main nitrogen-containing gaseous substances are HCN hydrogen cyanide and NH₃ ammonia.

The nitrogen volatile components in their chemical composition and release rate depend on temperature, coal age, release time, heating rate, composition of the gaseous medium. Thus, when the volatile matter content drops from 40% to 10%, the fraction of released carbon is reduced from 53% to 20%. Also, the molecular bond breakage temperature of the particle has increased from 475 °C for many volatile coal to 725 °C for anthracite.

3. METHODS OF REDUCING NITROGEN OXIDE EMISSIONS

Optimizing emission reductions, considering the lowest possible investment and exploitation costs, involves a thorough study and the need for changes to be made to combustion systems (primary measures) and additional measures.

It is important, in order to be able to develop an optimal overall concept of both the environment and the exploitation, to know the changes to be made in the combustion systems (primary measures) and their impact on the plant as a whole, as well as the additional measures that need to be taken applied to reduce nitrogen oxide emissions (bypass measures) and their financial influence on all installations [3,4].

3.1. Primary measures to reduce NOx emissions

There are many primary emission abatement measures (burning changes) to suppress the formation of nitrogen oxides in combustion plants. All these measures aim at modifying the operating or design parameters of the combustion plants so that the formation of nitrogen oxides is reduced or that the already formed nitrogen oxides are transformed into the boiler before they are emitted [5].

When introducing primary measures (burning changes), it is important to avoid negative impacts on boiler operation and the formation of other pollutants. Thus, the following criteria must be considered for low NO_x operations:

- Operating safety (example stable ignition over the load range);
- Safety in operation (to prevent, for example, corrosion, erosion, deposition, slagging, overheating of pipes, etc.);
- the ability to burn a wide range of fuels;
- complete combustion (to reduce carbon levels in ash, up to 5% unbound carbon in fly ash is a common requirement to market fly ash to the cement industry.) Full combustion is also desirable to avoid high carbon monoxide emissions carbon);
- lowest pollutant emissions, i.e. avoiding the formation of other pollutants, e.g. contaminant organic matter (POM), or N₂O;
- undesirable minimum consequences for the flue gas cleaning equipment;
- low maintenance costs.

The primary measures to reduce nitrogen oxide emissions are:

- Excessive air excess.

3.2. Secondary measures to reduce NO_x emissions

Applying primary measures leads to a significant decrease in the concentration of nitrogen oxides in combustion gases as they leave the outbreak, but not always enough to meet international NO_x emission norms on the combustion basin. A cleaning (nitrogen reduction) of flue gas must also be carried out. These measures are referred to as secondary measures and aim at retaining nitrogen oxides in the combustion gases before they are disposed of on the chimney in the environment [5,6].

In fossil fuel power plants, flue gas treatment can be done using selective catalytic reduction (SCR) and non-catalytic selective reduction (SNCR). The two processes can be used alone or in combination with combustion modifications [7].

- Selective Catalytic Reduction (SCR) is the most common secondary detoxification process. In selective catalytic reduction, the conversion of nitrogen oxides into nitrogen

and water results from the reaction with ammonia in the presence of a catalyst

- Non-Catalytic Selective Reduction (SNCR) is usually used when the expense for denoxing should not be too high, or there is a risk of poisoning the catalyst if the SCR process is used. The necessary condition, however, is to work at high and optimal temperatures, capable of providing the thermal energy required for the decomposition and vaporization of the reducing agent which is injected into the combustion gas stream.

In order to reduce the emissions of nitrogen oxides and to comply with the NO_x emission limit value in the combustion gases, unit no. 6 from Power Plant Rovinari both primary and non-catalytic selective non-catalytic (SNCR) methods were applied with urea injection.

SNCR mainly comprises [7]:

- control unit located at the control room of the energy group;
- The urea solution preparation and storage station;
- The urea solution distribution station at the + 45m elevation of the boiler.

The SNCR installation does not have an own operating station at the control panel of the power unit, so it is necessary to configure operating screens within the distributed control system.

The following facilities / equipment are provided:

- Fully equipped urea solution preparation plant: The plant is sized to produce an amount of 12500 kg liquid reagent in each batch.
- Fully equipped urea storage facility: ensures the storage of the NO_x reducing agent in the storage tank and the pumping of the NO_x reducing agent to the mixing and dosing modules. The capacity of the storage tank is 100m³. Storage tank is equipped with overflow protection, liquid leakage indication, level indicator and temperature measurement.
- Dilution water pumping system: feeds the mixing and dosing modules with dilution water. The dilution water pumping station located in the front-left concrete tower boiler on the platform at 45.0 m in the vicinity of the mixing and dosing modules. The dilution water pressure is increased to approximately 8

bar in a booster pump station 1 + 1 (one in operation, one in reserve), flow rate: 14 m³/h.

- Mixing and dosing modules: The SNCR installation consists of 4 mixing and dosing modules that provide: the aqueous solution of the NO_x reducing agent.

- Compressed air station: The instrument compressed air circuit provided by a fully compressed air production plant, fully serviced, drives the pneumatic actuators installed on the pipes of: NO_x reduction solution; spraying air for the injectors.

- Command and control system: contains the control sequences for the entire boiler SNCR installation, including the communication interface with all parts of the SNCR installation and the boiler DCS. The NO_x controller inputs are the momentary NO_x concentration values provided by the boiler emission collection unit. The controller will calculate the hourly average values [7].

- Combustion gas temperature measuring system - for measuring the temperature of combustion gases in the furnace.

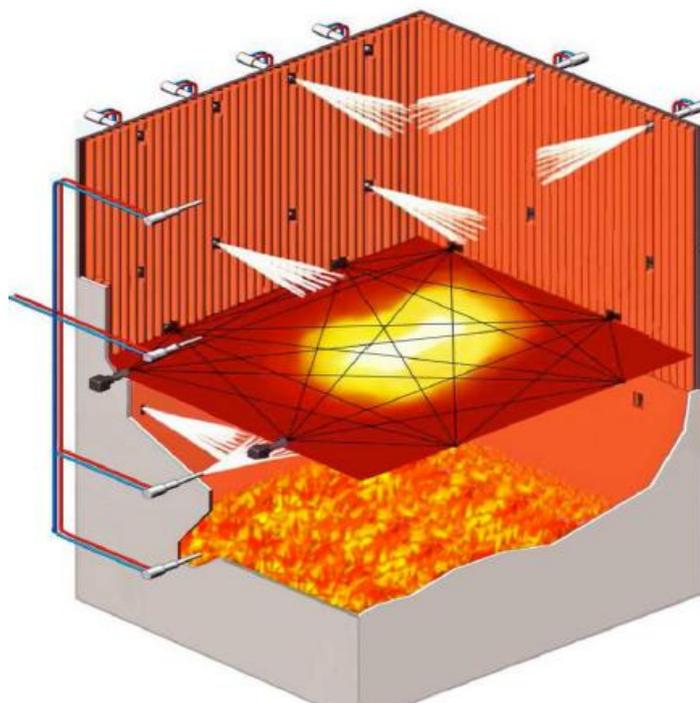


Figure 1 Non-Catalytic Selective Redaction Subsystem (SNCR) with Urea Injection [7]

The results of the NO_x emission measurements are centralized in Table 1.

Table 1 Average values of NO_x emissions

No	The year	Sources generators	Concentration average NO _x	Legal value [mg/Nm ³]	Quantities [t/an]
			[mg/Nm ³]		
1.	2017	Boiler 3	374,73	500 mg/Nm ³	1363,2537
		Boiler 4	393,69	500 mg/N m ³	1336,9182
		Boiler 6	346,31	500 mg/Nm ³	1391,1095
2.	2016	Boiler 3	367,6	500 mg/Nm ³	1669,026
		Boiler 4	409,20	500 mg/N m ³	1635,624
		Boiler 6	381,9	500 mg/Nm ³	1572,282
3.	2015	Boiler 3	350,7	500 mg/Nm ³	2917,9497
		Boiler 4	332,7	500 mg/Nm ³	3148,2093
		Boiler 5	421,4	500 mg/Nm ³	174,9765
		Boiler 6	358,1	500 mg/Nm ³	2832,3449

4.	2014	Boiler 3	354,70	500 mg/Nm ³	3402,2966
		Boiler 4	330	500 mg/Nm ³	561,0724
		Boiler 5	401,25	500 mg/Nm ³	1662,2535
		Boiler 6	435	500 mg/Nm ³	3637,7660
5.	2013	Boiler 3	446,61	500 mg/Nm ³	3.254,8442
		Boiler 4	-	RK	-
		Boiler 5	423,59	500 mg/Nm ³	2522,3594
		Boiler 6	388,36	500 mg/Nm ³	3145,2835
6.	2012	Boiler 3	434,80	500 mg/Nm ³	3581,2604
		Boiler 4	434,80	500 mg/Nm ³	1876,5528
		Boiler 5	450,77	500 mg/Nm ³	3226,7003
		Boiler 6	429,60	500 mg/Nm ³	3263,3677
7.	2011	Boiler 3,4	438,77	500 mg/Nm ³	7411,5454
		Boiler 5,6	450,77		3653,0802
8.	2010	Boiler 3,4	455	500 mg/Nm ³	7.955,2445
		Boiler 5,6	443		3.169,927
9.	2009	Boiler 3,4	406	500 mg/Nm ³	8096,284
		Boiler 5,6	322		3747,948

CONCLUSION

Formation of nitrogen oxides is a very complex process that depends on a many of factors.

Nitrogen oxides are formed from the nitrogen in the air and from the nitrogen in the fuel. Temperature plays an important role in the formation of nitrogen oxides. By lowering the volatile matter content, the amount of nitrogen released from the fuel decreases.

Reducing emissions of pollutants generated by high temperature units is a major concern. The realization of environmental investments in the case of already existing energy units generates important challenges namely: the first is the thermo mechanical installations itself and the second is the need to adapt the control systems of the boiler so that it is an integral part of the whole to reduce pollutant emissions.

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