Nitrogen oxide emissions reducing in cement production

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Abstract. In the European Union, the Russian Federation, as well as in a number of other countries, cement production is regulated by legislation on the best available technologies. Mandatory requirements (technological parameters, BAT-AELs) are imposed, first of all, on the emissions limitation of inorganic dust, nitrogen and sulfur oxides. The majority of Russian cement plants are currently characterized by the nitrogen oxide emissions state-established technological indicators’ excess. The technological indicators of the best available technologies and methods for reducing nitrogen oxide emissions operating in the Russian Federation and the EU countries are considered. It is demonstrated that the most efficient technologies are the staged fuel combustion and selective non-catalytic reduction (SNCR) of nitrogen oxides.

1. Introduction

A new environmental industrial policy based on the concept of integrated pollution prevention and control by introducing the best available technologies (BAT) has been developing and implementing in Russia since 2014 [1].

Technological rationing based on BAT principles means setting economically feasible goals for the introduction of resource-saving and waste-free industries, technological re-equipment, solving the problems of import substitution, the formation of a competitive industry that ensures the transition of the state’s economy from the raw materials export to an innovative development type.

The transition process to a new state regulation in the field of environmental protection is based on the BAT use and normatively regulated reduction of technogenic effect on environment [2-7].

In 2019, the Russian Federation started the process of issuing the integrated environmental permits for large enterprises in key industries. Among the first enterprises to receive the integrated environmental permits in December 2019 were three cement plants: a branch LLC “HeidelbergCement Rus” in the village of Novogurovsky, Joint-stock company “Iskitimcement” and LLC “South Ural Mining and Processing Company”.

Evaluation of technological, technical solutions, including the best available technologies, at these cement enterprises showed that there is an excess of nitrogen oxides emissions into the air (over the established industry technological indicators) at all enterprises, therefore, business entities have prepared the projects programs to improve environmental efficiency (PIEE), which were approved by the Interdepartmental Commission under the Ministry of Industry and Trade of the Russian Federation.
The problem of excess emissions of nitrogen oxides into the air currently exists at most Russian cement plants, in connection with which it is advisable to analyze the technological indicators and effective methods for reducing nitrogen oxides emissions in more detail.

2. Formation of nitrogen oxides NOₓ when baking Portland cement clinker
Nitrogen oxides (with a share NO about 95 % and N₂O about 5 %) are the key pollutants emitted into the atmosphere during cement production.

There are three ways of nitrogen oxides formation during the Portland cement clinker baking [8]: thermal nitrogen oxides (thermal NOₓ); fast nitrogen oxides (fast NOₓ) and fuel nitrogen oxides (fuel NOₓ).

Thermal NOₓ can be formed at high temperatures (t>1200 °C) and high concentration of oxygen during oxidation of atmospheric nitrogen with oxygen during combustion. With an increase in the flame temperature and the excess air ratio in the furnace, the amount of generated thermal NOₓ increases. Thermal NOₓ can be mainly formed by burning gaseous fuels (natural gas and liquefied petroleum gas) and fuels that do not contain nitrogen-containing substances.

Fast NOₓ can be formed in a burning fuel flame by complex reactions of radical interaction CH with nitrogen N₂ with HCN formation, which then is quickly disintegrated into NOₓ, CO₂ and H₂O. Content of fast NOₓ depends on the shape and temperature profile of the flame and increases during the combustion of enriched mixtures and during low-temperature combustion, reaching 25% of the total amount of the formed nitrogen oxides.

Fuel NOₓ can be formed from nitrogen-containing compounds that are part of solid and liquid fuels, especially coal. NOₓ formation mechanism consists in converting nitrogen-containing fuel compounds into ammonia NH₃ and HCN followed by additional oxidation to NOₓ.

NOₓ release greatly depends on the type of the process used. NOₓ emissions’ rates are rather high in long rotary kilns of the wet production process when the raw mixtures difficult to sinter are baked. NOₓ emissions decline with increasing fuel moisture. In dry kilns with cyclonic heat exchangers and calciners, part of the fuel is burned in the calciner at the temperatures up to 950-1000 °C, which leads to a decrease in total NOₓ emissions by reducing thermal NOₓ formation.

3. NOₓ emission levels in the kiln exhaust gases of rotary kilns, corresponding to BAT
Emission levels of nitrogen oxides in rotary kiln flue gases corresponding to BAT (BAT-Associated Emission Levels), are specified in the relevant regulatory documents (Table 1). In Russia, these levels are called sectoral technological indicators.

| Emissions of nitrogen oxides NOₓ from the rotary kiln, mg/m³ | ITG 6-2015, Russia, [8,9] | BREF CLM, EC, [10] | 17. BImSchV, Germany, [11] |
|---------------------------------------------------------------|---------------------------|--------------------|-----------------------------|
| - for kilns with a cyclonic heat exchanger                    | ≤ 500                     | <200-450           | 200                         |
| - for long kilns for wet production and Lepol type kilns      | ≤ 800                     | 400-800            | data unavailable            |

The values of nitrogen oxide emissions’ technological indicators, given in Table 1, are established in the Russian ITG 6-2015, are close to the emission levels of cement plants in the European Union (BREF CLM). However, when using special technologies, which will be discussed below, and when using alternative fuels (waste incineration), nitrogen oxide emissions in dry-type furnaces with cyclonic heat exchangers should be no more than 200 mg/m³ (17. BImSchV).

The cement plants’ operation analysis, carried out in 2017-2019, showed that currently none of the 57 Russian cement plants uses special technologies, and the levels of nitrogen oxide emissions often exceed 1000 mg/m³ [12-13].
4. Emissions reduction measures NO\textsubscript{x} in kiln gas

To reduce oxide emissions during cement production, the use of both primary technical solutions integrated into the technological process and the special technologies or their combination with primary measures are considered to be the best available technologies (Table 2, Figure 1) [8, 10,14].

| Technical solution                                      | Emission reduction efficiency, % | Emission data, mg/nm\textsuperscript{3} |
|--------------------------------------------------------|----------------------------------|----------------------------------------|
| Primary technical solutions:                           |                                  |                                        |
| • baking process optimization                          | 25                               | 1000                                   |
| • flame cooling                                        | 0-35                             | less 500-1000                          |
| • use of burners with low NO\textsubscript{x} emission | 0-35                             | less 500-1000                          |
| • staged fuel combustion, combustion of fuel in the middle of the kiln | 10-50                             | -                                      |
| • use of mineralizers                                   | 10-15                            | -                                      |
| Special technologies:                                  |                                  |                                        |
| • technology of selective non-catalytic reduction SNCR  | 30-90                            | 200-500                                |
| • technology of selective catalytic reduction SCR       | 43-95                            | 200-500                                |

For both environmental and economic reasons, NO\textsubscript{x} emission reductions can preferably be started with the implementation of the primary technical solutions integrated into the technological process. As it can be seen from Figure 1, staged fuel combustion is the most effective primary technical solution used in the EU countries.

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**Figure 1.** Various technical solutions’ application to reduce nitrogen oxide emissions [14].

4.1. Staged fuel combustion

Staged fuel combustion is used in dry-process cement kilns (Figure 2). The first combustion stage takes place in a rotary kiln under optimal clinker firing conditions. The second combustion stage is in the burner at the entrance to the furnace, where the reducing atmosphere is formed. This leads to the decomposition of some of the nitrogen oxides accumulated in the firing zone. At a high temperature,
NOx reduction reaction to elemental nitrogen takes place in this zone. At the third stage, fuel and tertiary air are fed to the calciner, which also results in a reducing atmosphere. At the same time, the number of NOx, formed during fuel combustion, is reduced as well as the amount of NOx, coming into the kiln from the outside. At the fourth final stage, the remaining tertiary air is fed to the top of the system for residual combustion.

**Figure 2.** Schematic representation of staged fuel combustion: a - the principle of staged fuel combustion; b - equipment location.

Combustion of lumpy fuel waste (for example, waste tires, tires, automobile tubes) is one of the options for the staged fuel combustion technology, while the combustion of fuel lumps is accompanied by the formation of a reducing atmosphere in the burnout zone. In the kilns equipped with baked heat exchangers and calciner, pieces of fuel are fed at the inlet to the kiln or calciner.

4.2. **Selective non-catalytic reduction of nitrogen oxides (SNCR)**

The technology of selective non-catalytic reduction of nitrogen oxides includes injection of an aqueous solution of ammonia into the flue gases (up to 25 % NH3) or aqueous solutions of ammonia or urea compounds for reduction NO till N2 (Figure 3):  
- urea \[ \text{NH}_2\text{CONH}_2 + 2 \text{NO} + \frac{1}{2} \text{O}_2 \rightarrow 2 \text{N}_2 + \text{CO}_2 + 2 \text{H}_2\text{O} \]  
- ammonia \[ 4 \text{NH}_3 + 4 \text{NO} + \text{O}_2 \rightarrow 4 \text{N}_2 + 6 \text{H}_2\text{O} \].

To ensure the sufficient contact time of the reducing agent with the flue gases, the optimum temperature should be 830 - 1050 °C.
If the enterprise uses the technology of staged fuel combustion already, then to further reduce NO\textsubscript{x} emissions, the SNCR technology needs to be applied. With the simultaneous use of staged combustion and selective non-catalytic reduction of nitrogen oxides, it is necessary that the temperature, dwell time and gas atmosphere in the reaction section are consistent with each other.

4.3. Selective catalytic reduction of nitrogen oxides (SCR)
In SCR technology nitrogen oxides are reduced to N\textsubscript{2} by means of NH\textsubscript{3} and catalyst at a temperature of about 300-400 °C. This technology is widely used to reduce NO\textsubscript{x} in other industries (for example, in thermal power plants with waste incineration), however, cement technology is practically not used.

SCR technology is used much less frequently, which is associated with a high cost (about 10 times higher than SNCR) and limited catalyst life.

In 2017, the authors of this report, together with the representatives of the German Cement Plants Association VDZ audited 3 Russian cement plants. The audit revealed NO\textsubscript{x} emissions excess at all the enterprises. Based on the audit results, German colleagues presented a comparative assessment of effective technologies (Table 3).

Table 3. Comparison of technology options to reduce NO\textsubscript{x} emissions [15].

| Index                        | Staged combustion | SNCR                                      | SCR                                           |
|------------------------------|-------------------|-------------------------------------------|-----------------------------------------------|
| General technology assessment| Very cost effective sufficiently high potential for NO\textsubscript{x} emissions reduction | Cost effective, medium / high NO\textsubscript{x} emissions reduction potential | Expensive and complex but effective technology with low NO\textsubscript{x} (~ 200 mg/m\textsuperscript{3}) and NH\textsubscript{3} emissions potential. |
| Applicability (according to [9]) | For dry and wet processing production plants with an upgraded kiln | For dry process plants | For dry process plants |
| Additional information on applicability | Most effective for kilns with heat exchanger, calciner and tertiary duct. Built-in calciner required | Can be combined with staged combustion | Requires wide space for equipment |
| Investment costs             | Low (can be high for complex modification projects) | Average | Very high |
Operating costs | Current costs will not change | Medium / High | Average
---|---|---|---
NO\textsubscript{x} emissions reduction rate | 10–50% | 30–90% | 43–95%
Potential risks | Risk of increased CO emissions in the absence of optimization | Danger of significant NH\textsubscript{3} overshoots in some cases (for example, when high reduction rates are achieved) | Risk of increased NH\textsubscript{3} emissions in the absence of optimization

5. Summary
Analysis of the technical solutions used to reduce nitrogen oxide emissions in cement production shows that the most preferable technologies are the staged fuel combustion and non-catalytic reduction of nitrogen oxides (SNCR). In the EU countries, especially in Germany, to reduce NO\textsubscript{x} emissions to less than 200 mg/m\textsuperscript{3} these two technologies are applied simultaneously.

By 2025, all large industrial enterprises should have obtained the integrated environmental permits. Therefore, today it is necessary to start preparations for IEP receiving – to conduct an internal environmental audit - to analyze the application of the best available technologies at the enterprise, as well as to compare the achieved technological indicators with the industry indicators established by the order of the Ministry of Natural Resources and Ecology of the Russian Federation. Information and technical guide on BAT (ITG 6-2015) in this case, serves as a methodological basis for conducting an internal audit. The cement production enterprises with non-achieved BAT technological indicators, in particular, in terms of nitrogen oxide emissions, first of all, should take a set of measures to optimize the process and conditions for burning the raw mixture and consider the use of technologies for the staged fuel combustion, as well as selective non-catalytic reduction of nitrogen oxides.

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