GOSPODARKA SUROWCAMI MINERALNYMI

Tom 18 2002 Zeszyt 4

TADEUSZ OLKUSKI*

The problem of nitrogen oxides in power industry

Key words

Nitric oxides, burning, emission

Abstract

A number of by–products, such as ash, slag, dust and toxic gases are produced during exothermal reaction of coal burning. The gases emitted into the atmosphere constitute the very serious problem due to considerable difficulties related to gases removal. This applies chiefly to sulfur and nitrogen oxides. In 1998, the Ministry of Environmental Protection, Natural Resources and Forestry issued the ordinance regarding the permissible level of pollutants emitted into the atmosphere as a result of hard coal burning. This ordinance was aimed at adjusting the Polish standards to European Union standards. Also the European Union countries modified their regulations and in the year of 2001 approved two Directives regarding the emission of sulfur dioxide and nitrogen dioxide.

The paper deals only with the nitrogen oxides problem. The genesis of their origin, the emission standards and the emission level have been presented. The mechanisms of converting the nitrogen into the nitrogen oxide and nitrogen dioxide have been discussed, as well as the impact of temperature on NO_x generation has been explained.

In the light of awareness with regard to the reasons for and effects of the nitrogen oxides, the efficient methods of counteraction have been presented. These include the primary methods involving the prevention of oxides generation, and secondary methods, restricting the emission of oxides already generated. The problem of nitrogen oxides is very complicated and requires further research and enhancing of the currently used reduction methods.

Introduction

The NO_x notion means the various forms of nitrogen oxides, above all the nitrogen oxide (NO), and nitrogen dioxide (NO_2). The nitrogen oxides are toxic gases, causing considerable

* M.Sc., Polish Academy of Sciences, Mineral and Energy Economy Research Institute; University of Mining and Metallurgy, Kraków, Poland.

Reviewed by Ph.D. Eng. Urszula Lorenz

hazards for human health, both as a result of direct inhaling, and through the reactions with the sulfur dioxide. These reactions cause the generation of the acid rain falls and produce the carcinogenic substances. NO_x substances are also responsible for destroying the protective ozone layer, even to as much as 50 percent of this layer destruction extent (Sloss 1991). The nitrogen oxides promote the generation of ozone, at the same time lowering the concentration of CH_4 gas in the atmosphere, which is also the greenhouse gas (Zanieczyszczenie... 1997). Due to the danger of health problems, the average annual concentration of nitrogen oxides in the atmospheric air should not exceed 100 μg per cubic meter (Kucowski et al. 1997). In the processes of fuel burning, chiefly the nitrogen oxides are emitted into the atmosphere, in the amount of 95—99% of their entire emission, which then becomes rapidly oxidated to NO_2 (Zanieczyszczenie... 1997). It is estimated that the natural emission is higher than the emission related to the man's activities. However, the concentration of NO_x is higher in the urban areas than in rural ones, which clearly and unambiguously shows the impact of the man on the environmental pollution.

1. Emission standards

In 1999, the Environmental Protection, Natural Resources and Forestry Ministry issued the ordinance regarding the permissible level of pollutants emitted into the atmosphere as a result of hard coal burning (Act Register 1998, No. 121, 793). The ordinance in question recognizes six kinds of thermal power of the source, determining for each source the allowable level of pollutants emission depending on the time when the operation of the source was commenced. Table 1 presents the data regarding exclusively nitrogen oxides, allowed to be introduced into the air, expressed in terms of nitrogen dioxide. For sources whose operation started before March 29. 1990 and the thermal power of which does not exceed 50 MW_t, the allowable rate of nitrogen entire site is equal to 400 mg per standard cubic meter. If the sources with larger thermal power are considered, this rate is increased to 540 mg per standard cubic meter. New systems and facilities, whose operation started after March 29. 1990 are subject to more stringent rules. They need to comply with the permissible value of 460 mg per standard cubic meter, and if the facility thermal power is less than 5 MW_t, this rate is not allowed to be higher than 400 mg per standard cubic meter. All the adjustments of the applicable norms and standards are aimed at bringing the Polish regulations to meet the Western European standards.

In 2001, the European Union approved two Directives regarding the restriction of the emission of sulfur dioxide and nitrogen dioxide into the atmosphere. The Directives in question present more stringent requirements with regard to the emission of sulfur dioxide and nitrogen oxides. These are the following documents:

Directive No. 2001/80/WE of the European Parliament and of the Council on the limitation of emissions certain pollutants into the air from large combustion plants, dated October 23. 2001; and Directive No. 2001/81/WE of the European Parliament and of the Council on national emission ceilings for certain atmospheric pollutants.

The first directive sets out the permissible emission level with regard to large emission, solid fuel fired sources, for 600 mg per standard cubic meter (Table 2). This applies to sources with

TABLE 1

Hard coal burning based nitrogen oxides (NO_2*) rates allowed to be introduced into the air, in accordance with the Ordinance of the Ministry of Environmental Protection, Natural Resources and Forestry, dated Sept. 8, 1998 (Act Register 1998, No. 121 item 793) — in milligrams per standard cubic meter of dry exhaust gases at the constant oxygen content of 6%

TABELA 1

Dopuszczalne do wprowadzania do powietrza ilości tlenków azotu (NO_2*) ze spalania węgla kamiennego według Rozporządzenia MOŚZNiL z dnia 8.09.1998 (Dz.U. 1998, 121, 793) — w [mg/Nm^3] suchych gazów odlotowych przy stałej zawartości tlenu 6%

Source thermal power MW_t	In sources, whose operations started		
	Prior to March 29. 1990		After March 29. 1990
	By December 31. 2005	From January 1 2006 to December 31. 2010	New installations
<5	400	400	400
≥5—50	400	400	460
≥50—100	540	540	460
≥100—300	540	540	460
≥300—500	540	540	460
≥500	540	540	460

* NO_2 means the sum of nitrogen oxides and nitrogen dioxide expressed in terms of nitrogen dioxide.

TABLE 2

Solid fuels burning based nitrogen oxides (NO_2*) rates allowed to be introduced into the air in the area of European Union (milligrams per standard cubic meter), in accordance with the Directive 2001/80/WE of the European Parliament and European Union Council, regarding the reduction of the emission of some pollutants from large sources of fuels burning, dated October 23. 2001

TABELA 2

Dopuszczalne do wprowadzania do powietrza ilości tlenków azotu (NO_2*) ze spalania paliw stałych w Unii Europejskiej [mg/Nm^3] według Dyrektywy 2001/80/WE Parlamentu Europejskiego i Rady Unii Europejskiej z dnia 23 października 2001 r. w sprawie ograniczenia emisji niektórych zanieczyszczeń powietrza z dużych źródeł spalania paliw

Source thermal power MW_t	Operation	
	By December 31. 2015	from January 1. 2016
50—500	600	600
>500	500	200

* NO_2 means the sum of nitrogen oxides and nitrogen dioxide expressed in terms of nitrogen dioxide.

thermal power 50 to 500 MW_t, however, solid fuel fired sources with thermal power exceeding 500 MW_t must comply with more stringent emission requirements, whose ceiling is at the level of 500 mg per standard cubic meter. After January 1st 2016, the allowable level of pollution emission for sources with thermal power anywhere between 50 and 500 MW_t will remain unchanged, but the solid fuel fired sources with thermal power exceeding 500 MW_t will be forced to restrict the emission to 200 mg per standard cubic meter. The second directive, determining the national ceilings regarding the emission of the harmful gases is aimed at restricting the eutrophication of soil in the area of the European Union. Owing to this directive, the nitrogen deposition that currently exceeds the critical rates in the area of the European Union should lower by some 30% compared with 1990 data. The ceilings of NO_x emission per year are diversified for the particular countries, e.g. 1167 thousand tons for the UK, 1051 thousand tons in Germany, 810 thousand tons in France, and 847 thousand tons for Spain. The total EU emission of NO_x, arrived at as a result of the aggregation of all national ceilings regarding the allowable emission of NO_x is not allowed to exceed 6519 thousand tons per year.

Attention should be paid to the fact that for the systems with power 50—500 MW_t, commissioned before March 1990, the Polish regulations anticipate even more stringent requirements (540 mg per standard cubic meter) than the European Union countries (600 mg per standard cubic meter). For the new installations with the same thermal power, Polish regulations set out the ceiling for 460 mg per standard cubic meter, which is also less than the corresponding EU requirement, equal to 600 mg per standard cubic meter. Admittedly, however, for hard coal fired NO_x sources with thermal power exceeding 500 MW_t, the EU standards are more stringent than Polish ones that allow the emission of 540 mg per standard cubic meter compared with the EU requirement of only 500 mg per standard cubic meter, and the anticipated level of permissible emission of 200 mg per standard cubic meter after December 31 2015. The Polish regulations do not specify the levels of emission to be applicable in Poland after 2010. If Poland enters the European Union by this time, the regulations identical as in European Union countries will start to be in force also in Poland.

2. Nitrogen oxides formation and the levels emission

From among various NO_x generation reasons, the natural emission may be recognized, caused by the biochemical processes occurring in the soil and seas and, as well as N_2 and O_2 reactions occurring in the atmosphere in the course of atmospheric discharges. The second reason is the anthropogenic emission, related to the man's activities. The anthropogenic emission involves chiefly fuels burning. The biggest producers of NO_x are: transportation sector (50%), electrical energy and heat generation sector (25%) (Sloss 1991). In 1991, in Poland, the total emission of nitrogen oxides expressed in terms of nitrogen dioxide rate was equal to 951 thousand tons, i.e. more than 25% less than in 1990 (1280 thousand tons) (Rocznik... 2001). The share of public utility power generation industry, amounting to 257 000 tons constituted some 27% of the total emission of NO_x in Poland in 1999. Compared with 1990 data, when the public utility power generation industry generated some 370 000 tons of nitrogen oxides, the emission was lower by as much as 33%.

It is estimated that from among the natural sources, some 5 million tons of NO_x per year come from the soil, 2—20 million tons of NO_x are generated by atmospheric discharges, further 0.5 million tons come from the oceans and 0.3—0.5 million tons of NO_x per year arrive from the stratosphere (International Energy Agency/OECD 1994). The authors, however, stress that these are only approximate data as the credible measurements are very hard to perform. The fossil fuels combustion causes the generation of some 20 million tons of NO_x per year, while the biomass firing is responsible for producing further 3—7 million tons of NO_x annually.

Nitrogen oxides are not only created in the soil, but are also absorbed by the soil. Some 90% of NO_x is built-up in the form of nitrogen acid (HNO_3) as a result of the reaction of NO_2 with OH radicals (Zanieczyszczenie... 1997).

In 1990, in the EU countries, public utility power plants, heat and power generation plants and finally heat-generating plants produces some 3759 000 tons of NO_x, which constituted 21% of the total anthropogenic emission of gaseous air pollutants (CORINAR 90 1996). In this year 1990, the district heating stations and household furnaces produced further 754 000 tons of NO_x (4%), while the industrial power plants and industrial firing contributed to the generation of 2439 000 tons (14%). The largest emission was reported in the road transportation sector, equal to 7846 thousand tons, or 44%.

The emission of nitrogen oxides coming from the big coal fired boilers is found anywhere between 200—1500 ppm (Tomeczek 1992).

Nitrogen oxides arising from the combustion processes may be divided into fuel oxides, thermal oxides and the so-called rapid oxides. The fuel oxides are generated as a result of releasing from the fuel the chemical compounds containing nitrogen at the presence of oxygen. The rate of NO_x depends on the N_2 content in the fuel, burning temperature and oxygen rate. According to Jasienko (1995), the nitrogen content in hard coal is between 0.6 and 2.8%, while the fluctuations of nitrogen content in the coal bed samples may amount to 20%. The impact of the combustion temperature on the nitrogen oxides generation has been presented in the Fig. 1.

However, not only the entire nitrogen is transformed into NO_x. Usually, this is merely 30—60%. The burning temperature, as well as the oxygen concentration, both play the most important role in this process. The second factor contributing to generating NO_x is the chemical reactions of the atmospheric nitrogen and oxygen. These reactions take place at the temperatures exceeding 1400 degrees Centigrade. These reactions are known as Zeldowicz reactions, while the resultant nitrogen oxides are called thermal ones. Their rate, as can be inferred from the very name, depends chiefly on the temperature. Also, the so-called rapid oxides can be recognized, generated in the first phase of the hydrocarbon firing, but this is applicable chiefly to gaseous fuels combustion. Their rate can be disregarded in the course of coal burning. Some 80% of NO_x generated in the course of coal burning are the fuel NO_x, while the remaining 20% are the thermal NO_x (Carpenter 1998; Laudyn et al. 1997; Zamorowski 1998).

When the coal is stoichiometrically fired in the boiler, at the considerable rate of excess air, nitrogen oxides NO generated from the molecular nitrogen are produced in accordance with the Zeldowicz reactions (Tomeczek 1992; Zeldowicz et al. 1947).

$$O + N_2 \leftrightarrow NO + N$$

$$N + O_2 \leftrightarrow NO + O$$

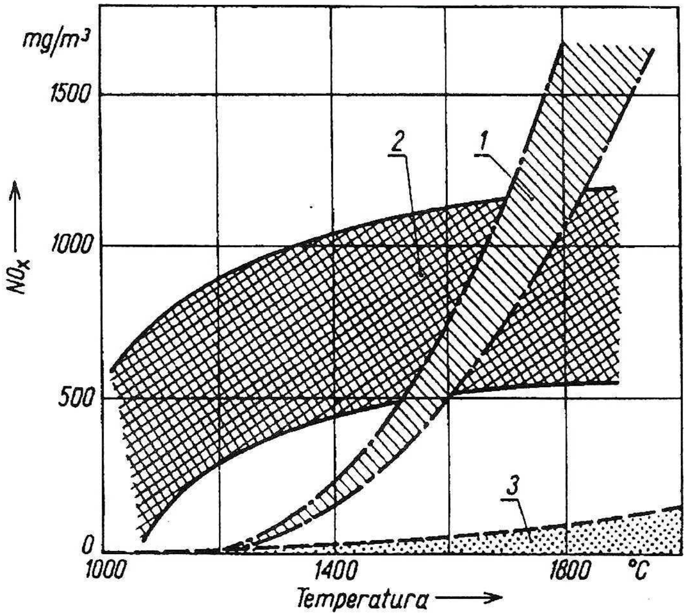

Fig. 1. Impact of combustion temperature on nitrogen oxides generation
1 — thermal oxides, 2 — fuel oxides, 3 — rapid oxides
Source: Laudyn et al. 1997

Rys. 1. Wpływ temperatury spalania na powstawanie tlenków azotu

Lavoie (Lavoie et al. 1970) found that also the following reaction takes place:

$$N + OH \leftrightarrow NO + H$$

Oxidizing of the atmospheric nitrogen depends above all on the temperature, while the fuel nitrogen conversion is subject to stoichiometry principles. The nitrogen from the fuel in the oxidizing environment is converted into the NO, while in the reduction environments, the said nitrogen is transformed into the N_2 molecule. According to Levy (1978), the coal is first degassed at the oxygen deficient high temperature atmosphere, while the nitrogen from the fuel is converted into the molecular nitrogen N_2. Then, the burning of the carbonizate takes place in the remaining rate of air, necessary for the reaction to occur. The NO is not produced in this case due to the fact that the entire organic nitrogen has already been transformed into the molecular nitrogen N_2. This gradual feeding of air into the combustion process has a very favorable impact on reducing the NO_x generation. In practice, special burners are used for this purpose, allowing the gradual mixing of secondary air with the mix of coal and primary air (PA). The rotary burners are characteristic of the lowest emission rates, while the cyclone furnaces are known to produce the largest emission rates.

3. Emission reduction methods

Knowing the mechanisms of nitrogen oxides generation, the adequate measures may be used. Generally speaking, two groups of methods for reducing the nitrogen oxides can be recognized. One group involves the nitrogen oxides generation counteraction, and is often called the primary method. The other group, involving the reduction of oxides already generated is called the secondary method.

The primary method involves the lowering of the combustion temperature and the control of mixing the fuel with the air. This can be obtained through:

— the application of the low emission burners,
— the two-stage burning (non stoichiometric),
— flue gas recirculation,
— load lowering.

All the aforesaid measures, applied to large combustion installations are capable of reducing the nitrogen oxides generation by as much as even 50 percent.

The secondary methods reducing the nitrogen oxides emission involve nitrogen removal from the exhaust gases after the burning zone. The following methods can be recognized, notably:

— selective catalytic reduction (SCR),
— selective non-catalytic reduction,
— combined flue gas desulphurisation and denitration.

For obvious reasons, it is better and cheaper to counteract the generation of the nitrogen oxides than to capture them later. Also, the modern fluidized bed boilers can be used, where the combustion temperature is anywhere between 800 and 900 degrees Centigrade, which considerably reduces the generation of nitrogen oxides.

The determination of the NO_x emission index for the large power industry boilers is very difficult, as this would require the inclusion of a number of parameters, such as boiler type, boiler load, fuel chemical composition, emission reduction methods and others. The Industrial Production Institute from Karlsruhe undertook the attempt to determine the NO_x index (Zanieczyszczenie... 1997), however, the efficiency of this method of calculations is not certain. The methods is based on the stoichiometric calculations of the mass balance of fuel being burned. The method includes the fuel parameters, above all the chemical composition and calorific value. These are the most important parameters characterizing the fuel with regard to its suitability for combustion processes. Also, the boiler parameters and the method of emission reduction are incorporated. The methods assumes the stoichiometric burning of all fuel content, i.e. C^{fuel}, $H_2{}^{fuel}$, $N_2{}^{fuel}$ and $S_2{}^{fuel}$. The method also assumes that the burning takes place without the air in excess, i.e. that the excess air index λ is equal to 1. All the stages of the calculations adopt standard conditions, i.e. the temperature equal to zero degrees Centigrade and pressure equal to 101.3 kPa. The particular stages of the calculations were presented by EMEP/CORINAR (EMEP/CORINAR 1996). However, this is not the applicable standard, therefore the details are not discussed here.

It can be assumed that for the conventional boilers, not equipped with any emission reducing system, at the load of 50—100%, each reduction of load by 1% causes the NO_x emission reduction by 0.3%. This applies only to pulverized fuel boilers (CITEPA/CORINAR 1992).

The NO_x reduction techniques and methods used currently allow to lower the NO_x emission to a less or more considerable extent. Depending on the method used, the obtainable reduction of the emission from the solid fuels is anywhere between 1 and 90%. This diversified efficiency with regard to the nitrogen oxides removal calls for detailed thinking of which method should be used. Table 3 presents the methods of NO_x emission reduction referring to the solid fuels.

TABLE 3

Possibilities of nitrogen oxides reduction depending on the method used [%]

TABELA 3

Możliwości redukcji tlenków azotu w zależności od stosowanej metody [%]

Method	NO_x reduction
Primary	
Low extent of excess air	1—15
Non-stoichiometric burning	30—60
Low emission burners	30—50
Secondary	
Selective catalytic reduction	80—90
Selected non-catalytic reduction	25—50
Total reduction SO_2/NO_x	
— adsorption processes	60—80
— catalytic reduction processes	80—99
— EB radiation processes	70—90
— alcalies injection processes	65—70
— wet processes	30—80

Source: Błasiak et al. 1995; Nowak et al. 1996; ENAP/CORINAR 1996; Kucowski et al. 1997

Summary

1. Nitrogen oxides are toxic gases and pose considerable hazards to health while in higher concentrations. Therefore, the more and more stringent requirements regarding the emission of these compounds into the atmosphere are introduced. In the years to come, as can be inferred from the European Union Directives, the requirements and standards in question will be subject to further tightening.

2. A considerable portion of nitrogen oxides is generated in conjunction with the men's activities. This is the anthropogenic emission coming chiefly from the transportation sector and

the electrical energy generation sector. Therefore, these industries should be subject to intense research into the restriction of the NO_x emission, as the possibilities of reductions are the biggest there.

3. The fuel oxides constitute the biggest problem in the power industry. These are the nitrogen oxides that are generated during the combustion process, and constitute some 80% of all nitrogen oxides produced at this stage of coal utilization. In order to reduce the NO_x emission, the low emission burners should be used, two-stage burning zone should be applied, as well as flue gases should be recirculated and the load should be lowered.

4. The combustion process should take place at lower temperatures in order to avoid generating thermal oxides.

REFERENCES

Błasiak W., Nowak W., 1995 — Metodyka modernizacji procesu spalania, redukcji NO_x oraz SO_2 w kotłach i piecach przemysłowych. Gospodarka Paliwami i Energią nr 11.

Carpenter A., 1998 — Switching to cheaper coals for power generation. CCC/01. IEA Coal Research. London, 87 pp.

CITEPA/CORINAR, 1992 — CORINAR Investory — Default emission factors handbook. Commission for the European Community. 2nd edition. Paris.

CORINAR 90, 1996 — Comprehensive summary report. Final Draft. Report of the European Environment Agency from the European Topic Centre on Air Emission, March 1996.

CORINAR Inventory, 1992 — Default emission factors handbook. 2nd edition, CEP, Paris.

Directive No. 2001/80/WE of the European Parliament and of the Council on the limitation of emissions certain pollutants into the air from large combustion plants, dated October 23 2001. (In Polish: Dyrektywa 2001/80/WE Parlamentu Europejskiego i Rady Unii Europejskiej z dnia 23 października 2001 r. w sprawie ograniczenia emisji niektórych zanieczyszczeń powietrza z dużych źródeł spalania paliw).

Directive No. 2001/81/WE of the European Parliament and of the Council on national emission ceilings for certain atmospheric pollutants. (In Polish: Dyrektywa 2001/81/WE Parlamentu Europejskiego i Rady Unii Europejskiej z dnia 23 października 2001 r. w sprawie krajowych pułapów emisji dla niektórych zanieczyszczeń powietrza atmosferycznego).

EMEP/CORINAR, 1996 — Atmospheric emission inventory guidebook, first edition. European Environment Agency. Copenhagen.

Hard coal burning based nitrogen oxides (NO_2*) rates allowed to be introduced into the air, in accordance with The Ordinance of the Ministry of Environmental Protection, Natural Resources and Forestry, dated Sept. 8 1998 (Act Register 1998 No. 121 item 793) — in milligrams per standard cubic meter of dry exhaust gases at the constant oxygen content of 6%. (In Polish: Rozporządzenie Ministra Ochrony Środowiska Zasobów Naturalnych i Leśnictwa z dnia 8.09.1998r w sprawie dopuszczalnych do wprowadzania do powietrza ilości substancji zanieczyszczających ze spalania węgla kamiennego (Dz.U. 1998, nr 121, poz. 793).

IEA/OECD, 1994 — Scoping Study: Energy and environmental technologies to respond to Global Climate Change Concerns, Paris.

Jasieńko S. i in., 1995 — Chemia i fizyka węgla. Oficyna Wydawnicza Politechniki Wrocławskiej, Wrocław.

Kucowski J., Laudyn D., Przekwas M., 1997 — Energetyka a ochrona środowiska. WNT, Warszawa.

Laudyn D., Pawlik M., Strzelczyk F., 1997 — Elektrownie. WNT, Warszawa.

Lavoie G.A., Heywood J.B., Kreck J.C., Comb. Sci. Technol. 1, 1970.

Levy J.M., Longwell J.P., Sarofim A.F., 1978 — Report to Energy and Environmental. Res. Corp. MIT, Cambridge.

Muezzinoglu A. (ed.), 1992 — Industrial air pollution assessment and control. Springer-Verlag.

Nowak W., Krzywiński J., 1996 — Technologie jednoczesnego odsiarczania oraz odazotowania spalin kotłowych. Gospodarka Paliwami i Energią nr 9.

Rocznik Statystyczny GUS 2001.
Sloss L.L., 1991 — NO_x emissions from coal combustion. IEA Coal Research, IEACR/36, London.
Tomeczek J., 1992 — Spalanie węgla. Skrypty Uczelniane Politechniki Śląskiej nr 1667, Gliwice.
Zamorowski K., 1998 — Możliwości redukcji emisji tlenków azotu w spalinach kotłów energetycznych. Energetyka nr 2, s. 85—90.
Zanieczyszczenie atmosfery. Źródła oraz metodyka szacowania wielkości emisji zanieczyszczeń. CIE, Warszawa 1997.
Zeldowicz J.B., Sadownikow P.J., Frank-Kamenetskij D.A., 1947 — Utlenianie azotu przy spalaniu. Akademia Nauk ZSRR, Instytut Chemii Fizycznej. Moskwa–Leningrad.

TADEUSZ OLKUSKI

PROBLEM TLENKÓW AZOTU W ENERGETYCE

Słowa kluczowe

Tlenki azotu, spalanie, emisja

Streszczenie

W procesach energetycznego spalania węgla powstaje wiele produktów ubocznych, takich jak popiół, żużel, pył oraz toksyczne gazy. Właśnie gazy emitowane do atmosfery stanowią największy problem ze względu na trudności z ich usuwaniem. Dotyczy to głównie tlenków siarki i azotu. W 1998 roku MOŚZNiL wydało Rozporządzenie dotyczące dopuszczalnych do wprowadzania do powietrza ilości substancji zanieczyszczających ze spalania węgla kamiennego. Rozporządzenie miało na celu dostosowanie polskich norm do norm obowiązujących w Unii Europejskiej. Również kraje Unii zmodyfikowały swoje przepisy i w 2001 roku przyjęły dwie dyrektywy dotyczące emisji dwutlenku siarki i azotu.

W artykule skoncentrowano się wyłącznie na problemie tlenków azotu. Przedstawiono genezę ich powstawania, normy emisji oraz wielkość emisji. Omówiono mechanizmy przechodzenia azotu w tlenek i dwutlenek azotu oraz pokazano wpływ temperatury na powstawanie NO_x. Znając przyczyny i skutki emisji tlenków azotu przedstawiono skuteczne metody przeciwdziałania temu zjawisku. Można do nich zaliczyć metody pierwotne, polegające na niedopuszczaniu do powstawania tlenków, oraz metody wtórne, ograniczające emisję tlenków już powstałych. Problem tlenków azotu jest bardzo złożony i wymaga jeszcze wielu badań i udoskonalania obecnie stosowanych metod redukcji.