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NITROUS OXIDE EMISSION – POTENTIAL DANGER, BALANCE AND REDUCTION POSSIBILITIES

The article presents major sources of nitrous oxide emission and indicates its role in greenhouse effect. The balance of nitrous oxide emission from technological processes of chemical industry and from combustion processes in energetic units was estimated. Attention was paid to potential possibilities of reducing nitrous oxide emission from these processes.

1. INTRODUCTION

An increased interest in nitrous dioxide is the result of a gradual increase of the gas concentration in the atmosphere, by approximately 0.3% per year [1]–[11]. Nitrous oxide is a relatively harmless gas and does not participate in the normal cycle of nitrogen in the troposphere. Its concentration in the atmosphere is not as yet detrimental to human health. However, nitrous oxide, together with such gases as, e.g., methane, carbon dioxide and chlorofluorocarbons, is one of the causes of the greenhouse effect and the depletion of the ozone layer [1], [3]. Nitrous oxide, which lifespan is 150–160 years, is in the stratosphere the source of nitric oxide, which causes decomposition of ozone. Nitric oxide because of its short life in the atmosphere (merely from 0.5 to 5 days) could not otherwise reach the level of the stratosphere. Participation of nitrous oxide in the depletion of the ozone layer is then indirect, but quite significant [14]. It is believed that nitric oxides, whose main source in the stratosphere is nitrous oxide, are responsible the depletion of almost half of the ozone layer. Consequently, when the concentration of nitrous oxide is doubled, the amount of stratospheric ozone will decrease by 12% [1], [3], [7]. Stratospheric ozone is the natural layer protecting us from excessive ultraviolet radiation, which increases the risk of skin cancer and weakens human immune system. Removing ozone from the stratosphere may cause global warming of our planet [1], [3]. Hence, since 1988 highly industrialised countries have

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been conducting research concerning analysis, measurement and balance of the sources of nitrous oxide production [1]–[9].

2. THE SOURCES OF NITROUS OXIDE PRODUCTION

Major sources of nitrous oxide emission into the atmosphere can be divided into natural and anthropogenic.

Natural sources comprise nitrous oxide emission from soil, oceans and midland waters. Small amounts of nitrous oxide are generated by sunlight. It is estimated that these sources constitute approximately 60–70% of the total nitrous oxide emission into the atmosphere [1]. Emission from these sources is believed to be a constant, so an increased concentration of nitrous oxide in the atmosphere that has been observed over some years is mainly of an anthropogenic character.

Anthropogenic sources are mainly the result of human performance. These are the processes of fuel combustion in power boilers, in stationary and mobile engines as well as biomass and waste combustion [1]–[11]. Another significant sources of nitrous oxide emission are technologies of chemical industry, such as production of nitric acid, adipic acid and other chemical compounds which include nitrogen. Big amounts of nitrous oxide are sent to the atmosphere as a result of using fertilizers [8], [9], [14]. Table 1 presents major sources of nitrous oxide emission [1], [3].

Table 1

Major sources of nitrous oxide emission into the atmosphere [1], [3]

Natural sources (sum) [Tg/year]	9.5–17.4
Soil in tropical zone	2.2–3.7
Soil in moderate zone	0.7–1.5
Oceans/ seas	2.0–4.0
Earth	4.6–8.2
Anthropogenic sources (sum) [Tg/year]	3.0–9.8
Fuel combustion	0.6–1.4
Combustion – stationary sources	0.1–0.3
Combustion – mobile sources	0.2–0.6
Biomass combustion	0.2–2.4
Nitric acid production	0.1–0.3
Adipic acid production	0.4–0.6
Plastics production	0.4–0.6
Fertilizers production	1.0–3.6

Numerous authors [3], [6], [7], [10] state that nitrous oxide emission into the atmosphere from fuel combustion may increase to 4.2–5.2 Tg/year. It would be then the biggest anthropogenic source of nitrous oxide emission into the atmosphere.

A special control of the fuel combustion seems to be crucial as well as the control of the installation which purifies fuels, which uses the selective non-catalytic reduction method (SNCR) [4]–[6], [11] and control of technological processes in chemical industry [8], [9].

2.1. FUEL COMBUSTION

During fuel combustion, apart from nitrogen oxides, sulphur dioxide and carbon oxide, nitrous oxide is also produced. Nitrous oxide concentration depends on the working conditions of the boiler, fuel type and interaction between specific pollutants [1]–[3].

An important factor which influences nitrous oxide concentration is combustion temperature. For a given fuel, nitrous oxide concentration decreases together with the rise of the combustion temperature. It was observed that the values of nitrous oxide concentration during brown coal combustion were lower than during hard coal combustion [6]. The nitrous oxide concentration is higher during fuel combustion in fluid boilers with circulation layer (40–153 ppm; 78.4–300 mg/m³) than in fluid boilers with bubble layer (6–103 ppm; 11.8–202 mg/m³) [10].

Introducing reducers to fuels in SNCR method is the reason of not so much quantitative, but rather qualitative changes in fuels. On the one hand, the reducer used (ammonia, urea, cyanuric acid, etc) reduces nitric oxide, and on the other hand, it produces waste products, which are the secondary atmosphere pollutants (e.g., nitrous oxide) [11]. Figure 1 shows the dependence of nitrous oxide production on the temperature and reducer used in SNCR method [11].

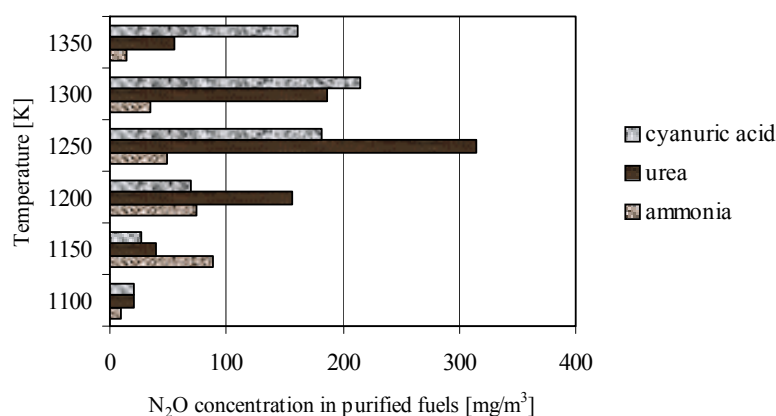


Fig. 1. Dependence of nitrous oxide production on temperature and reducer used in SNCR method

2.2. CHEMICAL PROCESSES

An important source of nitrous oxide emission into the atmosphere is chemical industry whose technological processes are responsible for the production of nitric acid, adipic acid, ammonia, urea and fertilizers (ammonium nitrate). Table 2 shows the values of nitrous oxide emission indicators of the above-mentioned chemical processes.

Table 2

Indicators of nitrous oxide emission from chemical processes [14]

Chemical processes	Emission indicator
Nitric acid production	3.4
Adipic acid production	150.0–300.0
Ammonia production	5.0
Urea production	1.0

3. THE BALANCE OF NITROUS OXIDE EMISSION

The balance of nitrous oxide emission from combustion processes was established based on the data from Austria consisting of the results of research on nitrous oxide concentration from 49 boilers of different power, boiler type and fuel type [7]. Figure 2 shows the dependence of nitrous oxide emission on the boiler power, whereas figure 3 shows the influence of the boiler type on nitrous oxide emission.

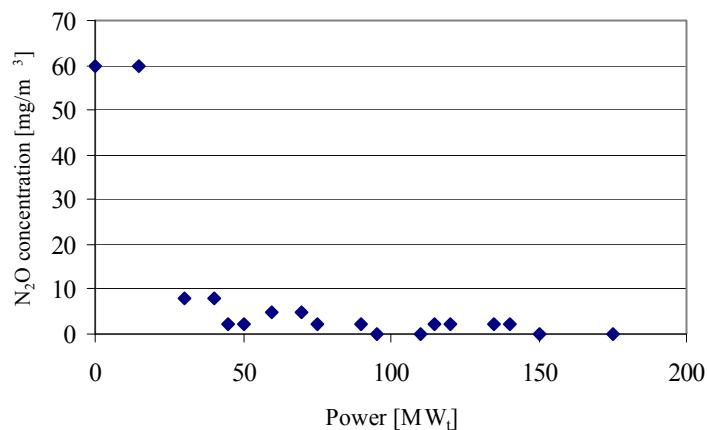


Fig. 2. Dependence of nitrous oxide emission on boiler power

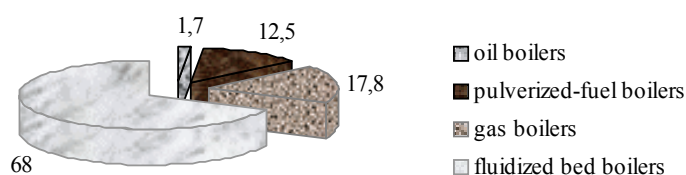


Fig. 3. The role of the boiler type in nitrous oxide emission

Figures 2 and 3 show that the highest nitrous oxide emissions were observed for the boilers of 40 MW_t power, and also during fuel combustion in fluidized-bed boilers. The balance of nitrous oxide emission from chemical processes was estimated taking account of three nitrogen plants, i.e., in Puławy, Kędzierzyn Koźle and Tarnów. The balance was based on their production capacity for nitric acid, ammonia and urea, and the indicators of nitrous oxide emission. The overall nitrous oxide emission from these plants during 1998–2004 is presented in figure 4, whereas the balance of national nitrous oxide emission from the main sources of emission, produced on the basis of statistic data [12], is shown in figure 5.

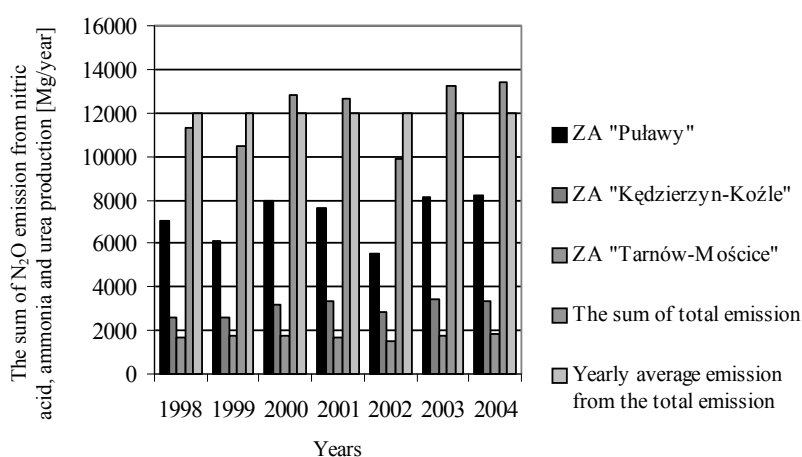


Fig. 4. Total emission of nitrous oxide from nitrogen plants

Yearly average total nitrous oxide emission from nitrogen plants in Poland coming from seven-year production of nitric acid, ammonia and urea amounts to 11969 Mg/year. Figure 5 shows that the emission of nitrous oxide from nitrogen plants “Puławy”, “Kędzierzyn Koźle” and “Tarnów–Mościce” constitutes 95% in general nitrous oxide emission from chemical processes, whereas in global emission in Poland – 19%. Comparing the results of nitrous oxide emission from all the sources (figure 5), it can be said that agriculture is responsible for 70% of the total emission.

During the government session on 4th November 2003 it was stated that further rise above 10–15% till 2020 in nitrous oxide emission in relation to the value of 52800 Mg/year from 2001 is rather unlikely [13]. Nitrous oxide emission due to agricultural activity in the following years will to a large extent depend on the agricultural policy of EU.

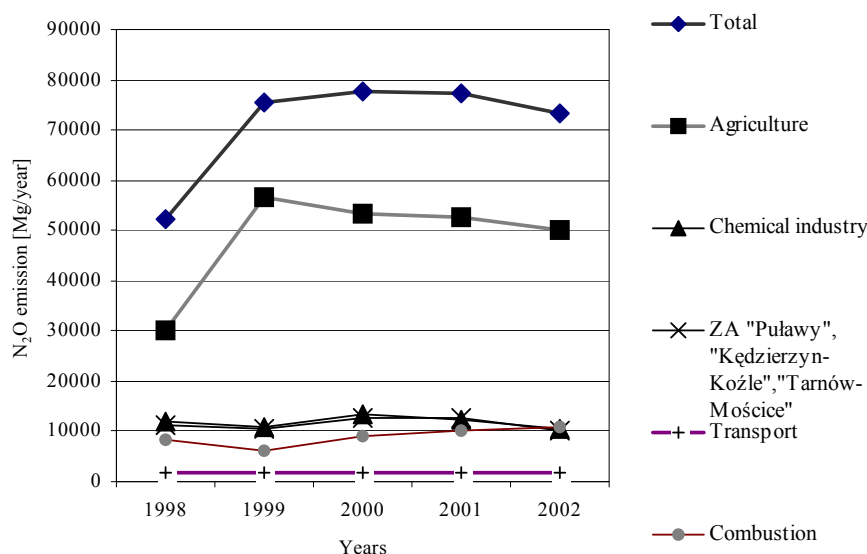


Fig. 5. Balance of nitrous oxide emission in Poland

4. POSSIBILITIES OF NITROUS OXIDE REDUCTION

Because of quite significant indirect role of nitrous oxide in the ozone layer depletion, attention is nowadays paid to the possibility of reducing nitrous oxide emission [8]–[11]. The choice of the method depends on the characteristics of plant, its location and technical requirements.

In the processes of fuel combustion, it is especially important to meet the requirements for the work of a boiler, fuel type and process temperature. In the presence of additives (e.g., carbohydrates), nitrous oxide concentration drops rapidly [11]. The influence of the additives on the nitrous oxide concentration can be explained by SNCR mechanism [1]–[3], [11], which shows that carbohydrates introduced to fuels of high rates of oxygen concentration generate at high temperature a high level of radicals (OH, H, O, N). These radicals react with nitrous oxide at almost the same rate as with nitric oxide, reducing it to nitrogen. A decrease in the load of fluidized-bed boiler causes the drop of combustion temperature, which in turn determines interactions between specific pollutants. Injection of calcium compounds to the boiler decreases ni-

trous oxide emission by 30% [3]–[6], [10].

In technological processes of chemical industry, there are various modifications of SCR (selective catalytic reduction) method of nitrous oxide before expander or after waste gases expander, preferably together with nitric oxide reduction [8], [9].

5. CONCLUSIONS

The air is the component of natural environment, into which more and more various pollutants are introduced. They are the cause of ecological threat. However, nitrous oxide concentration in the atmosphere does not so far constitute a potential threat to humans and its concentration is not regulated by separate environment protection rules. However, in the future, the gas may pose a serious problem, e.g., because of removing ozone from the atmosphere and increasing the greenhouse effect on the Earth. The data presented in this article can be useful for performing a research in this field.

REFERENCES

- [1] HULGAARD T., *Nitrous Oxide from Combustion*, TU Lyngby, Denmark, 1991.
- [2] MILLER J., BOWMAN C., *Mechanism and Modelling of Nitrogen Chemistry and Combustion*, Prog. Energy Combust. Sci., 1989, Vol. 15, pp. 287–338.
- [3] PELZ G., *N₂O-Emissionen aus kohlegefeuerten Kraftwerksanlagen*, Padeborn, 1993.
- [4] FRITZ U., MEYER-PITTRUFF R., *Das SNCR-Verfahren mit verschiedenen Verfahrenshilfsstoffen unter Minimierung der Sekundäremissionen NH₃ und N₂O*, Chem.-Ing.-Tech., 1993, Vol. 65, pp. 1348–1350.
- [5] KOEBEL M., ELSNER M., *Ensticklung von Abgasen nach dem SNCR-Verfahren: Ammoniak oder Harnstoff als Reduktionsmittel*, Chem.-Ing.-Tech., 1992, Vol. 64, pp. 934–937.
- [6] LECKNER B., KARLSSON M., *Influence of Additives on Selective Non-catalytic Reduction of NO with NH₃ in Circulating Fluidized Bed Boilers*, Ind. Eng. Chem. Res., 1991, Vol. 30, pp. 2396–2404.
- [7] VITOVEC W., HACKL A., *Pyrogenic N₂O Emissions in Austria, measurements at 45 combustion sources*, Proceedings of the 5th International Workshop on Nitrous Oxide Emissions, Tsukuba, Japan, 1–3.07.1992, pp. 41–47.
- [8] REIMER R. et al., *Abatement of N₂O Emissions Produced in the Adipic Acid Industry*, Environmental Progress, 1994, Vol. 13, pp. 134–137.
- [9] PERES-RAMIREZ J., KAPTELN F., SCHÖFFEL K., MOULIJN J., *Formation and control of N₂O in nitric acid production. Where do we stand today?* Applied Catalysis B: Environmental, 2003, Vol. 44, pp. 117–151.
- [10] NOWAK W., *Emisja zanieczyszczeń z kotłów fluidalnych*, Mat. konf. nauk. tech. Niskoemisyjne techniki spalania '96, Ustroń–Zawodzie, 28–30.03.1996, pp. 103–113.
- [11] KUROPKA J., *Analiza wpływu różnych parametrów na skuteczność selektywnej redukcji niekatalitycznej tlenków azotu ze spalin*, Raporty Instytutu Inżynierii i Ochrony Środowiska Politechniki Wrocławskiej, 1997, SPR nr 44, pp. 44.
- [12] *Materiały i opracowania statystyczne GUS „Ochrona Środowiska”*, Warszawa, 2004.
- [13] *Strategia redukcji emisji gazów cieplarnianych do roku 2020*, Ministerstwo Środowiska, Warszawa, 2003.

- [14] RADOVIĆ U., *Zanieczyszczenie atmosfery – źródła oraz metody oszacowania emisji zanieczyszczeń*, Wydawnictwo PWN, Warszawa, 1997.

EMISJA TLENKU DIAZOTU –
POTENCJALNE ZAGROŻENIE, BILANS I MOŻLIWOŚCI REDUKCJI

Przedstawiono główne źródła emisji tlenku diazotu oraz wskazano na jego udział w powstawaniu efektu cieplarnianego. Dokonano szacunkowego bilansu emisji tlenku diazotu z procesów technologicznych przemysłu chemicznego oraz z procesów spalania w kotłach energetycznych. Zwrócono uwagę na potencjalne możliwości ograniczenia emisji tlenku diazotu pochodzącego z tych procesów.