

CONTROL OF NITROGEN OXIDES

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Summary

Oxides of nitrogen belong to a group of highly reactive gases, some of which play an essential role in pollution problems, namely photochemical smog, ground level ozone, acid rain, acidification and eutrophication of water and soils, visibility impairment, and damage to natural ecosystems, cultural heritage and crops.

Major pollution concern is in nitric oxide (NO) and nitrogen dioxide (NO₂). NO is formed at high temperature, but immediately turns into NO₂ in the atmosphere. Nitrous oxide N₂O is a greenhouse gas.

The dominant part of anthropogenic emissions is attributed to combustion and transportation. The NO_x are produced by combustion of nitrogen-containing fuels and high-temperature oxidation of molecular nitrogen in air.

Strategies for reducing NO_x emissions are based on either primary measures for prevention of NO_x formation, which is the most cost-effective strategy; or post-combustion removal or destruction of nitrogen oxides. Primary measures for NO_x-reduction make use of modifications to combustion equipment or process. Post-combustion technologies remove NO_x from flue gas mostly by reduction of nitrogen oxides to harmless nitrogen, or by absorption processes.

1. Nitrogen Oxides

Seven different oxides of nitrogen are known to occur in the atmosphere. Nitric oxide (NO) and nitrogen dioxide (NO₂), together referred to as nitrogen oxides (NO_x), are the major air pollutants, for their role in atmospheric oxidation/reduction reactions with ozone, forming hazardous or detrimental substances. The most current unit of measure for NO_x is NO₂ mass equivalent (mg per Nm³ (normal cubic meter)) of NO plus NO₂. Also nitrous oxide (N₂O) is important due to its greenhouse gas effect (see *Pollution Control through Efficient Combustion Technology*).

Nitric oxide is a colorless, tasteless, toxic, nonflammable gas, almost insoluble in water. At the point of discharge NO is the predominant form of NO_x. In the atmosphere, it is readily converted to the much more harmful NO₂.

Nitrogen dioxide is a yellowish-orange to reddish-brown toxic, strongly oxidizing and corrosive gas with a characteristic pungent, irritating odor. In the atmosphere a portion of NO₂ is converted into nitric acid (HNO₃) and ammonium salts. Nitrate aerosol is

removed from the atmosphere through wet or dry deposition processes, similar to those that remove sulfate aerosol.

At high concentrations, both NO and NO₂ can be toxic to humans, animals, plants and other living organisms and in the atmosphere react with other pollutants, forming toxic and irritating chemicals, such as peroxyacetal nitrate (PAN) and fine atmospheric particles that cause respiratory and bronchial health problems. The main environmental problems associated with NO_x emissions are:

- photochemical smog;
- ground level ozone;
- acid rain;
- visibility impairment;
- acidification and eutrophication of water and soils; and
- damage to natural ecosystems, cultural heritage and crops.

Although natural sources also contribute to NO_x emissions, the dominant part is attributed to human activities, in particular combustion and transportation. The concentration of nitrogen oxides in urban and industrial areas can be 10 to 100 times as much as in non-urban areas. Concentrations of NO₂ in rural areas are close to background levels. However, nitrogen oxides can travel long distances in the upper atmosphere, contributing to elevated ozone levels and acidic depositions far away from the sources.

Annual *mean* concentrations of NO₂ in urban are 20 – 90 µg.m⁻³. Urban outdoor levels of NO₂ vary according to time of day, season, and meteorological conditions. Typically, urban concentrations peak during the rush hours. Levels are also higher in winter, because of domestic heating. Since conversion of NO to NO₂ is a photochemical reaction, which depends on solar intensity, concentrations are often greater on warm, sunny days.

1.1. Photochemical Smog

Photochemical smog is a brownish-yellow haze over urban areas, resulting from reactions between primary air pollutants in the presence of high sunlight intensity. It reduces visibility and has negative impacts on human health, vegetation and materials. Components of photochemical smog include a number of toxic compounds such as ground-level ozone, NO_x, SO₂, PAN, VOC, acidic aerosols and gases, and particulate matter.

1.2. Acid Deposition

Nitrogen oxides contribute 25 to 30 % to the acidity of rain. Rain out of nitric acid is the main wet removal mechanism of atmospheric NO_x, while direct scavenging is insignificant. Nitrogen oxides, mainly NO₂, are converted to HNO₃ by reacting with free radicals and other compounds by either of two different reaction mechanisms depending on the photochemical activity, i.e. day and night time. During daytime when the photolysis of ozone forms OH radicals in the atmosphere, NO₂ reacts with OH to

form HNO₃ by:



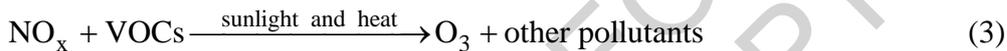
During nighttime, when photochemical activities are not available NO₂ forms HNO₃ by another pathway, involving intermediate formation of NO₃ and N₂O₅:



The effects of acid rain on the environment include damage to forests; deterioration of buildings, historical monuments, and materials; and acidification of lakes and rivers, which become unsuitable for the many fish species and aquatic vegetations.

1.3. Ground Level Ozone

Ozone is created at ground level by a chemical reaction between NO_x and VOCs in the presence of heat and sunlight. Peak ozone levels typically occur during hot, stagnant summers.



Ozone, when high in the stratosphere, protects the earth from harmful ultraviolet rays, however at ground level it is a toxic air pollutant (see *Pollution Control through Efficient Combustion Technology*).

2. Sources of NO_x-emissions

Natural sources of NO_x include soil release, metabolism of organic substances, lightning, volcanoes, forest fires, and transportation or transformation from the stratosphere.

Major anthropogenic sources of NO_x are combustion and industrial processes, including nitric acid production, metal ore smelting, and fertilizer production (see *Pollution Control in Industrial Processes* and *Pollution Control in Transportation*). Almost half of the NO_x-emissions originate from mobile sources, the remainder mainly from power plants and industrial boilers. The proportion from different sources varies considerably between nations and regions depending on industrialization, economic development and regulatory strategies. Worldwide annual emissions of anthropogenic NO_x are estimated at approximately 50 million metric tons. The United States generates about 20 million metric tons of NO_x per year, about 40 % of which emitted from mobile sources.

3. Formation of NO_x

Nitrogen oxides formed under technical combustion conditions contain typically 5 to 10 % of NO₂. At high temperatures only NO is stable and residence times in boiler or gas cleaning plant are inadequate in converting NO to the higher oxidation state. Once NO is emitted into the atmosphere, it is converted into NO₂ by atmospheric oxidation chemistry. Consequently, further discussion on the chemistry of NO_x formation will

focus on NO. Some N₂O is produced at low temperature, as prevailing in fluidized bed units, especially when firing sewage sludge. Measured values of N₂O in flue gases are always well below 50 mg m⁻³.

3.1. Formation of NO

Under ambient conditions the equilibrium concentration of NO in air is quite low, but it rises strongly at the usual combustion temperatures, even attaining several percent above 3000° C. Typically, flue gas contains some 10 to 1500 mg m⁻³ with the first value typical for low temperature combustion of natural gas, the latter for high temperature combustion of N-containing fuels, e.g. in cement kilns.

Sources of NO are on the one hand atmospheric nitrogen (N₂) present in combustion air and on the other hand fuel nitrogen (fuel-N), i.e., organic nitrogen in fuel or waste. Unlike most other pollutants, NO formation and emission are almost impossible to predict from purely kinetic considerations, given the importance of mixing and other physical parameters. There are three different routes of NO formation, with their relative importance depending upon:

- prevailing temperatures,
- the concentrations of free radicals in the flame and post-flame zones,
- gas flow and mixing characteristics,
- residence time,
- fuel/air-ratio and
- fuel type and composition.

Formation of NO occurs by the following fundamentally different mechanisms:

1. *Thermal-NO* – High-temperature oxidation of atmospheric nitrogen by oxygen.

Thermal-NO is produced at high temperatures from nitrogen and oxygen in combustion air. The process involves both oxygen and nitrogen free radicals and is strongly enhanced by high temperatures, both thermodynamically and kinetically.

2. *Fuel-NO* – Oxidation of fuel-bound nitrogen compounds.

Fuel-NO is formed by oxidation of fuel-N; when N-containing compounds are released as volatiles at comparatively low temperatures and are partly converted into NO. Part of the fuel-N remains in the solid residue of the fuel, to be released in the later stages of combustion; hence, N occurs under various forms in these intermediate stages, with various interactions.

3. *Prompt-NO* – Reaction of molecular nitrogen with hydrocarbon free radicals generated by combustion of hydrocarbons.

Prompt-NO is formed in the flame front by reaction of nitrogen molecules with a host of free radicals produced from the combustion of hydrocarbons.

Although these three sources of NO can be distinguished theoretically, it is still impractical to differentiate their respective contributions since the intermediates and reaction products are largely identical and the resulting NO later in the process may either be enhanced or reduced. Figure 1 shows the typical temperature dependence of thermal-, fuel- and prompt-NO.

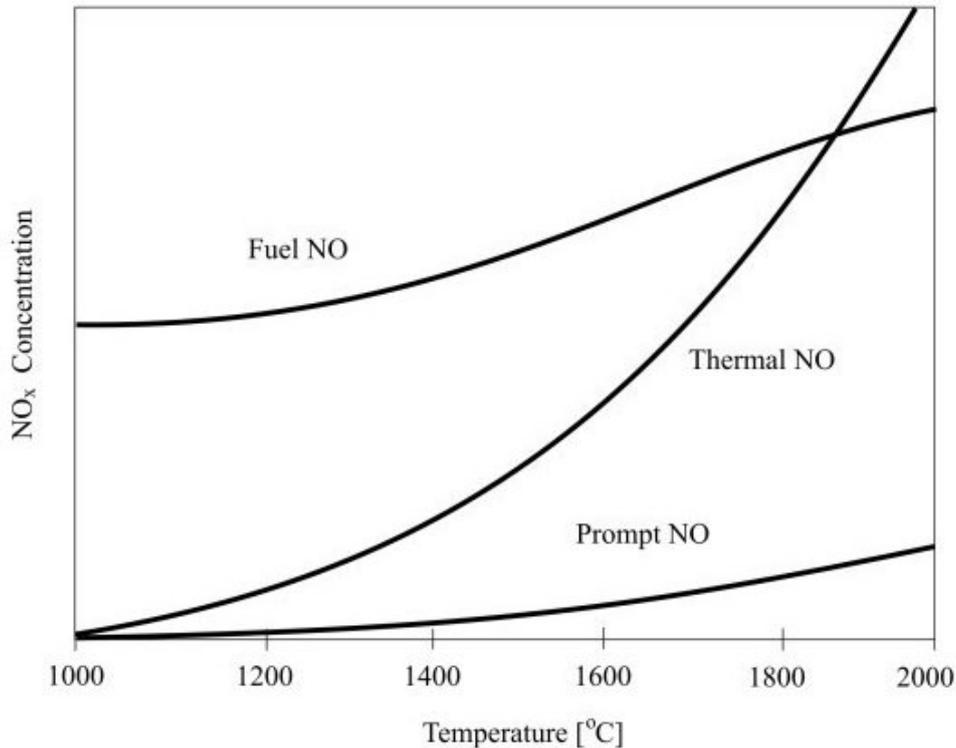


Figure 1: Different NO_x sources as a function of temperature

Fuel- and thermal-NO are dominant sources of NO_x-emissions, but their relative importance strongly varies:

- at very high temperatures and when firing fuels with low fuel-N content, thermal-NO is the prevailing source;
- fuel-NO is important when firing fuels such as coal, containing significant amounts of organic nitrogen. In low temperatures combustion systems, fuel-NO often predominates over thermal-NO.

Fuel-NO can have significant importance in waste incineration, due to the relatively low temperatures and the high N content in many kinds of waste, such as grass clippings, protein-rich food wastes, polyurethanes and amides (nylons), leather, hair, sewage sludge, etc.

The contribution of prompt-NO is insignificant compared with those from thermal- and fuel-NO and often ignored, except in hydrocarbon combustion.

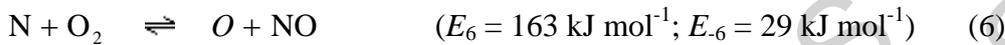
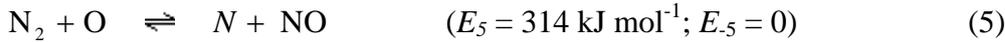
3.1.1. Thermal-NO

Zeldovich postulated a mechanism of thermal-NO formation, explaining the role of

nitrogen contained in air. Although nitrogen and oxygen coexist in the atmosphere without reacting with each other, they do combine at high temperature to form NO by the overall reaction:



Molecular nitrogen, with its triple bond, is unreactive. Thermal nitrogen fixation occurs markedly only in high temperature combustion processes (above 1600° C), as in thermal power plants or cement kilns. The formation of thermal-NO is determined by a set of highly temperature dependent chain reactions, referred to as Zeldovich mechanism:



Both forward reactions (5) and (6) have very high activation energies, so their rates are negligible at low temperatures and considerably increase at higher temperatures.

3.1.2. Fuel-NO

When N-containing fuel is burned, fuel-NO forms by oxidation of nitrogen present in the fuel and can be particularly important when firing fuels containing considerable amounts of organic nitrogen. The N-content of fuels and wastes varies considerably: N-content is typically 1 - 2 % in coal, 0 - 0.5 % in petroleum fuels, and 0.7 – 1.0 % for most wastes. Industrial waste may contain considerable amounts of organic nitrogen compounds. High N-content up to 7 %, by weight, of dry matter can be found in verge grass and sewage sludge.

Fuel-NO forms by the mechanism shown in Figure 2:

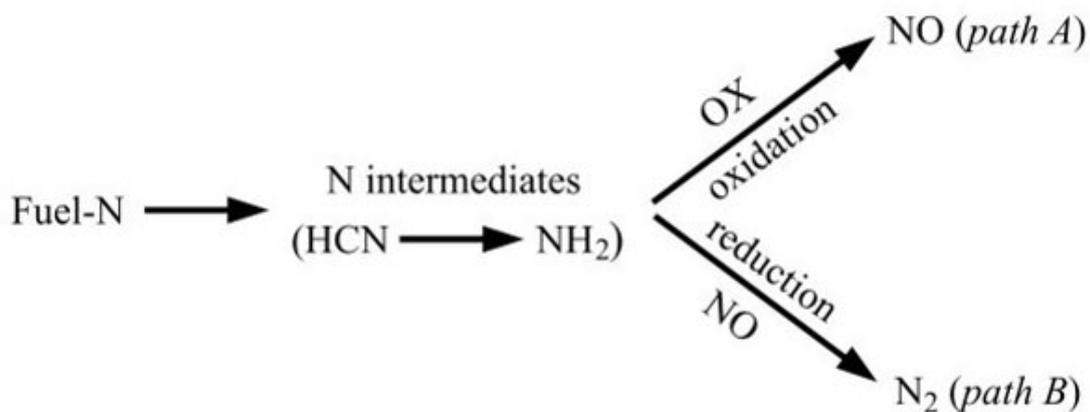


Figure 2: Simplified reaction pathway of fuel-N formation.

1. Fuels undergo thermal decomposition (pyrolysis) prior to entering the combustion zone, rapidly forming intermediate nitrogen compounds, such as cyanide (HCN mainly) and amine species (NH₃, NH₂ and NH). The rate at

which fuel-N is released varies with combustion temperature, heating rate, and chemical structure of fuels.

2. Subsequently, these newly formed compounds are subject to two competitive reaction paths, their relative share depending on the availability of oxidant in combustion, and each path comprising several successive or parallel reactions:
 - Path A (fuel-lean conditions) by oxidation of secondary intermediate N-containing compounds by oxygen containing species OX (mainly O and OH) forming NO;
 - Path B (fuel-rich conditions) by reduction of secondary intermediate N-containing compounds by N-containing substances, mainly NO itself, into N₂.

The formation of fuel-NO depends much less on combustion temperature than that of thermal-NO. However, final fuel-N conversion to NO depends strongly on oxygen concentration and other reaction conditions, such as mixing. The relative amount of fuel-N converted to NO is referred to as NO-yield. This yield decreases as the N-content in the fuel increases.

3.1.3. Prompt-NO

Prompt-NO typically occurs in turbulent diffusion flames where temperatures may be as low as 1300° C. There, NO is formed by an extremely rapid mechanism, solely active in hydrocarbon flames and featuring reactions between atmospheric nitrogen and fuel-derived hydrocarbon radicals (e.g. CH₃, CH₂, CH, CHO).

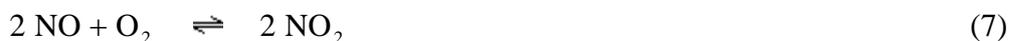
Prompt-NO arises in early stages of combustion, the existence of hydrocarbon species being limited to this stage, with eventual conversion of intermediate products to NO through reactions with O and OH.

The amount of NO formed depends strongly on the fuel-air ratio: maximum prompt-NO occurs in the fuel-rich region and drops off sharply as fuel-air ratios decrease below 1.4.

3.2. Formation of NO₂

In the flue gas NO_x concentrations remain basically at the values found during their formation at high temperature. Direct NO₂ formation during combustion processes is less likely. When NO is emitted it becomes thermodynamically unstable. In the atmosphere oxidation of NO to NO₂ occurs at a rate dictated by reaction kinetics.

The reduction of NO to N₂, is limited by its high activation energy (about 375 kJ mol⁻¹). Thus, at low temperatures NO preferentially oxidizes to NO₂ rather than being reduced to N₂. The overall reaction of NO₂ formation in the atmosphere is described as:



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Biographical Sketches

Sarantuyaa Zandaryaa is a Postdoctoral Research fellow at the United Nations University (UNU) and the Tokyo University in Japan. She is an Environmental Engineer by training.

She was born in Bayanbulag, Mongolia. Her educational background includes B.Sc. (1993) and M.Sc. (1995) from Mongolian University of Science and Technology and Ph.D. in Environmental Engineering

(2001) from University of Rome “La Sapienza”, Italy. She obtained Diploma on Environmental Management at the International Postgraduate Programme on Environmental Management (CIPSEM) at Dresden University of Technology, Germany, in 1997. She was a Visiting PhD student at Pennsylvania State University, USA, in 1999.

Dr. Sarantuyaa Zandaryaa was Professor of Environmental Engineering and Head of Environmental Engineering Department at the Mongolian University of Science and Technology. She has lectured at European universities for academic, policy-making, and international audiences and worked on several national and international research projects. She received a research grant “Young Researchers’ Project 2001-2002” from University of Rome “Tor Vergata”, Italy. She advised and coordinated UN-ESCAP environmental projects in Mongolia.

Her current research focuses on environment and sustainability, with emphasis on zero emissions approach and material flow analysis for assessing sustainability at national and local levels and integrating environmental considerations into economic and social policy-making. She has also been involved in research activities on urban ecosystems management.

Dr. Zandaryaa is author/co-author of numerous refereed research journal and conference papers, and project reports. She is co-editor of a book entitled “Environmental Engineering and Renewable Energy” (Elsevier, 1998) and serves as a peer-reviewer for the Journal of Air & Waste Management Association.

She was awarded full scholarships from the Government of Mongolia and Ministry of Foreign Affairs of Italy. In 2002, she was awarded Japan Society for the Promotion of Science (JSPS) Postdoctoral Fellowship. She is a member of the Mongolian National Committee for UNESCO-International Hydrology Programme (IHP).

Alfons Buekens was born in Aalst, Belgium; he obtained his M.Sc. (1964) and his Ph.D (1967) at Ghent University (RUG) and received the K.V.I.V.-Award (1965), the Robert De Keyser Award (Belgian Shell Co., 1968), the Körber Foundation Award (1988) and the Coca Cola Foundation Award (1989). Dr. Buekens was full professor at the Vrije Universiteit Brussel (VUB), since 2002 emeritus. He lectured in Ankara, Cochabamba, Delft, Essen, Sofia, Surabaya, and was in 2002 and 2003 Invited Professor at the Tohoku University of Sendai.

Since 1976 he acted as an Environmental Consultant for the European Union, for UNIDO and WHO and as an Advisor to Forschungszentrum Karlsruhe, T.N.O. and VITO. For 25 years, he advised the major industrial Belgian Bank and conducted more than 600 audits of enterprise.

Main activities are in thermal and catalytic processes, waste management, and flue gas cleaning, with emphasis on heavy metals, dioxins, and other semi-volatiles. He coordinated diverse national and international research projects (Acronyms Cycleplast, Upcycle, and Minidip). Dr. Buekens is author of one book, edited several books and a Technical Encyclopedia and authored more than 90 scientific publications in refereed journals and more than 150 presentations at international congresses. He is a member of Editorial Boards for different journals and book series.

He played a role in the foundation of the Flemish Waste Management Authority O.V.A.M., of a hazardous waste enterprise INDAVER, and the Environmental Protection Agency B.I.M./I.B.G.E. He was principal ministerial advisor in Brussels for matters regarding Environment, Housing, and Classified Enterprise (1989). Since 1970 he has been a Member of the Board of the Belgian Consumer Association and of Conseur, grouping more than a million members in Belgium, Italy, Portugal, and Spain.

He is licensed expert for conducting Environmental Impact Assessments (Air, Water, Soil) and Safety Studies regarding large accidents (Seveso Directive).