Nitrogen Oxides - Abatement and Control

An Online Continuing Education Course for Engineers

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Nitrogen Oxides - Abatement and Control

When we try to look only at one thing in Nature, we find it connected to everything else.

John Muir

Nitrogen oxides (NOx) are a very interesting and important family of air polluting chemical compounds. This course explains why NOx are important air pollutants and how NOx are formed and react in the atmosphere. This course also discusses the principles on which all NOx control and pollution prevention technologies are based; available NOx technologies for various combustion sources; and performance of different NOx technologies.

WHY SHOULD WE CONTROL NOx?

NOx represent a family of seven compounds. Actually, the U.S. Environmental Protection Agency (EPA) regulates only nitrogen dioxide (NO_2) as a surrogate for this family of compounds because it is the most prevalent form of NOx in the atmosphere that is generated by anthropogenic (human) activities. NO_2 is not only an important air pollutant by itself, but also reacts in the atmosphere to form ozone (O_3) and acid rain. It is important to note that the ozone that we want to minimize is tropospheric ozone; that is, ozone in the ambient air that we breathe. We are not talking about stratospheric ozone in the upper atmosphere that we cannot breathe. Stratospheric ozone protects us and the troposphere from ionizing radiation coming from the sun.

EPA has established National Ambient Air Quality Standards (NAAQS) for NO_2 and tropospheric ozone. The NAAQS define levels of air quality that are necessary, with a reasonable margin of safety, to protect public health (primary standard) and public welfare (secondary standard) from any known or anticipated adverse effects of pollution. The primary and secondary standard for NO_2 is 0.053 parts per million (ppm) (100 micrograms per cubic meter), annual arithmetic mean concentration.

Tropospheric ozone has been and continues to be a significant air pollution problem in the United States and is the primary constituent of smog. Large portions of the country do not meet the ozone NAAQS and thereby expose large segments of the population to unhealthy levels of ozone in the air. NO_2 reacts in the presence of air and ultraviolet light (UV) in sunlight to form ozone and nitric oxide (NO). The NO then reacts with free radicals in the atmosphere, which are also created by the UV acting on volatile organic compounds (VOC). The free radicals then recycle NO to NO_2. In this way, each molecule of NO can produce ozone multiple times.[40] This will continue until the VOC are reduced to short chains of carbon compounds that cease to be photo reactive (a reaction caused by light). A VOC molecule can usually do this about 5 times.

In addition to the NO_2 and Ozone NAAQS concerns, NOx and sulfur oxides (SOx) in the atmosphere are captured by moisture to form acid rain. Acid rain, along with cloud and dry deposition, severely affects certain ecosystems and directly affects some segments of our economy. All of these facts indicate an obvious need to reduce NOx emissions. However, to successfully do so, we must understand the generation and control of the NOx family of air pollutants.

WHAT IS A NITROGEN OXIDE?

Diatomic molecular nitrogen (N_2) is a relatively inert gas that makes up about 80% of the air we breathe. However, the chemical element nitrogen (N), as a single atom, can be reactive and have ionization levels (referred to as valence states) from plus one to plus five. Thus nitrogen can form several different oxides. Using the Niels Bohr model of the atom, valence state relates to the number of electrons which are either deficient (positive valence) or surplus (negative valence) in the ion when compared with the neutral molecule. The family of NOx compounds and their properties are listed in Table 1.

Table 1. Nitrogen Oxides (NOx)

Formula	Name	Nitrogen Valence	Properties
N_2O	nitrous oxide	1	colorless gas water soluble
NO N_2O_2	nitric oxide dinitrogen dioxide	2	colorless gas slightly water soluble
N_2O_3	dinitrogen trioxide	3	black solid water soluble, decomposes in water
NO_2 N_2O_4	nitrogen dioxide dinitrogen tetroxide	4	red-brown gas very water soluble, decomposes in water
N_2O_5	dinitrogen pentoxide	5	white solid very water soluble, decomposes in water

Oxygen ions are always at valence minus 2. Depending upon the number of oxygen ions (always balanced by the valence state of nitrogen), NOx can react to either deplete or enhance ozone concentrations. The nitrogen ion in these oxides really does a dance in which it has (at different times) various numbers of oxygen ions as partners. Nitrogen changes its number of partners when it changes its ionization energy level. This happens whenever NOx: (1) is hit with a photon of ionizing radiation (UV or a shorter wavelength light); (2) is hit with enough photons that together transfer enough energy to change its ionization level; (3) is catalyzed; (4) is stimulated sufficiently by thermal (IR) energy; (5) reacts with a chemically oxidizing or reducing radical (an ionized fragment of a molecule); or (6) reacts with a chemically oxidizing or reducing ion (an atom with unbalanced electrical charge).

When any of these oxides dissolve in water and decompose, they form nitric acid (HNO_3) or nitrous acid (HNO_2). Nitric acid forms nitrate salts when it is neutralized. Nitrous acid forms nitrite salts. Thus, NOx and its derivatives exist and react either as gases in the air, as acids in droplets of water, or as a salt. These gases, acid gases and salts together contribute to pollution effects that have been observed and attributed to acid rain.

Nitrous oxide (N_2O), NO, and NO_2 are the most abundant nitrogen oxides in the air. N_2O (also known as laughing gas) is produced abundantly by biogenic sources such as plants and yeasts. It is only mildly reactive, and is an analgesic (i.e., unlike an anaesthetic you still feel pain, but you feel so good that you just don't mind it). N_2O is an ozone depleting substance which reacts with O_3 in both the troposphere (i.e., below 10,000 feet above sea level) and in the stratosphere (50,000 - 150,000 feet). N_2O has a long half-life, estimated at from 100 to 150 years.

Oxidation of N_2O by O_3 can occur at any temperature and yields both molecular oxygen (O_2) and either NO or two NO molecules joined together as its dimer, dinitrogen dioxide (N_2O_2). The NO or N_2O_2 then oxidizes quickly (in about two hours) to NO_2. The NO_2 then creates an ozone molecule out of a molecule of oxygen (O_2) when it gets hit by a photon of ionizing radiation from sunlight. N_2O is also a "Greenhouse Gas" which, like carbon dioxide (CO_2), absorbs long wavelength infrared radiation to hold heat radiating from Earth, and thereby contributes to global warming.

Emissions of NOx from combustion are primarily in the form of NO. According to the Zeldovich equations, NO is generated to the limit of available oxygen (about 200,000 ppm) in air at temperatures above 1,300°C (2,370°F). At temperatures below 760°C (1,400°F), NO is either generated in much lower concentrations or not at all. Combustion NO is generated as a function of air to fuel ratio and is more pronounced when the mixture is on the fuel-lean side of the stoichiometric ratio[50] (the ratio of chemicals which enter into reaction). The Zeldovich equations are:

$$N_2 + O \rightarrow NO + N$$

$$N + O_2 \rightarrow NO + O$$

$$N + OH \rightarrow NO + H$$

Except for NO from soils, lightning and natural fires, NO is largely anthropogenic (i.e., generated by human activity). Biogenic sources are generally thought to account for less than 10% of total NO emissions. NO produces the same failure to absorb oxygen into the blood as carbon monoxide (CO). However, since NO is only slightly soluble in water, it poses no real threat except to infants and very sensitive individuals.

NO_2 is present in the atmosphere and in acid rain. It produces nitric acid (HNO_3) when dissolved in water. When NO_2 reacts with a photon to make O_2 become O_3, NO_2 becomes NO. This NO is then oxidized within hours to NO_2 by radicals from the photo reaction of VOC. Therefore, our present ozone concentration is the product of both NOx and VOC pollution.

Dinitrogen trioxide (N_2O_3) and dinitrogen tetroxide (N_2O_4) exist in very small concentrations in flue gas. However, they exist in such low concentrations in the atmosphere that both their presence and their effect are often ignored. N_2O_4 is two NO_2 molecules joined together (another dimer) and reacts like NO_2; so, the presence of N_2O_4 may be masked by the more abundant NO_2.

Dinitrogen pentoxide (N_2O_5) is the most highly ionized form of nitrogen oxide. It is generated in air in a very small concentration, unless it is emitted from a process (such as a nitric acid production facility) that is specifically designed to generate it. N_2O_5 is highly reactive, and forms nitric acid (HNO_3) when it decomposes in water.

Some experts feel that NO_2 is a good surrogate for NOx because NO is rapidly converted to NO_2, and N_2O has such a long life because it is not highly reactive. Others feel that due to their role in forming ozone, both NO and NO_2 should be considered NOx. Still others feel that all nitrogen oxides (including N_2O) need to be regulated. NO and NO_2 are certainly the most plentiful forms of NOx and they are largely (but not exclusively) from anthropogenic sources. N_2O is largely biogenic, and as such is not subject to regulation. For environmental purposes, using the concentration of NO_2 as a surrogate for the concentration of NOx has seemed to suffice, for it is the precursor for ozone.

WHERE DOES NOx COME FROM?

Automobiles and other mobile sources contribute about half of the NOx that is emitted. Electric power plant boilers produce about 40% of the NOx emissions from stationary sources.[34] Additionally, substantial emissions are also added by such anthropogenic sources as industrial boilers, incinerators, gas turbines, reciprocating spark ignition and Diesel engines in stationary sources, iron and steel mills, cement manufacture, glass manufacture, petroleum refineries, and nitric acid manufacture. Biogenic or natural sources of nitrogen oxides include lightning, forest fires, grass fires, trees, bushes, grasses, and yeasts.[1] These various sources produce differing amounts of each oxide. The anthropogenic sources are approximately shown as:

Mobile Sources	Electric Power Plants	Everything Else
50%	20%	30%

This shows a graphic portrayal of the emissions of our two greatest sources of NOx. If we could reduce the NOx emissions from just these two leading categories, we might be able to live with the rest. However, don't expect either of these categories to become zero in the foreseeable future. We cannot expect the car, truck, bus, and airplane to disappear.

In all combustion there are three opportunities for NOx formation. They are:

1. Thermal NOx - The concentration of "thermal NOx" is controlled by the nitrogen and oxygen molar concentrations and the temperature of combustion. Combustion at temperatures well below 1,300°C (2,370°F) forms much smaller concentrations of thermal NOx.

2. Fuel NOx - Fuels that contain nitrogen (e.g., coal) create "fuel NOx" that results from oxidation of the already-ionized nitrogen contained in the fuel.

3. Prompt NOx - Prompt NOx is formed from molecular nitrogen in the air combining with fuel in fuel-rich conditions which exist, to some extent, in all combustion. This nitrogen then oxidizes along with the fuel and becomes NOx during combustion, just like fuel NOx. The abundance of prompt NOx is disputed by the various writers of articles and reports - probably because they each are either considering fuels intrinsically containing very large or very small amounts of nitrogen, or are considering burners that are intended to either have or not have fu… h regions in the flame.

HOW DOES NOx AFFECT T…

Because NOx are tra… has a brownish color and the rare N_2O_3 is black), t… h and, therefore, have a lifetime of at least sev… photo reaction of VOC to make more ozone, NC… le of traveling considerable distances before creati… arth's surface and allow the atmospheric effects to … noted in EPA reports back in the 1970's. These re… a plume of ozone that extends more than a hu… 100 parts per billion (ppb). Another report cited the… blem was not just on the sea coast. Since ozone i… nomenon is a measure of the effect and the persist…

Differences in the distan… neration of ozone may be related to differences … orological and air quality factors. It is impo… plant plumes may travel relatively long distances … and NO_2 . These pollutants can thus be available to participate in … actions at distant locations on the following day.[41] Figure 1 shows a map of NOx concentration drawn by the Center for Air Pollution Impact and Trend Analysis (CAPITA) at Washington University in St. Louis and reported to the Ozone Transport Assessment Group, a national workgroup that addressed the problem of ground-level ozone (smog) and the long-range transport of air pollution across the Eastern United States. OTAG was a partnership among the EPA, the Environmental Council of the States (ECOS) and various industry and environmental groups with the goal of developing a thoughtful assessment and a consensus agreement for reducing ground-level ozone and the pollutants that cause it. The animated version of Figure 1 shows the trajectory of NOx emissions moving with the weather over an 8 day period.

Figure 2 is a map of ozone concentration that shows the same trajectory over the 8 day period. The animated version shows concentrations of both NOx and ozone moving with the weather for several hundred miles.[5]