

## 10.8: Pollutant Gaseous Oxides

### Carbon Monoxide

Carbon dioxide,  $\text{CO}_2$ , which is an essential ingredient of the atmosphere, but a potential cause of global warming at elevated levels, was discussed in some detail in Section 10.6. Carbon monoxide,  $\text{CO}$ , is an air pollutant of some concern because of its direct toxicity to humans. Carbon monoxide is toxic because it binds to blood hemoglobin and prevents the hemoglobin from transporting oxygen from the lungs to other tissues. Global and regional levels of atmospheric carbon monoxide are too low to be of concern. However, local levels in areas with heavy automobile traffic can become high enough to pose a health hazard and on some congested urban streets have reached levels of 50–100 ppm. The use of exhaust pollution control devices on automobiles have lowered these levels significantly during the last 30 years. The numerous fatal cases of carbon monoxide poisoning that occur each year are almost always the result of improperly vented heating devices in indoor areas.

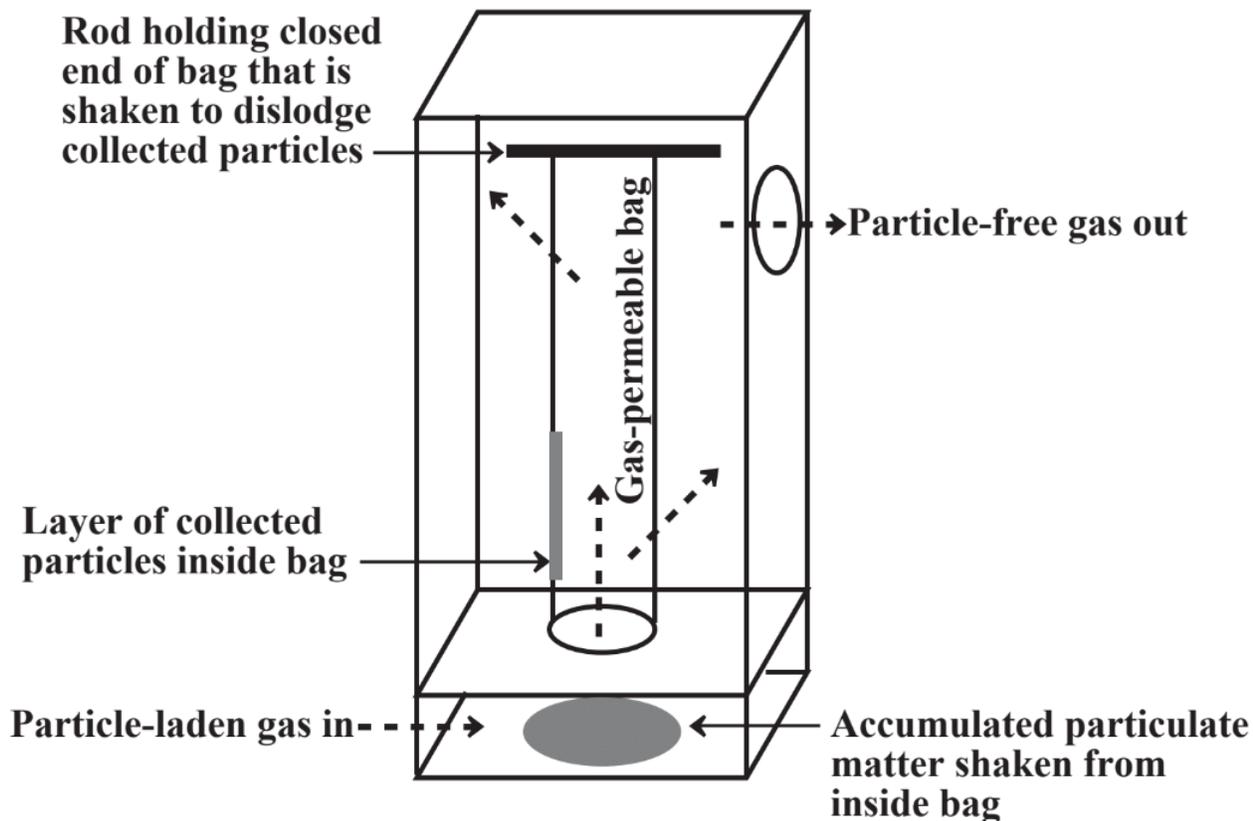


Figure 10.6. Illustration of a unit of a single bag in a baghouse for removal of particulate matter from a gas stream. The flow of gas is illustrated by the dashed lines. A bag is mounted on an opening in a plate such that particle-laden gas is forced up through the inside of the cylindrical bag and is filtered through the bag walls, then flows out as filtered gas. The particulate matter accumulates on the inside of the bag. Periodically, the gas flow through the bag is stopped and the rod suspending the closed upper end of the bag is shaken to dislodge particulate matter from the bag walls, which is collected at the bottom of the apparatus.

Carbon monoxide is produced by partial combustion of fuels, largely in the internal combustion engine. Carbon monoxide emissions can be reduced by careful control of combustion conditions. Running the exhaust along with pumped air over an exhaust catalyst can oxidize carbon monoxide to nontoxic carbon dioxide



Modern automobile engines use precise computerized control of engine operating parameters along with exhaust catalysts to control carbon monoxide emissions.

### Sulfur Dioxide

Sulfur dioxide enters the atmosphere as the result of the following:

- Direct emissions from volcanoes

- Atmospheric oxidation of  $\text{H}_2\text{S}$  emitted to the atmosphere by bacteria and from geothermal sources (volcanoes, hot springs, geysers)
- Atmospheric oxidation of dimethyl sulfide,  $(\text{CH}_3)_2\text{S}$ , emitted to the atmosphere from marine organisms
- Pollutant sources from the combustion of organic sulfur and iron pyrite,  $\text{FeS}_2$ , in fossil fuels

The pollutant sources are of most concern because of their contribution to local and regional air pollution problems and because they are sources that humans can do something about.

The fate of sulfur dioxide in the atmosphere is oxidation and reaction with water to produce sulfuric acid. The overall process is complex and not completely understood, but it can be described by the reaction.



This process is generally rather slow in the atmosphere, but it can be quite rapid under conditions of photochemical smog formation (see Section 10.11) in which highly reactive oxidizing species are present. It is very important because it is the main mechanism for forming acid rain, which can be directly harmful to vegetation, fish (especially fingerlings), and materials, such as building stone that can be attacked by acid. Sulfur dioxide forms aerosol droplets of sulfuric acid in the atmosphere. As a result, much of the Eastern United States is covered by a slight haze of sulfuric acid droplets during much of the year. In recent years, some volcanic eruptions have blasted enough sulfur dioxide into the atmosphere to produce a sufficient amount of sunlight-reflecting sulfuric acid aerosol to cause a noticeable cooling of the atmosphere.

In addition to indirect effects from the formation of acid rain, sulfur dioxide affects some plants directly, causing leaf necrosis (death of leaf tissue). Another symptom of sulfur dioxide phytotoxicity (toxicity to plants) is chlorosis, a bleaching or yellowing of green leaves.

The most straightforward means of reducing sulfur dioxide emissions is to avoid having sulfur in fuels. As discussed below, sulfur compounds are removed from natural gas and petroleum. Coal often has high levels of sulfur, and during recent years there has been a major shift to low sulfur coal in power plants. Much of the pyritic sulfur,  $\text{FeS}_2$ , can be washed from coal because it exists in a separate mineral phase that can be separated from the combustible organic matter in coal. However, about half of the sulfur in coal typically is bound to the coal as organic sulfur, and cannot be removed.

A number of coal-fired power plants have installed systems for removing sulfur dioxide resulting from the combustion of coal. One such approach uses **fluidized bed combustion** in which pulverized coal is blasted into a hot bed of calcium oxide, where the coal is burned, and sulfur dioxide is bound by the following reaction.



Some of the  $\text{CaSO}_3$  product is oxidized to  $\text{CaSO}_4$ . Another approach uses a slurry of calcium hydroxide (lime,  $\text{Ca}(\text{OH})_2$ ) to react with sulfur dioxide in stack gas.

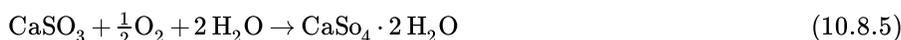


Although effective in removing sulfur dioxide, this process uses enormous quantities of limestone ( $\text{CaCO}_3$ ) as a source of lime and produces huge quantities of byproduct.

### Green Chemistry and Sulfur Dioxide

The problem of sulfur in fuel provides an excellent illustration of the potential for the application of green chemistry to the elimination of a pollution problem. Sulfur is a valuable raw material required in the manufacture of sulfuric acid, one of the largest volume chemicals made. Hydrogen sulfide,  $\text{H}_2\text{S}$ , occurs in large quantities in natural gas, such as that produced in the Canadian province of Alberta. This hydrogen sulfide must be removed from the natural gas. Rather than presenting a pollution problem, it is converted to elemental sulfur, then used to make sulfuric acid.

Another green chemistry approach to the reclamation of waste sulfur is practiced in Kalundborg, Denmark, the site of the world's most clearly recognizable system of industrial ecology (see Chapter 14). The huge coal-fired power plant in Kalundborg uses lime scrubbing to remove sulfur dioxide from stack gas. The calcium sulfite product of this process is oxidized,



to generate gypsum,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ . This mineral is then used to make wallboard, thus solving a pollution problem from the production of spent lime and a raw materials problem arising from the need for gypsum to make wallboard needed for building construction.

## Nitrogen Oxides

Nitrous oxide ( $\text{N}_2\text{O}$ ), colorless, odorless, nitric oxide ( $\text{NO}$ ), and pungent-smelling, red-brown nitrogen dioxide ( $\text{NO}_2$ ) occur in the atmosphere. Of these, nitrous oxide is generated by bacteria and its release is one of the ways in which chemically fixed nitrogen in the biosphere is returned to the atmosphere. It is not involved much with chemical processes in the troposphere, but undergoes photochemical dissociation in the stratosphere:



Both  $\text{NO}$  and  $\text{NO}_2$ , collectively designated as  $\text{NO}_x$ , are produced from natural sources, such as lightning and biological processes, and from pollutant sources. Pollutant concentrations of these gases can become too high locally and regionally, causing air pollution problems. A major pollutant source of these gases is the internal combustion engine in which conditions are such that molecular elemental nitrogen and oxygen react,



to produce  $\text{NO}$ . Combustion of fuels that contain organically bound nitrogen, such as coal, also produces  $\text{NO}$ . Atmospheric chemical reactions convert some of the  $\text{NO}$  emitted to  $\text{NO}_2$ .

Exposed to electromagnetic radiation of wavelengths below 398 nm, nitrogen dioxide undergoes photodissociation,



to produce highly reactive O atoms. The O atoms can participate in a series of chain reactions through which  $\text{NO}$  is converted back to  $\text{NO}_2$ , which can undergo photodissociation again to start the cycle over. Nitrogen dioxide is very reactive, undergoing photodissociation within a minute or two in direct sunlight.

Nitrogen dioxide,  $\text{NO}_2$ , is significantly more toxic than  $\text{NO}$ , although concentrations of  $\text{NO}_2$  in the outdoor atmosphere rarely reach toxic levels. Accidental releases of  $\text{NO}_2$  can be sufficient to cause toxic effects or even death. Brief exposures to 50–100 parts per million (ppm) of  $\text{NO}_2$  in air inflames lung tissue for 6–8 weeks followed by recovery. Exposure to 500 ppm or more of  $\text{NO}_2$  causes death within 2–10 days. Exposure to 100–500 ppm of  $\text{NO}_2$  causes a lung condition with the ominous name of *bronchiolitis fibrosa obliterans* that is fatal within 3–5 weeks after exposure. Fatal incidents of  $\text{NO}_2$  poisoning have resulted from accidental release of the gas used as an oxidant in rocket fuels and from burning of nitrogen-containing celluloid and nitrocellulose moving picture film (nitrocellulose has been used as an explosive and has long been banned in film because of catastrophic fires that killed numerous people). Plants exposed to nitrogen dioxide may suffer decreased photosynthesis, leaf spotting, and breakdown of plant tissue.

The release of  $\text{NO}$  from combustion sources can be reduced by limiting excess air so that there is not enough excess oxygen to produce  $\text{NO}$  according to Reaction 10.8.7. The production of  $\text{NO}$  is also reduced by relatively lower combustion temperatures. Exhaust catalytic converter reduce  $\text{NO}_x$  emissions from automobile exhausts. Scrubbing  $\text{NO}_x$  from furnace and power plant stack gases is difficult due to the low water solubilities of  $\text{NO}_x$  gases.

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