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10 PARTICLES IN THE ATMOSPHERE

10.1. PARTICLES IN THE ATMOSPHERE

Particles in the atmosphere, which range in size from about one-half millimeter (the size of sand or drizzle) down to molecular dimensions, are made up of an amazing variety of materials and discrete objects that may consist of either solids or liquid droplets.[1] A number of terms are commonly used to describe atmospheric particles; the more important of these are summarized in Table 10.1. Particles abound in the atmosphere. Even the Arctic, remote from sources of industrial pollution, is afflicted with an "Arctic Haze" of airborne particles from October to May each year. **Particulates** is a term that has come to stand for particles in the atmosphere, although *particulate matter* or simply *particles*, is preferred usage.

Table 10.1. Important Terms Describing Atmospheric Particles

Term	Meaning
Aerosol	Colloidal-sized atmospheric particle
Condensation aerosol	Formed by condensation of vapors or reactions of gases
Dispersion aerosol	Formed by grinding of solids, atomization of liquids, or dispersion of dusts
Fog	Term denoting high level of water droplets
Haze	Denotes decreased visibility due to the presence of particles
Mists	Liquid particles
Smoke	Particles formed by incomplete combustion of fuel

Particulate matter makes up the most visible and obvious form of air pollution. Atmospheric **aerosols** are solid or liquid particles smaller than 100 μm in diameter. Pollutant particles in the 0.001 to 10 μm range are commonly suspended in the air near sources of pollution such as the urban atmosphere, industrial plants, highways, and power plants.

Very small, solid particles include carbon black, silver iodide, combustion nuclei, and sea-salt nuclei (see Figure 10.1). Larger particles include cement dust, wind-blown soil dust, foundry dust, and pulverized coal. Liquid particulate matter, **mist**, includes raindrops, fog, and sulfuric acid mist. Particulate matter may be organic or inorganic; both types are very important atmospheric contaminants.
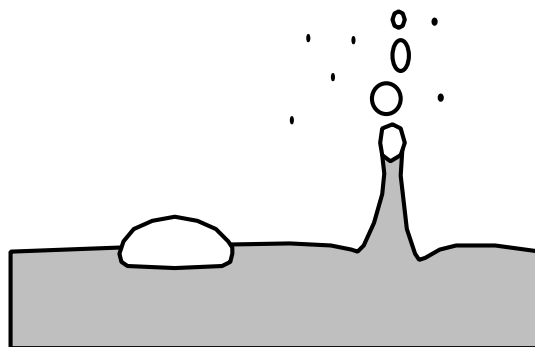

Figure 10.1. Bursting bubbles in seawater form small liquid aerosol particles. Evaporation of water from aerosol particles results in the formation of small solid particles of sea-salt nuclei.

Some particles are of biological origin, such as viruses, bacteria, bacterial spores, fungal spores, and pollen. In addition to organic materials, organisms may contribute to sulfate particulate matter in the atmosphere. Marine biological sources may contribute significantly to atmospheric aerosols.[2] Biogenic materials reacting in and on the surface of sea-salt aerosols produce some significant atmospheric chemical species, such as halogen radicals, and in so doing influence cycles involving atmospheric sulfur, nitrogen, and oxidants.[3]

As discussed later in this chapter, particulate matter originates from a wide variety of sources and processes, ranging from simple grinding of bulk matter to complicated chemical or biochemical syntheses. The effects of particulate matter are also widely varied. Possible effects on climate are discussed in Chapter 14. Either by itself, or in combination with gaseous pollutants, particulate matter may be detrimental to human health. Atmospheric particles may damage materials, reduce visibility, and cause undesirable esthetic effects. It is now recognized that very small particles have a particularly high potential for harm, including adverse health effects. In new ambient air quality standards for particulate matter issued in July 1997, the U. S. Environmental Protection Agency regulated particles 2.5 μm in diameter or less for the first time.

For the most part, aerosols consist of carbonaceous material, metal oxides and glasses, dissolved ionic species (electrolytes), and ionic solids. The predominant constituents are carbonaceous material, water, sulfate, nitrate, ammonium nitrogen, and silicon. The composition of aerosol particles varies significantly with size. The

very small particles tend to be acidic and often originate from gases, such as from the conversion of SO_2 to H_2SO_4. Larger particles tend to consist of materials generated mechanically, such as by the grinding of limestone, and have a greater tendency to be basic.

10.2. PHYSICAL BEHAVIOR OF PARTICLES IN THE ATMOSPHERE

As shown in Figure 10.2, atmospheric particles undego a number of processes in the atmosphere. Small colloidal particles are subject to *diffusion processes*. Smaller particles *coagulate* together to form larger particles. *Sedimentation* or *dry deposition* of particles, which have often reached sufficient size to settle by coagulation, is one of two major mechanisms for particle removal from the atmosphere. The other is *scavenging* by raindrops and other forms of precipitation. Particles also react with atmospheric gases.
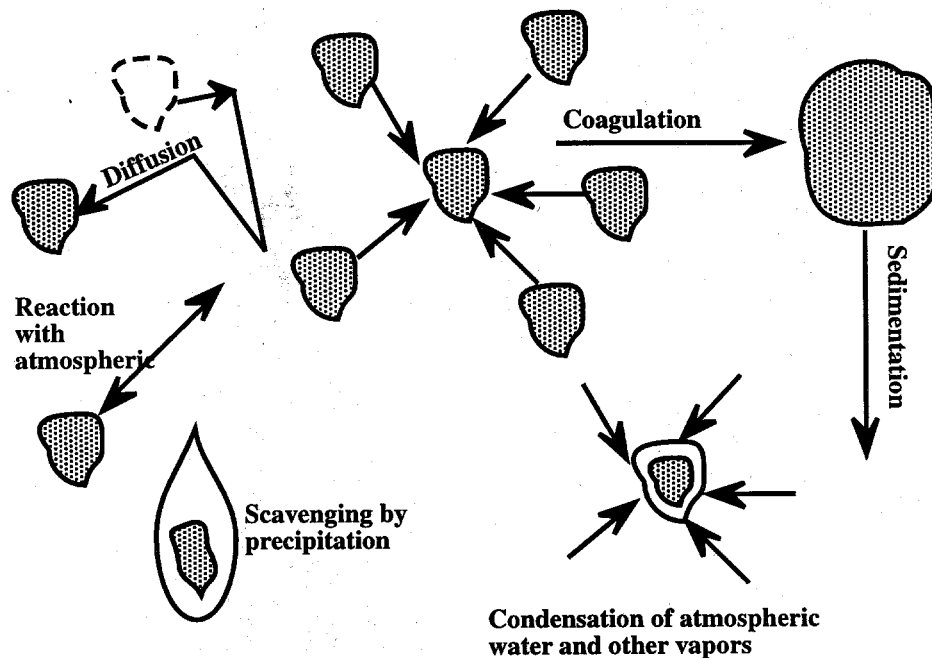

Figure 10.2. Processes that particles undergo in the atmosphere.

Particle size usually expresses the diameter of a particle, though sometimes it is used to denote the radius. The rate at which a particle settles is a function of particle diameter and density. The settling rate is important in determining the effect of the particle in the atmosphere. For spherical particles greater than approximately 1 μm in diameter, Stokes' law applies,

$$ = \frac{gd^2(\rho_1 - \rho_2)}{18} \tag{10.2.1}$$

where is the settling velocity in cm/sec, g is the acceleration of gravity in cm/sec^2, $_1$ is the density of the particle in g/cm^3, $_2$ is the density of air in g/cm^3, and is the viscosity of air in poise. Stokes' law can also be used to express the effective diameter of an irregular nonspherical particle. These are called **Stokes diameters** (aerodynamic diameters) and are normally the ones given when particle diameters are expressed. Furthermore, since the density of a particle is often not known, an arbitrary density of 1 g/cm^3 is conventionally assigned to $_1$; when this is done, the diameter calculated from Equation 10.2.1 is called the **reduced sedimentation diameter**.

Size and Settling of Atmospheric Particles

Most kinds of aerosol particles have unknown diameters and densities and occur over a range of sizes. For such particles, the term **mass median diameter (MMD)** may be used to describe aerodynamically equivalent spheres having an assigned density of 1 g/cm^3 at a 50% mass collection efficiency, as determined in sampling devices calibrated with spherical aerosol particles having a known, uniform size. (Polystyrene latex is commonly used as a material for the preparation of such standard aerosols.) The determination of MMD is accomplished by plotting the log of particle size as a function of the percentage of particles smaller than the given size on a probability scale. Two such plots are shown in Figure 10.3. It is seen from the plot that particles of aerosol X have a mass median diameter of 2.0 μm (ordinate corresponding to 50% on the abscissa). In the case of aerosol Y, linear extrapolation to sizes below the lower measurable size limit of about 0.7 μm gives an estimated value of 0.5 μm for the MMD.

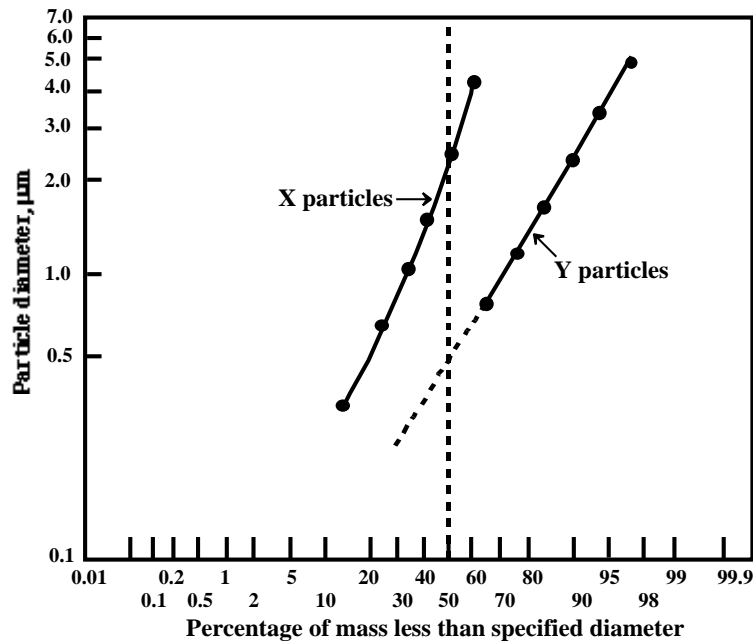Figure 10.3. Particle size distribution for particles of X (MMD = 2.0 μm) and Y (MMD = 0.5 μm).

The settling characteristics of particles smaller than about 1 μm in diameter deviate from Stokes' Law because the settling particles "slip between" air molecules. Extremely small particles are subject to **Brownian motion** resulting from random movement due to collisions with air molecules and do not obey Stokes' Law. Deviations are also observed for particles above 10 μm in diameter because they settle rapidly and generate turbulence as they fall.

10.3. PHYSICAL PROCESSES FOR PARTICLE FORMATION

Dispersion aerosols, such as dusts, formed from the disintegration of larger particles are usually above 1 μm in size. Typical processes for forming dispersion aerosols include evolution of dust from coal grinding, formation of spray in cooling towers, and blowing of dirt from dry soil.

Many dispersion aerosols originate from natural sources such as sea spray, windblown dust, and volcanic dust. However, a vast variety of human activities break up material and disperse it to the atmosphere. "All terrain" vehicles churn across desert lands, coating fragile desert plants with layers of dispersed dust. Quarries and rock crushers spew out plumes of ground rock. Cultivation of land has made it much more susceptible to dust-producing wind erosion.

However, since much more energy is required to break material down into small particles than is required for or released by the synthesis of particles through chemical synthesis or the adhesion of smaller particles, most dispersion aerosols are relatively large. Larger particles tend to have fewer harmful effects than smaller ones. As examples, larger particles are less *respirable* in that they do not penetrate so far into the lungs as smaller ones, and larger particles are relatively easier to remove from air pollution effluent sources.

Huge volcanic eruptions can cause highly elevated levels of particles in the atmosphere. These can be from the physical process of simply blowing as much as several cubic kilometers of volcanic dust as high as the stratosphere and through chemical processes, usually involving the production of sulfuric acid and sulfates from volcanic SO_2 and H_2S. A study of the 1982 eruption of El Chichon volcano in Mexico showed that volcanic glass, sodium chloride, and sulfate from the volcano were deposited in snow in Greenland.[4] The June 15, 1991 eruption of Mount Pinatubo in the Philippines caused perceptible perturbations in Earth's atmospheric solar and infrared radiation transmission.[5]

10.4. CHEMICAL PROCESSES FOR PARTICLE FORMATION

Chemical processes in the atmosphere convert large quantities of atmospheric gases to particulate matter. Among the chemical species most responsible for this conversion are the organic pollutants and nitrogen oxides that cause formation of ozone and photochemical smog (see Chapter 13) in the troposphere.[6] To an extent, therefore, control of hydrocarbon and NO_X emissions to reduce smog will also curtail atmospheric particulate matter pollution.

A major fraction of ambient particulate matter arises from atmospheric gas-to-particle conversion. Attempts to reduce particulate matter levels require control of the same organic and nitrogen oxide (NO_X) emissions that are precursors to urban and regional ozone formation.

Most chemical processes that produce particles are combustion processes, including fossil-fuel-fired power plants; incinerators; home furnaces, fireplaces, and stoves; cement kilns; internal combustion engines; forest, brush, and grass fires; and active volcanoes. Particles from combustion sources tend to occur in a size range below 1 μm. Such very small particles are particularly important because they are most readily carried into the alveoli of lungs (see pulmonary route of exposure to toxicants in Chapter 22) and they are likely to be enriched in more hazardous constituents, such as toxic heavy metals and arsenic. The latter characteristic can enable use of small particle analysis for tracking sources of particulate pollutants.

Inorganic Particles

Metal oxides constitute a major class of inorganic particles in the atmosphere. These are formed whenever fuels containing metals are burned. For example, particulate iron oxide is formed during the combustion of pyrite-containing coal:

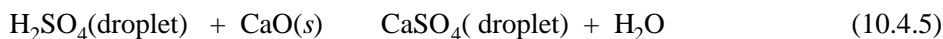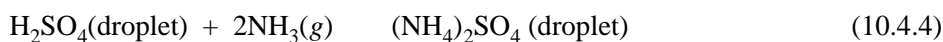$$3FeS_2 + 8O_2 \quad\quad Fe_3O_4 + 6SO_2 \tag{10.4.1}$$

Organic vanadium in residual fuel oil is converted to particulate vanadium oxide. Part of the calcium carbonate in the ash fraction of coal is converted to calcium oxide and is emitted into the atmosphere through the stack:

$$CaCO_3 + heat \quad\quad CaO + CO_2 \tag{10.4.2}$$

A common process for the formation of aerosol mists involves the oxidation of atmospheric sulfur dioxide to sulfuric acid, a hygroscopic substance that accumulates atmospheric water to form small liquid droplets:

$$2SO_2 + O_2 + 2H_2O \quad\quad 2H_2SO_4 \tag{10.4.3}$$

In the presence of basic air pollutants, such as ammonia or calcium oxide, the sulfuric acid reacts to form salts:

$$H_2SO_4(droplet) + 2NH_3(g) \quad\quad (NH_4)_2SO_4 \ (droplet) \tag{10.4.4}$$

$$H_2SO_4(droplet) + CaO(s) \quad\quad CaSO_4(\ droplet) + H_2O \tag{10.4.5}$$

Under low-humidity conditions water is lost from these droplets and a solid aerosol is formed.

The preceding examples show several ways in which solid or liquid inorganic aerosols are formed by chemical reactions. Such reactions constitute an important general process for the formation of aerosols, particularly the smaller particles.

Organic Particles

A significant portion of organic particulate matter is produced by internal combustion engines in complicated processes that involve pyrosynthesis and nitrogenous compounds. These products may include nitrogen-containing compounds and oxidized hydrocarbon polymers. Lubricating oil and its additives may also

contribute to organic particulate matter. A study of particulate matter emitted by gasoline auto engines (with and without catalysts) and diesel truck engines measured more than 100 compounds quantitatively.[7] Among the prominent classes of compounds found were *n*-alkanes, *n*-alkanoic acids, benzaldehydes, benzoic acids, azanaphthalenes, polycyclic aromatic hydrocarbons, oxygenated PAHs, pentacyclic triterpanes, and steranes (the last two classes of hydrocarbons are multiringed compounds characteristic of petroleum that enter exhaust gases from lubricating oil).

PAH Synthesis

The organic particles of greatest concern are PAH hydrocarbons, which consist of condensed ring aromatic (aryl) molecules. The most often cited example of a PAH compound is benzo(a)pyrene, a compound that the body can metabolize to a carcinogenic form:

Benzo(a)pyrene
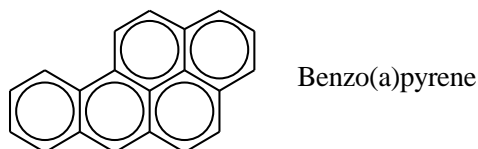
PAHs may be synthesized from saturated hydrocarbons under oxygen-deficient conditions. Hydrocarbons with very low molecular masses, including even methane, may act as precursors for the polycyclic aromatic compounds. Low-molar-mass hydrocarbons form PAHs by **pyrosynthesis**. This happens at temperatures exceeding approximately 500°C at which carbon-hydrogen and carbon-carbon bonds are broken to form free radicals. These radicals undergo dehydrogenation and combine chemically to form aryl ring structures which are resistant to thermal degradation. The basic process for the formation of such rings from pyrosynthesis starting with ethane is,

Polycyclic aromatic hydrocarbons
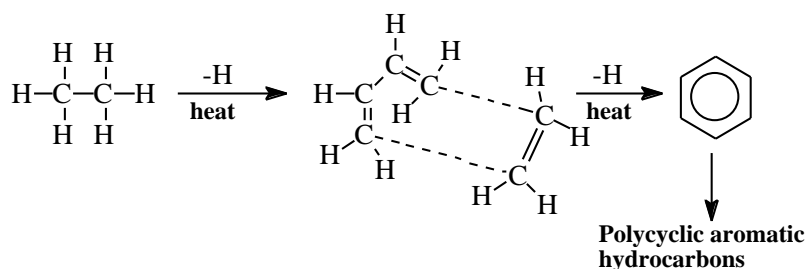
which results in the formation of stable PAH structures. The tendency of hydrocarbons to form PAHs by pyrosynthesis varies in the order aromatics > cycloolefins > olefins > paraffins. The existing ring structure of cyclic compounds is conducive to PAH formation. Unsaturated compounds are especially susceptible to the addition reactions involved in PAH formation.

Polycyclic aromatic compounds may be formed from higher alkanes present in fuels and plant materials by the process of **pyrolysis**, the "cracking" of organic compounds to form smaller and less stable molecules and radicals.

10.5. THE COMPOSITION OF INORGANIC PARTICLES

Figure 10.4 illustrates the basic factors responsible for the composition of inorganic particulate matter. In general, the proportions of elements in atmospheric particulate matter reflect relative abundances of elements in the parent material.

The source of particulate matter is reflected in its elemental compositon, taking into consideration chemical reactions that may change the composition. For example, particulate matter largely from an ocean spray origin in a coastal area receiving sulfur dioxide pollution may show anomalously high sulfate and corresponding low chloride content. The sulfate comes from atmospheric oxidation of sulfur dioxide to form nonvolatile ionic sulfate, whereas some chloride originally from the NaCl in the seawater may be lost from the solid aerosol as volatile HCl:

$$2SO_2 \; + \; O_2 \; + \; 2H_2O \qquad 2H_2SO_4 \tag{10.5.1}$$

$$H_2SO_4 \; + \; 2NaCl(particulate) \qquad Na_2SO_4(particulate) \; + \; 2HCl \tag{10.5.2}$$
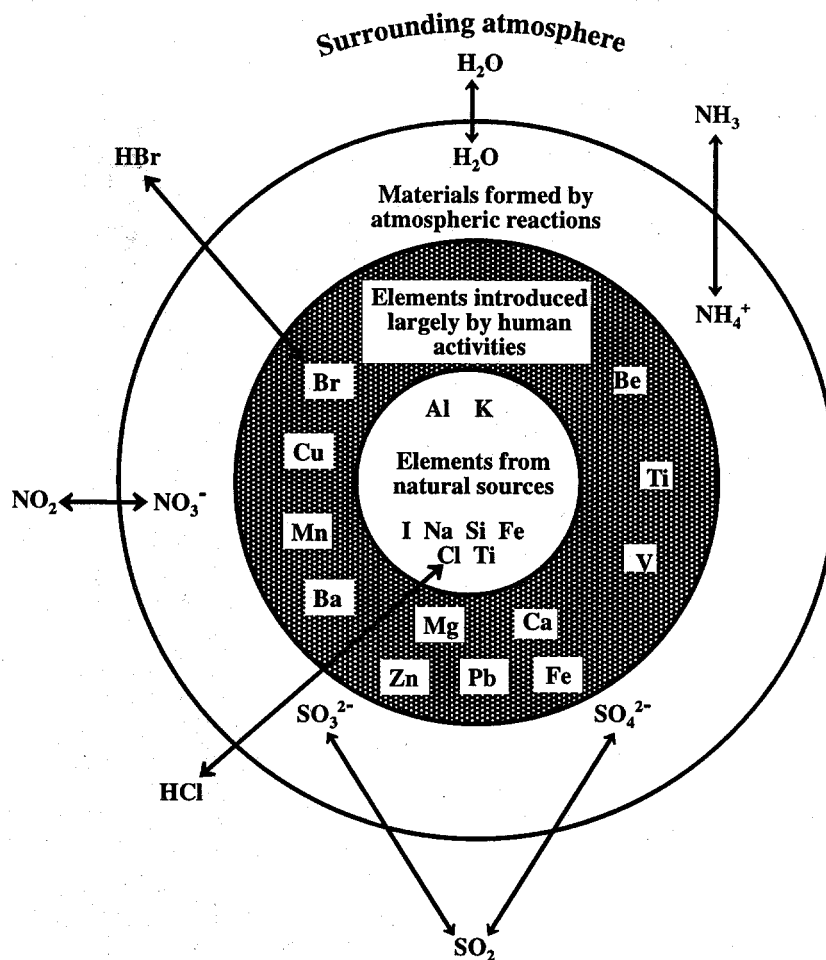

Figure 10.4. Some of the components of inorganic particulate matter and their origins.

Acids other than sulfuric acid can also be involved in the modification of sea-salt particles. An examination with an electron microscope equipped with an X-ray emission analyzer of sea-salt particles taken at Tsukuba, Japan, 50 km from the Pacific Coast, showed a marked deficiency of chloride.[8] This was attributed primarily to reaction with pollutant nitric acid as indicated by high levels of nitrate in the samples. The presence of significant levels of zinc in the particles indicated contamination from pollution sources. The chemical composition of atmospheric particulate matter is quite diverse. Among the constituents of inorganic particulate matter found in polluted atmospheres are salts, oxides, nitrogen compounds, sulfur compounds, various metals, and radionuclides. In coastal areas sodium and chlorine get into atmospheric particles as sodium chloride from sea spray. The major trace elements that typically occur at levels above 1 $\mu g/m^3$ in particulate matter are aluminum, calcium, carbon, iron, potassium, sodium, and silicon; note that most of these tend to originate from terrestrial sources. Lesser quantities of copper, lead, titanium, and zinc, and even lower levels of antimony, beryllium, bismuth, cadmium, cobalt, chromium, cesium, lithium, manganese, nickel, rubidium, selenium, strontium, and vanadium are commonly observed. The likely sources of some of these elements are given below:

- **Al, Fe, Ca, Si**: Soil erosion, rock dust, coal combustion

- **C**: Incomplete combustion of carbonaceous fuels

- **Na, Cl**: Marine aerosols, chloride from incineration of organohalide polymer wastes

- **Sb, Se**: Very volatile elements, possibly from the combustion of oil, coal, or refuse

- **V**: Combustion of residual petroleum (present at very high levels in residues from Venezuelan crude oil)

- **Zn**: Tends to occur in small particles, probably from combustion

- **Pb**: Combustion of leaded fuels and wastes containing lead

Particulate carbon as soot, carbon black, coke, and graphite originates from auto and truck exhausts, heating furnaces, incinerators, power plants, and steel and foundry operations, and composes one of the more visible and troublesome particulate air pollutants. Because of its good adsorbent properties, carbon can be a carrier of gaseous and other particulate pollutants. Particulate carbon surfaces may catalyze some heterogeneous atmospheric reactions, including the important conversion of SO_2 to sulfate.

Fly Ash

Much of the mineral particulate matter in a polluted atmosphere is in the form of oxides and other compounds produced during the combustion of high-ash fossil fuel. Much of the mineral matter in fossil fuels such as coal or lignite is converted during combustion to a fused, glassy bottom ash which presents no air pollution problems.

Smaller particles of **fly ash** enter furnace flues and are efficiently collected in a properly equipped stack system. However, some fly ash escapes through the stack and enters the atmosphere. Unfortunately, the fly ash thus released tends to consist of smaller particles that do the most damage to human health, plants, and visibility.

The composition of fly ash varies widely, depending upon the fuel. The predominant constituents are oxides of aluminum, calcium, iron, and silicon. Other elements that occur in fly ash are magnesium, sulfur, titanium, phosphorus, potassium, and sodium. Elemental carbon (soot, carbon black) is a significant fly ash constituent.

The size of fly ash particles is a very important factor in determining their removal from stack gas and their ability to enter the body through the respiratory tract. Fly ash from coal-fired utility boilers has shown a bimodal (two peak) distribution of size, with a peak at about 0.1 μm as illustrated in Figure 10.5.[9] Although only about 1-2 % of the total fly ash mass is in the smaller size fraction, it includes the vast majority of the total number of particles and particle surface area. Submicrometer particles probably result from a volatilization-condensation process during combustion, as reflected in a higher concentration of more volatile elements such as As, Sb, Hg, and Zn. Furthermore, the very small particles are the most difficult to remove by electrostatic precipitators and bag houses (see Section 10.11).
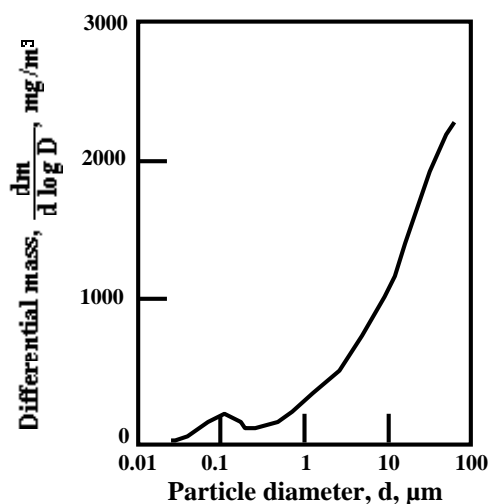

Figure 10.5. General appearance of particle-size distribution in coal-fired power plant ash. The data are given on differential mass coordinates, where M is the mass, so that the area under the curve in a given size range is the mass of the particles in that size range.

Asbestos

Asbestos is the name given to a group of fibrous silicate minerals, typically those of the serpentine group, approximate formula $Mg_3P(Si_2O_5)(OH)_4$. The tensile strength, flexibility, and nonflammability of asbestos have led to many uses including structural materials, brake linings, insulation, and pipe manufacture. In 1979, 560,000 metric tons of asbestos were used in the U.S. By 1988 annual consumption had dropped to 85,000 metric tons, most of it used for brake linings and pads, roofing products, cement/asbestos pipe, gaskets, heat-resistant packing, and specialty papers. In 1989, the U.S. Environmental Protection Agency announced regulations

that phased out most uses of asbestos by 1996.

Asbestos is of concern as an air pollutant because when inhaled it may cause asbestosis (a pneumonia condition), mesothelioma (tumor of the mesothelial tissue lining the chest cavity adjacent to the lungs), and bronchogenic carcinoma (cancer originating with the air passages in the lungs). Therefore, uses of asbestos have been severely curtailed and widespread programs have been undertaken to remove the material from buildings.

10.6. TOXIC METALS

Some of the metals found predominantly as particulate matter in polluted atmospheres are known to be hazardous to human health. All of these except beryllium are so-called "heavy metals." Lead is the toxic metal of greatest concern in the urban atmosphere because it comes closest to being present at a toxic level; mercury ranks second. Others include beryllium, cadmium, chromium, vanadium, nickel, and arsenic (a metalloid).

Atmospheric Mercury

Atmospheric mercury is of concern because of its toxicity, volatility, and mobility. Some atmospheric mercury is associated with particulate matter. Much of the mercury entering the atmosphere does so as volatile elemental mercury from coal combustion and volcanoes. Volatile organomercury compounds such as dimethylmercury, $(CH_3)_2Hg$, and monomethylmercury salts, such as CH_3HgBr, are also encountered in the atmosphere.

Atmospheric Lead

With the reduction of leaded fuels, atmospheric lead is of less concern than it used to be. However, during the decades that leaded gasoline containing tetraethyllead was the predominant automotive fuel, particulate lead halides were emitted in large quantities. This occurs through the action of dichloroethane and dibromoethane added as halogenated scavengers to prevent the accumulation of lead oxides inside engines. The lead halides formed,

$$Pb(C_2H_5)_4 + O_2 + \text{halogenated scavengers} \quad CO_2 + H_2O +$$
$$PbCl_2 + PbClBr + PbBr_2 \text{ (unbalanced)} \quad (10.6.1)$$
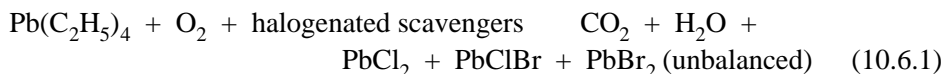
are volatile enough to exit through the exhaust system but condense in the air to form particles. During the period of peak usage of leaded gasoline in the early 1970s, about 200,000 tons of lead were entering the atmosphere each year by this route in the U.S.

Atmospheric Beryllium

Only about 350 metric tons of beryllium are used each year in the U.S. for the formulation of specialty alloys used in electrical equipment, electronic instrumentation, space gear, and nuclear reactor components, so that distribution of beryllium is by no means comparable to that of other toxic metals such as lead or

mercury. However, because of its "high tech" applications, consumption of beryllium may increase in the future.

During the 1940s and 1950s, the toxicity of beryllium and beryllium compounds became widely recognized; it has the lowest allowable limit in the atmosphere of all the elements. One of the main results of the recognition of beryllium toxicity hazards was the elimination of this element from phosphors (coatings which produce visible light from ultraviolet light) in fluorescent lamps.

10.7. RADIOACTIVE PARTICLES

Some of the radioactivity detected in atmospheric particles is of natural origin. This activity includes that produced when cosmic rays act on nuclei in the atmosphere to produce radionuclides, including ^{7}Be, ^{10}Be, ^{14}C, ^{39}Cl, ^{3}H, ^{22}Na, ^{32}P, and ^{33}P. A significant natural source of radionuclides in the atmosphere is **radon**, a noble gas product of radium decay. Radon may enter the atmosphere as either of two isotopes, ^{222}Rn (half-life 3.8 days) and ^{220}Rn (half-life 54.5 seconds). Both are alpha emitters in decay chains that terminate with stable isotopes of lead. The initial decay products, ^{218}Po and ^{216}Po, are nongaseous and adhere readily to atmospheric particulate matter.

The catastrophic 1986 meltdown and fire at the Chernobyl nuclear reactor in the former Soviet Union spread large quantities of radioactive materials over a wide area of Europe. Much of this radioactivity was in the form of particles.[10]

One of the more serious problems in connection with radon is that of radioactivity originating from uranium mine tailings that have been used in some areas as backfill, soil conditioner, and a base for building foundations. Radon produced by the decay of radium exudes from foundations and walls constructed on tailings. Higher than normal levels of radioactivity have been found in some structures in the city of Grand Junction, Colorado, where uranium mill tailings have been used extensively in construction. Some medical authorities have suggested that the rate of birth defects and infant cancer in areas where uranium mill tailings have been used in residential construction are significantly higher than normal. The combustion of fossil fuels introduces radioactivity into the atmosphere in the form of radionuclides contained in fly ash. Large coal-fired power plants lacking ash-control equipment may introduce up to several hundred millicuries of radionuclides into the atmosphere each year, far more than either an equivalent nuclear or oil-fired power plant.

The radioactive noble gas ^{85}Kr (half-life 10.3 years) is emitted into the atmosphere by the operation of nuclear reactors and the processing of spent reactor fuels. In general, other radionuclides produced by reactor operation are either chemically reactive and can be removed from the reactor effluent, or have such short half-lives that a short time delay prior to emission prevents their leaving the reactor. Widepread use of fission power will inevitably result in an increased level of ^{85}Kr in the atmosphere. Fortunately, biota cannot concentrate this chemically unreactive element.

The above-ground detonation of nuclear weapons can add large amounts of radioactive particulate matter to the atmosphere. Among the radioisotopes that have been detected in rainfall collected after atmospheric nuclear weapon detonation are ^{91}Y, ^{141}Ce, ^{144}Ce, ^{147}Nd, ^{147}Pm, ^{149}Pm, ^{151}Sm, ^{153}Sm, ^{155}Eu, ^{156}Eu, ^{89}Sr, ^{90}Sr,

^{115m}Cd, ^{129m}Te, ^{131}I, ^{132}Te, and ^{140}Ba. (Note that "m" denotes a metastable state that decays by gamma-ray emission to an isotope of the same element.) The rate of travel of radioactive particles through the atmosphere is a function of particle size. Appreciable fractionation of nuclear debris is observed because of differences in the rates at which the various debris constituents move through the atmosphere.

## 10.8. THE COMPOSITION OF ORGANIC PARTICLES

Organic atmospheric particles occur in a wide variety of compounds. For analysis, such particles can be collected onto a filter; extracted with organic solvents; fractionated into neutral, acid, and basic groups; and analyzed for specific constituents by chromatography and mass spectrometry. The neutral group contains predominantly hydrocarbons, including aliphatic, aromatic, and oxygenated fractions. The aliphatic fraction of the neutral group contains a high percentage of long-chain hydrocarbons, predominantly those with 16-28 carbon atoms. These relatively unreactive compounds are not particularly toxic and do not participate strongly in atmospheric chemical reactions. The aromatic fraction, however, contains carcinogenic polycyclic aromatic hydrocarbons, which are discussed below. Aldehydes, ketones, epoxides, peroxides, esters, quinones, and lactones are found among the oxygenated neutral components, some of which may be mutagenic or carcinogenic. The acidic group contains long-chain fatty acids and nonvolatile phenols. Among the acids recovered from air-pollutant particulate matter are lauric, myristic, palmitic, stearic, behenic, oleic, and linoleic acids. The basic group consists largely of alkaline N-heterocyclic hydrocarbons such as acridine:
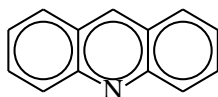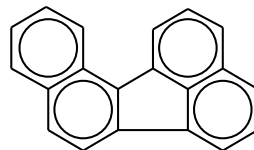

Acridine

Polycyclic Aromatic Hydrocarbons

Polycyclic aromatic hydrocarbons (PAH) in atmospheric particles have received a great deal of attention because of the known carcinogenic effects of some of these compounds, which are discussed in greater detail in Chapter 23. Prominent among these compounds are benzo(a)pyrene, benz(a)anthracene, chrysene, benzo-(e)pyrene, benz(e)acephenanthrylene, benzo(j)fluoranthene, and indenol. Some representative structures of PAH compounds are given below:
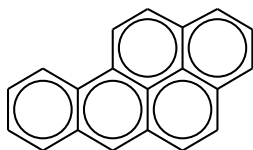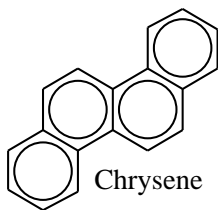

Benzo(a)pyrene   Chrysene   Benzo(j)fluoranthene

Elevated levels of PAH compounds of up to about 20 µg/m^3 are found in the atmosphere. Elevated levels of PAHs are most likely to be encountered in polluted

urban atmospheres, and in the vicinity of natural fires such as forest and prairie fires. Coal furnace stack gas may contain over 1000 μg/m^3 of PAH compounds, and cigarette smoke almost 100 μg/m^3.

Atmospheric polycyclic aromatic hydrocarbons are found almost exclusively in the solid phase, largely sorbed to soot particles. Soot itself is a highly condensed product of PAHs. Soot contains 1–3% hydrogen and 5–10% oxygen, the latter due to partial surface oxidation. Benzo(a)pyrene adsorbed on soot disappears very rapidly in the presence of light yielding oxygenated products; the large surface area of the particle contributes to the high rate of reaction. Oxidation products of benzo(a)-pyrene include epoxides, quinones, phenols, aldehydes, and carboxylic acids as illustrated by the composite structures shown below:
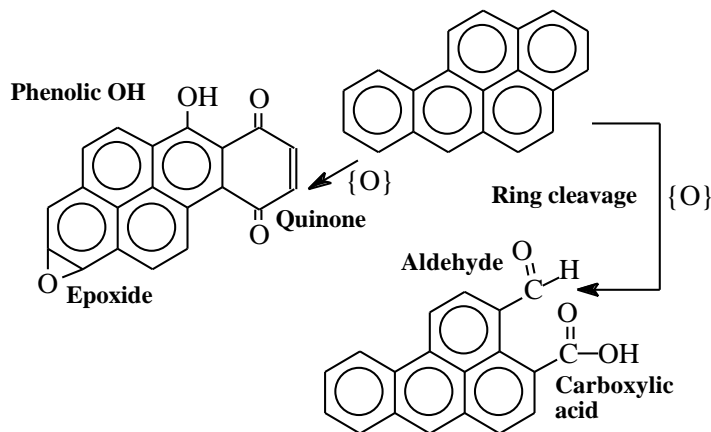
Carbonaceous Particles from Diesel Engines

Diesel engines emit significant levels of carbonaceous particles.[11] Although an appreciable fraction of these particles have aerodynamic diameters less than 1 μm, they may exist as aggregates of several thousand smaller particles in clusters up to 30 μm in diameter. This particulate matter consists largely of elemental carbon, although as much as 40% of the particle mass consists of organic extractable hydro-carbons and hydrocarbon derivatives including organosulfur and organonitrogen compounds.

10.9. EFFECTS OF PARTICLES

Atmospheric particles have numerous effects. The most obvious of these is reduction and distortion of visibility. They provide active surfaces upon which heterogeneous atmospheric chemical reactions can occur, and nucleation bodies for the condensation of atmospheric water vapor, thereby exerting a significant influence upon weather and air pollution phenomena.

The most visible effects of aerosol particles upon air quality result from their optical effects. Particles smaller than about 0.1 μm in diameter scatter light much like molecules, that is, Rayleigh scattering. Generally, such particles have an insignificant effect upon visibility in the atmosphere. The light-scattering and intercepting properties of particles larger than 1 μm are approximately proportional

to the particles' cross-sectional areas. Particles of 0.1 μm – 1 μm cause interference phenomena because they are about the same dimensions as the wavelengths of visible light, so their light-scattering properties are especially significant.

Atmospheric particles inhaled through the respiratory tract may damage health. Relatively large particles are likely to be retained in the nasal cavity and in the pharynx, whereas very small particles are likely to reach the lungs and be retained by them. The respiratory system possesses mechanisms for the expulson of inhaled particles. In the ciliated region of the respiratory system, particles are carried as far as the entrance to the gastrointestinal tract by a flow of mucus. Macrophages in the nonciliated pulmonary regions carry particles to the ciliated region.

The respiratory system may be damaged directly by particulate matter that enters the blood system or lymph system through the lungs. In addition, the particulate material or soluble components of it may be transported to organs some distance from the lungs and have a detrimental effect on these organs. Particles cleared from the respiratory tract are to a large extent swallowed into the gastrointestinal tract.

A strong correlation has been found between increases in the daily mortality rate and acute episodes of air pollution. In such cases, high levels of particulate matter are accompanied by elevated concentrations of SO_2 and other pollutants, so that any conclusions must be drawn with caution.

10.10. WATER AS PARTICULATE MATTER

Droplets of water are very widespread in the atmosphere. Although a natural phenomenon, such droplets can have significant and sometimes harmful effects. The most important such consequence is reduction of visibility, with accompanying detrimental effects on driving, flying, and boat navigation. Water droplets in fog act as carriers of pollutants. The most important of these are solutions of corrosive salts, particularly ammonium nitrates and sulfates, and solutions of strong acids. As discussed in Chapter 14, Section 14.3, the pH of water in acidic mist droplets collected during a Los Angeles acidic fog has been as low as 1.7, far below that of acidic precipitation. Such acidic mist can be especially damaging to the respiratory tract because it is very penetrating.

Arguably the most significant effect of water droplets in the atmosphere is as aquatic media in which important atmospheric chemical processes occur. The single most significant such process may well be the oxidation of S(IV) species to sulfuric acid and sulfate salts. The S(IV) species so oxidized include $SO_2(aq)$, HSO_3^-, and SO_3^{2-}. Another important oxidation that takes place in atmospheric water droplets is the oxidation of aldehydes to organic carboxylic acids.

The hydroxyl radical, HO•, is very important in initiating atmospheric oxidation reactions such as those noted above. Hydroxyl radical as HO• can enter water droplets from the gas-phase atmosphere, it can be produced in water droplets photo-chemically, or it can be generated from H_2O_2 and $•O_2^-$ radical-ion, which dissolve in water from the gas phase and then produce HO• by solution chemical reaction:

$$H_2O_2 + •O_2^- \qquad HO• + O_2 + OH^- \tag{10.10.1}$$

Several solutes can react photochemically in aqueous solution (as opposed to the gas phase) to produce hydroxyl radical. One of these is hydrogen peroxide:

$$H_2O_2(aq) + h \qquad 2HO\cdot(aq) \qquad\qquad (10.10.2)$$

Nitrite as NO_2^- or HNO_2, nitrate (NO_3^-), and iron(III) as $Fe(OH)^{2+}(aq)$ can also react photochemically in aqueous solution to produce $HO\cdot$. It has been observed that ultraviolet radiation at 3l3 nm and simulated sunlight can react to produce $HO\cdot$ radical in authentic samples of water collected from cloud and fog sources.[12] Based on the results of this study and related investigations, it may be concluded that the aqueous-phase formation of hydroxyl radical is an important, and in some cases dominant means by which this key atmospheric oxidant is introduced into atmospheric water droplets.

Iron is an inorganic solute of particular importance in atmospheric water. This is because of the participation of iron(III) in the atmospheric oxidation of sulfur(IV) to sulfur(VI)—that is, the conversion of $SO_2(aq)$, HSO_3^-, and SO_3^{2-} to sulfates and H_2SO_4.

10.11. CONTROL OF PARTICULATE EMISSIONS

The removal of particulate matter from gas streams is the most widely practiced means of air pollution control. A number of devices have been developed for this purpose which differ widely in effectiveness, complexity, and cost. The selection of a particle removal system for a gaseous waste stream depends upon the particle loading, nature of particles (size distribution), and type of gas-scrubbing system used.

Particle Removal by Sedimentation and Inertia

The simplest means of particulate matter removal is **sedimentation**, a phenomenon that occurs continuously in nature. Gravitational settling chambers may be employed for the removal of particles from gas streams by simply settling under the influence of gravity. These chambers take up large amounts of space and have low collection efficiencies, particularly for small particles.

Gravitational settling of particles is enhanced by increased particle size, which occurs spontaneously by coagulation. Thus, over time, the sizes of particles increase and the number of particles decreases in a mass of air that contains particles. Brownian motion of particles less than about 0.1 μm in size is primarily responsible for their contact, enabling coagulation to occur. Particles greater than about 0.3 μm in radius do not diffuse appreciably and serve primarily as receptors of smaller particles.

Inertial mechanisms are effective for particle removal. These depend upon the fact that the radius of the path of a particle in a rapidly moving, curving air stream is larger than the path of the stream as a whole. Therefore, when a gas stream is spun by vanes, a fan, or a tangential gas inlet, the particulate matter may be collected on a separator wall because the particles are forced outward by centrifugal force. Devices utilizing this mode of operation are called **dry centrifugal collectors** (cyclones).

Particle filtration

Fabric filters, as their name implies, consist of fabrics that allow the passage of gas but retain particulate matter. These are used to collect dust in bags contained in structures called *baghouses*. Periodically, the fabric composing the filter is shaken

to remove the particles and to reduce back-pressure to acceptable levels. Typically, the bag is in a tubular configuration as shown in Figure 10.6. Numerous other configurations are possible. Collected particulate matter is removed from bags by mechanical agitation, blowing air on the fabric, or rapid expansion and contraction of the bags.
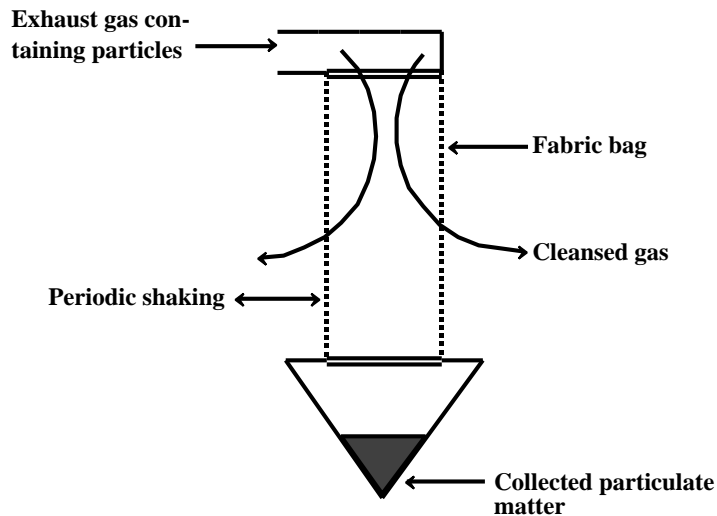

Figure 10.6. Baghouse collection of particulate emissions.

Although simple, baghouses are generally effective in removing particles from exhaust gas. Particles as small as 0.01 μm in diameter are removed, and removal efficiency is relatively high for particles down to 0.5 μm in diameter. Aided by the development of mechanically strong, heat-resistant fabrics from which the bags are fabricated, baghouse installations have increased significantly in the effort to control particulate emissions.

Scrubbers

A venturi scrubber passes gas through a device which leads the gas stream through a converging section, throat, and diverging section as shown in Figure 10.7. Injection of the scrubbing liquid at right angles to incoming gas breaks the liquid into very small droplets, which are ideal for scavenging particles from the gas stream. In the reduced-pressure (expanding and, therefore, cooling) region of the venturi, some condensation can occur of vapor from liquid initially evaporated in the generally hot waste gas, adding to the scrubbing efficiency. In addition to removing particles, venturis may serve as quenchers to cool exhaust gas, and as scrubbers for pollutant gases.

Ionizing wet scrubbers place an electrical charge on particles upstream from a wet scrubber. Larger particles and some gaseous contaminants are removed by scrubbing action. Smaller particles tend to induce opposite charges in water droplets in the scrubber and in its packing material and are removed by attraction of the opposite charges.
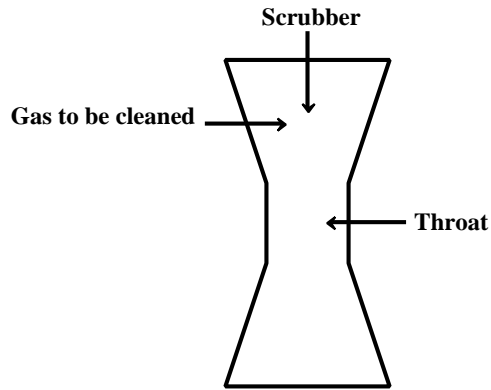
Figure 10.7. Venturi scrubber.

Electrostatic Removal

Aerosol particles may acquire electrical charges. In an electric field, such particles are subjected to a force, F (dynes), given by

$$F = Eq \tag{10.11.1}$$

where E is the voltage gradient (statvolt/cm) and q is the electrostatic charge on the particle (in esu). This phenomenon has been widely used in highly efficient **electrostatic precipitators**, as shown in Figure 10.8. The particles acquire a charge
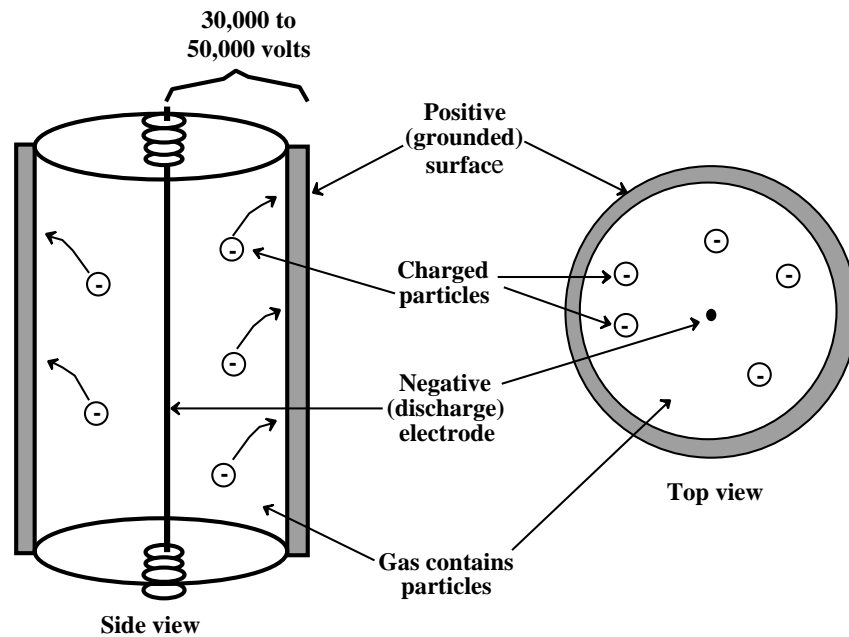

Figure 10.8. Schematic diagram of an electrostatic precipitator

when the gas stream is passed through a high-voltage, direct current corona. Because of the charge, the particles are attracted to a grounded surface from which they may be later removed. Ozone may be produced by the corona discharge. Similar devices used as household dust collectors may produce toxic ozone if not operated properly.

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QUESTIONS AND PROBLEMS

1. The maximum electrical charge that an atmospheric particle may attain in dry air is about 8 esu/cm^2. Where the charge of an electron is 4.77 x 10^{-10} esu, equal to the *elementary quantum of electricity* (the charge on 1 electron or proton), how many electrons per square centimeter of surface area is this?

2. For small charged particles, those that are 0.1 μm or less in size, an average charge of 4.77 x 10^{-10} esu, is normally assumed for the whole particle. What is the surface charge in esu/cm^2 for a charged spherical particle with a radius of 0.1 μm?

3. What is the settling velocity of a particle having a Stokes diameter of 10 μm and a density of 1 g/cm^3 in air at 1.00 atm pressure and 0°C temperature? (The viscosity of air at 0°C is 170.8 micropoise. The density of air under these conditions is 1.29 g/L.)

4. A freight train that included a tank car containing anhydrous NH_3 and one containing concentrated HCl was wrecked, causing both of the tank cars to leak. In the region between the cars a white aerosol formed. What was it, and how was it produced?

5. Examination of aerosol fume particles produced by a welding process showed that 2% of the particles were greater than 7 μm in diameter and only 2% were less than 0.5 μm. What is the mass median diameter of the particles?

6. What two vapor forms of mercury might be found in the atmosphere?

7. Analysis of particulate matter collected in the atmosphere near a seashore shows considerably more Na than Cl on a molar basis. What does this indicate?

8. What type of process results in the formation of very small aerosol particles?

9. Which size range encompasses most of the particulate matter mass in the atmosphere?

10. Why are aerosols in the 0.1–1 μm size range especially effective in scattering light?

11. Per unit mass, why are smaller particles more effective catalysts for atmospheric chemical reactions?

12. In terms of origin, what are the three major categories of elements found in atmospheric particles?

13. What are the five major classes of material making up the composition of atmospheric aerosol particles?

14. The size distribution of particles emitted from coal-fired power plants is bimodal. What are some of the properties of the smaller fraction in terms of potential environmental implications?