21.6 ACID RAIN

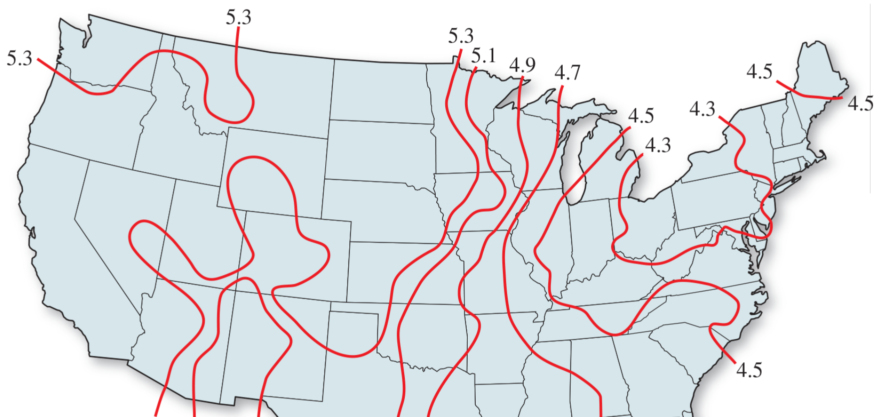
Every year acid rain causes hundreds of millions of dollars' worth of damage to stone buildings and statues throughout the world. The term *stone leprosy* is used by some environmental chemists to describe the corrosion of stone by acid rain (**Figure 21.20**). Acid rain is also toxic to vegetation and aquatic life. Many well-documented cases show dramatically how acid rain has destroyed agricultural and forest lands and killed aquatic organisms.

Figure 21.20 The effect of acid rain on marble.

Agencja Fotograficzna Caro/Alamy Stock Photo

Precipitation in the northeastern United States has an average pH of about 4.3 (**Figure 21.21**). Because atmospheric CO_2 in equilibrium with rainwater would not be expected to result in a pH less than 5.5, sulfur dioxide (SO_2) and, to a lesser extent, nitrogen oxides from auto emissions are believed to be responsible for the high acidity of rainwater. Acidic oxides, such as SO_2, react with water to give the corresponding acids. There are several sources of atmospheric SO_2. Nature itself contributes much SO_2 in the form of volcanic eruptions. Also, many metals exist combined with sulfur in nature. Extracting the metals often entails *smelting,* or *roasting,* the ores—that is, heating the metal sulfide in air to form the metal oxide and SO_2. For example:

$$2ZnS\,(s) + 3O_2\,(g) \longrightarrow 2ZnO\,(s) + 2SO_2\,(s)$$



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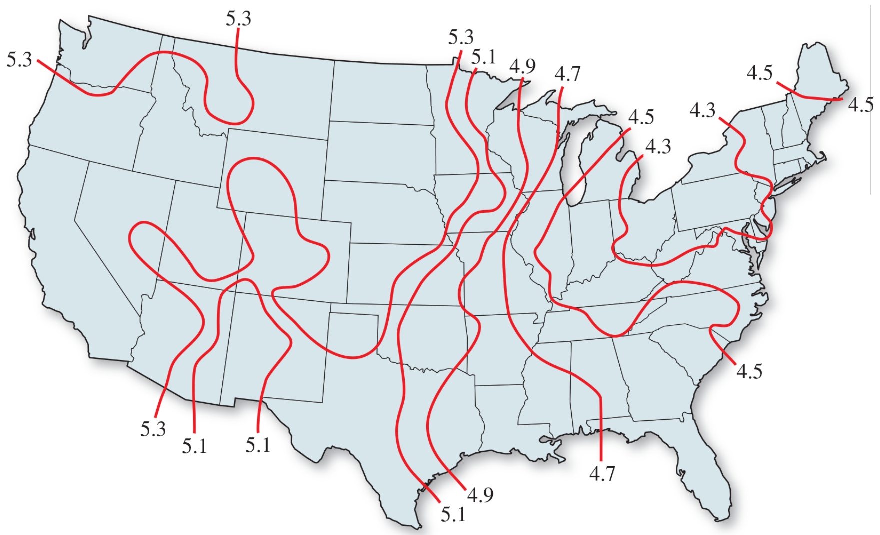

Figure 21.21 Mean precipitation pH in the United States in 1994. Most SO_2 comes from the midwestern states. Prevailing winds carry the acid droplets formed over the Northeast. Nitrogen oxides also contribute to acid rain formation.

The metal oxide can be reduced more easily than the sulfide (by a more reactive metal or in some cases by carbon) to the free metal.

Although smelting is a major source of SO_2, the burning of fossil fuels in industry, in power plants, and in homes accounts for most of the SO_2 emitted to the atmosphere (Figure 21.22). The sulfur content of coal ranges from 0.5 to 5 percent by mass, depending on the source of the coal. The sulfur content of other fossil fuels is similarly variable. Oil from the Middle East, for instance, is low in sulfur, whereas that from Venezuela has a high sulfur content. To a lesser extent, the nitrogen-containing compounds in oil and coal are converted to nitrogen oxides, which can also acidify rainwater.

Figure 21.22 Sulfur dioxide and other air pollutants being released into the atmosphere from a coal-burning power plant.

Larry Lee Photography/Corbis/Getty Images

All in all, some 50 to 60 million tons of SO_2 are released into the atmosphere each year! In the troposphere, SO_2 is almost all oxidized to H_2SO_4 in the form of aerosol, which ends up in wet precipitation or acid rain. The mechanism for the conversion of SO_2 to H_2SO_4 is quite complex and not fully understood. The reaction is believed to be initiated by the hydroxyl radical a coal-burning power plant.

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$$OH + SO_2 \longrightarrow HOSO_2$$

The $HOSO_2$ radical is further oxidized to SO_3.

$$HOSO_2 + O_2 \longrightarrow HO_2 + SO_3$$

The sulfur trioxide formed would then rapidly react with water to form sulfuric acid.

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

SO_2 can also be oxidized to SO_3 and then converted to SO_2SO_4 on particles by heterogeneous catalysis. Eventually, the acid rain can corrode limestone and marble $(CaCO_3)$. A typical reaction is

$$CaCO_3\,(s) + H_2SO_4\,(aq) \longrightarrow CaSO_4\,(s) + H_2O\,(l) + CO_2\,(g)$$

Video 21.1 Oil refining process.

Sulfur dioxide can also attack calcium carbonate directly.

$$2CaCO_3\,(s) + 2SO_2\,(g) + O_2\,(g) \longrightarrow 2CaSO_4\,(s) + 2CO_2\,(g)$$

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There are two ways to minimize the effects of SO_2 pollution. The most direct approach is to remove sulfur from fossil fuels before combustion, but this is technologically difficult to accomplish. A cheaper but less efficient way is to remove SO_2 as it is formed. For example, in one process powdered limestone is injected into the power plant boiler or furnace along with the coal (**Figure 21.23**). At high temperatures, the following decomposition occurs.

$$\underset{\text{limestone}}{CaCO_3\,(s)} \longrightarrow \underset{\text{quicklime}}{CaO\,(s)} + CO_2\,(g)$$

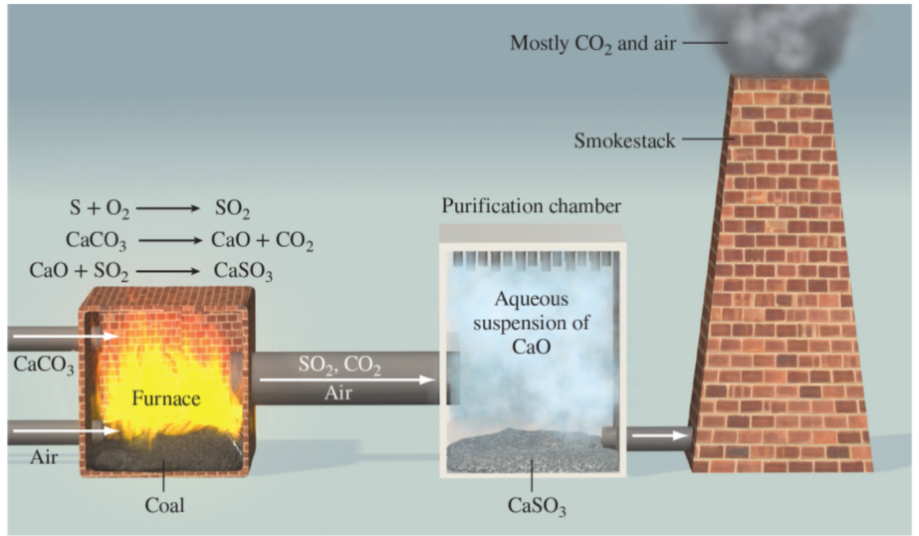

Figure 21.23 Common procedure for removing SO_2 from burning fossil fuel. Powdered limestone decomposes into CaO, which reacts with SO_2 to form $CaSO_3$. The remaining SO_2 is combined with an aqueous suspension of CaO to form $CaSO_3$.

The quicklime reacts with SO_2 to form calcium sulfite and some calcium sulfate.

$$CaO\,(s) + SO_2\,(g) \longrightarrow CaSO_3\,(s)$$
$$2CaO\,(s) + 2SO_2\,(g) + O_2\,(g) \longrightarrow 2CaSO_4\,(s)$$

To remove any remaining SO_2, an aqueous suspension of quicklime is injected into a purification chamber prior to the gases' escape through the smokestack. Quicklime is also added to lakes and soils in a process called *liming* to reduce their acidity (**Figure 21.24**). Installing a sulfuric acid plant near a metal ore refining site is also an effective way to cut SO_2 emission, because the SO_2 produced by roasting metal sulfides can be captured for use in the synthesis of sulfuric acid. This is a sensible way to turn what is a pollutant in one process into a starting material for another process!

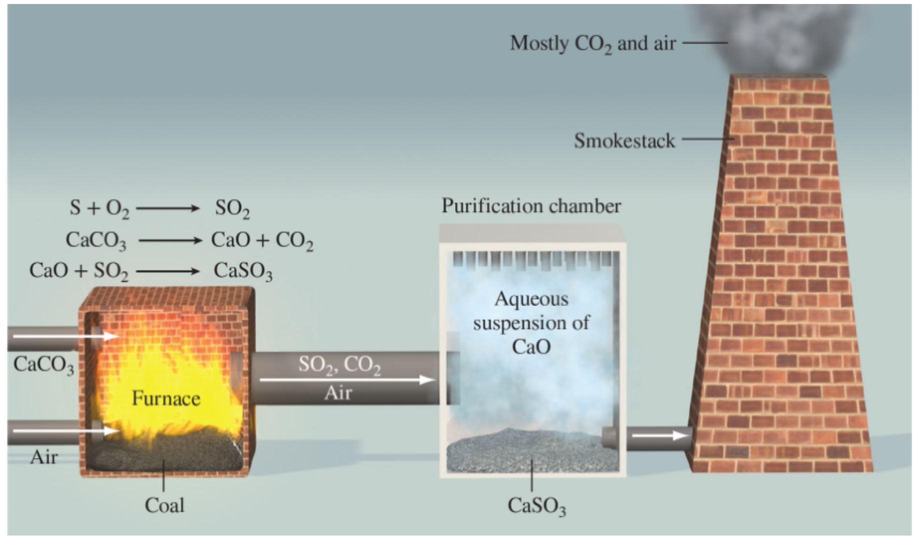

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Figure 21.24 Spreading calcium oxide (CaO) over acidified soil. This process is called liming.

Wayne Hutchinson/Alamy Stock Photo