A breath of fresh air

Clean air is a basic human need for a healthy life. Yet, advances in living standards (electricity on demand, automobiles, and consumer goods) contribute to air pollution in manufacturing, energy production, and the use of products. As scientists began to understand the connections between air pollution and industrialization, engineers developed technologies to minimize the damage. Molybdenum plays a central role in many of them.

Greenhouse gas emissions produced by burning fossil fuels such as coal and oil are today's most pressing air-quality problem. They drive global warming and climate change. However, there still are other serious air pollution challenges, such as acid rain, smog and particulates.

Acid rain

Readers of a certain age will remember when the impact of acid rain first became obvious in the late 1970s. The phrase "acid rain" was seared into the public consciousness by images of bare trees and dying lakes. Large areas of forests were affected, as once-healthy trees became weak and diseased. Acid rain destroys the protective coating on leaves and needles, reducing their ability to support the photosynthesis that trees and plants need to thrive. As the damage progresses, they become more susceptible to cold temperatures, insects and disease. Lakes and streams ironically turned crystal clear but, due to increased acidity of the water, fish populations and plant life suffered. The local ecosystem began to feel the effects as fish were taken out of the food chain and birds and other animals struggled to survive.

Acid rain also damages older buildings by slowly dissolving limestone and marble, speeding up natural erosion and causing the exposed stone to crumble away (see article on Cologne Cathedral in this issue). Indeed, Robert Angus Smith, the UK scientist credited with the first use of the term "acid rain" in the eighteenth century, noticed that stone buildings crumbled more readily in larger towns and cities where more coal was burned.

However, acid rain's effect was more widely felt as industrialization and the need for electric power progressed. It soon became apparent that fossil fuels, which often contain large amounts of sulfur, were at the root of the problem. Scientists have found that fossil-fuel fired power plants are the largest contributors to acid rain. When burned, fossil fuels release sulfur dioxide and various nitrogen oxide gases (NOx) that react with tiny droplets of water in the clouds to form sulfuric and nitric acids. On the pH scale which runs from zero (strongly acidic) to 14 (strongly alkaline), rain naturally has a value between five and six, whereas acidic rain has a pH value of around four. Because the pH scale is logarithmic, rain with a pH of four is ten times as acidic as rain with a pH of five, and 100 times as acidic as rain with a pH of six.

Smog and particulates

Even before acid rain became an issue, fossil fuels were well known for creating pollution problems. Heavy coal use to heat buildings resulted in the "pea-soup" fogs of Victorian London. This combination of smoke and fog became known as "smog," and it continues to exist in cities around the world today. Unlike Victorian smog, contemporary smog is mostly caused by automotive emissions, though the burning of coal, land and forest fires, and industrial activity can also be contributing factors where regulations are less stringent.

Smog brings with it significant health concerns. The ground-level ozone, sulfur dioxide, nitrogen oxides, and carbon monoxide contained in smog are most harmful to children, senior citizens, and anyone whose health is compromised by bronchitis, emphysema, or asthma. Premature deaths due to cancer and respiratory disease, and increased rates of birth defects and low birth weight have also been correlated with smog exposure.

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Acid rain caused by sulfurous fossil fuel emissions can wreak havoc on the natural environment, as evidenced by dead and dying forests and lakes. © istockphoto/ThomasTakacs

Smog is a serious problem in cities that strongly depend on automobiles. Los Angeles, located in a topographical basin that traps emissions, is a classic example. © istockphoto/Daniel Stein

Smog forms when gaseous emissions react under the influence of sunlight and heat with ammonia, moisture, and other compounds in the air to form the well-known brown haze. Particulates in vehicle exhaust emissions are also regarded as a health hazard. In fact, the European Union has classified particulate emissions from diesel engines as carcinogenic. The rapidly developing concerns regarding smog and particulate emissions in the 1960s spurred a drive to drastically reduce vehicle emissions even before acid rain emerged as a concern.

Molybdenum, a catalyst for change

Acid rain: Attempts to remove sulfur from the exhaust gases of power stations began in the nineteenth century. But flue gas desulfurization (FGD) units known as scrubbers did not become widespread until the 1980s and 90s. The most widely used FGD system for coal-fired power plants is the wet limestone-gypsum process in which sulfur dioxide and other acidic flue gases are neutralized by calcium carbonate. Scrubbers are very large vessels in which exhaust gases pass upwards through a spray containing the limestone slurry. Scrubber internals must withstand a very corrosive environment, so material choice is an important part of the design process. Highly corrosion-resistant molybdenum-containing alloys are used in modern systems to ensure long service life and prevent frequent costly replacement. Thus, FGD units are built using either molybdenum-containing stainless steel, or carbon steel covered with a molybdenum-containing nickel-based alloy.

Smog and particulates: Today's automotive catalytic converters use precious metals to break down smog-causing compounds. However, the sulfur naturally contained in fuels poisons the catalyst material and renders it ineffective. This means that low-sulfur fuel had to be widely available before carmakers could routinely fit catalytic converters to vehicles. At about the same time, elimination of lead from vehicle fuels required that new processes to boost octane be developed. These processes also used catalysts that were poisoned by sulfur, so desulfurization of vehicle fuels became a critical first step in smog reduction.

Molybdenum plays a crucial role in the hydrodesulfurization process used to produce low-sulfur liquid fuels and natural gas. In this process, fuel vapor flows over catalyst beds composed of molybdenum disulfide and smaller amounts of cobalt, nickel or tungsten. The molybdenum disulfide catalyst promotes a chemical reaction between free hydrogen and sulfur that removes sulfur from the fuel as hydrogen sulfide gas. Hydrogen sulfide is then converted to elemental sulfur, most of which is used to produce sulfuric acid. Today, more sulfur is produced worldwide from hydrodesulfurization than is mined.

Diesel engines present a more complex problem than gasoline engines because they emit a larger variety of pollutants that include many solid particles of soot. ›

Low-sulfur fuels, catalytic convertors, and diesel particulate filters have contributed to dramatic reductions in smog in cities around the world. Toronto is one city that has benefited greatly from these innovations. © istockphoto/slobo

Molybdenum-containing catalysts dramatically reduce the sulfur content of oil-based fuels. © Haldor Topsøe

Sulfur's detrimental role in diesel fuel is similar to its role in gasoline: it poisons the oxidation catalysts that improve particulate filters by removing gaseous emissions and "burning" fine soot particles that pass through the filters. Low-sulfur diesel fuel therefore makes the technology of converting pollution-causing constituents to harmless gases possible.

One hundred times cleaner

Even though smog was understood to play a role in health and environmental problems, the dual challenge of needing to reduce smog through the introduction of catalytic converters, but needing low-sulfur fuels to accomplish the goal, was difficult to solve. In the 1970s and 80s, parts of the U.S. legislated the use of reduced-sulfur fuels, spurring development of fuel desulfurization technology. In 1993 the European Commission, in order to improve urban air quality across Europe, required all gasoline and diesel fuel to meet new, cleaner specifications. To gradually reduce the sulfur content of fuels, the EU eventually mandated production of ultra-low sulfur (less than 10 ppm S) gasoline and diesel fuel by 2009.

A lifecycle assessment study analyzing ultra-low sulfur diesel (ULSD) compared the total lifetime environmental impact of a switch from the 2000-ppm diesel fuel of 1993 to today's 10-ppm ULSD in the EU. The study considered a number of environmental metrics relevant to vehicle use and performance. It calculated the following reductions for the use of ULSD:

- Acidification potential nearly 25% lower.
- Breathable particulates and other inorganic compounds down by 44%.
- Nearly 5% lower potential for smog creation.

In the European continent as a whole, the use of ULSD reduces annual sulfur dioxide emissions by more than three-quarters of a million tonnes (based on diesel consumption in road vehicles in 2011). Furthermore, sulfur dioxide emissions from diesel vehicles are now less than 1% of their 1993 values, despite a doubling of diesel fuel demand in the last 20 years.

In summary

Challenges to our natural world will no doubt continue to increase in line with our living standards and expectations, but the effective elimination of acid rain as an environmental issue and the drastic reduction in automotive emissions in the developed world show that it is not necessary to sacrifice one for the other. Molybdenum has contributed significantly to cleaner air. It has provided highly-corrosion resistant materials for power station FGD equipment. It is also a crucial catalyst used to remove sulfur from liquid and gaseous fuel, a process that enabled the mass introduction of automotive catalytic converters. These accomplishments demonstrate the power of innovation in solving some of the world's biggest problems, and molybdenum's remarkable contribution to those solutions. (Alan Hughes)