Chapter 14

ENVIRONMENTAL POLLUTION CONTROL

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1. WHY CONTROL POLLUTION?

The best-selling book, *Technology of Environmental Pollution Control* by Esber I. Shaheen,[1] serves as the primary technical reference for this chapter.

While addressing the question *What Is Life?* Margulis and Sagan[2] remind us that "every species of organism produces wastes that are incompatible with its own existence." As humans living on an ever-more-crowded planet, our main reason for abating pollution is self-preservation. Observing nature tells that that some day, if we don't control it, our own waste will kill us.

2. POLLUTION FROM PETROLEUM PROCESSING

This section describes the predominant gaseous, liquid and solid pollutants generated by the petroleum industry. It also explains why these pollutants can be harmful. Section 5 of this chapter describes selected pollution-control regulations, and Section 6 discusses technology for abating these pollutants.

2.1 Particulate Matter

The main sources of air pollution from petroleum refineries are listed in *Table 1*. Refineries can be significant sources of particulate matter (PM), which can irritate the respiratory tract. PM is especially harmful when it is associated with sulfur and nitrogen oxides (SOx and NOx).

Table 1. Main Sources of Refinery Air Pollution

Source	PM	SO_2	CO	VOC	NOx
Fluid catalytic cracking (FCC) units	x	x	x	x	x
Coking units	x	x	x	x	x
Compressor engines		x	x	x	x
Vapor recovery and flare systems		x	x	x	x
Vacuum distillation unit and condensers				x	
Sulfur recovery units		x	x		x
Waste water treatment plants				x	
Boilers and process heaters		x	x		x
Storage tanks				x	

PM = particulate matter
SO_2 = sulfur dioxide
CO = carbon monoxide
VOC = volatile organic compounds
NOx = nitric oxide (NO) and nitrogen dioxide (NO_2)

Most refinery PM comes from two sources – delayed coking units and the regenerators of fluid catalytic cracking (FCC) units. FCC regenerators also emit ammonia, which combines with SOx and NOx in the air to form ammonium sulfates and nitrates. According to the South Coast Air Quality Management District (AQMD)[3] in Southern California, 1 ton of ammonia can generate 6 tons of PM10 – airborne particulates with particle diameters less than 10 microns. PM2.5 stands for airborne particulates with diameters less than 2.5 microns.

2.2 Carbon Monoxide

In refineries, carbon monoxide (CO) is formed by incomplete combustion in boilers, process heaters, power plants, and FCC regenerators. CO is toxic because it binds strongly to the hemoglobin in blood, displacing oxygen. It is colorless and odorless, so without a special analyzer, it is hard to detect. This adds to its danger.

2.3 Sulfur Oxides

At oil and gas production sites, sulfur dioxide (SO_2) and sulfur trioxide (SO_3) are produced by the burning of sulfur-containing fuels. In oil refineries, SOx are produced by the combustion of sulfur-containing fuels, including the coke that is burned off of catalysts in FCC regenerators. SOx irritate the respiratory tracts of people and other animals. When adsorbed to particulate matter, SOx are especially bad. While gaseous SOx molecules are trapped by mucous in the upper respiratory tract, inhaled particulates can penetrate deep into lungs.

In the atmosphere, SOx react with water vapor to make sulfurous and sulfuric acids. The acids return to earth as “acid rain,” which poisons trees and contaminates lakes and rivers. Experts estimate that SO_2 can remain in the air for 2 to 4 days. During that time, it can travel 600 miles (1,000 km) before returning to the ground. Consequently, SO_2 emissions have caused a number of international disputes. Acid rain from neighboring countries in Eastern Europe may have caused the death of about ⅓ of Germany's forests. In the past, the United States and Canada argued bitterly about the cross-border impact of SOx emissions from U.S. power plants. Fortunately, since 1983, the passage and enforcement of clean-air legislation has reduced the problem dramatically.

2.4 Nitrogen Oxides, VOC, and Ozone

Like CO and SOx, nitric oxide (NO) and nitrogen dioxide (NO_2) are emitted by fired heaters, power plants and FCC regenerators. NOx also damage respiratory tissues and contribute to acid rain.

Ozone, a nasty component of smog, is generated by reactions between oxygen and NOx. The reactions are triggered by sunlight. In the troposphere, ozone reacts with volatile organic hydrocarbons (VOC) to form aldehydes, peroxyacetyl nitrate (PAN), peroxybenzoyl nitrate (PBN) and a number of other substances. PAN irritates nasal passages, mucous membranes, and lung tissue. Collectively, these compounds are called "photochemical smog." They are toxic to humans, animals and plants, and they accelerate the degradation of rubber and other materials. In some areas, smog looks like a brownish cloud just above the horizon. It makes for spectacular sunsets, but nothing else about it is good.

In the United States, areas with the worst air are Los Angeles, Houston, Eastern Connecticut, and New York. In recent years, due to better air in Los Angeles and worse air in Houston (caused in part by accidental releases from chemical plants along the Ship Channel), Houston led the United States in 1st-stage smog alerts.

Standards for selected pollutants in the air over Los Angeles are given in *Table 2*.

Table 2. Standards for Selected Pollutants in the Air over Los Angeles

	Maximum Allowable Concentration, ppm		
Pollutant	Warning	Alert	Danger
Carbon monoxide	100	200	300
Nitrogen oxides	3	5	10
Sulfur dioxide	3	5	10
Ozone	0.5	1.0	1.5

2.5 Chemicals that React with Stratospheric Ozone[4]

The previous section mentions the harmful effects of ground-level ozone. The stratosphere, located about 6 to 30 miles (10 to 50 km) above the ground, contains a layer of ozone that is beneficial, because it protects organisms from harmful ultraviolet-B (UV-B) solar radiation.

Over the past 3 decades, scientists have concluded that this protective shield has been damaged. Each year, an "ozone hole" forms over Antarctica. Ozone levels there can fall to 60% below normal. Even over the United States, stratospheric ozone levels are about 3% below normal in summer and 5% below normal in winter.

In the 1970s, scientists linked several man-made substances to ozone depletion, including carbon tetrachloride (CCl_4), chlorofluorocarbons (CFCs), halons, methyl bromide, and methyl chloroform. These chemicals leak from air conditioners, refrigerators, insulating foam, and some industrial processes. Winds carry them through the lower atmosphere into the stratosphere, where they react with strong solar radiation to release chlorine and bromine atoms. These atoms initiate chain reactions that consume ozone. Scientists estimate that a single chlorine atom can destroy 100,000 ozone molecules.

The 1998 and 2002 Scientific Assessments of Stratospheric Ozone firmly established the link between decreased ozone and increased UV-B radiation. In humans, UV-B is linked to skin cancer. It also contributes to cataracts and suppression of the immune system. The effects of UV-B on plant and aquatic ecosystems are not well understood. However, the growth of certain plants can be slowed by excessive UV-B. Some scientists suggest that marine phytoplankton, which are the foundation of the ocean food chain, are already under stress from UV-B. If true, this could adversely affect supplies of food from the oceans.

In 1987, 27 countries signed the Montreal Protocol, which recognized the international consequences of ozone depletion and committed the signators to limit production of ozone-depleting substances. Today, more than 180 nations have signed the Protocol, which now calls for the elimination of ozone-depleting chemicals.

In the United States, production of halons ended in January 1994. In January 1996, production virtually ceased for several other ozone-depleting chemicals, including CFCs, CCl_4, and methyl chloroform. New products less damaging to the ozone layer have gained popularity. For example, computer makers now use ozone-safe solvents to clean circuit boards, and automobile manufacturers use HFC-134a, an ozone-safe refrigerant, for air conditioners in new vehicles.

Studies indicate that the Montreal Protocol has been effective to date. The 2002 Scientific Assessment of Ozone Depletion shows that the rate of ozone depletion is slowing. Stratospheric concentrations of methyl chloroform are falling, indicating that emissions have been reduced. Concentrations of other ozone-depleting substances, such as CFCs, are also decreasing. It takes years for these substances to reach the stratosphere and release chlorine and bromine atoms. For this reason, stratospheric chlorine levels are still near their peak, but they are expected to decline slowly in years to come. If all parties to the Montreal Protocol abide by their commitments, the ozone layer may fully recovery during the second half of this century.

2.6 Greenhouse Gases[5,6]

In a greenhouse or in an automobile with the windows rolled up, sunlight comes in through the glass and gets absorbed by various objects inside. These objects reradiate the adsorbed energy as heat, which can't go back out through the glass, at least not very quickly. Consequently, on a sunny day the inside of a greenhouse and inside of a sealed car is hotter than the outside air.

In the earth's atmosphere, gases such as CO_2, CH_4, and N_2O are called "greenhouse gases," because they are nearly transparent to visible sunlight, but they absorb infrared (IR) radiation. In essence, they warm the atmosphere by slowing the release of heat into space. (The analogy with a real greenhouse isn't perfect, but it comes close.)

On average, every person in the world is responsible for just over a ton of CO_2 emissions each year. Most of this is due to the burning of fossil fuels in power plants and vehicles. According to some estimates, to prevent dangerous climate change while allowing for some increase in population, that number must be reduced to about 0.3 tons per person per year.

2.6.1 Global CO_2 and Temperature Balances

We are lucky to live on a planet that has a stable balance between *heat sources* (sunlight, volcanoes, forest fires, power plants, animal metabolism, natural radioactive decay, etc.) and *heat sinks* (consumption of sunlight by plants, radiation of heat into space, etc.). We also are lucky that our oceans and ice caps do such an excellent job of regulating temperature. In the past, when the amount of heat from sources exceeded the heat consumed by sinks, the ice caps shrank and sea level rose, but the average global temperature changed just a little – less than a few degrees. When heat sinks exceeded heat sources (for example, after a meteor strike or a major volcanic explosion hurled dust into the atmosphere, reducing incident sunlight for several months or even years), the ice caps grew and sea level fell, but again the average global temperature stayed nearly the same.

The oceans also serve as a buffer for carbon dioxide. On average, the oceans hold 60 times more CO_2 than the atmosphere. When dissolved in water, CO_2 forms carbonic acid (H_2CO_3), bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}). Sea water is slightly alkaline, with a surface pH of 8.2, so it readily reacts with H_2CO_3. However, rapid exchange with the atmosphere only occurs in the upper wind-mixed layer, which is about 300 feet (100 meters) thick. This layer contains roughly one atmosphere equivalent of CO_2.

CO_2 in its various forms is removed from the sea by foraminifera, coral reefs, and other marine organisms, which produce solid calcium carbonate, the main component of sea shells. About 30 to 50% of the CO_2 released into the air stays there. The rest goes into the hydrosphere and biosphere.

Table 3 provides estimates of the global carbon distribution.[7]

Table 3. Global Distribution of Carbon

Source	Moles of Carbon x 10^{18}	Relative to the Atmosphere
Sediments		
Carbonates	1530	28,500
Organic carbon	572	10,600
Land		
Organic carbon	0.065	1.22
Oceans		
CO_2 and H_2CO_3	0.018	0.3
HCO_3^-	2.6	48.7
CO_3^{2-}	0.33	6.0
Dead organic	0.23	4.4
Living organic	0.0007	0.01
Atmosphere		
CO_2	0.0535	1.0

2.6.2 Global Warming

The global greenhouse effect – also called global warming – concerns us now because atmospheric CO_2 concentrations are increasing faster than ever, and because most of the increase is due to industrial growth. Many scientists predict that unless we do something to impede global warming, it may:

- Increase the number and intensity of dangerous heat waves
- Increase severe storm activity
- Damage certain crops
- Raise the average sea level

These in turn will increase weather-related deaths, damage coastal cities and towns, and ruin coastal ecosystems.

It is still hard to find a consensus on global warming. Different experts use different models and even different data sets.[6] Some believe global warming is imminent and predict that it will cause catastrophic damage. Others are far less concerned. Until the science is more definitive, the global-warming debate will continue to be governed by Robinson's Rule of Expert Testimony:

"For any given PhD, there is an equal and opposite PhD."

2.7 Waste Water

Refineries generate contaminated process water, oily runoff, and sewage. Water is used by just about every process unit, especially those that require wash water, condensate, stripping water, caustic, or neutralization acids. Contaminated process water may contain suspended solids, dissolved salts, phenols, ammonia, sulfides, and other compounds. As much as possible, waste-water steams are purified and re-used. Present requirements ensure that the water going out of a refinery is at least as clean as the water coming in. Additional details are provided in Section 6.

2.8 Solid Waste

Solid wastes from petroleum processing may include the following:

- Cuttings from the drilling of oil wells
- Used drilling mud
- Spent catalyst and catalyst fines
- Acid sludge from alkylation units
- Sludge from the bottom of storage tanks
- Miscellaneous oil-contaminated solids

Wastes that cannot be recycled are cleaned on site, sent to land fills, or transported to reclamation facilities. Some of the technology used for cleanup and reclamation is discussed in Section 6.

2.9 Oil Spills

Large spills of oil from tankers are not very uncommon, but they can cause tremendous damage to the environment. Small spills come from leaks in tanks or mishaps during the loading or unloading of trucks, ships, or rail cars. Spills are discussed in more detail in Sections 3, 4, and 6.

3. ENVIRONMENTAL INCIDENTS

Pollution-causing incidents can be divided into four major categories:

1. Usual-practice pollution. In this case, we know that we are discharging waste into the environment. We know the associated risk, but we conclude that the cost of decreasing the discharge is too high. To different groups, "risk" and "cost" can mean entirely different things. Usually, nothing changes until some government body decides to force a change.

2. Accidental pollution. This category includes industrial accidents, some of which are described below. Post-disaster investigations often show that the accidents were preventable. In many cases, an entire industry learns from the accident and implements safeguards to prevent a recurrence.

3. Inappropriate response to pollution. As shown in the examples below, many industrial accidents would have been far less harmful if the people involved had responded in a more appropriate way. Inappropriate responses reflect lack of preparation, both mental and physical. Studies conclude that careful emergency planning coupled with thorough employee training (and re-training) prevents accidents and leads to faster, better responses to accidents.

4. Malicious acts. These include illegal "midnight dumping," cover-ups, sabotage, and acts of war.

The examples described below cover all four categories. In every case, the damage was mitigated by the heroic efforts of doctors, nurses, firemen, and/or cleanup crews. These people put themselves at risk to save the lives of others. When we give statistics for lost lives, we don't enumerate all the lives saved by these heroes, not because we don't want to, but because we can't find the numbers.

3.1 London Fog (1952)

In December 1952, thick fog rolled across many parts of the British Isles. In the Thames Valley, the fog mixed with smoke, soot and sulfur dioxide from coal-burning homes and factories, turning the air over London into a dense yellow mass. Due to a temperature inversion, the fog stayed put for several days, during which the city's hospitals filled to over-flowing. According to the Parliamentary Office of Science and Technology,[8] more than 4,000 people died that month because of the polluted air. Similar, less-severe episodes occurred in 1956, 1957, and 1962. The 1956 event killed more than 1,000 people.

London's deadly smog was caused by "usual-practice" pollution. Due to the widespread use of cheap, high-sulfur coal, the air in London had been bad for decades, but post-war growth made it worse than ever. In response to the incidents, Parliament passed Clean Air Acts in 1956 and 1962, prohibiting the use of high-sulfur fuels in critical areas.

3.2 Amoco Cadiz (1978)[9]

On March 16, 1978, the supertanker *Amoco Cadiz* was three miles off the coast of Brittany when its steering mechanism failed. The ship ran aground on the Portsall Rocks.

For two weeks, severe weather restricted cleanup efforts. The wreck broke up completely before any of the remaining oil could be pumped out, so the entire cargo – more than 1.6 million barrels of Arabian and Iranian crude oil – spilled into the sea.

The resulting slick was 18 miles wide and 80 miles long. It polluted 200 miles of coastline, including the beaches of 76 Breton communities. On several beaches, oil penetrated the sand to a depth of 20 inches. Piers and slips in small harbors were covered with oil. Other polluted areas included the pink granite rock beaches of Tregastel and Perros-Guirrec, and the popular bathing beaches at Plougasnou. The oil persisted for only a few weeks along exposed rocky shores, but in the areas protected from wave action, the oil remained as an asphalt crust for several years.

At the time, the *Amoco Cadiz* incident caused more loss of marine life than any other oil spill. Cleanup activities on rocky shores, such as pressure-washing, also caused harm. Two weeks after the accident, millions of dead mollusks, sea urchins, and other bottom-dwelling organisms washed ashore. Nearly 20,000 dead birds were recovered. About 9,000 tons of oysters died. Fish developed skin ulcerations and tumors.

Years later, echinoderms and small crustaceans had disappeared from many areas, but other species had recovered. Even today, evidence of oiled beach sediments can be seen in sheltered areas, and layers of sub-surface oil remain under many impacted beaches.

3.3 Bhopal, India (1984)

On December 2, 1984, a worker observed a build-up of pressure in a storage tank at the Union Carbide chemical plant near Bhopal, India. The tank contained about 15 tons of methylisocyanate (MIC), a chemical used to make pesticides. It is flammable, and at high concentrations it is deadly. At low concentrations, it causes lung damage and blindness.

The pressure increase probably was caused by water inside the tank. Water reacts with MIC to form methylamine and gaseous carbon monoxide. The reaction releases heat, which would have contributed to the pressure rise by vaporizing some MIC. Normally, a refrigeration unit would have controlled the temperature, but that unit had been out of service for several months. Eventually, the pressure rise opened a safety valve. When this happened, the vented gas should have been routed to a caustic scrubber, which would have absorbed and hydrolyzed the MIC, rendering it harmless. Instead, the vented gas went to the flare. The flare should have converted the MIC into relatively harmless CO_2, H_2O and N_2. But the flare system failed, perhaps because it wasn't designed to handle such a large surge of gas. Consequently, tons of MIC poured into the air and spread across the countryside, covering 25 square miles (65 square kilometers). If operators had noticed the leak immediately, they might have been able to stop it before it did much damage. But leak did not show up on their monitors because a critical panel had been removed from the control room.

How did water get into the tank? The MIC was stored under a blanket of dry nitrogen. Some experts suggest that the nitrogen was wet. Others guess that a water hose was inadvertently connected to the nitrogen line. A Union Carbide official suggested possible sabotage.

Even if the incident on December 2, 1984 was an accident, the MIC unit at Bhopal was a disaster waiting to happen. During a press conference, a Union Carbide executive acknowledged that the unit was in a state of sorry disrepair, and that its condition was so poor that it shouldn't have been running.

Up to 200,000 people were exposed to MIC in Bhopal and surrounding towns. More than 2,500 died. Thousands more suffered permanent lung and/or eye damage. All told, there were 524,000 personal injury claims, 2,800 lost-cattle claims, 4,600 business claims, and 3,400 wrongful death claims.

Eventually, Union Carbide reached a US$470 million settlement with the Parliament of India.

3.4 Chernobyl (1986)

SCRAM stands for "safety critical reactor ax man." It is a term from the early days of nuclear power development, when control rods were raised and lowered into the reactor core with a rope on a pulley. The ax man stood ready to cut the rope in an emergency, dropping all control rods all way down, shutting down the reactor.

After a SCRAM at the Chernobyl nuclear power plant near Pripyat, Ukraine, the cooling water pumps would stop due to lost electrical power. Emergency power was supplied by diesel generators, but starting the diesels took almost a minute. During the delay, residual heat remained in the reactor until the cooling pumps were running again.

To Deputy Chief Engineer Anatolij Diatlov, this delay was unacceptable. He thought of a solution. Right after a SCRAM, he knew, the plant's power turbines kept spinning for several minutes due to their massive inertia. Diatlov calculated that, as the turbines slowed down, they could produce enough power to run the water pumps until the diesels were up and running. He designed a complex network of switches to keep the current steady as the turbines lost momentum.

Diatlov talked to the chief engineer of the plant, who gave him permission to run his "electrical engineering" experiment. The test began on April 25, 1986, as Unit 4 was shutting down for long-delayed maintenance. With Diatlov's approval, the operators decided to run the test manually instead of using the unit's "unimaginative automatics."

At 2:00 PM, in violation of safety regulations, the operators switched off the emergency cooling system. Just after midnight on April 26th, they violated another rule by switching off the reactor's power-density controls.

Under manual operation, the reactor became unstable. At 1:07 AM, the power output suddenly dropped to 0.03 gigawatts (GW), far less than the specified minimum of 0.70 GW. To generate more power, the operators raised the control rods to the maximum height allowed by regulations. Diatlov ordered them to raise the rods further. When the operators balked, Diatlov insisted, and the operators complied.

At 1:23 AM, the power output seemed to be stable at 0.2 GW. The operators violated yet another regulation by disabling the emergency SCRAM, an automatic interlock designed to stop the reactor whenever the neutron flux exceeds a safe limit. (In modern nuclear power plants, it is physically impossible to disable this control.)

Now the experiment could begin. To see how long the turbine would spin without a supply of steam, they closed the valve that channelled steam from the reactor to the turbine. Steam that should have been taking heat out of the reactor was now trapped inside.

In less than 45 seconds, the reactor started to melt. Super-hot pellets of uranium-oxide fuel ruptured their zirconium-alloy containers, coming into direct contact with cooling water. The water flashed into steam, causing the first of two explosions that blew the top off the reactor. The second blast was caused by a H_2-CO-air explosion. The H_2 and CO were generated by reactions of zirconium and carbon with super-heated steam:

$$Zr + 2\,H_2O \rightarrow ZrO_2 + 2\,H_2$$
$$C + H_2O \rightarrow CO + H_2$$

About 15 tons of radioactive material from the reactor core was blown into the atmosphere, where it spread across Europe. More than 36 hours after the accident, plant personnel told local officials about the accident. About 14 hours after that – 50 hours after the accident – radiation from the explosion was detected by technicians at the Forsmark nuclear power plant in Sweden. That radiation was the first notification to the world outside the Soviet Union that something had happened in Pripyat.

At the site, more than 30 fires broke out, including an intensely hot graphite fire that burned until May 9. About 250 people fought the various fires. During 1800 helicopter sorties, pilots dropped 5000 tons of lead, clay, dolomite and boron onto the reactor. Near term, the explosion and high-level radiation killed 31 people, including operators, fire-fighters, and helicopter pilots. Thousands more died later.

In June 1987, 14 months after the disaster, some 27 villages within the restricted zone were still heavily contaminated, because the cleanup operation had stopped. Nearby cities and towns were reporting dramatic rises in thyroid diseases, anemia, and cancer. Hardest hit were children. Frequently, calves were born without heads, eyes, or limbs. The three remaining nuclear reactors were still running, and two new reactors were under construction. Despite ambient radiation levels 9 times higher than widely accepted limits, workers at the power-plant were living in newly built colonies inside the "dead zone."

During a trail that ended in August 1987, the Chernobyl plant director (Brukhanov) was convicted and sentenced to 10 years in a labor camp. The chief engineer (Fomin), and Diatlov received shorter sentences. The two operators were acquitted, but both of them died soon afterwards from radiation poisoning. More than 60 other workers were fired or demoted.

In 1991, Unit 2 was damaged beyond repair by a fire in the turbine room. That left Units 1 and 3, which kept running for the next nine years.

According to government figures, more than 4,000 Ukrainians who took part in the clean-up had died, and 70,000 were disabled by radiation. About 3.4 million of Ukraine's 50 million people, including some 1.26 million children, were affected by Chernobyl.[10] According to Gernadij Grushevoi, cofounder of the Foundation for he Children of Chernobyl, the long-term danger is even worse in Belorussia. In 1992, in testimony at the World Uranium Hearing,[11] he said, "… 70 percent of the radioactive stuff thrown up by the explosion at Chernobyl landed on White Russian territory. There is not a centimeter of White Russia where radioactive cesium cannot be found."

On December 14, 2000, the plant was shut down. The shut-down was expedited by the European Commission, which approved a US$585 million loan to help Ukraine build two new reactors, and by the European Bank for Reconstruction and Development, which provided US$215 million.

3.5 The Rhine (1986)[12]

On November 1, 1986, a fire broke out in a riverside warehouse at the Sandoz chemical plant in Schweizerhalle, Switzerland. While extinguishing the flames, firemen sprayed water over exploding drums of chemicals, washing as much as 30 tonnes of pesticides, chemical dyes and fungicides into the Rhine River. Up to 100 miles (160 km) downstream, the river was sterilized. All told, more than 500,000 eels and fish were killed. More than 50 million people in France, Germany, and The Netherlands suffered through drinking water alerts.

Afterwards, while checking the Rhine for chemicals as it rolled through Germany, officials discovered high levels of a herbicide (Atrazine) that wasn't on the list provided by Sandoz. Eventually, Ciba-Geigy admitted that it had spilled Atrazine into the river just a day before the Sandoz fire. As monitoring continued, more chemicals were discovered alerting German authorities to the fact that many different companies were discharging dangerous chemicals. BASF admitted to spilling more than a tonne of herbicide, Hoechst discovered a chlorobenzene leak, and Lonza confessed to "losing" 2,000 gallons (4,500 liters) of chemicals.

In response to the Sandoz disaster, companies all along the Rhine joined the Rhine Action Program for Ecological Rehabilitation, agreeing to cut the discharge of hazardous pollutants in half by 1995. Although many experts thought the target could never be reached, samples showed that from 1985 to 1992, mercury in the river at the German town of Bimmen-Lobith, near the Dutch border, fell from 6.0 to 3.2 tonnes, cadmium from 9.0 to 5.9 tonnes, zinc from 3,600 to 1,900 tonnes, and polychlorinated biphenyls (PCBs) from 390 to 90 kilograms.

The payoff for this program came in December 1990, when for the first time in 30 years a large Atlantic salmon was fished from the Sieg, a tributary of the Rhine in West-Central Germany. The catch proved what officials had hoped: If you clean the water and clear the way, someday the fish will come back. The event gave new life to the Salmon 2000 project, and further success followed. In 1994, researchers found recently hatched salmon in the Sieg, and 1996 a salmon was hooked near Baden-Baden. In 1998, encouraged by the success of the Rhine Action Program, targets were set to designate a large protected ecosystem from the mouth of the Rhine in The Netherlands to streams in the Jura Mountains, the Alps, the Rhine mountains, the Rhineland-Palatinate, the Black Forest, and the Vosges.

Meanwhile, not all of the Rhine's pollution problems have been solved. One of the most serious is a huge basin in the Netherlands, into which toxin-laden mud dredged from the Port of Rotterdam has been dumped since the 1970s. Contamination levels are falling, but several toxins are very stubborn.

All along the Rhine, the main source of remaining pollution comes from farm fertilizers, which seep into the river every time it rains.

3.6 Prince William Sound, Alaska (1989)

On March 23, 1989, the 987-foot supertanker Exxon *Valdez* left port carrying more than 1.2 million barrels of North Slope crude. The ship was headed south toward refineries in Benicia and Long Beach, California. At 10:53 PM, it cleared the Valdez Narrows and headed for Prince William Sound in the Gulf of Alaska. To avoid some small icebergs, Captain Joseph Hazelwood asked for and received permission to move to the northbound shipping lane. At 11:50 PM, just before retiring to his cabin, the captain gave control of the ship to the third mate, Gregory Cousins, instructing him to steer the vessel back into the southbound lane after it passed Busby Island.

Cousins did tell the helmsman to steer to the right, but the vessel didn't turn sharply enough. At 12:04 AM, it ran aground on Bligh Reef. It still isn't known whether Cousins gave the order too late, whether the helmsman didn't follow instructions properly, or if something went wrong with the steering system.

Captain Hazelwood returned to the bridge, where he struggled to hold the tanker against the rocks. This slowed the rate of oil leakage. He contacted the Coast Guard and the Alyeska Pipeline Service Company. The latter dispatched containment and skimming equipment. According to the official emergency plan, this equipment was supposed to arrive at a spill within 5 hours. In fact, it arrived in 13 hours – eight hours late.

The Exxon *Baton Rouge* was sent to off-load the un-spilled cargo and to stabilize the *Valdez* by pumping sea water into its ballast tanks. The oil transfer took several days. By the time it was finished, more than 250,000 barrels of oil had spilled into the Sound. Eventually, 33,000 birds and 1,000 otters died because of the spill.

Captain Hazelwood was tried and convicted of illegally discharging oil, fined US$50,000, and sentenced to 1000 hours of community service. Exxon spent US$2.2 billion to clean up the spill, continuing the effort until 1992 when both the State of Alaska and the U.S. Coast Guard declared the cleanup complete. The company also paid about US$1 billion for settlements and compensation.

Eleven thousand workers treated 1,200 miles (1,900 kilometers) of shoreline around Prince William Sound and the Gulf of Alaska, using 82 aircraft, 1,400 vessels, and 80 miles (128 kilometers) of oil-containing booms.

In response to the disaster, the U.S. Congress passed the Oil Pollution Act of 1990. The Act streamlined and strengthened the ability of the U.S. Environmental Protection Agency (EPA) to prevent and react to catastrophic oil spills. A trust fund, financed by a tax on oil, was established to pay for cleaning up spills when the responsible party cannot afford to do so. The Act requires oil storage facilities and vessels to submit plans to the Federal government, telling how they intend to respond to large oil discharges. EPA published regulations for above-ground storage facilities, and the U.S. Coast Guard published regulations for oil tankers. The Act also requires the development of area contingency plans to prepare for oil spills on a regional scale.

The efforts seem to be working. On July 10, 2004, *USA Today* reported:[13] "Not one drop of crude oil spilled into Prince William Sound from oil tankers in 2003 – the first spill-free year since the ships started carrying crude from the trans-Alaska pipeline terminal in 1977."

3.7 Kuwait (1991)

On January 25-27, 1991, during Iraqi's occupation of Kuwait, pumping stations at Mina Al-Ahmadi sent 4 to 6 million barrels of oil – 16 to 25 times more than the amount spilled by the Exxon *Valdez* – into the Arabian Gulf. On January 27, allied bombers stopped the spill by destroying the pumping stations.

Ad Daffi Bay and Abu Ali Island experienced the greatest pollution. The spill damaged sensitive mangrove swamps and shrimp grounds. Marine birds, such as cormorants, grebes, and auks, were killed when their plumage was coated with oil. The beaches around the shoreline were covered with oil and tar balls.

Despite the ongoing war, the clean-up of the oil spill proceeded rapidly. Kuwaiti crude is rich in light ends, and water in the Arabian Gulf water is relatively warm. For these reasons, about half of the spilled oil evaporated, Kuwaiti crude simply evaporated, leaving behind a thick emulsion which eventually solidified and sank to the bottom of the sea. Another 1.5 million barrels were recovered by skimming. Operators of sea-water cooled factories and desalination plants were concerned that the oil might foul their intake systems. To prevent this, protective booms that extended three feet (1 meter) below the surface were installed around intakes in Bahrain, Iran, Qatar, Saudi Arabia, and the United Arab Emirates.

On February 23-27, 1991, retreating Iraqi soldiers damaged three large refineries and blew up 732 Kuwaiti oil wells, starting fires on 650 of them. Up to 6 million barrels per day were lost between February 23 and November 8,

1991. Crews from 34 countries assembled to fight the oil-well fires. Initially, experts said the fires would rage for several years. But due to the development of innovative fire-fighting technology, the job took less than 8 months.

The oil-well fires burned more than 600 million barrels, enough to supply the United States for more than a month. The fire-fighting effort cost US$1.5 billion. Rebuilding Kuwait's refineries cost another US$5 billion. In all, Kuwait spent between US$30 and US$50 billion to recover from the Iraqi invasion.

3.8 Lessons Learned

Hopefully, we have learned from these terrible examples. Here are some suggested tenets:

Needs determine priorities. According Maslow's "Hierarchy of Needs," people must satisfy basic physiological needs before they can afford to focus on safety, love, self-esteem and self-actualization.[14]

Those of us lucky enough to live in wealthy countries are justly proud of our recent environmental progress, which qualifies as self-actualization. But in poorer countries, people are less inclined to care about long-term dangers of pollution. After the nuclear accident at Chernobyl, the power plant ran for 14 more years because the Soviet Union (and then Ukraine) needed electric power and decided that it was too expensive to build a new plant. After 1986, the old plant was staffed by workers who lived in towns where the ambient radiation exceeded the safety threshold by a factor of nine. Despite a second accident in 1991, and despite daily reminders of the dangers radiation, the workers stayed on because they needed jobs and couldn't find other work. Without incentives from the European Community, the Chernobyl nuclear power plant might still be running today.

Follow the rules. On their own or under duress, people ignore safety rules all the time, all over the world, not just in factories, but in homes and offices, on farms and highways. If we include exceeding the speed limit on public highways, it's safe to say that only a fraction of rule violations cause accidents. While the accidents can be tragic for the people who are involved, they seldom cause catastrophic damage to the environment.

When the consequences of an accident might be severe, adhering to safety rules is crucial. On the Exxon *Valdez*, Captain Hazelwood violated a U.S. Coast Guard guideline when he left the third mate in charge before the ship reached open water. At Chernobyl, Diatlov and his operators violated three major safety rules when they (a) shut off the emergency cooling water system, (b) raised the control rods too high, and (c) disabled the emergency SCRAM. Any one of the idled systems might have prevented the accident.

Encourage whistle-blowing. When told to raise the control rods too high, the Chernobyl operators hesitated, citing safety regulations. But when Diatlov insisted, the operators complied. Undoubtedly, the fear of losing their jobs outweighed their fear of breaking a rule. After all, they already had broken several rules, and nothing awful had happened.

Over the years, the U.S. Congress has passed at least seven laws to protect environmental whistle-blowers from retribution from their employers. Even so, according to Edmund Seebauer,[15] "Studies confirm the intuitive perception that whistleblowers tend to face hostility within their organizations and commonly leave their jobs, either voluntarily or otherwise. Lengthy and costly litigation often follows." Seebauer goes on to say: "Some employers are happy to hire workers who demonstrate such a strong commitment to high ethical standards. Nevertheless, there is no guarantee of employment, especially in a slow market. The whistleblower may lose seniority and retirement benefits, and must often move to another city. The needs of family members must be considered." When faced with these realities, insiders are reluctant to report environmental wrong-doing.

Smart companies encourage whistle-blowing. They send employees to courses that teach them about safety and environmental protection. They establish internal whistleblower hot lines and encourage employees to use them when they think their concerns haven't properly been addressed by the normal chain of command. These companies are smart. They recognize that, in today's litigious society, whistleblowers can save a company billions of dollars in fines and cleanup costs.

If your automation works, use it. Control systems aren't perfect. In fact, we have seen more than one process unit in which an advanced control application is so bad that the operators won't use it.

On the other hand, safety-related interlocks are equivalent to safety rules. They are there for a reason. They must not be broken. Operators, engineers, and managers should be trained to understand exactly how the controls work and why certain controls are critical. It the guidelines are wrong, unsafe or inadequate, they must be discussed thoroughly before changes are made.

Prepare, then test your preparation. In 1978, the world simply was not prepared for oil spills as large as the *Amoco Cadiz*. The main lesson learned there was that quick response is critical. By the time help finally arrived, the *Cadiz* was destroyed and its entire cargo was in the sea.

In 1987, the Alyeska Pipeline Service Company seemed better prepared for a large spill. As mentioned, in its emergency plan submitted to the federal government, Alyeska promised a 5-hour response to a 200,000-barrel oil spill in the Prince William Sound area. But after the Exxon *Valdez* ran aground, Alyeska took 13 hours to reach the ship. During those extra eight hours, the size of the oil spill more than doubled. Was it even possible for Alyeska to respond in five hours? We don't know. Was the plan ever tested? We don't know that either. We do know that, when filing its plan, Alyeska said: "It is highly unlikely that a spill of this magnitude would occur. Catastrophic events of this nature are further reduced because the majority of the tankers calling on Port Valdez are of American registry and all of these are piloted by licensed masters or pilots."

Despite the 8-hour delay, action by Alyeska and Exxon was relatively fast. Most of the oil stayed inside the ship until it was off-loaded. Consequently, instead of losing the entire cargo of 1.2 million barrels, "only" 250,000 barrels spilled into the sea.

If it's broken, don't run it. At Bhopal, the refrigeration system had been down for months. A faulty valve that should have sent the leaking gas to a scrubber sent it instead to the flare system, which failed. Operators didn't detect the leak immediately, because a key panel was missing from the control room. As stated by a Union Carbide executive, the plant should not have been running.

War is the biggest polluter of all.

4. ENVIRONMENTAL AGENCIES

Under pressure from the American public, in 1970 the U.S. Congress established the Environmental Protection Agency (EPA) and the Occupational Safety and Health Administration (OSHA). Together, these agencies are responsible for dramatic improvements in air and water quality and increases safety in workplaces throughout the United States.

4.1 Environmental Protection Agency

EPA's mission is "to enforce federal laws to control and abate pollution of air and water, solid waste, noise, radiation, and toxic substances. It is also to administer the Superfund for cleaning up abandoned waste sites, and award grants for local sewage treatment plants."

After its creation, EPA quickly took the following actions:

1. Established 10 regional offices throughout the nation.
2. In 1971, established National Ambient Air Quality Standards, which specified maximum permissible levels for major pollutants.
3. Required each state to develop plans to meet air quality standards.
4. Established and enforced emission standards for hazardous pollutants such as asbestos, beryllium, cadmium, and mercury.
5. Required a 90% reduction in emissions of VOC and carbon monoxide by 1975.
6. Published emission standards for aircraft.
7. Funded research and demonstration plants.
8. Furnished grants to states, cities, and towns to help them combat air and water pollution

EPA's law-enforcement efforts are supported by the National Enforcement Investigation Center in Denver, Colorado, which gives assistance to federal, state and local law enforcement agencies. This unit has helped to clamp down on the “midnight dumping” of toxic waste and the deliberate destruction or falsification of documents.

4.2 Other Environmental Agencies

Today, almost every U.S. state has an environmental agency. Arguably, the most famous of these is the California Air Resources Board (CARB), which pioneered regulations to mitigate smog in Los Angeles. In addition to administering state programs for improving air and water quality, the Texas Commission on Environmental Quality (TCEQ) participates in making plans to prevent and react to industrial terrorism.

Most countries have environmental agencies. As shown in *Table 4*, some are combined with public health departments, some are combined with energy agencies, and at least one is coupled with tourism. In addition to handling internal issues, most of these agencies administer their country’s participation in international treaties, such as the Kyoto Protocol.[16]

4.3 Occupational Safety and Health Administration

Pollution control and safety are two sides of the same coin. In the United States, the Occupational Safety and Health Administration (OSHA) is part of the U.S. Department of Labor. Its legislative mandate is to assure safe and healthful working conditions by:

- Enforcing the Occupational Safety and Health Act of 1970
- Helping states to assure safe and healthful working conditions
- Supporting research, information, education, and training in occupational safety and health

OSHA levies fines against unsafe people and companies. Not surprisingly, a large percentage of the safety infringements cited by OSHA have caused environmental damage or put the environment at risk.

Here is an example. In 1993 OSHA levied fines against the Manganas Painting Company for exposing its workers and the environment to lead during sand-blasting operations. The proposed fines totalled US$4 million. The contractor appealed, but in February 2002, it pled guilty to knowingly and illegally dumping 55 tons of lead-containing sandblasting material, in violation of the Resource Conservation and Recovery Act (RCRA).[17]

Under the Occupational Safety and Health Act, employers are responsible for ensuring a safe and healthy workplace. One key requirement is that all hazardous chemicals must be properly labeled. Workers must be taught how to handle the chemicals safely, and material safety data sheets must be available to any employee who wishes to see them.

Table 4. Environmental Agencies Around the World

Country	Agency
Australia	Department of the Environment and Heritage
Austria	Ministry of Agriculture, Forestry, Environment and Water Management
Brazil	Ministry of Environment
Canada	Environment Canada
China	China Council for International Cooperation on Environment and Development
Europe	European Environment Agency
Finland	Finnish Environmental Administration
Indonesia	Kementerian Lingkungan Hidup
India	Ministry of Environment and Forests
Japan	Department of the Environment of Japan
Kuwait	Environment Public Authority
Malaysia	Department of Environment Malaysia
Mexico	Secretariat of Environment and Natural Resources
Norway	Ministry of Environment
Saudi Arabia	Presidency of Meteorology and Environment
Singapore	National Environment Agency
South Africa	Department of Environmental Affairs and Tourism
Thailand	Ministry of Natural Resources and Environment
United Kingdom	Environment Agency
United States	Environmental Protection Agency

4.3.1 Material Safety Data Sheets (MSDS)

Material Safety Data Sheets (MSDS) include the following information:

Material identification. The name of the product and the manufacturer's name, address, and emergency phone number must be provided

Hazardous ingredients. The sheet must give the chemical name for all hazardous ingredients comprising more than 1% of the material. It must list cancer-causing materials if they comprise more that 0.1%. Listing only the trade name, only the Chemical Abstract Service (CAS) number, or only the generic name is not acceptable.

If applicable, exposure limits are listed in this section of the MSDS. The OSHA permissible exposure limit (PEL) is a legal, regulated standard. Other limits may also be listed. These include recommended exposure limits (REL) from the National Institute for Occupational Safety and Health (NIOSH) and threshold limit values (TLV) from the American Conference of Governmental Industrial Hygenists (ACGIH). Sometimes, short-term exposure and/or ceiling limits are shown. The ceiling limit should never be exceeded.

Physical properties. These include the appearance, color, odor, melting point, boiling point, viscosity, vapor pressure, vapor density, and evaporation rate. The vapour pressure indicates whether or not the chemical will vaporize when spilled. The vapor density indicates whether the vapor will rise or fall. Odor is important because a peculiar smell is the first indication that something has leaked.

Fire and explosion hazard data. This section provides the flash point of the material, the type of extinguisher that should be used if it catches fire, and any special precautions.

The flash point is the lowest temperature at which a liquid gives off enough vapor to form an explosive mixture with air. Liquids with flash points below 100°F (37.8°C) are called *flammable*, and liquids with flash points between 100 and 200°F (37.8 and 93.3°C) are called *combustible*. Flammable and combustible liquids require special handling and storage.

The four major types of fire extinguishers are Class A for paper and wood, Class B for flammable liquids or greases, Class C for electrical fires, and Class D for fires involving metals or metal alloys.

Health hazard data. This section defines the symptoms that result from normal exposure or overexposure to the material or one of its components. Toxicity information, such as the result of studies on animals, may also be provided. The information may also distinguish between the effects of acute (short term) and chronic (long-term) exposure. Emergency and first-aid procedures are included in this section.

Reactivity data. This section includes information on the stability of the material and special storage requirements.

Unstable chemicals can decompose spontaneously at certain temperatures and pressures. Some unstable chemicals decompose when they are shocked. Rapid decomposition produces heat, which may cause a fire and/or explosion. It also may generate toxic gas. Hazardous polymerization, which is the opposite of hazardous decomposition, also can produce enough heat to cause a fire or explosion.

Concentrated acids and reactive metals are hazards when mixed with water. They should be stored separately in special containers.

Spill, leak, and disposal procedures. This part of the MSDS gives general procedures, precautions and methods for cleaning up spills and disposing of the chemical.

Personal protection information. This section lists the protective clothing and equipment needed for the safe handling of the material. Requirements can differ depending on how the chemical is used and how much of it is used.

Protective equipment and clothing can include eye protection (safety glasses or face shields), skin protection (clothing, gloves, shoe covers), self-contained breathing equipment, and/or forced-air ventilation (fume hoods).

5. KEY REGULATIONS

In this section, we describe important environmental legislation. Most of our examples come from the United States. We apologize for this, but only a little. Historically, the United States has pioneered environmental regulations, and many countries have followed suit. Recently, the European Commission took the lead in promoting climate-control treaties, including the Rio and Kyoto Protocols. These are discussed in Sections 5.13.2 and 5.13.3.

5.1 Clean Air Acts

The first clear-air acts in the English-speaking world were implemented by Parliament in 1956, in response to the "deadly fog" incidents around London. Since then, the United States government has passed several clean-air acts, including:

- Clean Air Act of 1963
- Motor Vehicle Air Pollution Control Act of October 20, 1965
- Clean Air Act Amendments of October 15, 1967
- Air Quality Act of November 21, 1967
- Clean Air Act of 1970
- Clean Air Act Amendments of 1975, 1977, and 1990[18]

For convenience, the entire package often is called just the Clean Air Act (CAA) or the Clean Air Act Amendments (CAAA). Its continued strength demonstrates that Americans are serious about stopping air pollution.

The CAA of 1970 and its amendments contributed extensively to cleaner air in the United States. Significantly, it inspired similar legislation by many nations around the world. According to the EPA, between 1978 and 1988, lead pollution in the United States decreased by 89%, nitrogen oxides by 14%, carbon monoxide by 32%, sulfur dioxide by 37%, and ozone by 21%.

Since passage of the 1990 CAAA, individual and corporate polluters can be jailed for breaking environmental laws. Goals of the 1990 CAAA are:

1. To reduce SO_2 and NOx emissions from coal-burning power plants by 50% and 10%, respectively, by the year 2000.

2. To reduce smog, ozone, and carbon monoxide by requiring automakers to sell autos that burn clean alternative fuels in cities with bad air pollution.

3. To reduce airborne toxic chemicals by 75% in the 1990s by compelling plants to use the best available control technology (BACT), especially for chemicals suspected of causing cancer in humans.

The 1990 CAAA required EPA to set National Ambient Air Quality Standards (NAAQS) for pollutants considered harmful to public health and the environment. As shown in *Table 5*, EPA set two types of standards. Primary standards are designed to protect public health, including the health of sensitive people such as asthmatics, children, and the elderly. Secondary standards are designed to protect public welfare by improving visibility and decreasing damage to animals, crops, vegetation, and buildings. In the table, units of measure are parts per million (ppm) by volume, milligrams per cubic meter of air (mg/m^3), and micrograms per cubic meter of air ($\mu g/m^3$).

Table 5. U.S. National Ambient Air Quality Standards

Pollutant	**Primary Standard**	**Averaging Times**	**Secondary Standard**
Carbon monoxide	9 ppm (10 mg/m^3)	8-hour[1]	None
	35 ppm (40 mg/m^3)	1-hour[1]	None
Lead	1.5 µg/m^3	Quarterly	Same as Primary
Nitrogen dioxide	0.053 ppm (100 µg/m^3)	Annual	Same as Primary
PM10	50 µg/m^3	Annual[2]	Same as Primary
	150 µg/m^3	24-hour[1]	
PM2.5	15 µg/m^3	Annual[3]	Same as Primary
	65 µg/m^3	24-hour[4]	
Ozone	0.08 ppm	8-hour[5]	Same as Primary
	0.12 ppm	1-hour[6]	Same as Primary
Sulfur Oxides	0.03 ppm	Annual	–
	0.14 ppm	24-hour[1]	–
	–	3-hour[1]	0.5 ppm (1300 µg/m^3)

[1] Must not be exceeded more than once per year.

[2] Annual mean PM10 at each monitor in an area must not exceed 50 µg/m^3.

[3] The 3-year average of mean PM2.5 from all monitors must not exceed 15 µg/m^3.

[4] The 3-year average of the 98th percentile of 24-hour concentrations at each monitor in an area must not exceed 65 µg/m^3.

[5] The 3-year average of the fourth-highest daily-maximum 8-hour average concentrations of ozone in an area must not exceed 0.08 ppm.

[6] The standard is met when the expected number of days per calendar year with maximum hourly average concentrations above 0.12 ppm is less than or equal to 1.

The 1990 CAAA are designed to bring the United States into compliance with the NAAQS. The main sections of the Amendments are:

Title I – Non-Attainment
Title II – Mobile Sources
Title III – Air Toxics
Title IV – Acid Rain
Title V – Operating Permits
Title VI – Stratospheric Ozone and Global Climate Protection
Title VII – Enforcement
Title VIII – Miscellaneous (Outer Continental Shelf, Border Areas)
Title IX – Clean Air Research
Title X – Disadvantaged Business Concerns
Title XI – Clear Air Employment transition Assistance

Titles with a major impact on the petroleum processing industry are summarized below. State and local regulations can be more stringent than federal Clean Air Acts. For example, in the San Francisco Bay Area,[19] average daily CO emissions from oil refineries may not exceed 400 ppm, regardless of the CO concentration in ambient air.

5.1.1 Title I – Non-Attainment

Non-attainment categories. Title I divided cities and metropolitan areas into several categories for ozone (*marginal, moderate, serious, severe,* *extreme*) and two categories for carbon monoxide. Areas with *moderate* ozone had to achieve a 15% reduction in volatile organic compounds (VOC) by 1996. For areas with ozone problems that are *serious*, *severe* or *extreme*, VOC must be reduced by 3% per year until attainment is achieved. Major NOx sources had to reduce emissions by the same schedule, unless EPA agreed that NOx reduction would not be beneficial.

State Implementation Plans. Each American state was required to develop a state implementation plan (SIP) within 2 years. If EPA decided that an SIP was inadequate, it had the right to impose a federal implementation plan (FIP). In practice, EPA's first response was to ask for a revised SIP.

Ozone. Ground-level ozone is generated by photolytic reactions between NOx, VOC, and oxygen. Non-attainment ozone areas had to correct (update) their RACT, I/M, and CTG guidelines. RACT = reasonably available control technology, I/M = inspection and maintenance, CTG = control technology guidelines, and Non-CTG = plants that do not meet CTG.

Areas with moderate or worse air quality were required to use Stage II vapor recovery, in which special nozzles and coaxial hoses collect VOC from the fuel tanks of automobiles as they are being fuelled. The VOC are routed to a storage tank at the filling station. Moderate areas also were required to use basic I/M and RACT on new sources and on non-CTG existing sources from which potential NOx emissions exceeded 100 tons per year. For serious, severe and extreme ozone areas, RACT is required on plants from which NOx could exceed 50, 25, and 10 tons per year, respectively. These areas also had to implement transportation control measures (TCM) to limit the number of vehicles on the road. Extreme areas were required to add peak-hour traffic controls. Eleven new CTGs were issued for coatings in aerospace and shipbuilding factories, for marine vessels, and for consumer products.

CO and Particulates. For CO and PM10, Title I required oxygenated gasoline in the winter for areas where the ambient CO level exceeded 9.4 ppm. For areas where CO exceeded 12.7 ppm, enhanced I/M and predictions of "vehicle miles travelled" (VMT) were required. As in severe ozone areas, serious CO areas had to impose TCMs. Areas where PM10 levels exceeded EPA limits had to reach compliance by December 1994, with possible extensions to 2001. Moderate PM10 areas had to adopt RACT, and serious areas had to adopt BACT (best available control technology).

5.1.2 Title II – Mobile Sources

The mobile sources section of the 1990 CAA amendments promulgated regulations for automobiles, trucks, and other moving vehicles. It included the following sections:

Emission Standards. Full-useful-life emission standards for gasoline-powered vehicles are shown in *Table 6*. Tier I limits for automobiles were phased in between 1994 and 1996. Tier II standards are based on California's

LEV II program (LEV = low-emission vehicles). The Tier II phase-in began in January 2004. By 2009, sport utility vehicles (SUVs), minivans, and pickup trucks have to meet the same emission standards as automobiles. For the first time, vehicles and fuels are treated as a single system. Tier II allows vehicle manufacturers to certify a mix of vehicles ("fleet") if average NOx emissions for the fleet are less than 0.07 grams/mile (Bin 5). Tier II "bins" differ mainly in allowed NOx emissions. To obtain alternative motor vehicle credits, such as those described in the Energy Policy Act of 2004,[20] hybrid and alternative-fuel vehicles must meet or exceed Tier II, Bin 5 emission standards.

Table 6. Tier I & Tier II Emission Standards for Gasoline-Powered Vehicles (Full Useful Life)

	NMHC/ NMOG, gpm	CO gpm	NOx gpm	PM gpm	HCHO gpm
Tier 1					
LDV and LDT (<3,751 lbs.)	0.31	4.2	0.60	0.10	–
LDT (3,751-5,700 lbs.)	0.40	5.5	0.97	0.10	–
LDT (>5,750 lbs.)	0.56	7.3	1.53	0.12	–
Tier II					
Bin 6	0.09	4.2	0.09	0.01	0.018
Bin 5	**0.09**	**4.2**	**0.07**	**0.01**	**0.018**
Bin 4	0.07	2.1	0.04	0.01	0.011
Bin 3	0.055	2.1	0.03	0.01	0.011

gpm = grams/mile, LDV = light-duty vehicles, LDT = light-duty trucks

Reformulated Gasoline. Reformulated gasoline (RFG) is designed to reduce CO, air toxics, and VOC. Adding oxygen compounds lowers CO emissions, limiting benzene reduces air toxics, and controlling volatility limits VOC emissions. *Table 7* lists the RFG specification that took effect in 1995.

Table 7. Tier 1 RFG Specifications

Property	Specification
Oxygen, wt%	2.0 max
Benzene, vol%	1.0 max
RVP, Summer	
Class B (psi)	7.2 max
Class B (kPa)	50 max
Class C (psi)	8.1 max
Class C (kPa)	56 max
VOC (summer)	15% reduction
Air toxics	15% reduction
Sulfur	Same as 1990
T90, olefins, aromatics	Same as 1990

T90 = the temperature at which 90% of a gasoline blend evaporates.
RVP = Reid vapour pressure
Air toxics = benzene, formaldehyde, and butadiene

Oxygen can be added as ethanol, MTBE (methyl t-butyl ether), ETBE (ethyl t-butyl ether), or TAME (t-amyl methyl ether).

RFG was implemented in two phases. The Phase I program started in 1995 and mandated RFG for 10 large metropolitan areas. Several other cities and four entire states joined the program voluntarily. In the year 2000, about 35% of the gasoline in the United States was reformulated.

The regulations for Phase II, which took force in January 2000, are based on the EPA Complex Model, which estimates exhaust emissions for a region based on geography, time of year, mix of vehicle types, and – most important to refiners – fuel properties.

Low-sulfur gasoline. When fossil fuels are burned, the sulfur they contain is converted into SO_2 and sulfates. SO_2 contributes to acid rain, and sulfates become particulate matter. In the United States, the phase-in of low-sulfur gasoline began in January 2004. By 2006, the average sulfur level must be less than 30 wppm with a cap of 80 wppm. In parts of the Western U.S., the 30/80 rule will not take effect until 2007.

Low-sulfur diesel. From 1991 in Sweden, 1995 in California, and 1998 in the rest of the United States, the sulfur content of on-road diesel has been limited to <500 wppm sulfur. Recently, EPA imposed tighter limits on sulfur in both on-road and non-road diesel (*Table 8*). Non-road diesel is used in farm equipment, railroad engines, fork lifts, boats, and ships. Non-road rules also apply to diesel-powered generators, mining equipment, and baggage-handling equipment in airports.

Table 8. Clean Fuels: U.S. Limits on Sulfur in Gasoline and Diesel

	Fuel Sulfur Content, wppm		
	2004 Level	**Target Level**	**Target Date**
Gasoline	>300	30	2004 – 2008
Diesel, on-road	500	15	July 1, 2006
	-	-	July 1, 2010
Diesel, off-road	2000 – 3500	500	2007
	-	15	2010

5.1.3 Title III – Air Toxics

The 1990 CAA Amendments listed 189 hazardous air pollutants. It also told EPA to establish regulations for each pollutant and to publish a schedule for regulating the sources thereof. For the petroleum refining industry,[21] EPA issued regulations for the following:

2,2,4-Trimethylpentane
Benzene
Cresols/cresylic acid
Ethylbenzene
Hexane
Methyl ethyl ketone
Methyl-t-butylether (MTBE)
Naphthalne
Phenol
Toluene
Xylenes

Due to the shortage of environmental acronyms in 1990, the 1990 CAAA defined a few new ones – MACT and LAER – for maximum achievable control technology and lowest achievable emission rate. It stated that MACT must be used for new sources of air toxics, and it set a schedule for applying MACT to existing sources. Title III also required hazard assessments and risk management plans to protect against accidental releases of air toxics and other toxic chemicals. It also required the establishment of an independent chemical safety board to investigate major accidents, conduct research, and promulgate regulations for the reporting of accidental releases.

5.1.4 Title IV – Acid Rain

This Title required a 10 million ton per year reduction in SO_2 emissions from power plants, including those in refineries, with a goal of capping SO_2 emissions at about 8.9 million tons per year by 2000. Sources were given allowances based on previous emission reductions and past energy use. Each allowance is worth 1 ton per year of SO_2 and can be bought, sold, traded or banked to offset future emissions violations. Title IV also required a 2 million ton per year reduction in NOx emissions from power plants.

To measure SOx and NOx, continuous monitors are required. Opacity meters are required to measure PM, such as that emitted by FCC regenerators.

5.1.5 Title VIII – Enforcement

The 1990 CAAA made Clean Air Act easier to enforce, and also made them more consistent with other environmental statutes, including the Clean Water Act and the Resource Conservation and Recovery Act (RCRA). An array of new penalties were added, ranging from wrist slaps to jail time. Theses were enacted so officials could do a better job of matching a penalty to the severity of a crime.

Before 1990, criminal acts against the environment were misdemeanors, but the 1990 CAAA converted them into felonies. The CAAA also added sanctions for endangerment with air toxics. As an alternative to prosecuting every violation in court, EPA gained the authority to levy administrative fines up to US$200,000 and to issue field citations up to US$5,000. The fines can be challenged in court, but if the offender is found guilty, fines levied by the courts are likely to be higher than the fines levied by EPA.

In environmental lawsuits filed by citizens, courts gained the right to levy fines in addition to issuing injunctions. District courts were given jurisdiction over lawsuits filed against EPA for unreasonable delay, etc.

After the government proves that a violation has occurred, the burden of proof is on the accused. This makes it easier for EPA to convict and punish ongoing and recurring violations.

5.2 River and Harbor Act, Refuse Act

In 1899, the River and Harbor Act was passed to control obstructions to navigation. The Act required congressional approval for the building of bridges, dams, dikes, causeways, wharfs, piers, or jetties, either in or over a navigable waterway. The Act also made it illegal to discharge debris into navigable water without a permit. In 1966, a court held that the River and Harbor Act made it illegal to discharge industrial waste without a permit, not just directly into navigable waters, but also into associated tributaries and lakes, i.e., just about every puddle of open water in the United States. This led to the Refuse Act Permit Program of 1970, under which specific kinds of pollution are allowed under permits issued by the Army Corps of Engineers. Every application for a permit is reviewed by EPA. If EPA concludes that the discharge described in the application will harm the environment, the Army Corp of Engineers denies the permit.

The penalties for violating permits are severe. For a first offense, a person who violates a permit through negligence can be fined up to US$25,000 per day or imprisoned for up to a year. For a second offense, the maximum penalties double. For willful violations, fines can be as high as US$50,000 per day and prison terms can last 3 years. If a willful act causes serious bodily injury, the violator can be fined $250,000 or sent to jail for 15 years. In addition, the corporation that employs the guilty person can be fined up to $1,000,000. False reports also can be punished by fines or imprisonment.

In this context, “guilty person” refers to the corporate officer responsible for the facility from which the illegal discharge originates. In other words, a negligent act by a sloppy operator can send the Big Boss to jail.

Some examples of the fines levied under these Acts are:

Example 1. In June 1999, a pipeline ruptured in Bellingham, Washington, dumping 236,000 gallons of gasoline into nearby Hannah Creek and Whatcom Creek. The gasoline ignited, killing two boys and a young man. It also did extensive damage to waters, shorelines and other natural resources. In December 2002, two companies and three employees agree to pay damages and fines totaling US$36 million.

Example 2. After the 1989 oil spill in Prince William Sound, Exxon Shipping Company pled guilty to violating the Clean Water Act, the Refuse Act, and the Migratory Bird Treaty Act. In addition, Exxon Corporation pled guilty to violating the Migratory Bird Treaty Act. The corresponding fines – US$150 million – were the largest ever assessed for environmental pollution.

5.3 Federal Water Pollution Control Act

The original Federal Water Pollution Control Act (FWPCA) was approved on July 9, 1956. The present Act includes the following:

- Pollution Control Act Amendments of July 20, 1961

- Water Quality Act of October 2, 1965
- Clean Water Restoration Act of November 3, 1966
- Water Quality Improvement Act of April 3, 1970
- Federal Water Pollution Control Act of 1972
- Clean Water Acts of 1977, 1981, and 1987

The FWPCA of 1972 gave EPA greater authority to fight water pollution. While implementing the Act, EPA cooperates with the U.S. Coast Guard and the Secretary of the Interior. Individual states have primary responsibility for enforcing water quality standards, but if the states fail to meet expectations, EPA can take civil or criminal action under the Refuse Act.

The FWPCA prohibits the discharge of harmful amounts of oil into navigable waters. If oil is spilled, the owner or operator is liable for cleanup costs. Initially, the bill authorized $24.6 billion for water pollution control over three years. The goal of the law was to eliminate the pollution of U.S. waterways by municipal and industrial sources by 1985.

5.4 Clean Water Acts, Water Quality Act

The main objective of the Clean Water Acts (CWA) of 1977, 1981 and 1987 is to maintain the "chemical, physical, and biological integrity of the nation's waters." It seeks to have "water quality which provides for the protection and propagation of fish, shellfish and wildlife and provides for recreation in and on the water." Under these Acts, each state is required to set its own water quality standards. All publicly owned municipal sewage treatment facilities are required to use secondary treatment for wastewater. To help states and cities build new or improved water treatment plants, Congress provides construction grants, which are administered by EPA. EPA allocates funds to states, which in turn distribute money to local communities. Between 1972 and 1982, EPA approved construction grants worth nearly $33 billion. Between 1982 and 1992, another $24 billion was approved.

Community programs are monitored by EPA. They must meet treatment requirements to obtain permits under the National Pollutant Discharge Elimination System (NPDES).

The Water Quality Act of 1987 requires discharge permits for all point sources of pollution. More than 95% of all major facilities now comply with 5-year NPDES permits, which specify the types and amounts of pollutants that legally can be discharged. When permits are renewed, they can be modified to reflect more stringent regulations. Violators are subject to enforcement actions by EPA, including criminal prosecution.

The authority of the EPA was strengthened under the 1987 Clean Water Act. The allowable sizes of fines were increased, and violators found guilty of negligence could be sent to prison. Violators found guilty of endangerment can be fined up to US$250,000 and imprisoned for up to 15 years.

5.5 Marine Protection, Research, and Sanctuaries Act

The Marine Protection, Research, and Sanctuaries Act of 1972 gave authority to the EPA to protect oceans from indiscriminate dumping. The Agency designates sites at which dumping is allowed and issues dumping permits. Fines can be imposed for illegal dumping.

5.6 Safe Drinking Water Act

Since the 1970s, the assurance of safe drinking water has been a top priority for EPA, along with individual states and over 53,000 community water systems (CWSs). The CWSs supply drinking water to more than 260 million Americans – about 90% of the population.[22]

The Safe Drinking Water Act of 1974 was amended in 1977 and again in 1986. It empowered EPA to set national standards for drinking water from surface and underground sources. It also authorized EPA to give financial assistance to states, which are in charge of enforcing the standards. Aquifers are protected from wastes disposed in deep injection wells, from runoff from hazardous waste dumps, and from leaking underground storage tanks. In 1987, EPA also established maximum contaminant levels for volatile organics (VOC) and 51 manmade chemicals. Standards for other chemicals were added as their toxicity was determined. At present, health and safety standards have been established for 91 microbial, chemical, and radiological contaminants.

During 2005 – 2008, the EPA, the states, and the CWSs will continue to focus on supplying safe drinking water. In addition, they plan to work toward the following ambitious goal: By 2008, 95% of the population will have access to drinking water that meets all applicable health-based standards. To meet this goal, EPA identified five key objectives:

- To continue to develop and revise drinking water standards
- To implement drinking water standards and other program requirements
- To promote sustainable management of the nation's water infrastructure
- To protect sources of drinking water from contamination
- To assure that the water infrastructure is safe from terrorist and other intentional acts.

5.7 Resource Conservation and Recovery Act (RCRA)

In the United States, solid wastes are regulated by the following:

- Solid Waste Disposal Act of 1965
- Resources Recovery Act of 1970
- Resource Conservation and Recovery Act of 1976 (RCRA)

In 1965, the Solid Waste Disposal Act provided financial grants to develop and demonstrate new technologies in solid waste disposal. The Resources Recovery Act of 1970 emphasized recycling and by-product recovery.

By 1976, problems caused by the accumulation of large quantities of hazardous waste prompted Congress to pass the Resource Conservation and Recovery Act (RCRA). This legislation gave EPA the responsibility of developing a “cradle to grave” approach to hazardous waste.

Under RCRA, hazardous waste is tracked from its source to every destination, including final disposal. Tracking is based on transportation manifests, other required records, and the issuance of permits.

EPA classifies wastes according to four measurable characteristics, for which there are standardized tests. The characteristics are:

- Ignitibility
- Corrosivity
- Reactivity
- Extraction procedure toxicity (EP)

In 1980, the Waste Oil Recycling Act (WORA) empowered EPA to encourage the development of state and local programs for recycling waste motor oil. That same year, WORA was amended to strengthen its enforcement provisions.

A ***generator*** of hazardous waste is responsible for the following:

1. Determining if a waste is hazardous
2. Obtaining a facility permit if the waste is stored on the generator’s property for more than 90 days
3. Obtaining an EP identification number
4. Using appropriate containers and labeling them properly for shipment
5. Preparing manifests for tracking hazardous waste
6. Assuring through the manifest system that the waste arrives at the designated facility
7. Submitting to EPA an annual summary of activities

Prior to shipping hazardous waste, the generator must prepare a manifest which includes the following:

1. Name and address of the generator
2. Name of all transporters
3. Name and address of the facility designated to receive the waste
4. EPA identification number of all who will handle the waste
5. Department of Transportation (DOT) description of the waste
6. Amount of waste and number of containers
7. Signature certifying that the waste has been properly labeled and packaged in accordance with EPA and DOT regulations

To send waste away from its site, the generator must use EPA-approved transporters. It must also keep records of all hazardous waste shipments and immediately report those that fail to reach the facility shown on the manifest.

A ***transporter*** of hazardous waste must:

1. Obtain an EPA identification number
2. Comply with the manifest system for tracking hazardous waste
3. Deliver the entire quantity of hazardous waste to the facility specified by the manifest
4. Retain copies of manifests for three years
5. Comply with Department of Transportation rules for reporting discharges and spills.
6. Cleanup any spills that occur during transportation. All spills must be reported to both EPA and the DOT.

Any person who owns or operates a hazardous waste facility must receive a permit from the EPA. Standards for facilities that ***treat, store, or dispose*** of hazardous waste are designed to:

1. Promote proper treatment, storage, and methods of disposal
2. Provide states with minimum standards acceptable to EPA
3. Provide technical support to states that lack hazardous waste management programs

The RCRA amendments of 1984 and 1986 extended the act to cover underground storage tanks, especially those used for gasoline and other petroleum liquids. At the time, about 15% of the nation's 1.4 million gasoline storage tanks were leaking. Most of these leaks have since been repaired.

5.8 Superfund, CERCLA

Years ago, people were less aware of the dangers of dumping chemical wastes. On many properties, dumping was intensive and/or continuous. This created thousands of hazardous sites, many of which were uncontrolled and/or abandoned. On December 11, 1980, in response to public concern, Congress passed the Comprehensive Environmental Response Compensation and Liability Act (CERCLA), which authorized EPA to locate, investigate, and remediate the worst of these hazardous sites.

CERCLA established the Superfund, which provides emergency cleanup funds for chemical spills and hazardous waste dumps. The Superfund allows the government to take immediate action to cleanup spills or dumps where the responsible party cannot be identified easily. The Superfund draws about 90% of its money from taxes on oil and selected chemicals. The remainder comes from general tax revenues.

Except in an emergency, state agencies are consulted before the federal government takes action. When it does so, it uses one of three approaches:

1. If the owner of the hazardous site cannot readily be identified, the federal government may proceed with the cleanup
2. If the owner can be identified but refuses to clean the site, or if the owner's efforts are not up to par, the federal government can take charge of the cleanup. The owner must pay the cost, whatever it happens to be.

3. When the owner can be identified and decides to do the work, the federal government monitors the project and gives official approval when the work is completed according to standards.

CERCLA covers a wide range of sites. In addition to land-based dumps, it applies to spills into waterways, groundwater, and even the atmosphere. Initial funding for the Act was US$1.6 billion over 5 years. In 1986, the Superfund Amendment and Reauthorization Act (SARA) extended the program by five years and increased the fund to US$8.5 billion. It also tightened cleanup standards and enhanced EPA's enforcement powers. The Emergency Planning and Community Right-to-Know Act (EPCRA), also known as SARA Title III, encourages and supports emergency planning efforts at state and local levels. It also gives information to the public and local governments on potential chemical hazards in their communities. This piece of legislation has helped to reduce pollution and improve safety all across the land.

In 1984, Hazardous and Solid Waste Amendments (HSWA) were passed because citizens were concerned about the potential contamination of ground water by hazardous waste disposal sites.

In 1978, the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) of 1947 was amended to give EPA authority to control pollution from DDT, mercury, aldrin, toxaphene, parathion and related chemicals. About 1 billion pounds of pesticides, fungicides, and rodenticides are used every year in the United States. While they contribute enormously to the success of agriculture, they can be harmful to animals, birds and humans if not used properly.

5.9 Toxic Substances Control Act (TSCA)

The Toxic Substances Control Act (TSCA) of 1976 gave EPA the authority to regulate the development, distribution, and marketing of chemical products. Manufacturers, importers, and processors must notify EPA within 90 days before introducing a new chemical to the market. Certain tests (e.g., fish-kill tests) must be conducted to determine toxicity. Approved chemicals must bear warning labels.

Many chemicals are restricted or banned under TSCA.

- The manufacture, processing and distribution of completely halogenated chlorofluorocarbons (CFCs) is banned, except for a small number of essential applications.
- Chromium (VI) may not be used as a corrosion inhibitor in comfort cooling towers (CCTs) associated with air conditioning and refrigeration systems.
- Nitrosating agents may not be mixed with metalworking fluids that contain specific substances.
- The import, manufacture, processing, or distribution of PCBs is banned unless EPA agrees that the PCBs will be "totally enclosed."

5.10 Asbestos School Hazard Abatement Act

The Asbestos School Hazard Abatement Act (SHAA) of 1984 was passed to encourage the removal of asbestos from schools. In 1986, the Asbestos Hazard Emergency Response Act was passed to correct in deficiencies in the previous Act. The final rule, issued in 1987, required local education agencies to:

1. Inspect school buildings for asbestos-containing materials
2. Submit asbestos management plans to state governors
3. Reduce or completely eliminate all asbestos hazards

5.11 Stockholm Conference

The United Nations plays an important role in international pollution abatement. In June 1972, the U.N. Conference on the Human Environment was held in Stockholm, Sweden. The main purpose of the conference was to provide guidelines for action by governments and international environmental organizations. The conference took several important steps, including:

1. Approving a Declaration on Human Environment.
2. Approving an action plan based on five subject areas:
   - Human settlements
   - Environmental resource management
   - Pollutants of international significance
   - Training, education, and information
   - Development and the environment
3. Recommending the establishment of a new United Nations institution to coordinate international activities.

5.12 Control of Dumping at Sea

On November 13, 1972, the Convention on the Dumping of Wastes at Sea was agreed in London by representatives of 91 countries, including all of the world's principle maritime nations. The list of substances that may not be dumped includes biological and chemical warfare agents, certain kinds of oil, certain pesticides, durable plastics, poisonous metals and their compounds, and high-level radioactive waste. Enforcement is left to individual countries.

5.13 Climate Control: Rio and Kyoto[23,24]

5.13.1 Rio Earth Summit

In 1992, during the "Earth Summit" in Rio de Janeiro, 154 nations plus the European community signed the United Nations Framework Convention on

Climate Change (UNFCCC). At the time, the Earth Summit was the largest-ever gathering of Heads of State. Effective on March 21, 1994, the UNFCCC called on industrial nations to voluntarily reduce greenhouse gas emissions to 1990 levels by the year 2000.

In many respects, the Rio Declaration resembled the Declaration on Human Environment issued by the Stockholm Conference in 1972. The 27 non-binding principles of the Rio Declaration included the "polluter pays" concept and the "precautionary principle." The latter recommends that, before a construction project begins, an impact study should be conducted to identify and forestall potential harm to the environment.

The declaration asserted that present-day economic development should not undermine the resource base of future generations. It also affirmed that industrial nations pollute more than developing countries. (For example, on a per capita basis, the United States emits 25 times more CO_2 than India.) On the other hand, industrial nations have advanced technology and greater financial resources, which enable them to contribute more to environmental protection.

5.13.2 Kyoto Protocol

In 1997, representatives of 171 countries convened in Kyoto, Japan to strengthen the UNFCCC with specific, binding commitments. The Kyoto Protocol focused on controlling emissions of 6 greenhouse gases – CO_2, CH_4, N_2O, hydrofluorocarbons (HFCs), perfluorocarbons (PFCs) and sulfur hexafluoride (SF_6).

The last three chemicals do not act directly as greenhouse gases, but they deplete ozone in the upper atmosphere. Without an ozone layer, certain CO_2-consuming algae may no longer be protected from harmful UV radiation, and a major sink for CO_2 may be destroyed.

The Protocol divided countries into categories – industrialized (Annex I), economy-in-transition (EIT), developing, and least developed. *Table 9* lists several "Annex I" parties and their 1990 emissions of CO_2.

Table 9. 1990 Emissions of CO_2 by Selected Countries[23]

Country	1990 CO_2 Emissions (10^6 kg/year)	Emissions Relative to Japan
Australia	288,965	0.25
Canada	457,441	0.39
Iceland	2,172	0.0
Japan	1,173,360	1.00
Norway	35,533	0.03
Poland	414,930	0.35
Romania	171,103	0.15
Russia	2,388,720	2.04
USA	4,957,022	4.22
15 EC member states	3,322,990	2.83

The Protocol focused on establishing legally binding emissions targets, mechanisms for implementation, minimizing the burden placed on developing countries, accounting, reporting, review, and compliance. Parties to the Protocol agreed to develop internal climate-control programs entailing:

- National climate-change mitigation measures
- Provisions for developing and transferring environmental technology
- Provisions to maintain carbon sinks, such as forests, which remove more greenhouse gases from the air than they emit.
- Preparations for adapting to climate change
- Plans to engage in climate research and information exchange
- Plans to promote education, training and public awareness

The parties agreed to a 5% global reduction of greenhouse gases, versus 1990 levels, by 2008 – 2012. *Table 10* shows emissions targets for selected countries.

Table 10. Kyoto Protocol: Reduction Targets for Emissions of Greenhouse Gases

Country	Target[a]
European Community, Bulgaria, Czech Republic, Estonia, Latvia, Lithuania,	-8%
Liechtenstein, Monaco, Romania, Slovakia, Slovenia, Switzerland	-8%
United States[b]	-7%
Canada, Hungary, Japan, Poland	-6%
Croatia	-5%
New Zealand, Russia, Ukraine	No change
Norway	+1%
Australia[b]	+8%
Iceland	+10%

[a] The base year is 1990 for most countries. For some EIT countries, the base year is flexible.

[b] Declared that it will not ratify the Protocol.

By June 2001, more than 150 multi-country projects had been registered with the UNFCCC. Most of these related to renewable energy and energy efficiency, but the largest involved forest preservation or restoration.

5.13.3 Plan B for Climate Control: Contraction and Convergence

In 2002, the United States refused to ratify the Kyoto Protocol. Australia soon followed suit. Near the end of 2003, the European Union, the Protocol's biggest supporter, reported that only two member states – Sweden and the UK – were on course to meet their targets. An article in *New Scientist* by Fred Pearce[24] summarized his view of the Kyoto Protocol at the end of 2003.

"The Kyoto Protocol is dying a death of a thousand cuts," he wrote. "…These blows follow a history of bureaucratic squabbling and political posturing by the Protocol's signatories, and many observers now fear that it has been damaged beyond repair. So does the world have a Plan B for bringing the emissions of greenhouse gases under control?

"The answer is yes, and it goes by the name 'contraction and convergence,' or C&C. The idea has been around for a decade, but lately it has been gaining ever more influential converts, such as the UK's Royal Commission on Environmental Pollution, the UN Environment Programme, the European Parliament and the German Advisory Council on Global Change, which last week released a report supporting the idea…"

Pearce goes on to say that while Kyoto has become a convoluted, short-term measure to mitigate climate change, C&C could provide a simple, fair, long-term solution. Under C&C, per capita emissions will converge, year by year, towards a common target. In effect, after the target date, every person in the world would have an equal right to pollute.

"On the face of it," Pearce says, "C&C seems anathema to countries like the US, which would have to buy large numbers of pollution credits in the early years. But it does meet most of the criticisms made by the Bush administration of the Kyoto protocol.

"In particular, Bush called it unfair that Asian trading competitors, as developing nations, had no targets. Under C&C every nation would ultimately have the same target. Some, such as China, already have per-capita emissions in excess of targets they might have to meet by mid-century.

"But perhaps the greatest attraction of C&C is the complete break it would make from the horse-trading, short-term fixing and endless complications that have plagued efforts to bring the Kyoto Protocol into effect."

If the past can predict the future, politics will continue to dominate the debate about global warming until it becomes a clear and present danger. If so, we hope there will still be time to do something about it.

6. POLLUTION CONTROL TECHNOLOGY

In response to environmental regulation, the refining industry reduced pollution by:

- Reducing fugitive hydrocarbon emissions from valves and fittings
- Removing sulfur from refinery streams and finished products
- Adding tail-gas units to sulfur recovery plants
- Reducing the production of NOx in fired heaters
- Scrubbing SOx and NOx from flue-gases
- Reducing the production of CO_2 by increasing energy efficiency

The technology behind these actions is explained below.

6.1 Particulate Matter

In refineries, coking operations and FCC regenerators are the main sources of PM emissions. Coke-derived PM10 can be reduced by building enclosures around coke-handling equipment – conveyor belts, storage piles, rail cars, barges, and calciners.

For flue gas from FCC regenerators, many licensors offer scrubbing technology. ExxonMobil offers wet-gas scrubbing (WGS), which removes particulates, SOx and NOx.[25] UOP and Shell Global Solutions offer third-stage separator (TSS) technology, which removes PM in conjunction with flue-gas power recovery.[26]

6.2 Carbon Monoxide and VOC

CO from by partial combustion in FCC regenerators is converted to CO_2 in CO boilers. Flue gas from other boilers, process heaters, and power plants can also contain some CO, which can be diminished by the installation of high-efficiency burners and/or the implementation of advanced process control.

Fugitive emissions (leaks) from storage tanks, sewers, process units, seals, valves, flanges, and other fittings[27] can contain both CO and volatile organic compounds (VOC). Floating roofs can be added to open tanks, and tanks that already have a roof can be fitted with vapor recovery systems. Open grates above sewers can be replaced with solid covers. Emissions from seals, valves, etc., can be pin-pointed with portable combustible-gas detectors. Repairs can then be made at convenient times, e.g., during a maintenance shutdown.

6.3 Sulfur Oxides

Sources of SOx in refineries. Fuel-oil fired heaters and the regenerators of FCC units are major sources of refinery SOx and NOx emissions. The most obvious way to reduce SOx from a heater is to burn low-sulfur fuels. Switching fuels requires no capital investment, but it is probably the most expensive solution due to the relatively high cost of low-sulfur fuels.

A large fraction of the sulfur in the feed to an FCC unit ends up in coke on the catalyst. SOx are formed in the regenerator when the coke is burned away. Removing sulfur from FCC feed with a pretreater decreases SOx emissions.

Flue gas desulfurization. Processes for removing sulfur oxides from stack gases include dry absorption, wet absorption, carbon adsorption, and catalytic oxidation. As mentioned above, ExxonMobil offers wet-gas scrubbing (WGS) technology, which simultaneously removes particulates, SOx and NOx.[25]

Historically, wet flue-gas desulfurization processes used aqueous slurries of lime, dolomite, and/or sodium hydroxide. Sulfur oxides react with lime or limestone ($CaCO_3$) to produce calcium sulfate ($CaSO_4$) and calcium sulfite ($CaSO_3$), which precipitate from the scrubbing solution. The products move to a settling tank, in which the solid calcium salts separate from the solution as the scrubbed gas goes up the stack. After some time, the solids are removed and sent to a sanitary landfill. The solution is recycled, and fresh lime is added as needed.

The “dual alkali” approach starts with solutions or slurries of sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3), or sodium bicarbonate ($NaHCO_3$). These compounds react with SO_2 to give sodium sulfite (Na_2SO_3) and sodium bisulfite ($NaHSO_3$), which stay dissolved in the solution. Some of the sodium sulfite reacts with excess oxygen in the flue gas to give sodium sulfate. Sulfate and sulfite are removed by reaction with lime or limestone ($CaCO_3$). The sodium hydroxide solution is recycled. Make-up hydroxide is added as needed to compensate for losses. Selected dual-alkali reactions are shown below:

$2\,NaOH + SO_2 \rightarrow Na_2SO_3 + H_2O$
$Na_2CO_3 + SO_2 \rightarrow Na_2SO_3 + CO_2$
$Na_2SO_3 + \tfrac{1}{2}\,O_2 \rightarrow Na_2SO_4$
$Na_2SO_3 + CaCO_3 \rightarrow CaSO_3 + Na_2CO_3$
$Na_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4 + 2\,NaOH$

In a carbon adsorption process developed by Lurgi, hot flue gas first goes through a cyclone or dust collector for particulate removal. The gas is cooled with water and sent to an adsorption tower packed with activated carbon. The carbon adsorbs SOx. Water is sprayed into the tower intermittently to remove the adsorbed gas as a weak aqueous acid. The scrubbed gas goes out the stack. The acid goes to the gas cooler, where it picks up additional SOx by reacting with incoming flue gas. Cooler discharge is sold as dilute sulfuric acid.

In the Reinluft carbon adsorption process, the adsorbent is a slowly moving bed of carbon. The carbon is made from petroleum coke and activated by heating under vacuum at 1100°F (593°C).

Flue-gas scrubbing with catalytic oxidation (Cat-Ox) is an adaptation of the contact sulfuric acid process, modified to give high heat recovery and low pressure drop. In the Monsanto process, particulates are removed from hot flue gas with a cyclone separator and an electrostatic precipitator. A fixed-bed converter uses solid vanadium pentoxide (V_2O_5) to catalyze the oxidization of SO_2 to SO_3. Effluent from the converter goes through a series of heat exchangers into a packed-bed adsorption tower, where it contacts recycled sulfuric acid. The tower overhead goes through an electrostatic precipitator, which removes traces of acid mist from the scrubbed gas. Liquid from the tower (sulfuric acid) is cooled and sent to storage. Some of the acid product is recycled to the absorption tower.

In a flue-gas desulfurization process from Mitsubishi Heavy Industries (MHI), manganese dioxide (MnO_2) is the absorption agent. The final product is ammonium sulfate $(NH_4)_2SO_4$, which is an excellent fertilizer. MHI claims better than 90% removal of SOx with this process.

The Wellman-Lord process uses a solution of potassium sulfite (K_2SO_3) as a scrubbing agent. K_2SO_3 adsorbs SO_2 to give potassium bisulfite ($KHSO_3$). The bisulfite solution is cooled to give potassium pyrosulfite ($K_2S_2O_5$). This can be stripped with steam to release SO_2, which is fed to a sulfuric acid plant.

FCC SOx transfer additives. Arguably, SOx transfer additives are the most cost-effective way to lower SOx emissions from a full-combustion FCC unit. These materials, first developed by Davison Chemical, react with SOx in the FCC regenerator to form sulfates (*Figure 1*). When the sulfated additive circulates to the riser/reactor section, the sulfate is chemically reduced to H_2S, which is recovered by amine absorption and sent to a sulfur plant.

In summary, sulfur that would have gone up the stack as SOx goes instead to the sulfur plant as H_2S.

In some units, SOx additives can reduce FCC SOx emissions by more than 70%. This can have a dramatic effect on the design and/or operation of upstream and downstream equipment – FCC feed pretreaters, FCC gasoline post-treaters, and flue-gas scrubbers for FCC regenerators.

FCC Regenerator (Oxidizing Environment)

Coke on catalyst (solid) + O_2 + $H_2O \rightarrow CO_2$ + SO_2, SO_3, H_ySO_x (gases)

SO_2, SO_3, H_ySO_x (gas) + M (solid) + $O_2 \rightarrow$ M●SO_4 (solid)

FCC Riser-Reactor (Reducing Environment)

M●SO_4 (solid) + 5 $H_2 \rightarrow$ M (solid) + H_2S (gas) + 4 H_2O (gas)

Figure 1. Mechanism of SOx transfer in FCC units.

Hydrogen Sulfide Removal. When sulfur-containing feeds pass through hydrotreaters or conversion units, some or most of the sulfur is converted into H_2S, which eventually ends up in off-gas streams. Amine absorbers remove the H_2S, leaving only 10-20 wppm in the treated gas streams. H_2S is steam-stripped from the amines, which are returned to the absorbers. The H_2S is piped to the refinery sulfur plant, where it is converted into sulfur.

6.4 Nitrogen Oxides

NOx are formed in several ways. In high-temperature heaters and FCC regenerators, NOx are produced by the reaction of nitrogen with oxygen. In FCC regenerators, NOx are produced from the nitrogen deposited with coke on spent catalysts. FCC NOx emissions go up when (a) the catalyst contains more combustion promoter, (b) when oxygen in the flue gas goes up, (c) at higher regenerator temperatures, and (d) at higher feed nitrogen contents. Combustion promoter is a noble-metal material that accelerates the reaction between CO and O_2 to form CO_2. By removing CO, the promoter inhibits the following reactions:

$$2\,NO + 2\,CO \rightarrow N_2 + 2\,CO_2$$
$$2\,NO_2 + 4\,CO \rightarrow N_2 + 4\,CO_2$$

Dual-alkali flue-gas scrubbing as described in Section 6.3 only removes about 20% of the NOx from a typical flue gas. Therefore, instead of simple scrubbing, chemical reducing agents are used. In selective catalytic reduction (SCR) processes, anhydrous ammonia is injected into the flue gas as it passes through a bed of catalyst at 500 to 950°F (260 to 510°C). The reaction between NOx and ammonia produces N_2 and H_2O.

The MONO-NOx process offered by Huntington Environmental Systems employs a non-noble metal catalyst. For SOx, NOx and VOC removal, Ducon uses ceramic honeycomb or plate-type catalysts in which titanium dioxide is the ceramic and the active coatings are vanadium pentoxide and tungsten trioxide (WO_3). The working catalyst temperature ranges from 600 to 800°F (315 to 427°C). For NOx abatement, Ducon provides complete ammonia injection systems with storage tanks, vaporizers and injection grids. Either anhydrous or aqueous ammonia can be used.

NOx-removal catalysts are offered by Haldor-Topsøe, KTI, and others. The Thermal DeNOx process offered by ExxonMobil is non-catalytic.

6.5 Greenhouse Gases, Stratospheric Ozone

Refineries have reduced emissions of greenhouse gases – primarily CO_2 – by improving energy efficiency, which cuts back on fuel requirements. Like other factories in countries that have signed the Montreal Protocol, refineries are switching to ozone-friendly heat-transfer fluids in air conditioners.

6.6 Waste Water

In refineries, the treatment of wastewater (*Table 11*) purifies process water, runoff from storms, and sewage. These may contain oil, suspended solids, dissolved salts, phenols, ammonia, sulfides, and other materials. They come from just about every process unit, especially those that use wash water, condensate, stripping water, caustic, or neutralization acids.

6.6.1 Primary Treatment

Primary treatment uses a settling pond to allow most hydrocarbons and suspended solids to separate from the wastewater. The solids drift to the bottom of the pond, hydrocarbons are skimmed off the top, and oily sludge is removed. Difficult oil-in-water emulsions are heated to expedite separation.

Acidic wastewater is neutralized with ammonia, lime, or sodium carbonate. Alkaline wastewater is treated with sulfuric acid, hydrochloric acid, carbon dioxide-rich flue gas, or sulfur.

Figure 2 is a simplified sketch of an API oil-water separator. The large capacity of these separators slows the flow of wastewater, allowing oil to float

Table 11. Refinery waste water treatment in a nutshell.

Designation	Source
Oil-Free Water	Oil-free storm runoff
	Steam turbine condensate
	Air-conditioner cooling water
	Cooling water from light-oil units (C_5-minus)
	Cooling-tower blowdown
	Clean water from treatment plants
Oily Cooling Water	Oily storm runoff
	Cooling water from heavy-oil units (C_5-plus)
	Uncontrolled blowdown
Process Water	Desalter water
	Excess sour water
	Water drawn from oil-storage tanks
	Accumulator draws
	Treating plant waste
	Barometric condeners
	Slop-oil breaks
	Ballast water
Sanitary Water	Employee locker rooms
	Cafeteria
	Office buildings
	Control rooms
	Destination
Oil-Free Water	Oil/water separator
Oily Cooling Water	Oil/water separator
Process Water	API Separator, activated sludge treatment
Sanitary Water	Municipal water treatment plant

to the surface and sludge to settle out. They are equipped with a series of baffles and a rotating endless-belt skimmer, which recovers floating oil. Accumulated sludge is removed through sludge hoppers at the bottom.

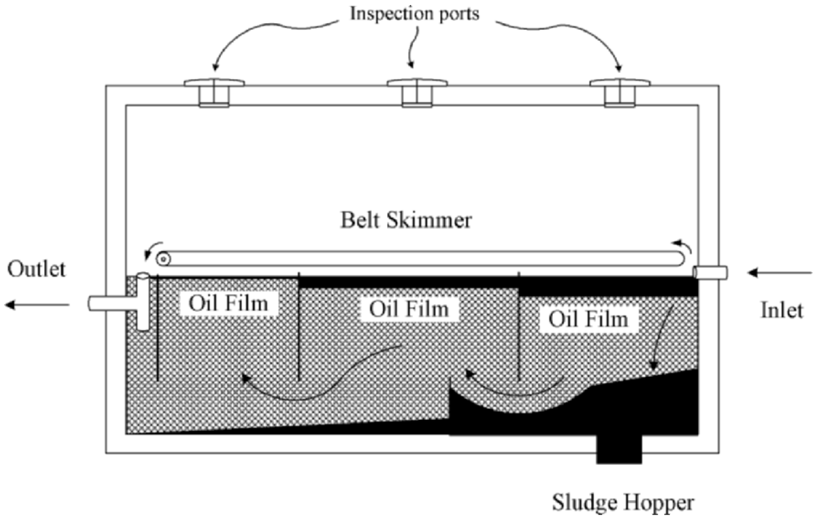

Figure 2. API oil/water separator: simplified sketch

6.6.2 Secondary Treatment

A small amount of suspended solids remains in the water after primary treatment. These are removed by filtration, sedimentation or air flotation. Flocculation agents may be added to consolidate the solids, making them easier to remove by sedimentation or filtration. Activated sludge, which contains waste-acclimated bacteria, digests water-soluble organic compounds, in either aerated or anaerobic lagoons. Steam-stripping is used to remove sulfides and ammonia, and solvent extraction is used to remove phenols.

6.6.3 Tertiary Treatment

Tertiary treatment removes specific pollutants, including traces of benzene and other partially soluble hydrocarbons. Tertiary processes include reverse osmosis, ion exchange, chlorination, ozonation, or adsorption onto activated carbon. Compressed air or oxygen can be used to enhance oxidation. Spraying water into the air or bubbling air through the water removes remaining traces of volatile chemicals such as phenol and ammonia.

6.7 Cleaning Up Oil Spills

Oil spills can be caused by natural seepage, leaky storage tanks, petroleum exploration and production activities, the on-purpose flushing of fuel tanks at sea, and accidents such as those described in Section 3.

The cleanup of oil spills includes containment, physical and mechanical removal, chemical and biological treatment, and natural forces. Land-based spills are easier to clean than spills onto open water, which are spread quickly by currents and winds.

6.7.1 Natural Forces

Several natural forces tend to remove oil spills. These include evaporation, spreading, emulsification, oxidation, and bacterial decomposition.

Evaporation. A large portion of an oil spill may simply evaporate before other methods can be used to recover or disperse the oil. Rates of evaporation depend on the ambient temperature and the nature of the oil.

Spreading. The fact that spilled oil spreads quickly across the surface of water is a “good news, bad news” story. The good news is that spreading increases rates of evaporation and air oxidation. The bad news is that the more dispersed the oil becomes, the harder it is to collect.

As with evaporation, rates of oil-spill dispersion depend upon ambient conditions and the nature of the oil. Not surprisingly, oil disperses best in fast-moving turbulent water.

Oxidation. Freshly spilled crude oil has a natural tendency to oxidize in air. Sunlight and turbulence stimulate the process. Oxidation products include organic acids, ketones and aldehydes, all of which tend to dissolve in water. As a spill ages, oxidation slows as "easy" molecules disappear from the mix. Compared to other natural forces, oxidation plays a minor role in removing oil spills.

Emulsification. When crude oil spills at sea, it emulsifies rapidly. Two kinds of emulsions are formed – oil-in-water and water-in-oil. Oil-in-water emulsions, in which water is the continuous phase, readily disperse, removing oil from the spill. However, this kind of emulsion requires the presence of surface-active agents (detergents).

The composition of water-in-oil emulsions varies from 30% to 80% water. These are extremely stable. After several days, they form "chocolate mousse" emulsions, which are annoyingly unresponsive to oxidation, adsorption, dispersion, combustion, and even sinking. The most effective method for mousse emulsions is physical removal. Mousse contains roughly 80% water, so after a 40 to 50% loss of light-ends through evaporation, a spill of 200,000 barrels oil can form 400,000 to 500,000 barrels of mousse.

6.7.2 Containment and Physical Removal

Booms. When oil is spilled on water, floating booms may be used for containment. A typical boom extends 4 inches (10 cm.) above the surface and 1 foot (30 cm.) below. Foam-filled booms are lightweight, flexible, and relatively inexpensive. Typically used for inland and sheltered waters, they are made from polyvinyl chloride (PVC) or polyurethane. Rectangular floats allow them to be wound onto a reel for storage.

Inflatable booms use less storage space and can be deployed from ships or boats in open water. Towed booms (*Figure 3*) are good for preventing dispersion of oil by winds and currents.

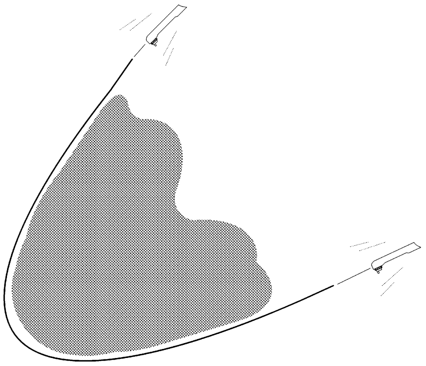

Figure 3. Boom barrier towed by ships

Beach booms are modified for use in shallow water or tidal areas. Water-filled tubes on the bottom of the boom elevate it above the beach when the water level is low and allow the boom to float when the water level rises.

Skimmers and pumps. After a spill is contained, skimmers and pumps can pick up the oil and move it into storage tanks. Weir skimmers are widely used because they are so simple. Modern designs are self-adjusting and circular so that oil can flow into the skimmer from any direction. They can be fitted with screw pumps, which enable them to process many different types of oil, including highly viscous grades. Cutting knives keep seaweed and trash from fouling the pumps. Screw pumps can develop high pressure differentials, which gives them higher capacities than other kinds of pumps.

Another kind of skimmer is an oleophilic ("oil loving") endless belt. The belt picks up oil as it passes across the top of the water. As of the belt returns to its starting point, it is squeezed through a wringer. Oil recovered by the wringer flows into containers, where it is stored until it can be moved to a land-based processing facility.

Another method uses a subsurface impeller to create a vortex, similar to the vortex that forms as water flows out of a bathtub. (Figure 4.) This funnels water down through the impeller and creates a bowl of oil in the middle of the vortex. A pump is used to remove oil from the bowl.

6.7.3 Adsorbents

Oil spills can be treated with absorbing substances or chemicals such as gelling agents, emulsifiers, and dispersants.

When applying adsorbents, it is important to spread them evenly across the oil and to give them enough time to work. When possible, innocuous substances should be used. Straw is cheap, and it can absorb between 8 and 30 times its own weight in oil. When it is saturated, the straw is loaded into boats with rakes or a conveyor system and transported to land. Oil can be recovered from the straw by passing it through a wringer.

Synthetic substances may also be used adsorbing oil spills. Polymers such as polypropylene, polystyrene, and polyurethane have been used successfully. Polyurethane foam is especially good. It can be synthesized onsite easily, even aboard a ship. It adsorbs oil readily and doesn't release its load unless it is squeezed. Best of all, a batch of polyurethane can be used again and again.

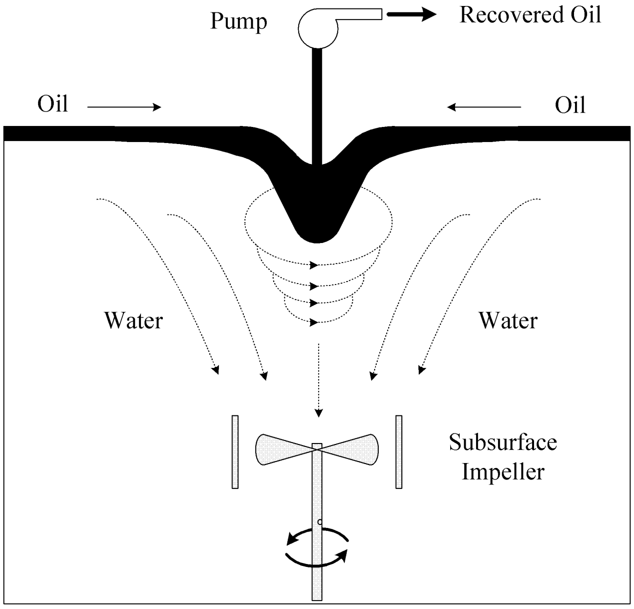

Figure 4. Free vortex skimmer for oil recovery

6.7.4 Dispersion Agents

Dispersion chemicals act like detergents. One part of the molecule is oil-soluble while the other is water-soluble. In effect, the oil dissolves in water and diffuses quickly away from the spill. Dispersants reduce the tendency of oil to cling to partly immersed solids, such as walls, docks, buoys and boats.

6.7.5 Non-dispersive Methods

Non-dispersive methods for removing oil spills include gelling, sinking, and burning.

Gelling. Fatty acids and 50% sodium hydroxide can be added to a spill to trigger a soap-forming reaction. The resulting gel does not disperse. Instead, it remains in place to block the spread of non-gelled oil.

Oil sinking. Sinking an oil spill keeps it from reaching shorelines, where it can devastate marine life. Sinking is best used in the open sea. In shallow water near the coast, it can cause more problems than it solves. Amine-treated sand is the most common sinking agent. To initiate sinking, a sand/water slurry is sprayed onto the oil slick through nozzles. The required sand/oil ratio is about 1-to-1. The oil sticks to the treated sand, which sinks toward the bottom of the sea. According to many experts, the oil-coated sand remains in place for many years. According to others, it can damage fragile ecosystems on the ocean floor.

During a full-scale test 15 miles from the coast of Holland, Shell Oil used amine-treated sand to sink a 100-ton slick of Kuwaiti crude in less than 45 minutes. Oil removal exceeded 95%.

Other materials have been used for oil sinking. These include talc, coal dust, cyclone-treated fly ash, sulfur-treated cement, and chalk. In general, a 1-to-1 ratio of sinker weight to oil weight is needed to sink a fresh spill. If weathering takes place, the density of the oil increases and less sinking agent is needed. It has been estimated that the cost for sinking is similar to the cost for dispersion. However, in open seas under high winds and waves, it may be difficult to spread the sinking agent.

Burning. Freshly spilled crude oil in a confined area may be combustible. However, after several hours, the spill may have thinned due to spreading and the most volatile components may have evaporated. If so, it may not be possible to ignite the remaining material. The addition of gasoline or kerosene can restore combustibility.

Burning is not used much anymore. It seldom removes much oil, and it can generate concentrated, unpredictable pockets of atmospheric CO and SO_2, both of which are poisonous.

6.7.6 Cleanup of Oil Contaminated Beaches

For cleaning oil from beaches, farm machinery and earthmoving equipment have been used to good effect. In many cases, a layer of straw is spread across the oil. After a few days, the oil-laden straw is raked onto a conveyor, screened to drop out sand, and sent to wringer. Recovered oil is trucked away to a refinery. The spent straw, which still contains some oil, can be blended with coal and burned in a power plant, or simply incinerated. The separated sand is washed and returned to the beach.

When beach pollution is severe, oily sand is removed with earthmoving equipment. When beach pollution is mild, sand removal may not be needed. Instead, detergents can be used. They must be used cautiously to minimize harm to marine life. Wave action does a great job of mixing detergent into the sand. Usually, the detergent is applied about one hour before high tide. When the tide comes in, the washing begins. If high-tide washing is inappropriate, high-pressure hoses can be used. Hoses are also effective for cleaning oil off of walls and rocks.

Froth flotation. In the froth-flotation process, oil-soaked sand from a polluted beach is poured into a vessel, where it is mixed with water and cleaned with a froth of air bubbles. Aided by chemical or physical pre-treatment, the froth strips oil away from the sand. Due to its low density and the action of the bubbles, the oil floats to the top of the vessel, where it is drawn off and sent to a separating chamber, where entrained water is removed. Tests show that sand containing 5,000 ppm of oil can be cleaned down to 130 ppm, generating effluent water with 165 ppm of oil. Usually, the cleaned sand is returned directly to the beach.

Hot water cleanup. When milder methods fail to give the desired degree of cleanup, hot water can mobilize some of the oil still trapped within the polluted sand. This method is used as a last resort because of the damage it does to inter-tidal ecosystems.

6.7.7 Amoco Cadiz Oil Spill Cleanup: A Case Study

As mentioned, for two weeks after the *Amoco Cadiz* ran aground off the coast of Brittany, severe weather restricted cleanup efforts. Eventually, the entire cargo – more than 1.6 million barrels of crude oil – spilled into the sea. The resulting slick was 18 miles wide and 80 miles long. The oil polluted 200 miles of coastline, including beaches, harbors and habitats for marine life.

A 2.5 mile permanent boom protected the Bay of Morlaix. Although it required constant monitoring, the boom functioned well because the bay was protected from severe weather and the brunt of the oil slick. In other areas, booms were largely ineffective due to strong currents, and also because they were not designed to handle such enormous amounts of oil. Skimmers were used in harbors and other protected areas. Vacuum trucks removed oil from piers and boat slips where seaweed was especially thick. “Honey wagons” – vacuum tanks designed to handle liquefied manure – were used to collect emulsified oil along the coast.

Oil-laden seaweed was removed from the beaches with rakes and front-end loaders. Farm equipment was used to plow and harrow the sand, making it more susceptible to wave and bacterial action. Prior to harrowing, chemical fertilizers and oleophilic bacteria were applied to the sand.

At first, authorities decided against using dispersants in sensitive areas and along the coastal fringe. Meanwhile, the spill formed a highly stable water-in-oil emulsion (“chocolate mousse”). On the open sea, the French Navy applied both dilute and concentrated dispersants, but good dispersion was hard to achieve because in some places the mousse emulsion was several centimeters thick. If dispersants been dropped from the air at the source of the spill – in days instead of weeks – the formation of mousse emulsion might have been prevented.

About 650 metric tons of chalk was applied in an effort to sink the oil. But after one month at sea, the oil was so viscous that the chalk just sat of top of it. Rubber powder made from ground-up tires was applied absorb the oil absorption. The French Navy used water hoses to spread most of the powder. Some was applied manually from small fishing boats. Because it stayed on top of the oil, the rubber powder had little effect; wave action wasn’t strong enough to mix it into the oil, most of which was trapped inside the chocolate mousse emulsion.

During the third and fourth months of the cleanup, high-pressure hot water (fresh water at 2,000 psi, 80º - 140ºC) was very effective in cleaning oil from rocky shores. A small amount of dispersant was applied to prevent oiling of clean rocks during the next high tide. The mouths of several rivers contained oyster beds and marshes that required manual cleaning. Soft mud river banks were cleaned with low-pressure water. To improve oil-collection efficiency, a sorbent was mixed with water and poured in front of the wash nozzles. The oil was collected downstream by a local invention called an "Egmolap." This device was good at collecting floating material in sheltered areas.

6.8 Solid Waste Recovery and Disposal

Contaminated solids are produced during the drilling of oil wells, the transportation of crude oil, and in oil refineries. All oil-contaminated solids are considered hazardous and must be sent to hazardous-waste landfills. The transportation and disposal of hazardous waste costs an order of magnitude more that the transportation and disposal of sanitary waste. Thus, there is a huge economic incentive to remove oil from contaminated solids before they leave a site.

Table 12 shows the sources of solid wastes in a modern oil refinery. These data, provided by the American Petroleum Institute, are based on a "typical" 200,000 barrels-per-day high-conversion refinery. A plant this size produces about 50,000 tons per year of solid waste and about 250,000 tons per year of waste water. As discussed above, all waste water must be purified before it leaves the plant.

Table 12. Breakdown of Refinery Solid Wastes

Solid Waste	Percent of Total (wt%)
Pond sediments	8.4
Sludge from biological treatment	18.9
Solid from DAF/IAF treaters	15.4
API separator sludge	13.2
Miscellaneous sludge	17.5
Off-grade coke	1.9
Spent catalysts	6.4
Slop oil emulsion solids	4.4
Spent solvents, chemicals	3.8
Contaminated soils and other solids	6.7
Heat exchanger cleaning sludge	0.1
Tank sludge	3.4

DAF = dissolved air flotation
IAF = induced air flotation

6.8.1 Super-critical Fluid Extraction

A supercritical substance exists as a single fluid phase. Simultaneously, it can have liquid-like solvating powers and gas-like diffusivity and viscosity; its surface tension is zero. Ammonia, argon, propane, xenon, water, CO and CO_2 are used for supercritical extraction. The phase diagram in *Figure 5* shows that the super-critical region for CO_2 lies above 88°F (31°C) and 1058 psig (7.4 MPa). The CO_2 triple point, where solid, liquid and gas phases exist simultaneously, occurs at -69.9°F (-56.6°C) and 57.8 psig (0.5 MPa).

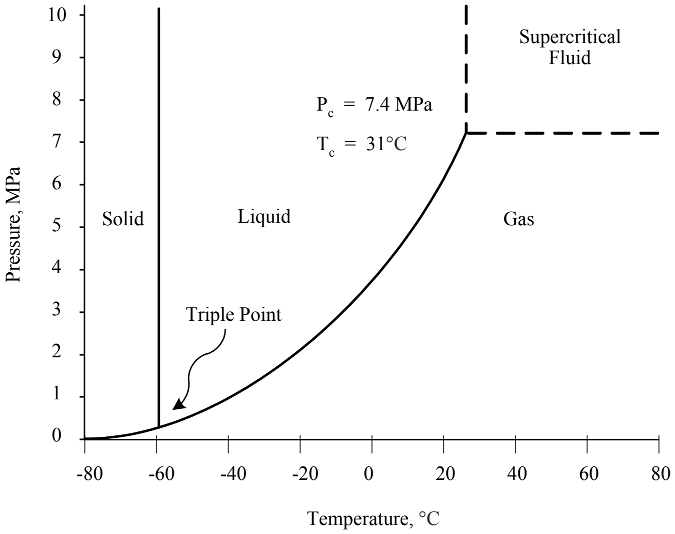

Figure 5. Phase diagram for carbon dioxide.

With non-toxic gases such as CO_2, the SFE process is simple. Untreated solids are placed in an extraction chamber and CO_2 is added. Pressurizing the CO_2 converts it into an effective solvent. By manipulating temperature and pressure, operators can extract the material of interest with high selectivity. After the extracted material dissolves in the CO_2, it goes to a collection vessel, where the pressure is reduced. At low pressure, CO_2 loses its solvating power and separates from the extract. The CO_2 is recovered, condensed and recycled. In SFE with CO_2, no liquid solvents are used. The CO_2 is recycled, so the process is not considered to be a contributor to global warming.

SFE is common in the food, pharmaceutical and cosmetic industries, where it extracts caffeine from coffee beans, bitter from hops, tar and nicotine from tobacco, and other natural compounds from spices, flowers, aromatic woods, and medicinal plants.

Since about 1990, SFE with CO_2 has been used in oil fields to remove oil from drill cuttings. CO_2 is especially good for this purpose because it can be used onsite. It is non-toxic (except when it suffocates), relatively unreactive, and it doesn't burn. On drill cuttings and other oil-contaminated soils and sands, it penetrates the mineral structure, removing both the free-oil phase and the oil trapped in the solid matrix. The process removes more than 99.9% of the oil, leaving no toxic residue. The required time is short – about 10 to 60 minutes per batch.

6.8.2 Sludge

According to RCRA, oil-containing sludge from storage tanks and refinery water treatment facilities is by definition hazardous, and should be sent to a hazardous land fill. In most cases, a lot of the sludge can be dissolved with detergents and/or or solvents (such as hot diesel oil) and blended into crude oil. Alternatively, dissolved sludge can go to delayed cokers, asphalt plants, carbon black plants, or cement kilns.

In one method, hot water and a chemical are circulated through the tank. On top of the water, a hydrocarbon such as diesel is added. The density difference between warm water and the hydrocarbons in the sludge causes the sludge to rise, allowing the chemical to strip out water and solids. The method recovers good-quality oil, which can be processed in the refinery, and leaves behinds a relatively clean layer of solids on the tank bottom.

Tanks associated with slurry oil from FCC units present an interesting challenge. It can be very expensive to take these tanks out of service, the sludge is loaded with finely divided FCC catalyst particles, and slurry-oil sludge is difficult to dissolve. Recently, a process called Petromax has been used to liquefy slurry-oil sludge, allowing it to be pumped out of tanks with ordinary equipment, even while the tanks are still in use.[28]

Some service companies use robots, cutting wands, and other sophisticated devices to clean tanks completely without sending people inside. These methods are especially valuable when the tank contents are toxic. One such company is Petrochemical Services, Inc., which pioneered the use of robots in tank-cleaning operations.

Blending mobilized sludge into crude oil is limited by specifications on basic sediment and water (BS&W). This seems equivalent to moving waste from one place to another, but it really isn't. The dissolution of tank sludge separates useful oil from inorganic solids (sand, clay, salts, and metal oxides) and refractory organics (asphaltenes, long-chain waxy paraffins, kerogen, and coke).

6.8.3 Spent Catalysts

Many refinery catalysts are regenerated several times. The regeneration of FCC catalysts occurs in the (aptly named) regenerator. Catalysts from fixed-bed units can be regenerated in place, but usually they are sent off-site to a facility that specializes in catalyst regeneration.

Eventually, even the hardiest catalysts reach the end of their useful life. When this happens, they are sent to a metals reclaimer, which recovers saleable products such as alumina, silica, MoO_3, V_2O_5, nickel metal, and various forms of cobalt.

The reclamation company makes money on both ends of the plant – from the refiner who must dispose of the catalyst, and from the customer who buys reclaimed products.

7. FICTION VS. FACT

In today's popular culture, Big Oil is a convenient villain. Catastrophic oil spills, tragic explosions, and price fluctuations capture front-page headlines, stimulate editorials, and spark conspiracy-theory discussions on talk radio and television news. *On Deadly Ground (1994)* is one of the latest in a succession of action films that portray oil executives as ruthless sociopaths.

This is understandable. The petroleum industry is far from blameless. Its early history was dominated by nature-despoiling oil booms and greedy oil barons. Its recent history is punctuated by ecological disasters.

But our personal experience differs from popular culture. Between us, we have been employed by three different oil companies, and we have provided services to scores of others. Without exception, the people we deal with – from managers and engineers to operators, and office workers – rank safety and environmental compliance as their top two work-place priorities.

Things used to be different. Before the 1970s, "miners' asthma," dead forests downwind from coal-fired power plants, and pools of poison around abandoned strip mines were just part of the price we paid for cheap power and minerals. In some locales, smoky flares in refineries were the rule, not the exception. More often than not, news of a river catching fire caused laughter instead of outrage.

In contrast, today we believe that our fundamental rights include clean air, clean water, and a healthy workplace. We are products of the same social movement that created the United States Environmental Protection Agency (EPA), the Occupational Safety and Health Administration (OSHA), and similar agencies around the world. We were part of that movement, as were many of the people who now work for Big Oil. Governments are providing the "stick" – steep fines and possible jail time for corporate executives – but the "carrot" comes from a basic change in our fundamental values.

We may never see a movie in which an oil executive saves the day. But someday, perhaps, public perception will catch up with the following reality: Accidents may happen and mistakes might be made, but their impact and frequency are minimized by the bright, devoted people who work in today's refineries. While providing us with clean fuels and basic chemicals, they do their level best to protect the world from pollution, making it a better place for all of us and our children.

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