INTRODUCTION

The last decade has brought about a significant change in industry attitude and practices in the handling of wastes and pollution. The concept of environmental management systems, personified by ISO 14001, the chemical industry’s Responsible Care program, and Western Europe’s EMAS, have raised the awareness and level of responsibility of industry to act in a more responsible manner that protects the public and preserves the environment. Despite this awareness, industry sectors continue to struggle innocently and in some cases act irresponsibly in their handling of waste and pollution issues.

This chapter provides an overview of industry practices in different heavy manufacturing sectors. The conventional waste handling practices, along with some of the pollution prevention strategies that are being implemented more frequently today, are covered.

THE CHEMICAL INDUSTRY

The U.S. chemicals and allied products industry consists of some 9125 multinational corporations whose primary business is the development, manufacturing, and marketing of industrial chemicals, pharmaceuticals, and other chemical products. The U.S. chemical industry is vital to the U.S. economy. It produces 1.9 percent of U.S. gross domestic product (GDP). It is the nation’s number one exporter. It supplies more than $1 out of every $10 of U.S. exports and consistently runs large international trade surpluses. It is a high-tech, research and development (R&D) oriented industry that is awarded about one out of every eight U.S. patents. It employs more than 1 million persons and it produces more than 70,000 different products. Most importantly, chemicals is a "keystone" industry -- one critical to the global competitiveness of other U.S. industries. Because so many modern products and businesses depend on chemicals, the international competitiveness of other U.S. industries requires a high-tech, globally competitive U.S. chemical industry that can supply new products at prices that give U.S. producers an edge.
Chemicals in many ways can be described as the foundation of a modern, progressive society. They are an integral and ever-increasing part of our complex technological world, making it possible for us to enjoy a high standard of living. Not only do pollution prevention (P2) practices in the chemical process industries (CPI) offer reduced costs in manufacturing operations, but they are essential in developing more efficient and safe means of manufacturing many of the chemical products we have grown to depend on.

PETROCHEMICAL MANUFACTURING PRACTICES

Natural gas and crude distillates such as naphtha from petroleum refining are used as feedstocks to manufacture a wide range of petrochemicals that are in turn used in the manufacture of consumer goods. Basic petrochemicals are manufactured by cracking, reforming, and other processes, and include olefins (such as ethylene, propylene, butylenes, and butadiene) and aromatics (such as benzene, toluene, and xylenes). The capacity of naphtha crackers is generally of the order of 250,000 to 750,000 metric tons per year (tpy) of ethylene production. Some petrochemical plants also have alcohol and oxo-compound manufacturing units on site. The base petrochemicals or products derived from them, along with other raw materials, are converted to a wide range of products. Among them are:

- Resins and plastics such as low-density polyethylene (LDPE), high-density polyethylene (HDPE), linear low-density polyethylene (LLDPE), polypropylene, polystyrene, and polyvinyl chloride (PVC);
- Synthetic fibers such as polyester and acrylic engineering polymers such as acrylonitrile butadiene styrene (ABS);
- Rubbers, including styrene butadiene rubber (SBR) and polybutadiene rubber (PBR);
- Solvents;

Industrial chemicals, including those used for the manufacture of detergents such as linear alkyl benzene (LAB) and of coatings, dyestuffs, agrochemicals, pharmaceuticals, and explosives.

Chemical compounds manufactured at petrochemical plants include methanol, formaldehyde, and halogenated hydrocarbons. Formaldehyde is used in the manufacture of plastic resins, including phenolic, urea, and melamine resins. Halogenated hydrocarbons are used in the manufacture of silicone, solvents, refrigerants, and degreasing agents.
Olefins (organics having at least one double bond for carbon atoms) are typically manufactured from the steam cracking of hydrocarbons such as naphtha. Major olefins manufactured include ethylene, propylene, butadiene, and acetylene. The olefins manufactured are used in the manufacture of polyethylene, including low-density polyethylene (LDPE) and high-density polyethylene (HDPE), and for polystyrene, polyvinyl chloride, ethylene glycol (used along with dimethyl terephthalate, DMT, as feedstock to the polyester manufacturing process), ethanol amines (used as solvents), polyvinyl acetate (used in plastics), polyisoprene (used for synthetic rubber manufacture), polypropylene, acetone (used as a solvent and in cosmetics), isopropanol (used as a solvent and in pharmaceuticals manufacturing), acrylonitrile (used in the manufacture of acrylic fibers and nitrile rubber), propylene glycol (used in pharmaceuticals manufacturing), and polyurethane. Butadiene is used in the manufacture of polybutadiene rubber (PBR) and styrene butadiene rubber (SBR). Other C\textsubscript{4} compounds manufactured include butanol, which is used in the manufacture of solvents such as methyl ethyl ketone.

The major aromatics (organics having at least one ring structure with six carbon atoms) manufactured include benzene, toluene, xylene, and naphthalene. Other aromatics manufactured include phenol, chlorobenzene, styrene, phthalic and maleic anhydride, nitrobenzene, and aniline. Benzene is generally recovered from cracker streams at petrochemical plants and is used for the manufacture of phenol, styrene, aniline, nitrobenzene, sulfonated detergents, pesticides such as hexachlorobenzene, cyclohexane (an important intermediate in synthetic fiber manufacture), and caprolactam, used in the manufacture of nylon. Benzene is also used as a solvent.

The main uses of toluene are as a solvent in paints, rubber, and plastic cements and as a feedstock in the manufacture of organic chemicals, explosives, detergents, and polyurethane foams. Xylenes (which exist as three isomers) are used in the manufacture of DMT, alkyd resins, and plasticizers. Naphthalene is mainly used in the manufacture of dyes, pharmaceuticals, insect repellents, and phthalic anhydride (used in the manufacture of alkyd resins, plasticizers, and polyester).

The largest user of phenol in the form of thermosetting resins is the plastics industry. Phenol is also used as a solvent and in the manufacture of intermediates for pesticides, pharmaceuticals, and dyestuffs. Styrene is used in the manufacture of synthetic rubber and polystyrene resins. Phthalic anhydride is used in the manufacture of DMT, alkyd resins, and plasticizers such as phthalates. Maleic anhydride is used in the manufacture of polyesters and, to some extent, for alkyd resins. Minor uses include the manufacture of malathion and soil conditioners. Nitrobenzene is used in the manufacture of aniline, benzidine, and dyestuffs and
as a solvent in polishes. Aniline is used in the manufacture of dyes, including azo dyes, and rubber chemicals such as vulcanization accelerators and antioxidants.

**SOLID WASTES**

Petrochemical plants generate significant amounts of solid wastes and sludges, some of which are hazardous because of the presence of toxic organics and heavy metals. Spent caustic and other hazardous wastes may be generated in significant quantities; examples are distillation residues associated with units handling acetaldehyde, acetonitrile, benzyl chloride, carbon tetrachloride, cumene, phthalic anhydride, nitrobenzene, methyl ethyl pyridine, toluene diisocyanate, trichloroethane, trichloroethylene, perchloroethylene, aniline, chlorobenzenes, dimethyl hydrazine, ethylene dibromide, toluenediamine, epichlorohydrin, ethyl chloride, ethylene dichloride, and vinyl chloride.

Petrochemical plants are typically large and complex, and the combination and sequence of products manufactured are often unique to the plant. Specific pollution prevention practices or source reduction measures are best determined by a dedicated technical staff. However, there are a number of broad areas where improvements are often possible, and site-specific emission reduction measures in these areas should be designed into the plant and targeted by plant management. A good practice target for a petrochemical complex is to reduce total organic emissions (including VOCs) from the process units to 0.6% of the throughput. Target maximum levels for air releases, per ton of product, are, for ethylene, 0.06 kg; for ethylene oxide, 0.02 kg; for vinyl chloride, 0.2 kg; and for 1,2-dichloroethane, 0.4 kg. Control of air emissions normally includes the capturing and recycling or combustion of emissions from vents, product transfer points, storage tanks, and other handling equipment. Catalytic cracking units should be provided with particulate removal devices. Particulate removal technologies include fabric filters, ceramic filters, wet scrubbers, and electrostatic precipitators. Gaseous releases are minimized by condensation, absorption, adsorption (using activated carbon, silica gel, activated alumina, and zeolites), and, in some cases, biofiltration and bioscrubbing (using peat or heather, bark, composts, and bioflora to treat biodegradable organics), and thermal decomposition.

Petrochemical waste waters often require a combination of treatment methods to remove oil and other contaminants before discharge. Separation of different streams (such as stormwater) is essential to minimize treatment requirements. Oil is recovered using separation techniques. For heavy metals, a combination of oxidation/reduction, precipitation, and filtration is used. For organics, a combination of air or steam stripping, granular activated carbon, wet oxidation, ion exchange, reverse osmosis, and electrodialysis is used. A typical system may
include neutralization, coagulation/flocculation, flotation/sedimentation/filtration, biodegradation (trickling filter, anaerobic, aerated lagoon, rotating biological contactor, and activated sludge), and clarification. A final polishing step using filtration, ozonation, activated carbon, or chemical treatment may also be required. Examples of pollutant loads that can be achieved are COD, less than 1 kg per 100 tons of ethylene produced; suspended solids, less than 0.4 kg/100 t; and dichloroethane less than 0.001 kg/100 t.

For solid and hazardous wastes, combustion (preceded in some cases by solvent extraction) of toxic organics is considered an effective treatment technology for petrochemical organic wastes. Steam stripping and oxidation are also used for treating organic waste streams. Spent catalysts are generally sent back to the suppliers. In some cases, the solid wastes may require stabilization to reduce the leachability of toxic metals before disposal of in an approved, secure landfill.

The generation of sludges should be minimized. Sludges must be treated to reduce toxic organics to nondetectable levels. Wastes containing toxic metals should be stabilized before disposal.

CHLOR-ALKALI PLANTS

There are three basic processes for the manufacture of chlorine and caustic soda from brine: the mercury cell, the diaphragm cell, and the membrane cell. Among these technologies, the membrane cell is the most modern and has both economic and environmental advantages. The other two processes generate hazardous wastes containing mercury or asbestos. Mercury cell technology is being phased out in worldwide production.

In the membrane process, the chlorine (at the anode) and the hydrogen (at the cathode) are kept apart by a selective polymer membrane that allows the sodium ions to pass into the cathodic compartment and react with the hydroxyl ions to form caustic soda. The depleted brine is dechlorinated and recycled to the input stage. As noted already, the membrane cell process is the preferred process for new plants. Diaphragm processes may be acceptable, in some circumstances, but only if nonasbestos diaphragms are used. The energy consumption in a membrane cell process is of the order of 2200 to 2500 kilowatt-hours per metric ton (kWh/t), as compared with 2400 to 2700 kWh/t of chlorine for a diaphragm cell process.

The major waste stream from the process consists of brine muds - the sludges from the brine purification step. The sludge is likely to contain magnesium, calcium, iron, and other metal hydroxides, depending on the source and purity of the brines. The muds are normally filtered or settled, the supernatant is recycled,
and the mud is dried and then landfilled. Chlorine is a highly toxic gas, and strict precautions are necessary to minimize risk to workers and possible releases during its handling. Major sources of fugitive air emissions of chlorine and hydrogen are vents, seals, and transfer operations. Acid and caustic waste waters are generated in both the process and the materials recovery stages of the operation. The following pollution prevention measures should be considered in plant operations:

- Use metal rather than graphite anodes to reduce lead and chlorinated organic matter.
- Resaturate brine in closed vessels to reduce the generation of salt sprays.
- Use noncontact condensers to reduce the amount of process wastewater.
- Scrub chlorine tail gases to reduce chlorine discharges and to produce hypochlorite.
- Recycle condensates and waste process water to the brine system.
- Recycle brine wastes, if possible.

For the chlor-alkali industry, an emergency preparedness and response plan is mandatory for potential uncontrolled chlorine and other releases. Carbon tetrachloride is sometimes used to scrub nitrogen trichloride (formed in the process) and to maintain its levels below 4% to avoid fire and explosion. Substitutes for carbon tetrachloride may have to be used, as the use of carbon tetrachloride may be banned in the near future because of its carcinogenicity. Implementation of cleaner production processes and pollution prevention measures can yield both economic and environmental benefits. The primary treatment technologies afforded to this manufacturing include the following: Caustic scrubber systems should be installed to control chlorine emissions from condensers and at storage and transfer points for liquid chlorine. Sulfuric acid used for drying chlorine should be neutralized before discharge. Brine muds should be discharged to lined settling ponds (or the equivalent) to prevent contamination of soil and groundwater. Effluents should be controlled for pH by neutralization. Settling and filtration are performed to control total suspended solids. Dechlorination of waste waters is performed using sulfur dioxide or bisulfite.

Daily monitoring for parameters other than pH (for effluents from the diaphragm process) is recommended. The pH in the liquid effluent should be monitored continuously. Chlorine monitors should be strategically located within the plant to detect chlorine releases or leaks on a continuous basis. Monitoring data should be analyzed and reviewed at regular intervals and compared with the operating standards so that any necessary corrective actions can be taken. Records of monitoring results should be kept in an acceptable format. The results should be reported to the responsible authorities and relevant parties, as required.
Preference should be given to the membrane process because it is less polluting characteristics over other technologies. In addition, the following pollution prevention measures should be considered for use with the membrane technology:

- Use metal instead of graphite anodes
- Resaturate brine in closed vessels
- Recycle brine wastes
- Scrub chlorine from tail gases to produce hypochlorite
- Provide lined settling ponds for brine muds

AGRO-INDUSTRY CHEMICALS

Mixed fertilizers contain two or more of the elements nitrogen, phosphorus, and potassium (NPK), which are essential for good plant growth and high crop yields. This subsection briefly addresses the production of ammonium phosphates (monoammonium phosphate, or MAP, and diammonium phosphate, or DAP), nitrophosphates, potash, and compound fertilizers.

Ammonium phosphates are produced by mixing phosphoric acid and anhydrous ammonia in a reactor to produce a slurry. This is referred to as the mixed acid route for producing NPK fertilizers; potassium and other salts are added during the process. The slurry is sprayed onto a bed of recycled solids in a rotating granulator, and ammonia is sparged into the bed from underneath. Granules pass to a rotary dryer followed by a rotary cooler. Solids are screened and sent to storage for bagging or for bulk shipment.

Nitrophosphate fertilizer is made by digesting phosphate rock with nitric acid. This is the nitrophosphate route leading to NPK fertilizers; as in the mixed-acid route, potassium and other salts are added during the process. The resulting solution is cooled to precipitate calcium nitrate, which is removed by filtration methods. The filtrate is neutralized with ammonia, and the solution is evaporated to reduce the water content. The process of prilling may follow. The calcium nitrate filter cake can be further treated to produce a calcium nitrate fertilizer, pure calcium nitrate, or ammonium nitrate and calcium carbonate. Nitrophosphate fertilizers are also produced by the mixed-acid process, through digestion of the phosphate rock by a mixture of nitric and phosphoric acids.

Potash (potassium carbonate) and sylvine (potassium chloride) are solution-mined from deposits and are refined through crystallization processes to produce fertilizer. Potash may also be dry-mined and purified by flotation.
Compound fertilizers can be made by blending basic fertilizers such as ammonium nitrate, MAP, DAP, and granular potash; this route may involve a granulation process.

The principal pollutants from the production of MAP and DAP are ammonia and fluorides, which are given off in the steam from the reaction. Fluorides and dust are released from materials-handling operations. Ammonia in uncontrolled air emissions has been reported to range from 0.1 to 7.8 kilograms of nitrogen per metric ton (kg/t) of product, with phosphorus ranging from 0.02 to 2.5 kg/t product (as phosphorous pentoxide, P$_2$O$_5$).

In nitrophosphate production, dust will also contain fluorides. Nitrogen oxides NO$_x$ are given off at the digester. In the evaporation stage, fluorine compounds and ammonia are released. Unabated emissions for nitrogen oxides from selected processes are less than 1000 milligrams per cubic meter (mg/m$^3$) from digestion of phosphate rock with nitric acid, 50-200 (mg/m$^3$) from neutralization with ammonia, and 30-200 mg/m$^3$ from granulation and drying. Dust is the primary air pollutant from potash manufacturing.

The volumes of liquid effluents from mixed fertilizer plants are reported to range from 1.4 to 50 cubic meters per metric ton (m$^3$/t) of product. Where water is used in scrubbers, the scrubbing liquors can usually be returned to the process. Effluents can contain nitrogen, phosphorus, and fluorine; the respective ranges of concentrations can be 0.7-15.7 kg/t of product (as N), 0.1-7.8 kg/t of product (as P$_2$O$_5$), and 0.1-3.2 kg/t of product.

Generally, there is little solid waste from a fertilizer plant, since dust and fertilizer spillage can be returned to the process. However, wastewater treatment operations will create toxic sludges that ultimately must be disposed of.

Materials handling and milling of phosphate rock should be carried out in closed buildings. Fugitive emissions can be controlled by, for example, hoods on conveying equipment, with capture of the dust in fabric filters. In the ammonium phosphate plant, the gas streams from the reactor, granulator, dryer, and cooler should be passed through cyclones and scrubbers, using phosphoric acid as the scrubbing liquid, to recover particulates, ammonia, and other materials for recycling. In the nitrophosphate plant, nitrogen oxide (NO$_x$) emissions should be avoided by adding urea to the digestion stage. Fluoride emissions should be prevented by scrubbing the gases with water. Ammonia should be removed by scrubbing. Phosphoric acid may be used for scrubbing where the ammonia load is high. The process water system should be balanced, if necessary, by the use of holding tanks to avoid the discharge of an effluent.
Additional pollution control devices beyond the scrubbers, cyclones, and baghouses that are an integral part of the plant design and operations are generally not required for mixed fertilizer plants. Good housekeeping practices are essential to minimize the amount of spilled material. Spills or leaks of solids and liquids should be returned to the process. Liquid effluents, if any, need to be controlled for TSS, fluorides, phosphorus, and ammonia. An effluent discharge of less than 1.5 m³/t product as P₂O₅ is realistic, but use of holding ponds makes feasible a discharge approaching zero. In many countries outside of the United States, wastewater treatment discharges are often used for agricultural purposes and may contain heavy metals. Of particular concern is the cadmium content.

NITROGENOUS FERTILIZER PLANTS

An important class of fertilizers is based on the production of ammonia, urea, ammonium sulfate, ammonium nitrate (AN), calcium ammonium nitrate (CAN), and ammonium sulfate nitrate (ASN). The manufacture of nitric acid used to produce nitrogenous fertilizers typically occurs on site and is therefore included here. Ammonia (NH₃) is produced from atmospheric nitrogen and hydrogen from a hydrocarbon source. Natural gas is the most commonly used hydrocarbon feedstock for new plants; other feedstocks that have been used include naphtha, oil, and gasified coal. Natural gas is favored over the other feedstocks from an environmental perspective.

Ammonia production from natural gas includes the following processes: desulfurization of the feedstock; primary and secondary reforming; carbon monoxide shift conversion and removal of carbon dioxide, which can be used for urea manufacture; methanation; and ammonia synthesis. Catalysts used in the process may include cobalt, molybdenum, nickel, iron oxide/chromium oxide, copper oxide/zinc oxide, and iron.

Urea fertilizers are produced by a reaction of liquid ammonia with carbon dioxide. The process steps include solution synthesis, where ammonia and carbon dioxide react to form ammonium carbamate, which is dehydrated to form urea; solution concentration by vacuum, crystallization, or evaporation to produce a melt; formation of solids by prilling (pelletizing liquid droplets) or granulating; cooling and screening of solids; coating of the solids; and bagging or bulk loading. The carbon dioxide for urea manufacture is produced as a by-product from the ammonia plant reformer.

Ammonium sulfate is produced as a caprolactam by-product from the petrochemical industry, as a coke by-product, and synthetically through reaction of ammonia with sulfuric acid. Only the third process is covered in our discussion. The reaction between ammonia and sulfuric acid produces an
ammonium sulfate solution that is continuously circulated through an evaporator
to thicken the solution and to produce ammonium sulfate crystals. The crystals
are separated from the liquor in a centrifuge, and the liquor is returned to the
evaporator. The crystals are fed either to a fluidized bed or to a rotary drum
dryer and are screened before bagging or bulk loading.

Ammonium nitrate is made by neutralizing nitric acid with anhydrous ammonia.
The resulting 80 to 90% solution of ammonium nitrate can be sold as is, or it
may be further concentrated to a 95 to 99.5% solution (melt) and converted into
prills or granules. The manufacturing steps include solution formation, solution
concentration, solids formation, solids finishing, screening, coating, and bagging
or bulk shipping. The processing steps depend on the desired finished product.
Calcium ammonium nitrate is made by adding ammonia calcite or dolomite to the
ammonium nitrate melt before prilling or granulating. Ammonium sulfate nitrate
is made by granulating a solution of ammonium nitrate and ammonium sulfate.
The production stages for nitric acid manufacture include vaporizing the
ammonia; mixing the vapor with air and burning the mixture over a
platinum/rhodium catalyst; cooling the resultant nitric oxide (NO) and oxidizing
it to nitrogen dioxide (NO₂) with residual oxygen; and absorbing the nitrogen
dioxide in water in an absorption column to produce nitric acid (HNO₃). Because
of the large quantities of ammonia and other hazardous materials handled on site,
an emergency preparedness and response plan is required.

Emissions to the atmosphere from ammonia plants include sulfur dioxide (SO₂),
nitrogen oxides (NOₓ), carbon monoxide (CO), carbon dioxide (CO₂), hydrogen
sulfide (H₂S), volatile organic compounds (VOCs), particulate matter, methane,
hydrogen cyanide, and ammonia. The two primary sources of pollutants, with
typical reported values, in kilograms per ton (kg/t) for the important pollutants,
are as follows:

- Flue gas from primary reformer: CO₂: 500 kg/t NH₃, NOₓ: 0.6-1.3 kg/t NH₃
  as NO₂, SO₂: less than 0.1 kg/t; CO: less than 0.03 kg/t.
- Carbon dioxide removal: CO₂: 1200 kg/t.

Nitrogen oxide emissions depend on the process features. Nitrogen oxides are
reduced, for example, when there is low excess oxygen, with steam injection;
when postcombustion measures are in place; and when low-NOₓ burners are in
use. Other measures will also reduce the total amount of nitrogen oxides emitted.
Concentrations of sulfur dioxide in the flue gas from the reformer can be
expected to be significantly higher if a fuel other than natural gas is used. Energy
consumption ranges from 29 to 36 gigajoules per metric ton (GJ/t) of ammonia.
Process condensate discharged is about 1.5 cubic meters per metric ton (m³/t) of
ammonia. Ammonia tank farms can release upward of 10 kg of ammonia per ton
of ammonia produced. Emissions of ammonia from the process have been
reported in the range of less than 0.04 to 2 kg/t of ammonia produced.
In a urea plant, ammonia and particulate matter are the emissions of concern. Ammonia emissions are reported as recovery absorption vent (0.1 to 0.5 kg/t), concentration absorption vent (0.1 to 0.2 kg/t), urea prilling (0.5 to 2.2 kg/t), and granulation (0.2 to 0.7 kg/t). The prill tower is a source of urea dust (0.5-2.2 kg/t), as is the granulator (0.1 to 0.5 kg/t).

Particulate matter are the principal air pollutant emitted from ammonium sulfate plants. Most of the particulates are found in the gaseous exhaust of the dryers. Uncontrolled discharges of particulates may be of the order of 23 kg/t from rotary dryers and 109 kg/t from fluidized-bed dryers. Ammonia storage tanks can release ammonia, and there may be fugitive losses of ammonia from process equipment.

The production of ammonium nitrate yields emissions of particulate matter (ammonium nitrate and coating materials), ammonia, and nitric acid. The emission sources of primary importance are the prilling tower and the granulator. Total quantities of nitrogen discharged are in the range of 0.01-18.4 kg/t of product. Values reported for calcium ammonium nitrate are in the range of 0.13 to 3 kg nitrogen per ton of product.

Solid wastes are principally spent catalysts that originate in ammonia production and in the nitric acid plant. Other solid wastes are not normally of environmental concern. It is important to note that hot ammonium nitrate, whether in solid or in concentrated form, carries the risk of decomposition and is unstable and may even detonate under certain circumstances. Special precautions are therefore required in its manufacture. Implementation of cleaner production processes and pollution prevention measures can yield both economic and environmental benefits. The following describes production-related targets that can be achieved by measures such as those described above. The numbers relate to the production processes before the addition of pollution control measures.

**PHOSPHATE FERTILIZER PLANTS**

Phosphate fertilizers are produced by adding acid to ground or pulverized phosphate rock. If sulfuric acid is used, single or normal, phosphate (SSP) is produced, with a phosphorus content of 16 to 21% as phosphorous pentoxide (P$_2$O$_5$). If phosphoric acid is used to acidulate the phosphate rock, triple phosphate (TSP) is the result. TSP has a phosphorus content of 43 to 48% as P$_2$O$_5$. 
SSP production involves mixing the sulfuric acid and the rock in a reactor. The reaction mixture is discharged onto a slow-moving conveyor in a den. The mixture is cured for 4 to 6 weeks before bagging and shipping.

Two processes are used to produce TSP fertilizers: run-of-pile and granular. The run-of-pile process is similar to the SSP process. Granular TSP uses lower-strength phosphoric acid (40%, compared with 50% for run-of-pile). The reaction mixture, a slurry, is sprayed onto recycled fertilizer fines in a granulator. Granules grow and are then discharged to a dryer, screened, and sent to storage.

Phosphate fertilizer complexes often have sulfuric and phosphoric acid production facilities. Sulfuric acid is produced by burning molten sulfur in air to produce sulfur dioxide, which is then catalytically converted to sulfur trioxide for absorption in oleum. Sulfur dioxide can also be produced by roasting pyrite ore. Phosphoric acid is manufactured by adding sulfuric acid to phosphate rock. The reaction mixture is filtered to remove phosphogypsum, which is discharged to settling ponds or waste heaps.

Fluorides and dust are emitted to the air from the fertilizer plant. All aspects of phosphate rock processing and finished product handling generate dust, from grinders and pulverizers, pneumatic conveyors, and screens. The mixer/reactors and dens produce fumes that contain silicon tetrafluoride and hydrogen fluoride. Liquid effluents are not normally expected from the fertilizer plant, since it is feasible to operate the plant with a balanced process water system. The fertilizer plant should generate minimal solid wastes.

In a fertilizer plant, the main source of potential pollution is solids from spills, operating upsets, and dust emissions. It is essential that tight operating procedures be in place and that close attention be paid to constant cleanup of spills and to other housecleaning measures. Product will be retained, the need for disposal of waste product will be controlled, and potential contamination of stormwater runoff from the property will be minimized. The discharge of sulfur dioxide from sulfuric acid plants should be minimized by using the double-contact, double-absorption process, with high-efficiency mist eliminators. Spills and accidental discharges should be prevented by using well-bounded storage tanks, by installing spill catchment and containment facilities, and by practicing good housekeeping and maintenance. Residues from the roasting of pyrites may be used by the cement and steel manufacturing industries. In the phosphoric acid plant, emissions of fluorine compounds from the digester/reactor should be minimized by using well-designed, well-operated, and well-maintained scrubbers. Design for spill containment is essential for avoiding inadvertent liquid discharges. An operating water balance should be maintained to avoid an effluent discharge.
The management of phosphogypsum tailings is a major problem because of the large volumes and large area required and because of the potential for release of dust and radon gases and of fluorides and cadmium in seepage. The following measures will help to minimize the impacts:

- Maintain a water cover to reduce radon gas release and dust emissions.
- Where water cover cannot be maintained, keep the tailings wet or revegetate to reduce dust. (Note, however, that the revegetation process may increase the rate of radon emissions.)
- Line the tailings storage area to prevent contamination of groundwater by fluoride. Where contamination of groundwater is a concern, a management and monitoring plan should be implemented.
- Phosphogypsum may find a use in the production of gypsum board for the construction industry.

Implementation of cleaner production processes and pollution prevention measures can yield both economic and environmental benefits. The following production-related targets can be achieved by measures such as those described above. The numbers relate to the production processes before the addition of pollution control measures. In sulfuric acid plants that use the double-contact, double-absorption process, emissions levels of 2 to 4 kilograms of sulfur dioxide per metric ton (kg/t) of sulfuric acid can be achieved, and sulfur trioxide levels of the order of 0.15 to 0.2 kg/t of sulfuric acid are attainable. Scrubbers are used to remove fluorides and acid from air emissions. The effluent from the scrubbers is normally recycled to the process.

If it is not possible to maintain an operating water balance in the phosphoric acid plant, treatment to precipitate fluorine, phosphorus, and heavy metals may be necessary. Lime can be used for treatment. Spent vanadium catalyst is returned to the supplier for recovery, or, if that cannot be done, is locked in a solidification matrix and disposed of in a secure landfill. Opportunities to use gypsum wastes as a soil conditioner (for alkali soil and soils that are deficient in sulfur) should be explored to minimize the volume of the gypsum stack.

COKE MANUFACTURING

Coke and coke by-products, including coke oven gas, are produced by the pyrolysis (heating in the absence of air) of suitable grades of coal. The process also includes the processing of coke oven gas to remove tar, ammonia (usually
recovered as ammonium sulfate), phenol, naphthalene, light oil, and sulfur before the gas is used as fuel for heating the ovens. This section provides an overview of the production of metallurgical coke and the associated by-products using intermittent horizontal retorts, as well as the pollution prevention practices.

In the coke-making process, bituminous coal is fed (usually after processing operations to control the size and quality of the feed) into a series of ovens, which are sealed and heated at high temperatures in the absence of oxygen, typically in cycles lasting 14 to 36 hours. Volatile compounds that are driven off the coal are collected and processed to recover combustible gases and other byproducts. The solid carbon remaining in the oven is coke.

The coke is taken to the quench tower, where it is cooled with a water spray or by circulating an inert gas (nitrogen), a process known as dry quenching. The coke is screened and sent to a blast furnace or to storage. Coke oven gas is cooled, and by-products are recovered. Flushing liquor, formed from the cooling of coke oven gas, and liquor from primary coolers contain tar and are sent to a tar decanter. Note that the coke oven gas has a heating value and can be used effectively in cogeneration-type projects.

An electrostatic precipitator is used to remove more tar from coke oven gas. The tar is then sent to storage. Ammonia liquor is also separated from the tar decanter and sent to wastewater treatment after ammonia recovery. Coke oven gas is further cooled in a final cooler. Naphthalene is removed in the separator on the final cooler. Light oil is then removed from the coke oven gas and is fractionated to recover benzene, toluene, and xylene. Some facilities may include an onsite tar distillation unit. The Claus process is normally used to recover sulfur from coke oven gas. During the coke quenching, handling, and screening operation, coke breeze is produced. It is either reused on site (e.g., in the sinter plant) or sold off site as a by-product.

The coke oven is a major source of fugitive air emissions. The coking process emits particulate matter (PM); volatile organic compounds (VOCs); polynuclear aromatic hydrocarbons (PAHs); methane, at approximately 100 grams per metric ton (g/t) of coke; ammonia; carbon monoxide; hydrogen sulfide (50-80 g/t of coke from pushing operations); hydrogen cyanide; and sulfur oxides, SO\textsubscript{x}, (releasing 30% of sulfur in the feed). Significant amount of VOCs may also be released in by-product recovery operations. For every ton of coke produced, approximately 0.7 to 7.4 kilograms (kg) of PM, 2.9 kg of SO\textsubscript{x}, (ranging from 0.2 to 6.5 kg), 1.4 kg of nitrogen oxides NO\textsubscript{x}, 0.1 kg of ammonia, and 3 kg of VOCs (including 2 kg of benzene) may be released into the atmosphere if there is no vapor recovery system. Coal-handling operations may account for about 10% of the particulate load. Coal charging, coke pushing, and quenching are major sources of dust emissions.
Wastewater is generated at an average rate ranging from 0.3 to 4 cubic meters (m³) per ton of coke processed. Major wastewater streams are generated from the cooling of the coke oven gas and the processing of ammonia, tar, naphthalene, phenol, and light oil. Process wastewater may contain 10 milligrams per liter (mg/l) of benzene, 1,000 mg/l of biochemical oxygen demand (BOD) (4 kg/t of coke), 1500 to 6000 mg/l of chemical oxygen demand (COD), 200 mg/l of total suspended solids (TSS), and 150 to 2,000 mg/l of phenols (0.3 to 12 kg/t of coke). Wastewaters also contain PAHs at significant concentrations (up to 30 mg/l), ammonia (0.1 to 2 kg nitrogen/t of coke), and cyanides (0.1-0.6 kg/t of coke). Coke production facilities generate process solid wastes other than coke breeze (which averages 1 kg/t of product).

Most of the solid wastes contain hazardous components such as benzene and PAHs. Waste streams of concern include residues from coal tar recovery (typically 0.1 kg/t of coke), the tar decanter (0.2 kg/t of coke), tar storage (0.4 kg/t of coke), light oil processing (0.2 kg/t of coke), wastewater treatment (0.1 kg/t of coke), naphthalene collection and recovery (0.02 kg/t of coke), tar distillation (0.01 kg/t of coke), and sludges from biological treatment of wastewater.

Pollution prevention in coke making is focused on reducing coke oven emissions and developing cokeless iron- and steelmaking techniques. Implementation of cleaner production processes and pollution prevention measures can yield both economic and environmental benefits. By way of some general guidelines, the generation rate for wastewater should be less than 0.3 m³/t of coke. New coke plants should not generate more than 1 kg of process solid waste (excluding coke breeze and biosludges) per ton of coke.

Baghouses are preferred over venturi scrubbers for controlling particulate matter emissions from loading and pushing operations because of the higher removal efficiencies. ESPs are effective for final tar removal from coke oven gas. Stack air emissions should be monitored continuously for particulate matter. Alternatively, opacity measurements of stack gases could suffice. Fugitive emissions should be monitored annually for VOCs.

Wastewater treatment systems include screens and settling tanks to remove total suspended solids, oil, and tar; steam stripping to remove ammonia, hydrogen sulfide, and hydrogen cyanide; biological treatment; and final polishing with filters. Wastewater discharges should be monitored daily for flow rate and for all parameters, except for dibenz(a,h)anthracene and benzo(a)pyrene. The latter should be monitored at least on a monthly basis or when there are process changes. Frequent sampling may be required during startup and upset conditions.
All process hazardous wastes except for coke fines should be recycled to coke ovens. Wastewater treatment sludges should be dewatered. If toxic organics are detectable, dewatered sludges are to be charged to coke ovens or disposed in a secure landfill or an appropriate combustion unit.

Solid hazardous wastes containing toxic organics should be recycled to a coke oven or treated in a combustion unit, with residues disposed of in a secure landfill. In summary, the key production and control practices that will lead to compliance with emissions guidelines can be summarized as follows:

- Use cokeless iron- and steelmaking processes, such as the direct reduction process for ironmaking, to eliminate the need for coke manufacturing.
- Where feasible, use dry quenching instead of wet quenching.
- Use vapor-recovery systems in light oil processing, tar processing and storage, naphthalene processing, and phenol and ammonia recovery operations.
- Recover sulfur from coke oven gas.
- Segregate process and cooling water.
- Recycle process solid wastes to the coke oven.

**DYE MANUFACTURING**

Dyes are soluble at some stage of the application process, whereas pigments, in general, retain essentially their particulate or crystalline form during application. A dye is used to impart color to materials of which it becomes an integral part. An aromatic ring structure coupled with a side chain is usually required for resonance and thus to impart color. Resonance structures cause displacement or appearance of absorption bands in the visible spectrum of light, and hence they are responsible for color. Correlation of chemical structure with color has been accomplished in the synthesis of dye using a chromogen-chromophore with auxochrome. Chromogen is the aromatic structure containing benzene, naphthalene, or anthracene rings. A chromophore group is a color giver or donor and is represented by the following radicals, which form a basis for the chemical classification of dyes when coupled with the chromogen: azo ( =N=N=); carbonyl (=C=O); carbon (=C≡C=); carbon-nitrogen (>C=NH or -CH=N-); nitroso (-NO or N-OH); nitro (-NO2 or =NO-OH); and sulfur (>C=S, and other carbon-sulfur groups). The chromogen-chromophore structure is often not sufficient to impart solubility and cause adherence of dye to fiber. The auxochrome or bonding affinity groups are amine, hydroxyl, carboxyl, and sulfonic radicals, or their derivatives. These auxochromes are important in the use classification of dyes. A listing of dyes by use classification comprises the following:
• *Acetate rayon dyes*: developed for cellulose acetate and some synthetic fibers

• *Acid dyes*: used for coloring animal fibers via acidified solution (containing sulfuric acid, acetic acid, sodium sulfate, and surfactants) in combination with amphoteric protein

• *Azoic dyes*: contain the azo group (and formic acid, caustic soda, metallic compounds, and sodium nitrate); especially for application to cotton

• *Basic dyes*: amino derivatives (and acetic acid and softening agents); used mainly for application on paper

• *Direct dyes*: azo dyes, and sodium salts, fixing agents, and metallic (chrome and copper) compounds; used generally on cotton-wool, or cotton-silk combinations

• *Mordant or chrome dyes*: metallic salt or lake formed directly on the fiber by the use of aluminum, chromium, or iron salts that cause precipitation in situ

• *Lake or pigment dyes*: form insoluble compounds with aluminum, barium, or chromium on molybdenum salts; the precipitates are ground to form pigments used in paint and inks

• *Sulfur or sulfide dyes*: contain sulfur or are precipitated from sodium sulfide bath; furnish dull shades with good fastness to light, washing, and acids but susceptible to chlorine and light

• *Vat dyes*: impregnated into fiber under reducing conditions and reoxidized to an insoluble color

Chemical classification is based on chromogen. For example, nitro dyes have the chromophore -NO₂. The *Color Index (C.I.)*, published by the Society of Dyers and Colourists (United Kingdom) in cooperation with the American Association of Textile Chemists and Colorists (AATC), provides a detailed classification of commercial dyes and pigments by generic name and chemical constitution.

Dyes are synthesized in a reactor, then filtered, dried, and blended with other additives to produce the final product. The synthesis step involves reactions such as sulfonation, halogenation,amination, diazotization, and coupling, followed by separation processes that may include distillation, precipitation, and crystallization.

In general, organic compounds such as naphthalene are reacted with an acid or an alkali along with an intermediate (such as a nitrating or a sulfonating compound) and a solvent to form a dye mixture. The dye is then separated from the mixture and purified. On completion of the manufacture of actual color, finishing operations, including drying, grinding, and standardization, are performed; these are important for maintaining consistent product quality.
Major solid wastes of concern include filtration sludges, process and effluent treatment sludges, and container residues. Examples of wastes considered toxic include wastewater treatment sludges, spent acids, and process residues from the manufacture of chrome yellow and orange pigments, molybdate orange pigments, zinc yellow pigments, chrome and chrome oxide green pigments, iron blue pigments, and azo dyes.

Dedicated effort should be made to substitute degradable and less toxic ingredients for highly toxic and persistent ingredients in this industry sector. Recommended pollution prevention measures include the following:

- Avoid the manufacture of toxic azo dyes and provide alternative dyestuffs to users such as textile manufacturers.
- Meter and control the quantities of toxic ingredients to minimize wastage.
- Reuse by-products from the process as raw materials or as raw material substitutes in other processes.
- Use automated filling to minimize spillage.
- Use equipment washdown waters as makeup solutions for subsequent batches.
- Return toxic materials packaging to suppliers for reuse, where feasible.
- Find productive uses for off-specification products to avoid disposal problems.
- Use high-pressure hoses for equipment cleaning to reduce the amount of wastewater generated.
- Label and store toxic and hazardous materials in secure areas.

Contaminated solid wastes are generally incinerated, and the flue gases, when acidic wastes, are scrubbed. Contaminated solid wastes should be incinerated under controlled conditions to reduce toxic organics to nondetectable levels, in no case exceeding 0.05 mg/kg or the health-based level. Emissions levels for the design and operation of each project must be established based upon national and local emissions standards.

**PHARMACEUTICALS MANUFACTURING**

The pharmaceutical industry includes the manufacture, extraction, processing, purification, and packaging of chemical materials to be used as medications for humans or animals. Pharmaceutical manufacturing is divided into two major stages: the production of the active ingredient or drug (primary processing, or manufacture) and secondary processing, the conversion of the active drugs into products suitable for administration. This section briefly deals with the synthesis of the active ingredients and their usage in drug formulations to deliver the
Formulation is also referred to as galenical production. The main pharmaceutical groups manufactured include:

- Proprietary ethical products or prescription only medicines (POM), which are usually patented products
- General ethical products, which are basically standard prescription-only medicines made to a recognized formula that may be specified in standard industry reference books
- Over-the-counter (OTC), or nonprescription, products

The products are available as tablets, capsules, liquids (in the form of solutions, suspensions, emulsions, gels, or injectables), creams (usually oil-in-water emulsions), ointments (usually water-in-oil emulsions), and aerosols, which contain inhalable products or products suitable for external use. Propellants used in aerosols include chlorofluorocarbons (CFCs), which are being phased out. Recently, butane has been used as a propellant in externally applied products. The major manufactured groups include:

- Antibiotics such as penicillin, streptomycin, tetracyclines, chloramphenicol, and antifungals
- Other synthetic drugs, including sulfa drugs, antituberculosis drugs, antileprotic drugs, analgesics, anesthetics, and antimalarials;
- Vitamins
- Synthetic hormones
- Glandular products drugs of vegetable origin, such as quinine, strychnine and brucine, emetine, and digitalis glycosides
- Vaccines and sera
- Other pharmaceutical chemicals such as calcium gluconate, ferrous salts, nikethamide, glycerophosphates, chloral hydrate, saccharin, antihistamines (including meclozine and buclozine), tranquilizers (including meprobamate and chloropromazine), antifilarials, diethyl carbamazine citrate, and oral antidiabetics, including tolbutamide and chlorpropamide;
- Surgical sutures and dressings

The principal manufacturing steps are as follows:
(a) Preparation of process intermediates
(b) Introduction of functional groups
(c) Coupling and esterification
(d) Separation processes such as washing and stripping
(e) Purification of the final product

Additional product preparation steps include granulation; drying; tablet pressing, printing, and coating; filling; and packaging. Each of these steps may generate air emissions, liquid effluents, and solid wastes.
The manufacture of penicillin, for example, involves batch fermentation-using 100 to 200 m³ batches-of maize steep liquor or a similar base, with organic precursors added to control the yield. Specific mold culture such as *Penicillium chrysogenum* for Type 11 is inoculated into the fermentation medium. Penicillin is separated from the fermentation broth by solvent extraction.

The product is further purified using acidic extraction. This is followed by treatment with a pyrogen-free distilled water solution containing the alkaline salt of the desired element. The purified aqueous concentrate is separated from the solvent in a supercentrifuge and pressurized through a biological filter to remove the final traces of bacteria and pyrogens.

The solution can be concentrated by freeze drying or vacuum spray drying. Oil-soluble procaine penicillin is made by reacting a penicillin concentrate (20-30%) with a 50% aqueous solution of procaine hydrochloride. Procaine penicillin crystallizes from this mixture.

In some countries, the manufacture of pharmaceuticals is controlled by Good Management Practices (GMP). Some countries require an environmental assessment (EA) report addressing the fate and toxicity of drugs and their metabolized by-products. The EA data relate to the parent drug, not to all metabolites, and include:

(a) Physical and chemical properties
(b) Biodegradability
(c) Photolysis propensity
(d) Aqueous toxicity to fish
(e) Prediction of existing or planned treatment plant to treat wastes and wastewaters
(f) Treatment sequences that are capable of treating wastes and wastewaters

Liquid effluents resulting from equipment cleaning after batch operation contain toxic organic residues. Their composition varies, depending on the product manufactured, the materials used in the process, and other process details. Cooling waters are normally recirculated. Some wastewaters may contain mercury, in a range of 0.1-4 milligrams per liter (mg/l), cadmium (10 to 600 mg/l), isomers of hexachlorocyclohexane, 1,2-dichloroethane, and solvents. Typical amounts released with the wastewater are 25 kilograms of biochemical oxygen demand (BOD) per metric ton of product (kg/t), or 2000 mg/l; 50 kg/t chemical oxygen demand (COD), or 4000 mg/l; 3 kg/t of suspended solids; and up to 0.8 kg/t of phenol.

The principal solid wastes of concern include process and effluent treatment sludges, spent catalysts, and container residues. Approximately 200 kg wastes per ton of product of waste are generated. Some solid wastes contain significant
concentrations of spent solvents and other toxic organics. Every effort should be made to replace highly toxic and persistent ingredients with degradable and less toxic ones.

PETROLEUM REFINING

Petroleum refining is one of the leading manufacturing industries in the United States in terms of its share of the total value of shipments of the U.S. economy. In relation to its economic importance, however, the industry is comprised of relatively few companies and facilities. The number of refineries operating in the United States can vary significantly depending on the information source. For example, in 1992, the Census Bureau counted 232 facilities and the Department of Energy reported 199 facilities.

In addition, EPA's Toxic Release Inventory (TRI) for 1993 identified 159 refineries. The differences lie in each organization's definition of a refinery. The Census Bureau's definition is based on the type of product that a facility produces and includes a number of very small operations producing a specific petroleum product, such as lubricating oils from other refined petroleum products. These small facilities often employ fewer than 10 people and account for only 1% to 2% of the petroleum refining industry's total value of shipments. In comparison to the typically much more complex, larger, and more numerous crude oil processing refineries, these facilities with their smaller and relatively simple operations do not warrant the same level of attention from an economic and environmental compliance standpoint, nor are the pollution prevention opportunities likely to be substantial, except on a collective basis. Refineries recognized by the Department of Energy tend to be only the larger facilities which process crude oil into refined petroleum products.

INDUSTRY DESCRIPTION AND PRACTICES

This section describes the major industrial processes within the petroleum refining industry, including the materials and equipment used, and the processes employed. The section is necessary for an understanding of the industry, and for grasping the interrelationship between the industrial processes and pollutant outputs and pollution prevention opportunities. This section specifically contains a description of commonly used production processes, associated raw materials, the by-products produced or released, and the materials either recycled or transferred off-site. This discussion, coupled with schematic drawings of the
identified processes, provides a description of where wastes may be produced in the process. This section also describes the potential fate (via air, water, and soil pathways) of these waste products.

Petroleum refining is the physical, thermal, and chemical separation of crude oil into its major distillation fractions which are then further processed through a series of separation and conversion steps into finished petroleum products. The primary products of the industry fall into three major categories: fuels (motor gasoline, diesel and distillate fuel oil, liquefied petroleum gas, jet fuel, residual fuel oil, kerosene, and coke); finished nonfuel products (solvents, lubricating oils, greases, petroleum wax, petroleum jelly, asphalt, and coke); and chemical industry feedstocks (naphtha, ethane, propane, butane, ethylene, propylene, butylenes, butadiene, benzene, toluene, and xylene). These petroleum products comprise about 40% of the total energy consumed in the United States and are used as primary input to a vast number of products, including: fertilizers, pesticides, paints, waxes, thickeners, solvents, cleaning fluids, detergents, refrigerants, anti-freeze, resins, sealants, insulations, latex, rubber compounds, hard plastics, plastic sheeting, plastic foam and synthetic fibers. About 90% of the petroleum products used in the United States are fuels with motor gasoline accounting for about 43% of the total.

The Standard Industrial Classification (SIC) code established by the Bureau of Census to track the flow of goods and services within the economy is 29 for the Petroleum Refining and Related Industries. The petroleum refining industry is classified as SIC 2911, which includes the production of petroleum products through distillation and fractionation of crude oil, redistillation of unfinished petroleum derivatives, cracking, or other processes. The related industries under SIC 29 are 2951, Asphalt Paving Mixtures and Blocks; 2952, Asphalt Felts and Coatings; 2992, Lubricating Oils and Greases; and 2999, Petroleum and Coal Products, Not Elsewhere Classified. Certain products that are produced by the petroleum refining industry are also produced by other industries, including 2865, Cyclic Organic Crudes and Intermediates, and Organic Dyes and Pigments; 2869, Industrial Organic Chemicals; 2819, Industrial Inorganic Chemicals, Not Elsewhere Classified; 2821, Plastic Materials, Synthetic Resins, Nonvulcanizable Elastomers; 2873, Nitrogenous Fertilizers; 4613, Refined Petroleum Pipelines; and 5171, Petroleum Bulk Stations and Terminals. Most crude oil distillation capacity is owned by large, integrated companies with multiple high-capacity refining facilities. Small refineries with capacities below 50,000 barrels per day, however, make up about half of all facilities, but only 14% of the total crude distillation capacity.

The United States is a net importer of crude oil and petroleum products. In 1994, imports accounted for more than 50% of the crude oil used in the United States and about 10% of finished petroleum products. The imported share of crude oil is
expected to increase as U.S. demand for petroleum products increases and the domestic production of crude oil declines. Imported finished petroleum products serve specific market niches arising from logistical considerations, regional shortages, and long-term trade relations between suppliers and refiners. Exports of refined petroleum products, which primarily consist of petroleum coke, residual fuel oil, and distillate fuel oil, account for about 4% of the U.S. refinery output. Exports of crude oil produced in the United States account for about one percent of the total U.S. crude oil produced and imported.

The petroleum refining industry in the United States has felt considerable economic pressures in the past two decades arising from a number of factors, including increased costs of labor; compliance with new safety and environmental regulations; and the elimination of government subsidies through the Crude Oil Entitlements Program which had encouraged smaller refineries to add capacity throughout the 1970s. A rationalization period began after crude oil pricing and entitlements were decontrolled in early 1981. The market determined that there was surplus capacity and the margins dropped to encourage the closure of the least efficient capacity. Reflecting these pressures, numerous facilities have closed in recent years. Between 1982 and 1994, the number of U.S. refineries as determined by the Department of Energy dropped from 301 to 176. Most of these closures have involved small facilities refining less than 50,000 barrels of crude oil per day. Some larger facilities, however, have also closed in response to economic pressures. Industry representatives cited complying with the increasing environmental regulations, particularly the requirements of the Clean Air Act Amendments of 1990, as the most important factor affecting petroleum refining in the 1990s. Despite the closing of refineries in recent years, total refinery output of finished products has remained relatively steady with slight increases in the past 2 to 3 years. Increases in refinery outputs are attributable to higher utilization rates of refinery capacity, and to incremental additions to the refining capacity at existing facilities as opposed to construction of new refineries.

Demand for refined petroleum products is expected to increase on the average by about 1.5% per year, which is slower than the expected growth of the economy. This slower rate of increase of demand will be due to increasing prices of petroleum products as a result of conservation, the development of substitutes for petroleum products, and rising costs of compliance with environmental and safety requirements.

Recent and future environmental and safety regulatory changes are expected to force the petroleum refining industry to make substantial investments in upgrading certain refinery processes to reduce emissions and alter product compositions. For example, industry estimates of the capital costs to comply with the 1990 Clean Air Act Amendments, which mandate specific product compositions, are about $35 to $40 billion. There is concern that in some cases it
may be more economical for some refineries to close down partially or entirely rather than upgrade facilities to meet these standards. In fact, the U.S. Departments of Energy and Commerce expect refinery shutdowns to continue through the early part of the new decade; however, total crude oil distillation capacity is expected to remain relatively stable as a result of increased capacity and utilization rates at existing facilities. Increases in demand for finished petroleum products will be filled by increased imports. Pressure to meet the Clean Air Amendments is a major driving force for pollution prevention programs in this industry sector.

**PROCESSES AND OPERATIONS**

Crude oil is a mixture of many different hydrocarbons and small amounts of impurities. The composition of crude oil can vary significantly depending on its source. Petroleum refineries are a complex system of multiple operations and the operations used at a given refinery depend upon the properties of the crude oil to be refined and the desired products. For these reasons, no two refineries are alike. Portions of the outputs from some processes are refed back into the same process, fed to new processes, fed back to a previous process, or blended with other outputs to form finished products. The major unit operations typically involved at petroleum refineries are described briefly below. In addition to those listed below, there are also many special-purpose processes that cannot be described here and which may play an important role in a facility's efforts to comply with pollutant discharge and product specification requirements.

Refining crude oil into useful petroleum products can be separated into two phases and a number of supporting operations. The first phase is desalting of crude oil and the subsequent distillation into its various components or "fractions." The second phase is made up of three different types of "downstream" processes: combining, breaking, and reshaping.

**Crude Oil Distillation and Desalting**

One of the most important operations in a refinery is the initial distillation of the crude oil into its various boiling point fractions. Distillation involves the heating, vaporization, fractionation, condensation, and cooling of feedstocks. This
subsection discusses the atmospheric and vacuum distillation processes which when used in sequence result in lower costs and higher efficiencies. This subsection also discusses the important first step of desalting the crude oil prior to distillation.

Desalting. Before separation into fractions, crude oil usually must first be treated to remove corrosive salts. The desalting process also removes some of the metals and suspended solids which cause catalyst deactivation. Desalting involves the mixing of heated crude oil with water (about 3 to 10% of the crude oil volume) so that the salts are dissolved in the water. The water must then be separated from the crude oil in a separating vessel by adding demulsifier chemicals to assist in breaking the emulsion and/or, more commonly, by applying a high potential electric field across the settling vessel to coalesce the polar saltwater droplets. The desalting process creates an oily desalter sludge and a high temperature salt water waste stream which is typically added to other process wastewaters for treatment in the refinery wastewater treatment facilities. The water used in crude desalting is often untreated or partially treated water from other refining process water sources.

Atmospheric Distillation. The desalted crude oil is then heated in a heat exchanger and furnace to about 750°F and fed to a vertical distillation column at atmospheric pressure where most of the feed is vaporized and separated into its various fractions by condensing on 30 to 50 fractionation trays, each corresponding to a different condensation temperature. The lighter fractions condense and are collected toward the top of the column. Heavier fractions, which may not vaporize in the column, are further separated later by vacuum distillation. Within each atmospheric distillation tower, a number of side streams (at least four) of low-boiling-point components are removed from the tower from different trays. These low-boiling point mixtures are in equilibrium with heavier components which must be removed. The side streams are each sent to a different small stripping tower containing four to 10 trays with steam injected under the bottom tray. The steam strips the light-end components from the heavier components and both the steam and light-ends are fed back to the atmospheric distillation tower above the corresponding side stream draw tray. Fractions obtained from atmospheric distillation include naphtha, gasoline, kerosene, light fuel oil, diesel oils, gas oil, lube distillate, and heavy bottoms. Most of these can be sold as finished products, or blended with products from downstream processes. Another product produced in atmospheric distillation, as well as many other refinery processes, is the light, noncondensible refinery fuel gas (mainly methane and ethane). Typically this gas also contains hydrogen sulfide and ammonia gases. The mixture of these gases is known as "sour gas" or "acid gas." The sour gas is sent to the refinery sour gas treatment system which separates the fuel gas so that it can be used as fuel in the refinery heating furnaces. Air emissions during atmospheric distillation arise from the combustion
of fuels in the furnaces to heat the crude oil, process vents and fugitive emissions. Oily sour water (condensed steam containing hydrogen sulfate and ammonia) and oil is also generated in the fractionators.

**Vacuum Distillation.** Heavier fractions from the atmospheric distillation unit that cannot be distilled without cracking under its pressure and temperature conditions are vacuum distilled. Vacuum distillation is simply the distillation of petroleum fractions at a very low pressure (0.2 to 0.7 psia) to increase volatilization and separation. In most systems, the vacuum inside the fractionator is maintained with steam ejectors and vacuum pumps, barometric condensers, or surface condensers. The injection of superheated steam at the base of the vacuum fractionator column further reduces the partial pressure of the hydrocarbons in the tower, facilitating vaporization and separation. The heavier fractions from the vacuum distillation column are processed downstream into more valuable products through either cracking or coking operations. A potential source of emissions from distillation of crude oil are the combustion of fuels in the furnace and some light gases leaving the top of the condensers on the vacuum distillation column. A certain amount of noncondensable light hydrocarbons and hydrogen sulfide pass through the condenser to a hot well, and then is discharged to the refinery sour fuel system or is vented to a process heater, flare, or another control device to destroy hydrogen sulfide. The quantity of these emissions depends on the size of the unit, the type of feedstock, and the cooling water temperature. If barometric condensers are used in vacuum distillation, significant amounts of oily wastewater can be generated. Vacuum pumps and surface condensers have largely replaced barometric condensers in many refineries to eliminate this oily wastewater stream. Oily sour water is also generated in the fractionators.

**Downstream Processing**

Certain fractions from the distillation of crude oil are further refined in thermal cracking (visbreaking), coking, catalytic cracking, catalytic hydrocracking, hydrotreating, alkylation, isomerization, polymerization, catalytic reforming, solvent extraction, Merox, dewaxing, propane deasphalting and other operations. These downstream processes change the molecular structure of hydrocarbon molecules either by breaking them into smaller molecules, joining them to form larger molecules, or reshaping them into higher quality molecules. For many of the operations, a number of different techniques are used in the industry.

**Thermal Cracking/Visbreaking.** Thermal cracking, or visbreaking, uses heat and pressure to break large hydrocarbon molecules into smaller, lighter molecules. The process has been largely replaced by catalytic cracking and some refineries no longer employ thermal cracking. Both processes reduce the production of less valuable products such as heavy fuel oil and cutter stock and increase the
feedstock to the catalytic cracker and gasoline yields. In thermal cracking, heavy gas oils and residue from the vacuum distillation process are typically the feed stocks. The feedstock is heated in a furnace or other thermal unit to up to 1000°F and then fed to a reaction chamber which is kept at a pressure of about 140 psig. Following the reactor step, the process stream is mixed with a cooler recycle stream, which stops the cracking reactions. The product is then fed to a flasher chamber, where pressure is reduced and lighter products vaporize and are drawn off. The lighter products are fed to a fractionating tower where the various fractions are separated. The "bottoms" consist of heavy residue, part of which is recycled to cool the process stream leaving the reaction chamber; the remaining bottoms are usually blended into residual fuel (refer to Fig. 1).

Figure 1. Flow diagram of thermal cracker unit.

Air emissions from thermal cracking include emissions from the combustion of fuels in the process heater, vents, and fugitive emissions. A sour water stream is generated in the fractionator.
Coking. Coking is a cracking process used primarily to reduce refinery production of low-value residual fuel oils to transportation fuels, such as gasoline and diesel. As part of the upgrading process, coking also produces petroleum coke, which is essentially solid carbon with varying amounts of impurities, and is used as a fuel for power plants if the sulfur content is low enough. Coke also has nonfuel applications as a raw material for many carbon and graphite products including anodes for the production of aluminum, and furnace electrodes for the production of elemental phosphorus, titanium dioxide, calcium carbide and silicon carbide. A number of different processes are used to produce coke; both delayed coking and fluid coking are the most widely used processes. Fluid coking produces a higher grade of coke. In delayed coking operations, the same basic process as thermal cracking is used except feed streams are allowed to react longer without being cooled. The delayed coking feed stream of residual oils from various upstream processes is first introduced to a fractionating tower where residual lighter materials are drawn off and the heavy ends are condensed. The heavy ends are removed and heated in a furnace to about 900 to 1000°F and then fed to an insulated vessel called a coke drum where the coke is formed. When the coke drum is filled with product, the feed is switched to an empty parallel drum. Hot vapors from the coke drums, containing cracked lighter hydrocarbon products, hydrogen sulfide, and ammonia, are fed back to the fractionator where they can be treated in the sour gas treatment system or drawn off as intermediate products.

Steam is then injected into the full coke drum to remove hydrocarbon vapors, water is injected to cool the coke, and the coke is removed. Typically, high-pressure water jets are used to cut the coke from the drum.

Air emissions from coking operations include the process heater flue gas emissions, fugitive emissions and emissions, that may arise from the removal of the coke from the coke drum. The injected steam is condensed and the remaining vapors are typically flared. Wastewater is generated from the coke removal and cooling operations and from the steam injection. In addition, the removal of coke from the drum can release particulate emissions and any remaining hydrocarbons to the atmosphere.

Catalytic Cracking. Catalytic cracking uses heat, pressure and a catalyst to break larger hydrocarbon molecules into smaller, lighter molecules. Catalytic cracking has largely replaced thermal cracking because it is able to produce more gasoline with a higher octane and less heavy fuel oils and light gases. Feedstocks are light and heavy oils from the crude oil distillation unit which are processed primarily into gasoline as well as some fuel oil and light gases. Most catalysts used in catalytic cracking consist of mixtures of crystalline synthetic silica-alumina, termed "zeolites," and amorphous synthetic silica-alumina. The catalytic cracking
processes, as well as most other refinery catalytic processes, produce coke which collects on the catalyst surface and diminishes its catalytic properties. The catalyst, therefore, needs to be regenerated continuously or periodically essentially by burning the coke off the catalyst at high temperatures. The method and frequency in which catalysts are regenerated are a major factor in the design of catalytic cracking units. A number of different catalytic cracking designs are currently in use, including fixed-bed reactors, moving-bed reactors, fluidized-bed reactors, and once-through units. The fluidized- and moving-bed reactors are by far the most prevalent.

Fluidized-bed catalytic cracking units (FCCUs) are the most common catalytic cracking units. In the fluidized-bed process, oil and oil vapor preheated to 500 to 800°F is contacted with hot catalyst at about 1,300°F either in the reactor itself or in the feed line (called the ‘riser’) to the reactor. The catalyst is in a fine, granular form which, when mixed with the vapor, has many of the properties of a fluid. The fluidized catalyst and the reacted hydrocarbon vapor separate mechanically in the reactor and any oil remaining on the catalyst is removed by steam stripping. The cracked oil vapors are then fed to a fractionation tower where the various desired fractions are separated and collected. The catalyst flows into a separate vessel(s) for either single- or two-stage regeneration by burning off the coke deposits with air.

In the moving-bed process, oil is heated to up to 1300°F and is passed under pressure through the reactor where it comes into contact with a catalyst flow in the form of beads or pellets. The cracked products then flow to a fractionating tower where the various compounds are separated and collected. The catalyst is regenerated in a continuous process where deposits of coke on the catalyst are burned off. Some units also use steam to strip remaining hydrocarbons and oxygen from the catalyst before being fed back to the oil stream. In recent years moving-bed reactors have largely been replaced by fluidized-bed reactors.

Catalytic cracking is one of the most significant sources of air pollutants at refineries. Air emissions from catalytic cracking operations include: the process heater flue gas emissions, fugitive emissions, and emissions generated during regeneration of the catalyst. Relatively high concentrations of carbon monoxide can be produced during regeneration of the catalyst which is typically converted to carbon dioxide either in the regenerator or further downstream in a carbon monoxide waste heat boiler. In addition, a significant amount of fine catalyst dust is produced in FCCUs as a result of the constant movement of the catalyst grains against each other. Much of this dust, consisting primarily of alumina and relatively small amounts of nickel, is carried with the carbon monoxide stream to the carbon monoxide burner.
The catalyst dust is then separated from the resulting carbon dioxide stream via cyclones and/or electrostatic precipitators and is sent off-site for disposal or treatment. Generated wastewater is typically sour water from the fractionator containing some oil and phenols. Wastewater containing metal impurities from the feed oil can also be generated from the steam used to purge and regenerate catalysts.

*Catalytic Hydrocracking.* Catalytic hydrocracking normally utilizes a fixed-bed catalytic cracking reactor with cracking occurring under substantial pressure (1,200 to 2,000 psig) in the presence of hydrogen. Feedstocks to hydrocracking units are often those fractions that are the most difficult to crack and cannot be cracked effectively in catalytic cracking units. The feedstocks include middle distillates, cycle oils, residual fuel oils, and reduced crudes.

The hydrogen suppresses the formation of heavy residual material and increases the yield of gasoline by reacting with the cracked products. However, this process also breaks the heavy sulfur- and nitrogen-bearing hydrocarbons and releases these impurities to where they could potentially foul the catalyst. For this reason, the feedstock is often first hydrotreated to remove impurities before being sent to the catalytic hydrocracker. Sometimes hydrotreating is accomplished by using the first reactor of the hydrocracking process to remove impurities. Water also has a detrimental effect on some hydrocracking catalysts and must be removed before being fed to the reactor. The water is removed by passing the feed stream through a silica gel or molecular sieve dryer. Depending on the products desired and the size of the unit, catalytic hydrocracking is conducted in either single-stage or multi-stage reactor processes. Most catalysts consist of a crystalline mixture of silica-alumina with small amounts of rare earth metals. Hydrocracking feedstocks are usually first hydrotreated to remove the hydrogen sulfide and ammonia that will poison the catalyst. Sour gas and sour water streams are produced at the fractionator, however, if the hydrocracking feedstocks are first hydrotreated to remove impurities, both streams will contain relatively low levels of hydrogen sulfide and ammonia. Hydrocracking catalysts are typically regenerated off-site after 2 to 4 years of operation. Therefore, few or no emissions are generated from the regeneration processes. Air emissions arise from the process heater, vents, and fugitive emissions.

*Hydrotreating/Hydroprocessing.* Hydrotreating and hydroprocessing are similar processes used to remove impurities such as sulfur, nitrogen, oxygen, halides, and trace-metal impurities that may deactivate process catalysts. Hydrotreating also upgrades the quality of fractions by converting olefins and diolefins to paraffins for the purpose of reducing gum formation in fuels. Hydroprocessing, which typically uses residuals from the crude distillation units, also cracks these heavier molecules to lighter, more saleable products. Both hydrotreating and hydroprocessing units are usually placed upstream of those processes in which
sulfur and nitrogen could have adverse effects on the catalyst, such as catalytic reforming and hydrocracking units. The processes utilize catalysts in the presence of substantial amounts of hydrogen under high pressure and temperature to react the feedstocks and impurities with hydrogen. The reactors are nearly all fixed-bed with catalyst replacement or regeneration done after months or years of operation often at an off-site facility. In addition to the treated products, the process produces a stream of light fuel gases, hydrogen sulfide, and ammonia. The treated product and hydrogen-rich gas are cooled after they leave the reactor before being separated. The hydrogen is recycled to the reactor. The off-gas stream may be very rich in hydrogen sulfide and light fuel gas. The fuel gas and hydrogen sulfide are typically sent to the sour gas treatment unit and sulfur recovery unit. Catalysts are typically cobalt or molybdenum oxides on alumina, but can also contain nickel and tungsten. Air emissions from hydrotreating may arise from process heater flue gas, vents, and fugitive emissions.

**Alkylation.** Alkylation is used to produce a high-octane gasoline blending stock from the isobutane formed primarily during catalytic cracking and coking operations, but also from catalytic reforming, crude distillation and natural gas processing. Alkylation joins an olefin and an isoparaffin compound using either a sulfuric acid or a hydrofluoric acid catalyst. The products are alkylates including propane and butane liquids. When the concentration of acid becomes less than 88%, some of the acid must be removed and replaced with stronger acid. In the hydrofluoric acid process, the slipstream of acid is redistilled. Dissolved polymerization products are removed from the acid as a thick dark oil. The concentrated hydrofluoric acid is recycled and the net consumption is about 0.3 pounds per barrel of alkylates produced. Hydrofluoric acid alkylation units require special engineering design, operator training, and safety equipment precautions to protect operators from accidental contact with hydrofluoric acid, which is an extremely hazardous substance. In the sulfuric acid process, the sulfuric acid removed must be regenerated in a sulfuric acid plant which is generally not a part of the alkylation unit and may be located off-site. Spent sulfuric acid generation is substantial; typically in the range of 13 to 30 pounds per barrel of alkylate. Air emissions from the alkylation process may arise from process vents and fugitive emissions.

**Isomerization.** Isomerization is used to alter the arrangement of a molecule without adding or removing anything from the original molecule. Typically, paraffins (butane or pentane from the crude distillation unit) are converted to isoparaffins having a much higher octane. Isomerization reactions take place at temperatures in the range of 200 to 400°F in the presence of a catalyst that usually consists of platinum on a base material. Two types of catalysts are currently in use. One requires the continuous addition of small amounts of organic chlorides which are converted to hydrogen chloride in the reactor. In
such a reactor, the feed must be free of oxygen sources including water to avoid deactivation and corrosion problems. The other type of catalyst uses a molecular sieve base and does not require a dry and oxygen free feed. Both types of isomerization catalysts require an atmosphere of hydrogen to minimize coke deposits; however, the consumption of hydrogen is negligible. Catalysts typically need to be replaced about every 2 to 3 years or longer. Platinum is then recovered from the used catalyst off-site. Light ends are stripped from the product stream leaving the reactor and are then sent to the sour-gas treatment unit. Some isomerization units utilize caustic treating of the light fuel gas stream to neutralize any entrained hydrochloric acid. This will result in a calcium chloride (or other salts) waste stream. Air emissions may arise from the process heater, vents, and fugitive emissions. Wastewater streams include caustic wash and sour water.

**Polymerization.** Polymerization is occasionally used to convert propene and butene to high-octane gasoline blending components. The process is similar to alkylation in its feed and products, but is often used as a less expensive alternative to alkylation. The reactions typically take place under high pressure in the presence of a phosphoric acid catalyst. The feed must be free of sulfur, which poisons the catalyst; basic materials, which neutralize the catalyst; and oxygen, which affects the reactions. The propene and butene feed is washed first with caustic to remove mercaptans (molecules containing sulfur), then with an amine solution to remove hydrogen sulfide, then with water to remove caustics and amines, and finally dried by passing through a silica gel or molecular sieve dryer. Air emissions of sulfur dioxide may arise during the caustic washing operation. Spent catalyst, which typically is not regenerated, is occasionally disposed as a solid waste. Wastewater streams will contain caustic wash and sour water with amines and mercaptans.

**Catalytic Reforming.** Catalytic reforming uses catalytic reactions to process primarily low-octane heavy straight run (from the crude distillation unit) gasolines and naphthas into high-octane aromatics (including benzene). There are four major types of reactions which occur during reforming processes: (1) dehydrogenation of naphthenes to aromatics; (2) dehydrocyclization of paraffins to aromatics; (3) isomerization; and (4) hydrocracking. The dehydrogenation reactions are very endothermic, requiring that the hydrocarbon stream be heated between each catalyst bed. All but the hydrocracking reaction release hydrogen which can be used in the hydrotreating or hydrocracking processes. Fixed-bed or moving-bed processes are utilized in a series of three to six reactors. Feedstocks to catalytic reforming processes are usually hydrotreated first to remove sulfur, nitrogen, and metallic contaminants. In continuous reforming processes, catalysts can be regenerated one reactor at a time, once or twice per day, without disrupting the operation of the unit. In semiregenerative units, regeneration of all reactors can be carried out simultaneously after 3 to 24 months of operation by
first shutting down the process. Because the recent reformulated gasoline rules have limited the allowable amount of benzene in gasoline, catalytic reforming is being used less as an octane enhancer than in past years.

Air emissions from catalytic reforming arise from the process heater gas and fugitive emissions. The catalysts used in catalytic reforming processes are usually very expensive and extra precautions are taken to ensure that catalyst is not lost. When the catalyst has lost its activity and can no longer be regenerated, the catalyst is usually sent off-site for recovery of the metals. Subsequent air emissions from catalyst regeneration are, therefore, relatively low. Relatively small volumes of wastewater containing sulfides, ammonia, and mercaptans may be generated from the stripping tower used to remove light ends from the reactor effluent.

**Solvent Extraction.** Solvent extraction uses solvents to dissolve and remove aromatics from lube-oil feed stocks, improving viscosity, oxidation resistance, color and gum formation. A number of different solvents are used, with the two most common being furfural and phenol. Typically, feed lube stocks are contacted with the solvent in a packed tower or rotating disk contactor. Each solvent has a different solvent-to-oil ratio and recycle ratio within the tower. Solvents are recovered from the oil stream through distillation and steam stripping in a fractionator. The stream extracted from the solvent will likely contain high concentrations of hydrogen sulfide, aromatics, naphthenes and other hydrocarbons and is often fed to the hydrocracking unit. The water stream leaving the fractionator will likely contain some oil and solvents.

**Chemical Treating.** In petroleum refining, chemical treating is used to remove or change the undesirable properties associated with sulfur, nitrogen, or oxygen compound contaminates in petroleum products. Chemical treating is accomplished by either extraction or oxidation (also known as sweetening), depending upon the product. Extraction is used to remove sulfur from the very light petroleum fractions, such as propane/propylene (PP) and butane/butylene (BB). Sweetening, though, is more effective on gasoline and middle distillate products. A typical extraction process is "Merox" extraction. Merox extraction is used to remove mercaptans (organic sulfur compounds) from PP and BB streams. PP streams may undergo amine treating before the Merox extraction to remove excess H₂S which tends to fractionate with PP and interferes with the Merox process. A caustic prewash of the PP and BB removes any remaining trace H₂S prior to Merox extraction. The PP and BB streams are passed up through the trays of an extraction tower. Caustic solution flowing down the extraction tower absorbs mercaptan from the PP and BB streams. The rich caustic is then regenerated by oxidizing the mercaptans to disulfide in the presence of aqueous Merox catalyst and the lean caustic recirculated to the extraction tower. The disulfide is insoluble in the caustic and can be separated.
Oxidation or "sweetening" is used on gasoline and distillate fractions. A common oxidation process is also a Merox process that uses a solid catalyst bed. Air and a minimum amount of alkaline caustic ("mini-alky" operation) is injected into the hydrocarbon stream. As the hydrocarbon passes through the Merox catalyst bed, sulfur mercaptans are oxidized to disulfide. In the sweetening Merox process, the caustic is not regenerated. The disulfide can remain with the gasoline product, since it does not possess the objectionable odor properties of mercaptans; hence, the product has been "sweetened."

In the extraction process, a waste oily disulfide stream leaves the separator. Air emissions arise from fugitive hydrocarbons and the process vents on the separator which may contain disulfides.

**Dewaxing.** Dewaxing of lubricating oil base stocks is necessary to ensure that the oil will have the proper viscosity at lower ambient temperatures. Two types of dewaxing processes are used: selective hydrocracking and solvent dewaxing. In selective hydrocracking, one or two zeolite catalysts are used to selectively crack the wax paraffins. Solvent dewaxing is more prevalent. In solvent dewaxing, the oil feed is diluted with solvent to lower the viscosity, chilled until the wax is crystallized, and then filtered to remove the wax. Solvents used for the process include propane and mixtures of methyl ethyl ketone (MEK) with methyl isobutyl ketone (MIBK) or MEK with toluene. Solvent is recovered from the oil and wax through heating and two-stage flashing, followed by steam stripping. The solvent-recovery stage results in solvent-contaminated water which typically is sent to the wastewater treatment plant. The wax either is used as feed to the catalytic cracker or is deoiled and sold as industrial wax. Air emissions may arise from fugitive emissions of the solvents.

**Propane Deasphalting** Propane deasphalting produces lubricating oil base stocks by extracting asphaltenes and resins from the residuals of the vacuum distillation unit. Propane is usually used to remove asphaltenes because of its unique solvent properties. At lower temperatures (100 to 140°F), paraffins are very soluble in propane and at higher temperatures (about 200°F) all hydrocarbons are almost insoluble in propane. The propane deasphalting process is similar to solvent extraction in that a packed or baffled extraction tower or rotating disk contactor is used to mix the oil feedstocks with the solvent. In the tower method, four to eight volumes of propane are fed to the bottom of the tower for every volume of feed flowing down from the top of the tower. The oil, which is more soluble in the propane dissolves and flows to the top. The asphaltene and resins flow to the bottom of the tower where they are removed in a propane mix. Propane is recovered from the two streams through two-stage flash systems followed by steam stripping in which propane, is condensed and removed by cooling at high pressure in the first stage and at low pressure in the second stage. The asphalt
recovered can be blended with other asphalts or heavy fuels, or can be used as feed to the coker. The propane recovery stage results in propane-contaminated water which typically is sent to the wastewater treatment plant. Air emissions may arise from fugitive propane emissions and process vents.

Supporting Operations

Many important refinery operations are not directly involved in the production of hydrocarbon fuels but serve in a supporting role. Some of the major supporting processes are described below.

**Wastewater Treatment.** Relatively large volumes of water are used by the petroleum refining industry. Four types of wastewater are produced: surface water runoff, cooling water, process water, and sanitary wastewater. Surface water runoff is intermittent and will contain constituents from spills to the surface, leaks in equipment and any materials that may have collected in drains. Runoff surface water also includes water coming from crude and product storage tank roof drains.

A large portion of water used in petroleum refining is used for cooling. Cooling water typically does not come into direct contact with process oil streams and therefore contains less contaminants than process wastewater. Most cooling water is recycled over and over with a bleed or blowdown stream to the wastewater treatment unit to control the concentration of contaminants and the solids content in the water. Cooling towers within the recycle loop cool the water using ambient air. Some cooling water, termed "once through," is passed through a process unit once and is then discharged directly without treatment in the wastewater treatment plant. The water used for cooling often contains chemical additives such as chromates, phosphates, and antifouling biocides to prevent scaling of pipes and biological growth. It should be noted that many refineries in the United States no longer use chromates in cooling water as antifouling agents; however, this is not the case in other parts of the world. Although cooling water usually does not come into direct contact with oil process streams, it also may contain some oil contamination due to leaks in the process equipment.

Water used in processing operations also accounts for a significant portion of the total wastewater. Process wastewater arises from desalting crude oil, steam stripping operations, pump gland cooling, product fractionator reflux drum drains, and boiler blowdown. Because process water often comes into direct contact with oil, it is usually highly contaminated. Petroleum refineries typically utilize primary and secondary wastewater treatment technologies. Primary wastewater treatment consists of the separation of oil, water and solids in two stages. During the first stage, an API separator, a corrugated plate interceptor, or other separator design is used. Wastewater moves very slowly through the
A separator allowing free oil to float to the surface and be skimmed off, and solids to settle to the bottom and be scraped off to a sludge collecting hopper. The second stage utilizes physical or chemical methods to separate emulsified oils from the wastewater. Physical methods may include the use of a series of settling ponds with a long retention time, or the use of dissolved air flotation (DAF). In DAF, air is bubbled through the wastewater, and both oil and suspended solids are skimmed off the top. Chemicals, such as ferric hydroxide or aluminum hydroxide, can be used to coagulate impurities into a froth or sludge which can be more easily skimmed off the top. Some wastes associated with the primary treatment of wastewater at petroleum refineries may be considered hazardous and include API separator sludge, primary treatment sludge, sludges from other gravitational separation techniques, float from DAF units, and wastes from settling ponds.

After primary treatment, the wastewater can be discharged to a publicly owned treatment works or undergo secondary treatment before being discharged directly to surface waters under a National Pollution Discharge Elimination System (NPDES) permit. In secondary treatment, dissolved oil and other organic pollutants may be consumed biologically by microorganisms. Biological treatment may require the addition of oxygen through a number of different techniques, including activated sludge units, trickling filters, and rotating biological contactors. Secondary treatment generates biomass waste which is typically treated anaerobically and then dewatered.

Some refineries employ an additional stage of wastewater treatment called polishing to meet discharge limits. The polishing step can involve the use of activated carbon, anthracite coal, or sand to filter out any remaining impurities, such as biomass, silt, trace metals, and other inorganic chemicals, as well as any remaining organic chemicals.

Certain refinery wastewater streams are treated separately, prior to the wastewater treatment plant, to remove contaminants that would not easily be treated after mixing with other wastewater. One such waste stream is the sour water drained from distillation reflux drums. Sour water contains dissolved hydrogen sulfide and other organic sulfur compounds and ammonia which are stripped in a tower with gas or steam before being discharged to the wastewater treatment plant.

Wastewater treatment plants are also a significant source of refinery air emissions and solid wastes. Air releases arise from fugitive emissions from the numerous tanks, ponds and sewer system drains. Solid wastes are generated in the form of sludges from a number of the treatment units.
Gas Treatment and Sulfur Recovery. Sulfur is removed from a number of refinery process off-gas streams (sour gas) in order to meet the SOₓ emissions limits of the CAA and to recover saleable elemental sulfur. Process off-gas streams, or sour gas, from the coker, catalytic cracking unit, hydrotreating units and hydropricessing units can contain high concentrations of hydrogen sulfide mixed with light refinery fuel gases. Before elemental sulfur can be recovered, the fuel gases (primarily methane and ethane) need to be separated from the hydrogen sulfide. This is typically accomplished by dissolving the hydrogen sulfide in a chemical solvent. Solvents most commonly used are amines, such as diethanolamine (DEA). Dry adsorbents such as molecular sieves, activated carbon, iron sponge and zinc oxide are also used. In the amine solvent processes, DEA solution or another amine solvent is pumped to an absorption tower where the gases are contacted and hydrogen sulfide is dissolved in the solution. The fuel gases are removed for use as fuel in process furnaces in other refinery operations. The amine-hydrogen sulfide solution is then heated and steam stripped to remove the hydrogen sulfide gas.

Current methods for removing sulfur from the hydrogen sulfide gas streams are typically a combination of two processes: the Claus Process followed by the Beaven process, the Scot process, or the Wellman-Land Process. The Claus process consists of partial combustion of the hydrogen sulfide-rich gas stream (with one-third the stoichiometric quantity of air) and then reacting the resulting sulfur dioxide and unburned hydrogen sulfide in the presence of a bauxite catalyst to produce elemental sulfur.

Since the Claus process by itself removes only about 90% of the hydrogen sulfide in the gas stream, the Beaven, SCOT, or Wellman-Land processes are often used to further recover sulfur. In the Beaven process, the hydrogen sulfide in the relatively low-concentration gas stream from the Claus process can be almost completely removed by absorption in a quinone solution.

The dissolved hydrogen sulfide is oxidized to form a mixture of elemental sulfur and hydro-quinone. The solution is injected with air or oxygen to oxidize the hydro-quinone back to quinone. The solution is then filtered or centrifuged to remove the sulfur and the quinone is then reused.

The Beaven process is also effective in removing small amounts of sulfur dioxide, carbonyl sulfide, and carbon disulfide that are not affected by the Claus process. These compounds are first converted to hydrogen sulfide at elevated temperatures in a cobalt molybdate catalyst prior to being fed to the Beaven unit. Air emissions from sulfur recovery units will consist of hydrogen sulfide, SOₓ, and NOₓ in the process tail gas as well as fugitive emissions and releases from vents.
The SCOT process is also widely used for removing sulfur from the Claus tail gas. The sulfur compounds in the Claus tail gas are converted to hydrogen sulfide by heating and passing it through a cobalt-molybdenum catalyst with the addition of a reducing gas. The gas is then cooled and contacted with a solution of diisopropanolamine (DIPA) which removes all but trace amounts of hydrogen sulfide. The sulfide-rich DIPA is sent to a stripper where hydrogen sulfide gas is removed and sent to the Claus plant. The DIPA is returned to the absorption column.

Additive Production. A number of chemicals (mostly alcohols and ethers) are added to motor fuels to either improve performance or meet federal and state environmental requirements. Since the 1970s, alcohols (methanol and ethanol) and ethers have been added to gasoline to increase octane levels and reduce carbon monoxide generation in place of the lead additives which were being phased out as required by the 1970 Clean Air Act. In 1990, the more stringent Clean Air Act Amendments established minimum and maximum amounts of chemically combined oxygen in motor fuels as well as an upper limit on vapor pressure. As a result, alcohol additives have been increasingly supplemented or replaced with a number of different ethers which are better able to meet both the new oxygen requirements and the vapor pressure limits.

The most common ethers being used as additives are methyl tertiary butyl ether (MTBE), and tertiary amyl methyl ether (TAME). Many of the larger refineries manufacture their own supplies of MTBE and TAME by reacting isobutylene and/or isoamylene with methanol. Smaller refineries usually buy their supplies from chemical manufacturers or the larger refineries.

Isobutylene is obtained from a number of refinery sources, including the light naphtha from the FCCU and coking units, the by-product from steam cracking of naphtha or light hydrocarbons during the production of ethylene and propylene, catalytic dehydrogenation of isobutane, and conversion of tertiary butyl alcohol recovered as a by-product in the manufacture of propylene oxides. Several different processes are currently in use to produce MTBE and TAME from isobutylene and methanol. Most processes use a two-stage acidic ion-exchange resin catalyst. The reaction is exothermic and cooling to the proper reaction temperature is critical in obtaining the optimal conversion efficiency. The process usually produces an MTBE or TAME stream and a relatively small stream of unreacted hydrocarbons and methanol. The methanol is extracted in a water wash and the resulting methanol-water mixture is distilled to recover the methanol for recycling.
Heat Exchanger Cleaning. Heat exchangers are used abundantly throughout petroleum refineries to heat or cool petroleum process streams. The heat exchangers consist of bundles of pipes, tubes, plate coils, or steam coils enclosing heating or cooling water, steam, or oil to transfer heat indirectly to or from the oil process stream. The bundles are cleaned periodically to remove accumulations of scales, sludge and any oily residues.

Because chromium has almost been eliminated as a cooling water additive, wastes generated from the cleaning of heat exchanger bundles no longer account for a significant portion of the hazardous wastes generated at refining facilities. The sludge generated may contain lead or chromium, although some refineries which do not produce leaded gasoline and which use non-chrome corrosion inhibitors typically do not generate sludge that contains these constituents. Oily wastewater is also generated during heat exchanger cleaning.

Blowdown System. Most refinery process units and equipment are manifolded into a collection unit, called the blowdown system. Blowdown systems provide for the safe handling and disposal of liquid and gases that either are automatically vented from the process units through pressure relief valves, or that are manually drawn from units. Recirculated process streams and cooling water streams are often manually purged to prevent the continued buildup of contaminants in the stream. Part or all of the contents of equipment can also be purged to the blowdown system prior to shutdown before normal or emergency shutdowns.

Blowdown systems utilize a series of flash drums and condensers to separate the blowdown into its vapor and liquid components. The liquid is typically composed of mixtures of water and hydrocarbons containing sulfides, ammonia, and other contaminants, which are sent to the wastewater treatment plant. The gaseous component typically contains hydrocarbons, hydrogen sulfide, ammonia, mercaptans, solvents, and other constituents and either is discharged directly to the atmosphere or is combusted in a flare. The major air emissions from blowdown systems are hydrocarbons in the case of direct discharge to the atmosphere and sulfur oxides when flared.
Blending. Blending is the final operation in petroleum refining. It consists of mixing the products in various proportions to meet specifications such as vapor pressure, specific gravity, sulfur content, viscosity, octane number, initial boiling point, and pour point. Blending can be carried out inline or in batch blending tanks. Air emissions from blending are fugitive VOCs from blending tanks, valves, pumps and mixing operations.

Storage Tanks. Storage tanks are used throughout the refining process to store crude oil and intermediate process feeds for cooling and further processing. Finished petroleum products are also kept in storage tanks before transport off site. Storage tank bottoms are mixtures of iron rust from corrosion, sand, water, and emulsified oil and wax, which accumulate at the bottom of tanks. Liquid tank bottoms (primarily water and oil emulsions) are periodically drawn off to prevent their continued buildup.

Tank bottom liquids and sludge are also removed during periodic cleaning of tanks for inspection. Tank bottoms may contain amounts of tetraethyl or tetramethyl lead (although this is increasingly rare because of the phaseout of leaded products), other metals, and phenols. Solids generated from leaded gasoline storage tank bottoms are listed as a RCRA hazardous waste. Even if equipped with floating tops, storage tanks account for considerable VOC emissions at petroleum refineries. A study of petroleum refinery emissions found that the majority of tank losses occurred through tank seals on gasoline storage tanks.

Cooling Towers. Cooling towers cool heated water by circulating the water through a tower with a predetermined flow of ambient air pushed with large fans. A certain amount of water exits the system through evaporation, mist droplets and as bleed or blowdown to the wastewater treatment system. Therefore, makeup water in the range of about 5% of the circulation rate is required.

MATERIAL BALANCE INFORMATION

Raw material input to petroleum refineries is primarily crude oil; however, petroleum refineries use and generate an enormous number of chemicals, many of which leave the facilities as discharges of air emissions, wastewater, or solid waste. Pollutants generated typically include VOCs, carbon monoxide (CO), sulfur oxides (SO₂), nitrogen oxides (NOₓ), particulates, ammonia (NH₃) hydrogen sulfide (H₂S) metals, spent acids, and numerous toxic organic compounds.
When discussing material outputs of the petroleum refining industry, it is important to note the relationship between the outputs of the industry itself and the outputs resulting from the use of refinery products. Petroleum refineries play an important role in the U.S. economy, supplying approximately 40% of the total energy used in the United States and virtually all of the energy consumed in the transportation sector.

The pollutant outputs from the refining facilities, however, are modest in comparison to the pollutant outputs realized from the consumption of petroleum products by the transportation sector, electric utilities, chemical manufacturers, and other industrial and commercial users.

Air emissions from refineries include fugitive emissions of the volatile constituents in crude oil and its fractions, emissions from the burning of fuels in process heaters, and emissions from the various refinery processes themselves. Fugitive emissions occur throughout refineries and arise from the thousands of potential fugitive emission sources such as valves, pumps, tanks, pressure relief valves and flanges.

Although individual leaks are typically small, the sum of all fugitive leaks at a refinery can be one of its largest emission sources. Fugitive emissions can be reduced through a number of techniques, including improved leak resistant equipment, reducing the number of tanks and other potential sources and, perhaps the most effective method, an ongoing Leak Detection and Repair (LDAR) program.

The numerous process heaters used in refineries to heat process streams or to generate steam (boilers) for heating or steam stripping, can be potential sources of SO₂, NOₓ, CO, particulate matter and hydrocarbons emissions. When operating properly and when burning cleaner fuels such as refinery fuel gas, fuel oil, or natural gas, these emissions are relatively low. If, however, combustion is not complete, or heaters are fired with refinery fuel pitch or residuals, emissions can be significant.

The majority of gas streams exiting each refinery process contain varying amounts of refinery fuel gas, hydrogen sulfide and ammonia. These streams are collected and sent to the gas treatment and sulfur recovery units to recover the refinery fuel gas and sulfur. Emissions from the sulfur recovery unit typically contain some H₂S, SO₂, and NOₓ.

Other emissions sources from refinery processes arise from periodic regeneration of catalysts. These processes generate streams that may contain relatively high levels of carbon monoxide, particulates and VOCs. Before being discharged to the atmosphere, such off-gas streams may be treated first through a carbon
monoxide boiler to burn carbon monoxide and any VOCs, and then through an electrostatic precipitator or cyclone separator to remove particulate matter.

Wastewaters consist of cooling water, process water, sanitary sewage water, and storm water. Wastewaters are treated in on-site wastewater treatment facilities and then discharged to POTWs or discharged to surfaces waters under NPDES permits. In addition, some facilities use underground injection of some wastewater streams.

Many refineries unintentionally release, or have unintentionally released in the past, liquid hydrocarbons to ground water and surface waters. At some refineries contaminated groundwater has migrated off-site and resulted in continuous "seeps" to surface waters. While the actual volume of hydrocarbons released in such a manner is relatively small, there is the potential to contaminate large volumes of groundwater and surface water, possibly posing a substantial risk to human health and the environment.

There are a variety of other wastes that are generated from many of the refining processes, and petroleum-handling operations, as well as wastewater treatment. Both hazardous and nonhazardous wastes are generated, treated, and disposed.

Residual refinery wastes are typically in the form of sludges, spent process catalysts, filter clay, and incinerator ash. Treatment of these wastes includes incineration, land treating off-site, landfiling onsite, landfiling off-site, chemical fixation, neutralization, and other treatment methods.

A significant portion of the nonpetroleum product outputs of refineries is transported off-site and sold as by-products. These outputs include sulfur, acetic acid, phosphoric acid, and recovered metals. Metals from catalysts and from the crude oil that have deposited on the catalyst during the production often are recovered by third-party recovery facilities.

Table 1 provides a summary of the typical material outputs from major petroleum refining operations. Where possible, typical quantities and concentrations of pollutants are reported. These should be considered very approximate figures since no two refinery operations are identical. However, they do provide a general idea of the quantities, flows, and levels of different types of priority pollutants handled by refinery operations.
Table 1. Material Outputs from Selected Petroleum Refining Processes

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<th>Air emissions</th>
<th>Process waste water</th>
<th>Residual wastes generated</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Process: Crude oil desalting</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heater stack gas (CO, SO(_x), NO(_x), hydrocarbons and particulates), fugitive emissions (hydrocarbons)</td>
<td>Flow = 2.1 gal/bbl oil, H(_2)S, NH(_x), phenol, high levels of SS, dissolved solids, high BOD, high temperature</td>
<td>Crude oil/desalter sludge (iron rust, clay, sand, water, emulsified oil and wax, metals)</td>
</tr>
<tr>
<td><strong>Process: Atmospheric distillation and vacuum distillation</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heater stack gas (CO, SO(_x), NO(_x), hydrocarbons and PM), vents and fugitive emissions (hydrocarbons); steam ejector emissions (hydrocarbons), heater stack gas (CO, SO(_x), NO(_x), Hydrocarbons, and PM), vents and fugitive emissions (hydrocarbons)</td>
<td>Flow = 26.0 Gal/Bbl Oil, H(_2)S NH(_x), suspended solids, chlorides, mercaptans, phenol, elevated pH</td>
<td>Typically, little or no residual waste generated</td>
</tr>
<tr>
<td><strong>Process: Thermal Cracking/Visbreaking</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heater stack gas (CO, SO(_x), NO(_x), HCs and PM), vents, and fugitive emissions (HCs)</td>
<td>Flow = 2.0 Gal/Bbl Oil, H(_2)S NH(_x), phenol, suspended solids, high pH, BOD, COD</td>
<td>Typically, little or no residual waste generated</td>
</tr>
<tr>
<td><strong>Process: Coking</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heater stack gas (CO, SO(_x), NO(_x), hydrocarbons and PM), vents and fugitive emissions (HCs) and decoking emissions (HCs and PM)</td>
<td>Flow = 1.0 Gal/Bbl High pH, H(_2)S, NH(_x), SS, COD</td>
<td>Coke dust (carbon particles and HCs)</td>
</tr>
<tr>
<td><strong>Process: Catalytic cracking</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Air emissions</td>
<td>Process waste water</td>
<td>Residual wastes generated</td>
</tr>
<tr>
<td>---------------</td>
<td>---------------------</td>
<td>-------------------------</td>
</tr>
<tr>
<td>Heater stack gas (CO, SO(_x), NO(_x), HCs and PM), fugitive emissions (HCs) and catalyst regeneration (CO, NO(_x), SO(_x), and PM)</td>
<td>Flow = 15.0 gal/bbl high levels of oil, SS, phenols, cyanides, H(_2)S, NH(_3), high pH, BOD, COD</td>
<td>Spent catalysts (metals from crude oil and hydrocarbons), spent catalyst fines from ESps (aluminum silicate and metals)</td>
</tr>
<tr>
<td><strong>Process: Catalytic Hydrocracking</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heater stack gas (CO, SO(_x), NO(_x), hydrocarbons and PM), fugitive emissions (hydrocarbons) and catalyst regeneration (CO, NO(_x), SO(_x), and catalyst dust)</td>
<td>Flow = 2.0 Gal/Bbl High COD, SS, H(_2)S, relatively low levels of BOD</td>
<td>Spent catalysts fines (metals from crude oil, and hydrocarbons).</td>
</tr>
<tr>
<td><strong>Process: Hydrotreating/hydroprocessing</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heater stack gas (CO, SO(_x), NO(_x), hydrocarbons and PM), vents and fugitive emissions (HCs) and catalyst regeneration (CO, NO(_x), SO(_x))</td>
<td>Flow = 1.0 gal/bbl H(_2)S, NH, High pH, phenols, SS, BOD, COD</td>
<td>Spent catalyst fines (aluminum silicate and metals)</td>
</tr>
<tr>
<td><strong>Process: Alkylation</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heater stack gas (CO, SO(_x), NO(_x), HCs and PM), vents and fugitive emissions (HCs)</td>
<td>Low pH, SS, dissolved solids, COD, H(_2)S, spent sulfuric acid</td>
<td>Neutralized alkylation sludge (sulfuric acid or calcium fluoride, HCs)</td>
</tr>
<tr>
<td><strong>Process: Isomerization</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heater stack gas (CO, SO(_x), NO(_x), HCs and PM), HCl (potentially in light ends), vents and fugitive emissions (HCs)</td>
<td>Low pH, chloride salts, caustic wash, relatively low H(_2)S, and NH(_3)</td>
<td>Calcium chloride sludge from neutralized HCl gas</td>
</tr>
<tr>
<td><strong>Process: Polymerization</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Air emissions</td>
<td>Process waste water</td>
<td>Residual wastes generated</td>
</tr>
<tr>
<td>---------------</td>
<td>---------------------</td>
<td>--------------------------</td>
</tr>
<tr>
<td>H₂S, from caustic washing</td>
<td>H₂S, NH₃, caustic wash, mercaptans and ammonia, high pH</td>
<td>Spent catalyst containing phosphoric acid</td>
</tr>
</tbody>
</table>

**Process: Catalytic Reforming**

- Heater stack gas (CO, SOₓ, NOₓ, HCs and PM), fugitive emissions (hydrocarbons) and catalyst regeneration (CO, NOₓ, SOₓ)
- Fugitive emissions: SOₓ, NOₓ, HCs and PM, high levels of oil, SS, COD.
- Relatively low H₂S
- Spent catalyst fines from electrostatic precipitators (alumina silicate and metals)

**Process: Solvent Extraction**

- Fugitive solvents
- Oil and solvents
- Little or no residual wastes generated

**Process: Dewaxing**

- Fugitive solvents, heaters
- Oil and solvents
- Little or no residual wastes generated

**Process: Propane deasphalting**

- Heater stack gas (CO, SOₓ, NOₓ, HCs and PM), fugitive propane
- Oil and propane
- Little or no residual wastes generated

**Process: Merox treating**

- Vents and fugitive emissions (HCs and disulfides)
- Little or no wastewater generated
- Spent Merox caustic solution, waste oil-disulfide mixture

**Process: Wastewater treatment**

- Fugitive emissions (H₂S, NH₃, and HCs)
- Not Applicable
- API separator sludge (phenols, metals and oil), chemical precipitation sludge (chemical coagulants, oil), DAF floats, biological sludges (metals, oil, SS), spent lime

**Process: Gas treatment and sulfur recovery**
INDUSTRY PRACTICES

Air emissions
SO\textsubscript{x}, NO\textsubscript{x}, and H\textsubscript{2}S from vent and tail gas emissions

Process waste water
H\textsubscript{2}S, NH\textsubscript{3}, amines, Stretford solution

Residual wastes generated
Spent catalyst

\textit{Process: Blending}

Fugitive emissions (HCs).
Little or no wastewater generated.
Little or no residual waste generated.

\textit{Process: Heat exchanger cleaning}

Periodic fugitive emissions (HCs.)
Oily wastewater generated
Heat exchanger sludge (oil, metals, and SS)

\textit{Process: Storage tanks}

Fugitive emissions (hydrocarbons).
Water drained from tanks contaminated with tank product.
Tank bottom sludge (iron rust, clay, sand, water, emulsified oil and wax, metals).

\textit{Process: Blowdown and flaring operations}

Combustion products (CO, SO\textsubscript{x}, NO\textsubscript{x}, and HCs) from flares, fugitive emissions
Little or no wastewater generated
Little or no residual waste generated

\textit{Sources:}

POLLUTION PREVENTION PRACTICES AND OPPORTUNITIES

The Pollution Prevention Act of 1990 (PPA) requires facilities to report information about the management of TRI chemicals in waste and efforts made to eliminate or reduce those quantities. These data have been collected annually in the TRI reporting Form R beginning with the 1991 reporting year. The following discussions are based on a review of data between the years 1992 and 1995 and is meant to provide a basic understanding of the quantities of waste handled by the industry, the methods typically used to manage this waste, and recent trends, practices, and opportunities for further pollution prevention. From the yearly data it is apparent that the portion of the wastes reported as recycled on-site has increased and the portions treated or managed through energy recovery on-site have decreased between 1992 and 1995. Table 2 shows that the petroleum refining industry managed about 1.6 billion pounds of production-related waste. 
(total quantity of TRI chemicals in the waste from routine production operations) in 1993 (column B). Column C reveals that of this production-related waste, 30% was either transferred off-site or released to the environment. Column C is calculated by dividing the total TRI transfers and releases by the total quantity of production-related waste. In other words, about 70 percent of the industry’s TRI wastes were managed on-site through recycling, energy recovery, or treatment as shown in columns E, F, and G, respectively. The majority of waste that is released or transferred off-site can be divided into portions that are recycled off-site, recovered for energy off-site, or treated off-site as shown in columns H, I, and J, respectively. The remaining portion of the production related wastes (4%), shown in column D, is either released to the environment through direct discharges to air, land, water, and underground injection, or it is disposed of off-site. In general, toxic chemical releases have been declining. Reported releases dropped by 42.7% between 1988 and 1993, with declining trends continued throughout the 1990s. Although on-site releases have decreased, the total amount of reported toxic waste has not declined because the amount of toxic chemicals transferred off-site has increased. Transfers have increased from 3.7 billion pounds in 1991 to 4.7 billion pounds in 1993. Better management practices have led to increases in off-site transfers of toxic chemicals for recycling. The amount of TRI chemicals generated by the petroleum refining industry provides a gross profile of the types and relative amounts of toxic chemical outputs from refining processes. Additional information, which can be related back to possible compliance requirements, is available from the distribution of chemical releases across specific media within the environment.

Table 2. Source Reduction and Recycling Activity for Petroleum Industry

<table>
<thead>
<tr>
<th>Year</th>
<th>Quantity of production-related waste (10^6lbs.)^a</th>
<th>% Released and transferred^b</th>
<th>% Released and disposed off-site^c</th>
<th>On-site</th>
<th>Off-site</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>E</td>
<td>F</td>
</tr>
<tr>
<td>1992</td>
<td>1476</td>
<td>24%</td>
<td>3%</td>
<td>10%</td>
<td>37%</td>
</tr>
<tr>
<td>1993</td>
<td>1600</td>
<td>30%</td>
<td>4%</td>
<td>14%</td>
<td>36%</td>
</tr>
</tbody>
</table>
The petroleum refining industry releases 75% of its total TRI poundage to the air, 24% to the water (including 20% to underground injection and 4 percent to surface waters), and 1% to the land. This release profile differs from other TRI industries which average approximately 59% to air, 30% to water, and 10% to land. Examining the petroleum refining industry’s TRI reported toxic chemical releases highlights the likely origins of the large air releases for the industry.

According to TRI data, the petroleum refining industry releases (discharges to the air, water, or land without treatment) and transfers (shipped off-site) a total of 482 million pounds of pollutants per year, made up of 103 different chemicals. This represents about 11% of the total pounds of TRI chemicals released and transferred by all manufacturers in a year. In comparison, the chemical industry generates on the average 2.5 billion pounds per year, accounting for 33% of all releases and transfers.

Overall, the petroleum refining industry’s releases declined between 1988 and 1993. Between 1991 and 1993 the decrease in releases was 6.7% compared to the average for all industries of 18%. In the same period, however, transfers were reported to increase 65%, which is higher than the average increase in transfers of 25% for all manufacturing industries.

A large portion of the increases were in the form of transfers to recycling. Spent sulfuric acid generated in the alkylation process makes up about half of all transfers of TRI listed chemicals off-site. At the facility level, the industry reported a level of pollution prevention activities of 42% of all refineries which is slightly higher than the overall average of about 35% of TRI reporting facilities.

Comparisons of the reported pounds released or transferred per facility demonstrate that the petroleum refining industry is far above average in its pollutant releases and transfers per facility when compared to other TRI
industries. Of the twenty manufacturing SIC codes listed in the TRI database, the mean amount of pollutant release per facility (including petroleum refining) was approximately 120,000 pounds.

The TRI releases of the average petroleum refining facility (SIC 2911) were 404,000 pounds, making the industry 3.4 times higher in per facility releases than for other industries. For transfers, the mean of petroleum refining facilities was about 13 times as much that of all TRI manufacturing facilities (202,000 pounds transferred off-site per facility compared to 2,626,000 per refinery). These high releases and transfers per facility reflect the large volumes of material processed at a relatively small number of facilities.

Of the top 10 most frequently reported toxic chemicals on the TRI list, the prevalence of volatile chemicals explains the air intensive toxic chemical loading of the refining industry. Nine of the 10 most commonly reported toxic chemicals are highly volatile. Seven of the 10 are aromatic hydrocarbons (benzene, toluene, ethylbenzene, xylene, cyclohexane, 1,2,4-trimethylbenzene, and ethylbenzene).

Aromatic hydrocarbons are highly volatile compounds and make up a portion of both crude oil and many finished petroleum products. Ammonia, the ninth most commonly reported toxic chemical, is also released and transferred from petroleum refineries in large quantities. Ammonia may be found in high concentrations in process water streams from steam distillation processes and in refinery sour gas. The primary means of release to the environment is through underground injection of wastewater and emissions to air.

Gasoline blending additives (i.e., methanol, ethanol, and MTBE) and chemical feedstocks (propylene, ethylene, and naphthalene) are also commonly reported to TRI. Additives and chemical feedstocks are, for the most part, released as air emissions due to their high volatility. A significant portion of the remaining chemicals of the reported TRI toxic chemicals are metals compounds, which are typically transferred off-site for recovery or as a component of hazardous wastes.

Although it is not the most frequently reported toxic chemical released or transferred, sulfuric acid is generated in by far the largest quantities. Spent sulfuric acid is primarily generated during the alkylation process. The acid is typically transferred off-site for regeneration.

Table 3 provides a summary of the toxicity and fate information for the principal hazardous chemicals released by petroleum refinery operations. The table provides descriptions of the most common routes by which these pollutants enter the environment as a result of common refinery practices and operations.
Table 3. Toxicity and Environmental Fate Information.

**Ammonia CAS #7664-41-7**

**Sources.** Ammonia is formed from the nitrogen bearing components of crude oil and can be found throughout petroleum refineries in both the gaseous and aqueous forms. Gaseous ammonia often leaves distillation, cracking and treating processes mixed with the sour gas or acid gas along with refinery fuel gases and hydrogen sulfide. Aqueous ammonia is present in the sourwater generated in the vacuum distillation unit and steam strippers or fractionators. Some release sources include fugitive emissions, sour gas stripper, sulfur units, and wastewater discharges.

**Toxicity.** Anhydrous ammonia is irritating to the skin, eyes, nose, throat, and upper respiratory system. Ecologically, ammonia is a source of nitrogen (an essential element for aquatic plant growth) and may therefore contribute to eutrophication of standing or slow-moving surface water, particularly in nitrogen-limited waters such as the Chesapeake Bay. In addition, aqueous ammonia is moderately toxic to aquatic organisms.

**Carcinogenicity.** There is currently no evidence to suggest that this chemical is carcinogenic.

**Environmental Fate.** Ammonia combines with sulfate ions in the atmosphere and is washed out by rainfall, resulting in rapid return of ammonia to the soil and surface waters. Ammonia is a central compound in the environmental cycling of nitrogen. Ammonia in lakes, rivers, and streams is converted to nitrate.

**Physical Properties.** Ammonia is a corrosive and severely irritating gas with a pungent odor.

**Toluene CAS #108-88-3**

**Sources.** Toluene is a component of crude oil and is therefore present in many refining operations. Toluene is also produced during catalytic reforming and is sold as one of the large volume aromatics used as feedstocks in chemical manufacturing. Its volatile nature makes fugitive emissions its largest release source. Point air sources may arise during the process of separating toluene from other aromatics and from solvent dewaxing operations where toluene is often used as the solvent.

**Toxicity.** Inhalation or ingestion of toluene can cause headaches, confusion, weakness, and memory loss. Toluene may also affect the way the kidneys and liver function. Reactions of toluene in the atmosphere contribute to ozone formation. Ozone can affect the respiratory system, especially in sensitive individuals such as asthma or allergy sufferers. Unborn animals were harmed when high levels of toluene were inhaled by their mothers, although the same effects were not seen when the mothers were fed large quantities of toluene. Note that these results may reflect similar difficulties in humans.

**Carcinogenicity.** There is currently no evidence to suggest carcinogenicity.
Environmental Fate. A portion of releases of toluene to land and water will evaporate. Toluene may also be degraded by microorganisms. Once volatilized, toluene in the lower atmosphere will react with other atmospheric components contributing to the formation of ground-level ozone and other air pollutants.

Physical Properties. Toluene is a volatile organic chemical.

Xylenes (Mixed Isomers) CAS #1330-20-7

Sources. Xylene isomers are a component of crude oil and are therefore present in many refining operations. Xylenes are also produced during catalytic reforming and are sold as one of the large-volume aromatics used as feedstocks in chemical manufacturing. Xylenes volatile nature make fugitive emissions the largest release source. Point air sources may arise during the process of separating xylene from other aromatics.

Toxicity. Xylenes are rapidly absorbed into the body after inhalation, ingestion, or skin contact. Short-term exposure of humans to high levels of xylenes can cause irritation of the skin, eyes, nose, and throat, difficulty in breathing, impaired lung function, impaired memory, and possible changes in the liver and kidneys. Both short- and long-term exposure to high concentrations can cause effects such as headaches, dizziness, confusion, and lack of muscle coordination. Reactions of xylenes in the atmosphere contribute to the formation of ozone in the lower atmosphere. Ozone can affect the respiratory system, especially in sensitive individuals such as asthma or allergy sufferers.

Carcinogenicity. There is currently no evidence to suggest that this chemical is carcinogenic.

Environmental Fate. A portion of releases to land and water will quickly evaporate, although some degradation by microorganisms will occur. Xylenes are moderately mobile in soils and may leach into groundwater, where they may persist for many years. Xylenes are VOCs. As such, xylenes will react with other atmospheric components, contributing to the formation of ground-level ozone and other air pollutants.

Methyl Ethyl Ketone CAS #78-93-3

Sources. Methyl ethyl ketone (MEK) is used in some refineries as a solvent in lube oil dewaxing. Its extremely volatile characteristic makes fugitive emissions its primary source of releases to the environment.

Toxicity. Breathing moderate amounts of methyl ethyl ketone (MEK) for short periods of time can cause adverse effects on the nervous system ranging from headaches, dizziness, nausea, and numbness in the fingers and toes to unconsciousness. Its vapors are irritating to the skin, eyes, nose, and throat and can damage the eyes. Repeated exposure to moderate to high amounts may cause liver and kidney effects.
**Carcinogenicity.** No agreement exists over the carcinogenicity of MEK. One source believes MEK is a possible carcinogen in humans based on limited animal evidence. Other sources believe that there is insufficient evidence to make any statements about possible carcinogenicity.

**Environmental Fate.** Most of the MEK released to the environment will end up in the atmosphere. MEK can contribute to the formation of air pollutants in the lower atmosphere. It can be degraded by microorganisms living in water and soil.

**Physical Properties.** Methyl ethyl ketone is a flammable liquid.

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**Propylene CAS # 115-07-1**

**Sources.** Propylene (propene) is one of the light ends formed during catalytic and thermal cracking and coking operations. It is usually collected and used as a feedstock to the alklylation unit. Propylene is volatile and soluble in water making releases to both air and water significant.

**Toxicity.** At low concentrations, inhalation of propylene causes mild intoxication, a tingling sensation, and an inability to concentrate. At higher concentrations, unconsciousness, vomiting, severe vertigo, reduced blood pressure, and disordered heart rhythms may occur. Skin or eye contact with propylene causes freezing burns. Reaction of propylene (see environmental fate) in the atmosphere contributes to the formation of ozone in the lower atmosphere. Ozone can affect the respiratory system, especially in sensitive individuals such as asthma or allergy sufferers. Ecologically, similar to ethylene, propylene has a stimulating effect on plant growth at low concentrations, but inhibits plant growth at high levels.

**Carcinogenicity.** There is currently no evidence to suggest that this chemical is carcinogenic.

**Environmental Fate.** Propylene is degraded principally by hydroxyl ions in the atmosphere. Propylene released to soil and water is removed primarily through volatilization. Hydrolysis, bioconcentration, and soil adsorption are not expected to be significant fate processes of propylene in soil or aquatic ecosystems. Propylene is readily biodegraded by microorganisms in surface water.

**Physical Properties.** Propylene is a volatile organic chemical.

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**Benzene CAS # 71-43-2**

**Sources.** Benzene is a component of crude oil. It is also produced during catalytic reforming and is sold as one of the large volume aromatics used as feedstocks in chemical manufacturing. Benzene's volatile nature makes fugitive emissions the largest release source.
Toxicity. Short-term inhalation of benzene affects the central nervous system and respiratory system. Chronic exposure causes bone marrow toxicity in animals and humans, causing suppression of the immune system and development of leukemia. Ingestion of benzene is rare. Reactions of benzene in the atmosphere contributes to the formation of ozone in the lower atmosphere (troposphere).

Carcinogenicity. Benzene is a known human carcinogen.

Environmental Fate. A portion of benzene releases to soil and surface waters evaporate rapidly. Benzene is highly mobile in the soil and may leach to groundwater. Once in groundwater, it is likely biodegraded by microorganisms only in the presence of oxygen. Benzene is not expected to significantly adsorb to sediments, bioconcentrate in aquatic organisms, or break down in water. Atmospheric benzene is broken down through reacting with chemical ions in the air; this process is greatly accelerated in the presence of other air pollutants such as nitrogen oxides or sulfur dioxide. Benzene is fairly soluble in water and is removed from the atmosphere in rain. As a volatile chemical, benzene in the lower atmosphere will react with other atmospheric components, contributing to the formation of ground-level ozone and other air pollutants, which can contribute to respiratory illnesses in both the general and highly susceptible populations, such as asthmatics and allergic sufferers.

In addition to chemicals covered under TRI, many other chemicals are released. For example, the EPA Office of Air Quality Planning and Standards has compiled air pollutant emission factors for determining the total air emissions of priority pollutants (e.g., VOCs, SO₂, NOₓ, CO, particulates, etc.) from many refinery sources. The EPA Office of Aerometric Information Retrieval System (AIRS) contains a wide range of information related to stationary sources of air pollution, including the emissions of a number of air pollutants which may be of concern within a particular industry. With the exception of volatile organic compounds (VOCs), there is little overlap with the TRI chemicals reported above.

Control technologies employed for the handling of air emissions normally include the capture and recycling or combustion of emissions from vents, product transfer points, storage tanks, and other handling equipment. Boilers, heaters, other combustion devices, cokers, and catalytic units may require particulate matter controls. Use of a carbon monoxide boiler is normally a standard practice in the fluidized catalytic cracking units. Catalytic cracking units should be provided with particular removal devices. Steam injection in flaring stacks can reduce particulate matter emissions.

Refinery wastewaters often require a combination of treatment methods to remove oil and contaminants before discharge. Separation of different streams,
such as stormwater, cooling water, process water, sanitary, and sewage, is essential for minimizing treatment requirements. A typical system may include sour water stripper, gravity separation of oil and water, dissolved air flotation, biological treatment, and clarification. A final polishing step using filtration, activated carbon, or chemical treatment may also be required. Achievable pollutant loads per ton of crude processed include BOD, 6 g; COD, 50 g; suspended solids, 10 g; and oil and grease, 2 g.

Sludge treatment is usually performed using land application (bioremediation) or solvent extraction followed by combustion of the residue or by use for asphalt, where feasible. In some cases, the residue may require stabilization prior to disposal to reduce the leachability of toxic metals. Oil is recovered from slops using separation techniques such as gravity separators and centrifuges.

Implementation of pollution prevention measures can yield both economic and environmental benefits. However, a balance on energy usage and environmental impacts may have to be struck. New refineries should be designed to maximize energy conservation and reduce hydrocarbon losses. A good target for simple refineries (i.e., refineries with distillation, catalytic reforming, hydrotreating, and off-site facilities) is that the total quantity of oil consumed as fuel and lost in production operations should not exceed 3.5% of the throughput. For refineries with secondary conversion units (i.e., hydrocrackers or lubricating oil units), the target should be 5-6% (and, in some cases, up to 10%) of the throughput. Fugitive VOC emissions from the process units can be reduced to 0.05% of the throughput, with total VOC emissions of less than 1 kg per ton of crude (or 0.1% of throughput). Methods of estimating these figures include emissions monitoring, mass balance, and inventories of emissions sources. Design assumptions should be recorded to allow for subsequent computation and reduction of losses. Vapor recovery systems to control losses of VOCs from storage tanks and loading areas should achieve 90-100% recovery.

Plant operators should aim at using fuel with less than 0.5% sulfur (or an emissions level corresponding to 0.5% sulfur in fuel). High-sulfur fuels should be directed to units equipped with SOx controls. Fuel blending is another option. A sulfur recovery system that achieves at least 97% (but preferably over 99%) sulfur recovery should be used when the hydrogen sulfide concentration in tail gases exceeds 230 mg/Nm³. The total release of sulfur dioxide should be below 0.5 kg per ton for a hydroskimming refinery and below 1 kg per ton for a conversion refinery. A wastewater generation rate of 0.4 m³/t of crude processed is achievable with good design and operation, and new refineries should achieve this target as a minimum. The generation rate of solid wastes and sludges should be less than 0.5% of the crude processed, with a target of 0.3%.
As already noted, petroleum refineries are complex plants, and the combination and sequence of processes is usually very specific to the characteristics of the raw materials (crude oil) and the products. Specific pollution prevention or source reduction measures can often be determined only by the technical staff of the specific refinery operation. However, there are a number of general areas where improvements are often possible, and site-specific waste reduction measures in these areas should be designed into the plant and targeted by management of operating plants. Areas where efforts should be concentrated are summarized in Table 4.

Although numerous cases have been documented where petroleum refineries have simultaneously reduced pollution outputs and operating costs through pollution prevention techniques, there are often barriers to their implementation. The primary barrier to most pollution prevention projects is cost. Many pollution prevention options simply do not pay for themselves, or the economics often appear marginal. Corporate investments typically must earn an adequate return on invested capital for the shareholders and some pollution prevention options at some facilities may not meet the requirements set by company policies. Additionally, the equipment used in the petroleum refining industry are very capital intensive and have very long lifetimes. This reduces the incentive to make process modifications to (expensive) installed equipment that is still useful.

It should be emphasized however, that pollution prevention techniques are, nevertheless, often more cost-effective than pollution reduction through end-of-pipe treatment technologies. A case study based on the Amoco/EPA joint study claimed that the same pollution reduction currently realized through end-of-pipe regulatory requirements at the Amoco facility could be achieved at 15 percent the current costs using pollution prevention techniques. To better understand some of the broad areas of pollution prevention practices listed in Table 4, the following provides a summary of these widespread pollution prevention techniques found to be effective at petroleum refineries.

**Process and Equipment Modification Practices**

**Place secondary seals on storage tanks.** One of the largest sources of fugitive emissions from refineries is storage tanks containing gasoline and other volatile products. These losses can be significantly reduced by installing secondary seals on storage tanks. An Amoco/EPA joint study estimated that VOC losses from storage tanks could be reduced 75 to 93%. Equipping an average tank with a secondary seal system was estimated to cost about $20,000.
### Table 4. Recommended Pollution Prevention Practices

<table>
<thead>
<tr>
<th>Area of Opportunity</th>
<th>Recommended pollution prevention practice</th>
</tr>
</thead>
</table>
| **Reduction of air emissions** | 1. Minimize losses from storage tanks and product transfer areas by methods such as vapor recovery systems and double seals.  
2. Minimize SOx emissions either through desulfurization of fuels, to the extent feasible, or by directing the use of high-sulfur fuels to units equipped with SOx emissions controls.  
3. Recover sulfur from tail gases in high-efficiency sulfur recovery units.  
4. Recover nonsilica-based (i.e., metallic) catalysts and reduce particulate emissions.  
5. Use low-NOx burners to reduce nitrogen oxide emissions.  
6. Avoid and limit fugitive emissions by proper process design and maintenance.  
7. Keep fuel usage to a minimum. |
| **Elimination or reduction of pollutants** | 8. Consider reformate and other octane boosters instead of tetraethyl lead and other organic lead compounds for octane boosting.  
9. Use nonchrome-based inhibitors in cooling water, where inhibitors are needed.  
10. Use long-life catalysts and regenerate to extend the catalysts’ life cycle. |
| **Recycling and reuse** | 11. Recycle cooling water and, where cost-effective, treated wastewater.  
12. Maximize recovery of oil from oily waste waters and sludges. Minimize losses of oil to the effluent system.  
13. Recover and reuse phenols, caustics, and solvents from their spent solutions.  
14. Return oily sludges to coking units or crude distillation units. |
| **Operating procedures** | 15. Segregate oily waste waters from stormwater systems.  
16. Reduce oil losses during tank drainage carried out to remove water before product dispatch.  
17. Optimize frequency of tank and equipment cleaning to avoid accumulating residue at the bottom of the tanks.  
18. Prevent solids and oily wastes from entering the drainage system. |
19. Institute dry sweeping instead of washdown to reduce wastewater volumes.
20. Establish and maintain an emergency preparedness and response plan and carry out frequent training.
21. Practice corrosion monitoring, prevention, and control in underground piping and tank bottoms.
22. Establish leak detection and repair programs.

Establish leak detection and repair program. Fugitive emissions are one of the largest sources of refinery hydrocarbon emissions. A leak detection and repair (LDAR) program consists of using a portable VOC detecting instrument to detect leaks during regularly scheduled inspections of valves, flanges, and pump seals. Leaks are then repaired immediately or are scheduled for repair as quickly as possible. A LDAR program could reduce fugitive emissions 40 to 64%, depending on the frequency of inspections.

Regenerate or eliminate filtration clay. Clay from refinery filters must periodically be replaced. Spent clay often contains significant amounts of entrained hydrocarbons and, therefore, must be designated as hazardous waste. Back washing spent clay with water or steam can reduce the hydrocarbon content to levels so that it can be reused or handled as a nonhazardous waste. Another method used to regenerate clay is to wash the clay with naphtha, dry it by steam heating and then feed it to a burning kiln for regeneration. In some cases clay filtration can be replaced entirely with hydrotreating.

Reduce the generation of tank bottoms. Tank bottoms from crude oil storage tanks constitute a large percentage of refinery solid waste and pose a particularly difficult disposal problem because of the presence of heavy metals. Tank bottoms comprise of heavy hydrocarbons, solids, water, rust and scale. Minimization of tank bottoms is carried out most cost effectively through careful separation of the oil and water remaining in the tank bottom. Filters and centrifuges can also be used to recover the oil for recycling.

Minimize solids leaving the desalter. Solids entering the crude distillation unit are likely to eventually attract more oil and produce additional emulsions and sludges. The amount of solids removed from the desalting unit should, therefore, be maximized. A number of techniques can be used, such as using low-shear mixing devices to mix desalter wash water and crude oil; using lower pressure water in the desalter to avoid turbulence; and replacing the water jets used in some refineries with mud rakes which add less turbulence when removing settled solids.
Minimize cooling-tower blowdown. The dissolved solids concentration in the recirculating cooling water is controlled by purging or blowing down a portion of the cooling-water stream to the wastewater treatment system. Solids in the blowdown eventually create additional sludge in the wastewater treatment plant. However, the amount of cooling tower blowdown can be lowered by minimizing the dissolved solids content of the cooling water. A significant portion of the total dissolved solids in the cooling water can originate in the cooling water makeup stream in the form of naturally occurring calcium carbonates. Such solids can be controlled either by selecting a source of cooling tower makeup water with less dissolved solids or by removing the dissolved solids from the makeup water stream. Common treatment methods include cold lime softening, reverse osmosis, or electrodialysis.

Install vapor recovery for barge loading. Although barge loading is not a factor for all refineries, it is an important emissions source for many facilities. One of the largest sources of VOC emissions identified during the Amoco/EPA study was fugitive emissions from loading of tanker barges. It was estimated that these emissions could be reduced 98% by installing a marine vapor loss control system. Such systems could consist of vapor recovery or VOC destruction in a flare.

Minimize FCCU decant oil sludge. Decant oil sludge from the fluidized bed catalytic cracking unit (FCCU) can contain significant concentrations of catalyst fines. These fines often prevent the use of decant oil as a feedstock or require treatment which generates an oily catalyst sludge. Catalysts in the decant oil can be minimized by using a decant-oil catalyst removal system. One system incorporates high voltage electric fields to polarize and capture catalyst particles in the oil. The amount of catalyst fines reaching the decant oil can be minimized by installing high-efficiency cyclones in the reactor to shift catalyst fines losses from the decant oil to the regenerator where they can be collected in the electrostatic precipitator.

Control of heat-exchanger cleaning solids. In many refineries, using high pressure water to clean heat exchanger bundles generates and releases water and entrained solids to the refinery wastewater treatment system. Exchanger solids may then attract oil as they move through the sewer system and may also produce finer solids and stabilized emulsions that are more difficult to remove. Solids can be removed at the heat-exchanger cleaning pad by installing concrete overflow weirs around the surface drains or by covering drains with a screen. Other ways to reduce solids generation are by using antifoulants on the heat exchanger bundles to prevent scaling and by cleaning with reusable cleaning chemicals that also allow for the easy removal of oil.
Control of surfactants in wastewater. Surfactants entering the refinery wastewater streams will increase the amount of emulsions and sludges generated. Surfactants can enter the system from a number of sources, including washing unit pads with detergents; treating gasolines with an end point over 400°F; thereby producing spent caustics; cleaning tank truck tank interiors; and using soaps and cleaners for miscellaneous tasks. In addition, the overuse, and mixing of the organic polymers used to separate oil, water, and solids in the wastewater treatment plant can actually stabilize emulsions. The use of surfactants should be minimized by educating operators, by routing surfactant sources to a point downstream of the DAF unit and by using dry cleaning, high-pressure water, or steam to clean oil surfaces of oil and dirt.

Thermal treatment of applicable sludges. The toxicity and volume of some deoiled and dewatered sludges can be further reduced through thermal treatment. Thermal sludge treatment units use heat to vaporize the water and volatile components in the feed and leave behind a dry solid residue. The vapors are condensed for separation into the hydrocarbon and water components. Non-condensible vapors are either flared or sent to the refinery amine unit for treatment and use as refinery fuel gas.

Eliminate use of open ponds. Open ponds used to cool, settle out solids, and store process water can be a significant source of VOC emissions. Wastewater from coke cooling and coke VOC removal is occasionally cooled in open ponds where VOCs easily escape to the atmosphere. In many cases, open ponds can be replaced with closed storage tanks.

Remove unnecessary storage tanks from service. Since storage tanks are one of the largest sources of VOC emissions, a reduction in the number of these tanks can have a significant impact. The need for certain tanks can often be eliminated through improved production planning and more continuous operations. By minimizing the number of storage tanks, tank bottom solids and decanted wastewater may also be reduced.

Replace old boilers. Older refinery boilers can be a significant source of SO₂, NOₓ, and particulate emissions. It is possible to replace a large number of old boilers with a single new cogeneration plant with emissions controls.

Modify the FCCU to allow the use of catalyst fines. Some FCCUs can be modified to recycle some of the catalyst fines generated.

Reduce the use of 55-gallon drums. Replacing 55-gallon drums with bulk storage can minimize the chances of leaks and spills.
Install rupture disks and plugs. Rupture disks on pressure-relief valves and plugs in open-ended valves can reduce fugitive emissions.

Install high pressure power washer. Chlorinated solvent vapor degreasers can be replaced with high-pressure power washers which do not generate spent solvent hazardous wastes.

Refurbish or eliminate underground piping. Underground piping can be a source of undetected releases to the soil and groundwater. Inspecting, repairing, or replacing underground piping with surface piping can reduce or eliminate these potential sources.

Waste Segregation and Separation Practices

Segregate process waste streams. A significant portion of refinery waste arises from oily sludges found in combined process/storm sewers. Segregation of the relatively clean rainwater runoff from the process streams can reduce the quantity of oily sludges generated. Furthermore, there is a much higher potential for recovery of oil from smaller, more concentrated process streams.

Control solids entering sewers. Solids released to the wastewater sewer system can account for a large portion of a refinery's oily sludges. Solids entering the sewer system (primarily soil particles) become coated with oil and are deposited as oily sludges in the API oil/water separator. Because a typical sludge has a solids content of 5 to 30% by weight, preventing 1 lb of solids from entering the sewer system can eliminate 3 to 20 pounds of oily sludge. An Amoco/EPA study estimated that at the Yorktown facility 1000 tons of solids per year enter the refinery sewer system. Solids controls methods include using a street sweeper on paved areas, paving unpaved areas, planting ground cover on unpaved areas, relining sewers, cleaning solids from ditches and catch basins, and reducing heat-exchanger bundle cleaning solids by using antifoulants in cooling water.

Improve recovery of oils from oily sludges. Because oily sludges make up a large portion of refinery solid wastes, any improvement in the recovery of oil from the sludges can significantly reduce the volume of waste. There are a number of technologies currently in use to mechanically separate oil, water and solids, including belt filter presses, recessed chamber pressure filters, rotary vacuum filters, scroll centrifuges, disk centrifuges, shakers, thermal driers, and centrifuge-drier combinations.

Identify benzene sources and install upstream water treatment. Benzene in wastewater can often be treated more easily and effectively at the point, where it is generated rather than at the wastewater treatment plant after it is mixed with other wastewater.
Recycling Practices

Recycle and regenerate spent caustics. Caustics used to absorb and remove hydrogen sulfide and phenol contaminants from intermediate and final product streams can often be recycled. Spent caustics may be saleable to chemical recovery companies if concentrations of phenol or hydrogen sulfide are high enough. Process changes in the refinery may be needed to raise the concentration of phenols in the caustic to make recovery of the contaminants economical. Caustics containing phenols can also be recycled on-site by reducing the pH of the caustic until the phenols become insoluble thereby allowing physical separation. The caustic can then be treated along with the refinery wastewaters.

Use oily sludges as feedstock. Many oily sludges can be sent to a coking unit or the crude distillation unit where they become part of the refinery products. Sludge sent to the coker can be injected into the coke drum with the quench water, injected directly into the delayed coker, or injected into the coker blowdown contactor used in separating the quenching products. Use of sludge as a feedstock has increased significantly in recent years and is currently carried out by most refineries. The quantity of sludge that can be sent to the coker is restricted by coke quality specifications which may limit the amount of sludge solids in the coke. Coking operations can be upgraded, however, to increase the amount of sludge that they can handle.

Control and reuse FCCU and coke fines. Significant quantities of catalyst fines are often present around the FCCU catalyst hoppers and reactor and regeneration vessels. Coke fines are often present around the coker unit and coke storage areas. The fines can be collected and recycled before being washed to the sewers or migrating off-site via the wind. Collection techniques include dry sweeping the catalyst and coke fines and sending the solids to be recycled or disposed of as nonhazardous waste. Coke fines can also be recycled for fuel use. Another collection technique involves the use of vacuum ducts in dusty areas (and vacuum hoses for manual collection) which run to a small baghouse.

Recycle lab samples. Lab samples can be recycled to the oil recovery system.

Training and Supervision

Train personnel to reduce solids in sewers. A facility training program which emphasizes the importance of keeping solids out of the sewer systems will help reduce that portion of wastewater treatment plant sludge arising from the everyday activities of refinery personnel.
Train personnel to prevent soil contamination. Contaminated soil can be reduced by educating personnel on how to avoid leaks and spills.

Material Substitution

Use nonhazardous degreasers. Spent conventional degreaser solvents can be reduced or eliminated through substitution with less toxic and/or biodegradable products.

Eliminate chromates as an anti-corrosive. Chromate-containing wastes can be reduced or eliminated in cooling tower and heat exchanger sludges by replacing chromates with less toxic alternatives such as phosphates.

Use high-quality catalysts. By using catalysts of a higher quality, process efficiencies can be increased while the required frequency of catalyst replacement can be reduced.

Replace ceramic catalyst support with activated alumina supports. Activated alumina supports can be recycled with spent alumina catalyst.

ALUMINUM MANUFACTURING

INDUSTRY DESCRIPTION AND PRACTICES

The United States' aluminum industry annually produces about $39.1 billion in products and exports. U.S. companies are the largest single producer of primary aluminum. The U.S. industry operates more than 300 plants in 35 states, produces more than 23 billion pounds of metal annually, and employs more than 145,000 people with an annual payroll of about $5 billion.

Aluminum is the second most abundant metallic element in the earth's crust after silicon. It weighs about one-third as much as steel or copper; is malleable, ductile, and easily machined and cast; and has excellent corrosion resistance and durability. Measured in either quantity or value, aluminum's use exceeds that of any other metal except iron, and it is critical to many segments of the world economy. Some of the many uses for aluminum are in transportation (automobiles, airplanes, trucks, railcars, marine vessels, etc.), packaging (cans, foil, etc.), construction (windows, doors, siding, etc.), consumer durables (appliances, cooking utensils, etc.), electrical transmission lines, and machinery.
Aluminum recovery from scrap (recycling) has become an important component of the aluminum industry. A common practice since the early 1900s, aluminum recycling is not new. It was, however, a low-profile activity until the late 1960s when recycling of aluminum beverage cans finally vaulted recycling into the public consciousness. Sources for recycled aluminum include automobiles, windows and doors, appliances, and other products.

The top markets for the industry are transportation, beverage cans and other packaging, and building construction. In the 1990s transportation first emerged as the largest market for aluminum, at about one-quarter of the market, with passenger cars accounting for the vast majority of the growth. That trend has continued each subsequent year. Automotive and light truck applications accounted for almost 5.2 billion pounds of aluminum in 2000, or about one-fifth of industry shipments. In 2000, transportation accounted for 32.5% of all U.S. shipments. That same year aluminum passed plastic—with average content of 257 lb per vehicle—to become the third most-used material in automobiles. Automakers are increasingly choosing aluminum to improve fuel economy, reduce emissions, and enhance vehicle performance.

Containers and packaging rank second to transportation with 20.4% of the market, thanks to shipments of 4,992 million pounds in products such as beverage cans, food containers, and household and institutional foil. Product producers and consumers are increasingly using foil because it has numerous applications.

Largely because of products in the residential, industrial, commercial, farm, and highway sectors, the 1999 building and construction market accounted for 3,237 millions of pounds of net shipments, good for 13.1% of total shipments and the third largest domestic market for aluminum.

MANUFACTURING

Aluminum originates as an oxide called alumina. Deposits of bauxite ore are mined and refined into alumina—one of the feedstocks for aluminum metal. Then alumina and electricity are combined in a cell with a molten electrolyte called cryolite. Direct-current electricity is passed from a consumable carbon anode into the cryolite, splitting the aluminum oxide into molten aluminum metal and carbon dioxide. The molten aluminum collects at the bottom of the cell and is periodically "tapped" into a crucible and cast into ingots. While continual progress has been made over the more than 110-year history of aluminum processing to reduce the amount of electricity used, there are currently no viable alternatives to the electrometallurgical process. Between materials recovery and ongoing innovative research and development efforts, the aluminum industry is
constantly searching for areas where energy and costs can be reduced. In the past two decades, the energy efficiency of the production of metal has improved by about 20%.

PRODUCTS

The U.S. aluminum supply comprises three basic sources:

- **Primary** (domestic production from ore material)
- **Imports** (of primary and secondary ingot and mill products) and
- **Recycled** (metal recovered from scrap, also known as secondary recovery)

In 2000, the nation's total aluminum supply was 10.69 million metric tons, a decrease of 4.1% from 1999. Since 1990 the nation's total supply has expanded at an average rate of 3.4% annually. In 2000, primary production increased to 34.3% of total supply, and imports rose to 33.5%, while secondary recovery accounted for 32.2%.

Fabricated products include the following:

- **Castings**. The automotive industry is the largest market for aluminum castings and cast products make up more than half of the aluminum used in cars. Cast aluminum transmission housings and pistons have been virtually universal in cars and trucks throughout the world for years.
- **Extrusions**. To many designers and materials specifiers, extruded aluminum is the material of choice for countless applications. Experts chose aluminum profiles because extrusion offers so many design options: various alloys can be readily formed into complex shapes; extrusion tooling is inexpensive; lead times for custom shapes or prototypes are relatively brief; many different finishes are available; and the life cycle value of the product remains high because of aluminum's recyclability.
- **Mill products**.

ENERGY USE

The aluminum industry is a major user of electricity, spending more than $2 billion per year on energy. Since the electrolytic process is the only commercially proven method of producing aluminum, the industry has on its own pursued opportunities to reduce its use of electricity. In the past 50 years, the average
amount of electricity needed to make a pound of aluminum has been slashed from 12 kilowatt hours to about 7 kilowatt hours.

RECYCLING

Total aluminum industry supply in 2001 was 10.69 million metric tons, 33% of which was recycled aluminum. Of the 101 billion aluminum cans shipped in 2000, 62.1% (63 billion) were recycled. Almost 90% of automotive aluminum is reclaimed and recycled. Recycling of aluminum saves energy and removes some 95% of emissions association with making new aluminum from ore. Recycling is also a critical component of the industry, both from its contributions to the environment and because of the favorable economic impact on production. This dual benefit is probably the reason aluminum beverage cans now account for virtually all of the beverage can market, and most of the total single-serve beverage market. The contribution of recycling has had a positive impact on the industry with energy savings brought about with the increased proportion of recycled metal as a resource. For instance, the energy used to produce aluminum is saved for future reuse through recycling. Recycling saves almost 95% of the energy needed to produce aluminum from its original source, bauxite ore. As of 2000, over one-third of the total U.S. aluminum supply is provided through recycling. Aluminum is the most commonly recycled postconsumer metal in the world.

The production of aluminum begins with the mining and beneficiation of bauxite. At the mine (usually of the surface type), bauxite ore is removed to a crusher. The crushed ore is then screened and stockpiled, ready for delivery to an alumina plant. In some cases, ore is upgraded by beneficiation (washing, size classification, and separation of liquids and solids) to remove unwanted materials such as clay and silica.

At the alumina plant, the bauxite ore is further crushed to the correct particle size for efficient extraction of the alumina through digestion by hot sodium hydroxide liquor. After removal of "red mud" (the insoluble part of the bauxite) and fine solids from the process liquor, aluminum trihydrate crystals are precipitated and calcined in rotary kilns or fluidized bed calciners to produce alumina (Al₂O₃). Some alumina processes include a liquor purification step.

Primary aluminum is produced by the electrolytic reduction of the alumina. The alumina is dissolved in a molten bath of fluoride compounds (the electrolyte), and an electric current is passed through the bath, causing the alumina to dissociate to form liquid aluminum and oxygen. The oxygen reacts with carbon in the
electrode to produce carbon dioxide and carbon monoxide. Molten aluminum collects in the bottom of the individual cells or pots and is removed under vacuum into tapping crucibles. There are two prominent technologies for aluminum smelting: prebake and Soderberg. The following discussions focus on the prebake technology, with its associated reduced air emissions and energy efficiencies.

Raw materials for secondary aluminum production are scrap, chips, and dross. Pretreatment of scrap by shredding, sieving, magnetic separation, drying, and so on is designed to remove undesirable substances that affect both aluminum quality and air emissions. The prevailing process for secondary aluminum production is smelting in rotary kilns under a salt cover. Salt slag can be processed and reutilized. Other processes (smelting in induction furnaces and hearth furnaces) need no or substantially less salt and are associated with lower energy demand, but they are only suitable for high-grade scrap.

Depending on the desired application, additional refining may be necessary. For demagging (removal of magnesium from the melt), hazardous substances such as chlorine and hexachloroethane are often used, which may produce dioxins and dibenzofurans. Other, less hazardous methods, such as adding chlorine salts, are available. Because it is difficult to remove alloying elements such as copper and zinc from an aluminum melt, separate collection and separate reutilization of different grades of aluminum scrap are necessary. Note that secondary aluminum production uses substantially less energy than primary production (less than 10-20 gigajoules per metric ton (GJ/t) of aluminum produced, compared with 164 GJ/t for primary production).

POLLUTION PREVENTION PRACTICES AND OPPORTUNITIES

At the bauxite production facilities, dust is emitted to the atmosphere from dryers and materials-handling equipment, through vehicular movement, and from blasting. Although the dust is not hazardous, it can be a nuisance if containment systems are not in place, especially on the dryers and handling equipment. Other air emissions could include NOx, SOx, and other products of combustion from the bauxite dryers. Ore washing and beneficiation yield process wastewaters containing suspended solids. Runoff from precipitation may also contain suspended solids. At the alumina plant, air emissions can include bauxite dust from handling and processing, limestone dust from limestone handling, burnt lime dust from conveyors and bins, alumina dust from materials handling, red mud dust and sodium salts from red mud stacks (impoundments), caustic aerosols
from cooling towers, and products of combustion such as sulfur dioxide and
nitrogen oxides from boilers, calciners, various mobile equipment, and kilns. The
calciners may also emit alumina dust and the kilns, burnt lime dust.

Although alumina plants do not normally discharge effluents, heavy rainfalls can
result in surface runoff that exceeds what the plant can use in the process. The
excess may require treatment.

The main solid waste from the alumina plant is red mud (as much as 2 tons of
mud per ton of alumina produced), which contains oxides of alumina, silicon,
iron, titanium, sodium, calcium, and other elements. The pH is typically between
10 and 12. Disposal is to an impoundment.

Hazardous wastes from the alumina plant include spent sulfuric acid from
descaling in tanks and pipes. Salt cake may be produced from liquor purification
if this is practiced.

In the aluminum smelter, air emissions include alumina dust from handling
facilities; coke dust from coke handling; gaseous and particulate fluorides; sulfur
and carbon dioxides and various dusts from the electrolytic reduction cells;
gaseous and particulate fluorides; sulfur dioxide; tar vapor and carbon
particulates from the baking furnace; coke dust, tars, and polynuclear aromatic
hydrocarbons (PAHs) from the green carbon and anode-forming plant; carbon
dust from the rodding room; and fluxing emissions and carbon oxides from
smelting, anode production, casting, and finishing operations. The electrolytic
reduction cells (pot line) are the major source of the air emissions, with the
gaseous and particulate fluorides being of prime concern. The anode effect
associated with electrolysis also results in emissions of carbon tetrafluoride (CF₄)
and carbon hexafluoride (C₂F₆), which are greenhouse gases of concern because
of their potential for global warming. Emissions numbers that have been reported
for uncontrolled gases from smelters are 20 to 80 kg/t for particulates, 6 to 12
kg/t for hydrogen fluoride, and 6-10 kg/t for fluoride particulates. Corresponding
concentrations are 200 to 800 mg/m³; 60 to 120 mg/m³; and 60 to 100 mg/m³.
An aluminum smelter produces 40 to 60 kg of mixed solid wastes per ton of
product, with spent cathodes (spent pot and cell linings) being the major fraction.
The linings consist of 50% refractory material and 50% carbon. Over the useful
life of the linings, the carbon becomes impregnated with aluminum and silicon
oxides (averaging 16% of the carbon lining), fluorides (34% of the lining), and
cyanide compounds (about 400 parts per million). Contaminant levels in the
refractory portion of linings that have failed are generally low. Other by-products
for disposal include skim, dross, fluxing slags, and road sweepings.
Atmospheric emissions from secondary aluminummelting include hydrogen chloride and fluorine compounds. Demagging may lead to emissions of chlorine, hexachloroethane, chlorinated benzenes, and dioxins and furans. Chlorinated compounds may also result from the melting of aluminum scrap that is coated with plastic. Salt slag processing emits hydrogen and methane. Solid wastes from the production of secondary aluminum include particulates, pot lining refractory material, and salt slag. Particulate emissions containing heavy metals are also associated with secondary aluminum production.

Pollution prevention is always preferred to the use of end-of-pipe pollution-control facilities. Therefore every attempt should be made to incorporate cleaner production processes and facilities to limit, at source, the quantity of pollutants generated.

In the bauxite mine, where beneficiation and ore washing are practiced, a tailings slurry of 79% solids is produced for disposal. The preferred technology is to concentrate these tailings and dispose of them in the mined-out area. A concentration of 25 to 30% can be achieved through gravity settling in a tailings pond. The tailings can be further concentrated, using a thickener, to 30-50%, yielding a substantially volume-reduced slurry.

The alumina plant discharges red mud in a slurry of 25 to 30% solids, and this also presents an opportunity to reduce disposal volumes. Modern technology, in the form of high-efficiency deep thickeners, and large-diameter conventional thickeners, can produce a mud of 50-60% solids concentration. The lime used in the process forms insoluble solids that leave the plant along with the red mud. These lime-based solids can be minimized by recycling the lime used as a filtering aid to digestion to displace the fresh lime that is normally added at this point. Also, effluent volume from the alumina plant can be minimized or eliminated by good design and operating practices: reducing the water added to the process, segregating condensates and recycling to the process, and using rainwater in the process. Using the prebake technology rather than the Soderberg technology for aluminum smelting is a significant pollution prevention measure. In the smelter, computer controls and point feeding of aluminum oxide to the centerline of the cell help reduce emissions, including emissions of organic fluorides such as CF₄, which can be held at less than 0.1 kg/t aluminum. Energy consumption is typically 14 megawatt hours per ton (MWh/t) of aluminum, with prebake technology. Soderberg technology uses 17.5 MWh/t. Gas collection efficiencies for the prebake process is better than for the Soderberg process: 98% versus 90%. Dry scrubber systems using aluminum oxide as the adsorbent for the
cell gas permit the recycling of fluorides. The use of low-sulfur tars for baking anodes helps control SO$_2$ emissions. Spent pot linings are removed after they fail, typically because of cracking or heaving of the lining. The age of the pot linings can vary from 3 to 10 years. By improving the life of the lining through better construction and operating techniques, discharge of pollutants can be reduced. Note that part of the pot-lining carbon can be recycled when the pots are relined. Emissions of organic compounds from secondary aluminum production can be reduced by thoroughly removing coatings, paint, oils, greases, and the like from raw feed materials before they enter the melt process. European experience has shown that red mud produced at the alumina plant can be reduced from 2 t/t alumina to about 1 t/t alumina through implementation of good industrial practices.

At bauxite facilities, the major sources of dust emissions are the dryers, and emissions are controlled with electrostatic precipitators (ESPs) or baghouses. Removal efficiencies of 99% are achievable. Dust from conveyors and material transfer points is controlled by hoods and enclosures. Dust from truck movement can be minimized by treating road surfaces and by ensuring that vehicles do not drop material as they travel. Dusting from stockpiled material can be minimized by the use of water sprays or by enclosure in a building.

At the alumina plant, pollution control for the various production and service areas is implemented as follows:

- **Bauxite and limestone handling and storage:** Dust emissions are controlled by baghouses.
- **Lime kilns:** Dust emissions are controlled by baghouse systems. Kiln fuels can be selected to reduce SO$_x$ emissions; however, this is not normally a problem, since most of the sulfur dioxide that is formed is absorbed in the kiln.
- **Calciners:** Alumina dust losses are controlled by ESPs; SO$_2$ and NO$_x$ emissions are reduced to acceptable levels by contact with the alumina.
- **Red mud disposal:** The mud impoundment area must be lined with impervious clay prior to use to prevent leakage. Water spraying of the mud stack may be required to prevent fine dust from being blown off the stack. Longer term treatment of the mud may include reclamation of the mud, neutralization, covering with topsoil, and planting with vegetation.

In the smelter, primary emissions from the reduction cells are controlled by collection and treatment using dry sorbent injection; fabric filters or ESPs are used for controlling particulate matter. Primary emissions make up 97.5% of
total cell emissions; the balance consists of secondary emissions that escape into
the potroom and leave the building through roof ventilators. Wet scrubbing of the
primary emissions can also be used, but large volumes of toxic waste liquors will
need to be treated or disposed of. Secondary emissions result from the periodic
replacement of anodes and other operations; the fumes escape when the cell hood
panels have been temporarily removed. While wet scrubbing can be used to
control the release of secondary fumes, the high-volume, low-concentration gases
offer low scrubbing efficiencies, have high capital and operating costs, and
produce large volumes of liquid effluents for treatment. Wet scrubbing is seldom
used for secondary fume control in the prebake process.

When anodes are baked on-site, the dry scrubbing system using aluminum oxide
as the adsorbent is used. It has the advantage of being free of waste products, and
all enriched alumina and absorbed material are recycled directly to the reduction
cells. Dry scrubbing may be combined with incineration for controlling emissions
of tar and volatile organic compounds (VOCs) and to recover energy. Wet
scrubbing can also be used but is not recommended, since a liquid effluent, high
in fluorides and hydrocarbons, will require treatment and disposal.

Dry scrubber systems applied to the pot fumes and to the anode baking furnace
result in the capture of 97% of all fluorides from the process.

The aluminum smelter solid wastes, in the form of spent pot lining, are disposed
of in engineered landfills that feature clay or synthetic lining of disposal pits,
provision of soil layers for covering and sealing, and control and treatment of
any leachate. Treatment processes are available to reduce hazards associated with
spent pot lining prior to disposal of the lining in a landfill. Other solid wastes
such as bath skimmings are sold for recycling, while spalled refractories and
other chemically stable materials are disposed of in landfill sites.

Modern smelters using good industrial practices are able to achieve the following
in terms of pollutant loads (all values are expressed on an annualized basis):
hydrogen fluoride, 0.2-0.4 kg/t; total fluoride, 0.3-0.6 kg/t; particulates, 1 kg/t;
sulfur dioxide, 1 kg/t; and nitrogen oxides, 0.5 kg/t. CF₄ emissions should be
less than 0.1 kg/t.

For secondary aluminum production, the principal treatment technology
downstream of the melting furnace is dry sorbent injection using lime, followed
by fabric filters. Waste gases from salt slag processing should be filtered as well.
Waste gases from aluminum scrap pretreatment that contain organic compounds
of concern may be treated by postcombustion practices.
Air emissions should be monitored regularly for particulate matter and fluorides. Hydrocarbon emissions should be monitored annually on the anode plant and baking furnaces. Liquid effluents should be monitored weekly for pH, total suspended solids, fluoride, and aluminum and at least monthly for other parameters. Monitoring data should be analyzed and reviewed at regular intervals and compared with the operating standards so that any necessary corrective actions can be taken.

IRON AND STEEL

INDUSTRY DESCRIPTION AND PRACTICES

Steel is an alloy of iron usually containing less than 1% carbon. The process of steel production requires several sequential steps. The two types of steelmaking technology in use today are the basic oxygen furnace (BOF) and the electric arc furnace (EAF). Although these two technologies use different input materials, the output for both furnace types is molten steel which is subsequently formed into steel mill products. The BOF input materials are molten iron, scrap, and oxygen. In the EAF, electricity and scrap are the input materials used. BOFs are typically used for high tonnage production of carbon steels, while EAFs are used to produce carbon steels and low tonnage alloy and specialty steels. The processes leading up to steelmaking in a BOF are very different than the steps preceding steelmaking in an EAF; the steps after each of these processes producing molten steel are the same.

Steel manufacturing may be defined as the chemical reduction of iron ore, using an integrated steel manufacturing process or a direct reduction process. In the conventional integrated steel manufacturing process, the iron from the blast furnace is converted to steel in a BOF. As noted, it can also be made in an electric arc furnace (EAF) from scrap steel and, in some cases, from direct reduced iron. An emerging technology, direct steel manufacturing, produces steel directly from iron ore. In the BOF process, coke making and iron making precede steelmaking; these steps are not necessary with an EAF. Pig iron is manufactured from sintered, pelletized, or lump iron ores using coke and limestone in a blast furnace. It is then fed to a BOF in molten form along with scrap metal, fluxes, alloys, and high-purity oxygen to manufacture steel. In some integrated steel mills, sintering (heating without melting) is used to agglomerate fines and so recycle iron-rich material such as mill scale.
When making steel using a BOF, coke-making and iron-making precede steelmaking; these steps are not needed for steelmaking with an EAF. Coke, which is the fuel and carbon source, is produced by heating coal in the absence of oxygen at high temperatures in coke ovens. Hence, merchant coke plants are needed to support industry based on this technology. Pig iron is then produced by heating the coke, iron ore, and limestone in a blast furnace. In the BOF, molten iron from the blast furnace is combined with flux and scrap steel where high-purity oxygen is injected. This process, with coke-making, iron-making, steelmaking, and subsequent forming and finishing operations is referred to as fully integrated production. Alternatively, in an EAF, the input material is primarily scrap steel, which is melted and refined by passing an electric current from the electrodes through the scrap. The molten steel from either process is formed into ingots or slabs that are rolled into finished products. Rolling operations may require reheating, rolling, cleaning, and coating the steel. Descriptions of both steelmaking processes follow.

**Basic Oxygen Furnace Technology**

The process of making steel in a BOF is preceded by coke-making and ironmaking operations. In coke-making, coke is produced from coal. In ironmaking, molten iron is produced from iron ore and coke. Each of these processes and the subsequent steelmaking process in the BOF are briefly described below.

**Coke-making.** Coal processing typically involves producing coke, coke gas and by-product chemicals from compounds released from the coal during the coke-making process. Coke is carbon-rich and is used as a carbon source and fuel to heat and melt iron ore in ironmaking. The coke-making process starts with bituminous pulverized coal charge which is fed into the coke oven through ports in the top of the oven. After charging, the oven ports are sealed and the coal is heated at high temperatures (1600 to 2300°F) in the absence of oxygen. Coke manufacturing is done in a batch mode where each cycle lasts for 14 to 36 hours. A coke oven battery comprises a series of 10 to 100 individual ovens, side-by-side, with a heating flue between each oven pair. Volatile compounds are driven from the coal, collected from each oven, and processed for recovery of combustible gases and other coal by-products. The solid carbon remaining in the oven is the coke. The necessary heat for distillation is supplied by external combustion of fuels (e.g., recovered coke oven gas, blast furnace gas) through flues located between ovens.

At the end of the heating cycle, the coke is pushed from the oven into a rail quench car. The quench car takes it to the quench tower, where the hot coke is cooled with a water spray. The coke is then screened and sent to the blast furnace
or to storage. In the by-products recovery process, volatile components of the coke oven gas stream are recovered including the coke oven gas itself (which is used as a fuel for the coke oven), naphthalene, ammonium compounds, crude light oils, sulfur compounds, and coke breeze (coke fines).

During the coke quenching, handling, and screening operation, coke breeze is produced. Typically, the coke breeze is reused in other manufacturing processes on-site (e.g., sintering) or sold off-site as a by-product.

Coke-making is perhaps the major environmental concern in this industry. Both air emissions and quench water are the key problems. As a result, many steelmakers have turned in recent years to pulverized coal injection, which substitutes coal for coke in the blast furnace. The use of pulverized coal injection can replace roughly 25-40% of the coke in the blast furnace thereby reducing the amount of coke needed and the associated emissions. It is also common practice to inject other fuels, such as natural gas, oil, and tar/pitch to replace a portion of the coke.

Quench water from coke-making is also an area of significant environmental concern. In Europe, many plants have implemented technology to shift from water quenching to dry quenching which eliminates suspected carcinogenic PM and VOCs. However, major construction changes are required for such a solution and considering the high capital costs of coke batteries, combined with the depressed state of the steel industry and increased regulations for coke-making, it is unlikely that new facilities will be constructed. Instead, many countries with steelmaking industries are experiencing increases in the amount of coke imported.

Iron ore, coke, and limestone are fed into the top of the blast furnace. Heated air is forced into the bottom of the furnace through a bustle pipe and tuyeres (orifices) located around the circumference of the furnace. The carbon monoxide from the burning of the coke reduces iron ore to iron.

The acid part of the ores reacts with the limestone to create a slag which is drawn periodically from the furnace. This slag contains unwanted impurities in the ore. Among the most common impurities is sulfur from the fuels. When the furnace is tapped, iron is removed through one set of runners and molten slag via another. The molten iron is tapped into refractory-lined cars for transport to the steelmaking furnaces. Residuals from the process are mainly sulfur dioxide or hydrogen sulfide, which are driven off from the hot slag. The slag is the largest by-product generated from the ironmaking process and is reused extensively in the construction industry.
Blast furnace flue gas is cleaned and used to generate steam to preheat the air coming into the furnace, or it may be used to supply heat to other plant processes. The cleaning of the gas may generate air pollution control dust in removing coarse particulates (which may be reused in the sintering plant or landfilled), and water treatment plant sludge in removing fine particulates by venturi scrubbers. Sintering (briefly described earlier) is the process that agglomerates fines (including iron ore fines, dusts, coke breeze, water treatment plant sludge, coke breeze, and flux) into a porous mass for charging to the blast furnace. By means of the sintering operations, a mill can recycle iron-rich material, such as mill scale and processed slag. Not all mills have sintering capabilities. The input materials are mixed together, placed on a slow-moving grate or rotating/tilting mixer, and ignited. Windboxes under the grate draw air through the materials to deepen the combustion throughout the traveling length of the grate. The coke breeze provides the carbon source for sustaining the controlled combustion. In the process, the fine materials are fused into the sinter agglomerates, which can be reintroduced into the blast furnace along with ore. Air pollution control equipment removes the particulate matter generated during the thermal fusing process. For wet scrubbers, water treatment plant sludge is generally land disposed waste. If electrostatic precipitators or baghouses are used as the air pollution control equipment, the dry particulate matter that is captured are typically recycled as sinter feedstock, or is landfilled as solid waste.

Steelmaking. Molten iron from the blast furnace, flux, alloy materials, and scrap are placed in the BOF, melted and refined by injecting high-purity oxygen. A chemical reaction occurs, where the oxygen reacts with carbon and silicon generating the heat necessary to melt the scrap and oxidize the impurities. The operation is performed as a batch process with a cycle time of about 45 min. Slag is produced from impurities removed by the combination of the fluxes with the injected oxygen. Various alloys are added to produce different grades of steel. The molten steel is typically cast into slabs, beams, or billets.

Waste products from the basic oxygen steelmaking process include slag, carbon monoxide, and oxides of iron emitted as dust. Also, when the hot iron is poured into ladles or the furnace, iron oxide fumes are released and some of the carbon in the iron is precipitated as graphite (called kish). The BOF slag can be processed to recover the high-metallic portions for use in sintering or blast furnaces, but its applications as a saleable construction material are more limited than those of the blast furnace slag. Basic oxygen furnaces are equipped with air pollution control systems for containing, cooling, and cleaning the volumes of hot gases and sub-micron fumes that are released during the process. Water is used to quench or cool the gases and fumes to temperatures at which they can be
effectively treated by the gas cleaning equipment. The resulting waste streams from the pollution control operations include dust and water treatment plant sludge. About 1000 gallons of water per ton of steel is typically used in a wet scrubber in order to effectively remove air pollutants. The primary pollutants captured from the off-gases are TSS and metals such as zinc and lead.

Electric Arc Furnace Technology

In the steelmaking process that uses an electric arc furnace (EAF), the primary raw material is scrap metal. The scrap metal is melted and refined using electrical energy. During melting, oxidation of phosphorus, silicon, manganese, carbon, and other materials occurs and a slag containing some of these oxidation products forms on top of the molten metal. Oxygen is used to decarburize the molten steel and to provide thermal energy. This is a batch process with a cycle time of about 2 to 3 hours. Since scrap metal is used instead of molten iron, there are no coke-making or ironmaking operations associated with steel production that uses an EAF.

This technology results in the production of metal dusts, slag, and gaseous products. Particulate matter and gases evolve together during the steelmaking process and are conveyed into a gas cleaning system. Emissions are cleaned using a wet or dry system. The particulate matter that is removed as emissions in the dry system is referred to as EAF dust, or EAF sludge if it is from a wet system. This waste is a listed hazardous waste under the RCRA. The composition of EAF dust can vary greatly depending on the scrap composition and furnace additives. The primary component is iron or iron oxides, and it may also contain flux (lime and/or fluorspar), zinc, chromium and nickel oxides (when stainless steel is being produced) and other metals associated with the scrap. The two primary hazardous constituents of EAF emission dust are lead and cadmium. Roughly 20 pounds of dust per ton of steel is expected, but as much as 40 pounds of dust per ton of steel may be generated, depending on production practices. Oils are burned off "charges" of oil-bearing scrap in the furnace. Small but not insignificant amounts of nitrogen oxides and ozone are generated during the melting process. The furnace is extensively cooled by water; however, this water is recycled through cooling towers.

Forming and Finishing Operations

Steel Forming. Whether the molten steel is produced using a BOF or an EAF, to convert it into a product, it must be solidified into a suitable shape and finished. The traditional forming method is called ingot teeming, and involves pouring the
metal into ingot molds, then allowing the steel to cool and solidify. The alternative method of forming steel is called continuous casting. This process bypasses several steps of the conventional ingot teeming process by casting steel directly into semifinished shapes. Molten steel is poured into a reservoir from which it is released into the molds of the casting machine. The metal is cooled as it descends through the molds, and before emerging, a hardened outer shell is formed. As the semifinished shapes proceed on the runout table, the center also solidifies, allowing the cast shape to be cut into lengths. Process contact water cools the continuously cast steel and is collected in settling basins along with oil, grease, and mill scale generated in the casting process. The scale settles out and is removed and recycled for sintering operations, if the mill has a sinter plant. Waste treatment plant sludge is also generated during the operation. The steel is further processed to produce slabs, strips, bars, or plates through various forming steps. The most common hot forming operation is hot rolling, where heated steel is passed between two rolls revolving in opposite directions. Hot rolling units may have as many as 13 stands, each producing an incremental reduction in thickness. The final shape and characteristics of a hot formed piece depend on the rolling temperature, the roll profile, and the cooling process after rolling. Wastes generated from hot rolling include waste treatment plant sludge and scale.

In subsequent cold forming, the cross-sectional area of unheated steel is progressively reduced in thickness as the steel passes through a series of rolling stands. Generally, wires, tubes, sheet and strip steel products are produced by cold-rolling operations. Cold forming is used to obtain improved mechanical properties, better machinability, special size accuracy, and the production of thinner gages than hot rolling can accomplish economically. During cold rolling, the steel becomes hard and brittle. To make the steel more ductile, it is heated in an annealing furnace. Process contact water is used as a coolant for rolling mills to keep the surface of the steel clean between roller passes. Cold rolling operations also produce a waste treatment plant sludge, primarily due to the lubricants applied during rolling. Grindings from resurfacing of the worn rolls and disposal of used rolls can be a significant contributor to the wastestream.

**Finishing Stages.** One of the most important aspects of a finished product is the surface quality. To prevent corrosion, a protective coating is usually applied to the steel product. Prior to coating, the surface of the steel must be cleaned so the coating will adhere to the steel. Mill scale, rust, oxides, oil, grease, and soil are chemically removed from the surface of steel using solvent cleaners, pressurized water or air blasting, cleaning with abrasives, alkaline agents or acid pickling. In the pickling process, the steel surface is chemically cleaned of scale, rust, and
other materials. Inorganic acids such as hydrochloric or sulfuric acid are most
commonly used for pickling. Stainless steels are pickled with hydrochloric,
nitric, and hydrofluoric acids. Spent pickle liquor is a hazardous waste, if it
contains considerable residual acidity and high concentrations of dissolved iron
salts. Pickling prior to coating may use a mildly acidic bath which is not
necessarily hazardous. Steel generally passes from the pickling bath through a
series of rinses. Alkaline cleaners may also be used to remove mineral oils and
animal fats and oils from the steel surface prior to cold rolling. Common alkaline
cleaning agents include: caustic soda, soda ash, alkaline silicates, and
phosphates. Steel products are often given a coating to inhibit oxidation and
extend the life of the product. Coated products can also be painted to further
inhibit corrosion. Common coating processes include: galvanizing (zinc coating),
tin coating, chromium coating, aluminizing, and terne coating (lead and tin).
Metallic coating application processes include hot dipping, metal spraying, metal
cladding (to produce bimetal products), and electroplating. Galvanizing is a
common coating process where a thin layer of zinc is deposited on the steel
surface.

MATERIAL BALANCE INFORMATION

There are a large number of outputs that are produced as a result of the
manufacturing of coke, iron, and steel, the forming of metals into basic shapes,
and the cleaning and scaling of metal surfaces. Many of these outputs,
categorized by process are listed in Table 5.

<table>
<thead>
<tr>
<th>Inputs</th>
<th>Outputs</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Coke oven gas by-products such as coal tar, light oil, ammonia liquor, and the remainder of the gas stream is used as fuel. Coal tar is typically refined to produce commercial and industrial products including pitch, creosote oil, refined tar, naphthalene, and bitumen.</td>
</tr>
<tr>
<td>Inputs</td>
<td>Outputs</td>
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<td>----------------------------------------------------------------------</td>
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<tr>
<td>Charging emissions (fine particles of coke generated during oven pushing, conveyor transport, loading and unloading of coke that are captured by pollution control equipment. Approximately 1 lb per ton of coke produced is captured and generally land disposed).</td>
<td>Ammonia, phenol, cyanide, and hydrogen sulfide.</td>
</tr>
<tr>
<td></td>
<td>Lime sludge, generated from the ammonia still.</td>
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<tr>
<td></td>
<td>Decanter tank tar sludge.</td>
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<tr>
<td></td>
<td>Benzene releases in coke by-product recovery operations.</td>
</tr>
<tr>
<td></td>
<td>Naphthalene residues, generated in the final cooling tower.</td>
</tr>
<tr>
<td></td>
<td>Tar residues.</td>
</tr>
<tr>
<td></td>
<td>Sulfur compounds, emitted from the stacks of the coke ovens.</td>
</tr>
<tr>
<td></td>
<td>Wastewater from cleaning and cooling (contains zinc, ammonia still lime, or decanter tank tar, tar distillation residues).</td>
</tr>
<tr>
<td></td>
<td>Coke oven gas condensate from piping and distribution system.</td>
</tr>
<tr>
<td></td>
<td>Ironmaking</td>
</tr>
<tr>
<td>Iron ore (primarily in the form of taconite pellets), coke, sinter, coal, limestone, heated air.</td>
<td>Slag, which is either sold as a by-product, primarily for use in the construction industry, or landfilled.</td>
</tr>
<tr>
<td></td>
<td>Residual sulfur dioxide or hydrogen sulfide.</td>
</tr>
<tr>
<td></td>
<td>Particulates captured in the gas, including the air pollution control dust or waste treatment plant sludge.</td>
</tr>
<tr>
<td></td>
<td>Iron is the predominant metal found in the process wastewater.</td>
</tr>
<tr>
<td></td>
<td>Blast-furnace gas (CO).</td>
</tr>
<tr>
<td>Inputs</td>
<td>Outputs</td>
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<tr>
<td>-----------------------------------------------------------------------</td>
<td>------------------------------------------------------------------------</td>
</tr>
<tr>
<td><strong>Steelmaking</strong></td>
<td>Basic oxygen furnace emission control dust and sludge, a metals bearing waste.</td>
</tr>
<tr>
<td>In the steelmaking process that uses a basic oxygen furnace (BOF), inputs include molten iron, metal scrap, and high-purity oxygen. In the steelmaking process that uses an electric arc furnace (EAF), the primary inputs are scrap metal, electric energy and graphite electrodes. For both processes, fluxes and alloys are added, and may include: fluorspar, dolomite, and alloying agents such as aluminum, manganese.</td>
<td>Electric arc furnace emission control dust and sludge; generally, 20 pounds of dust per ton of steel is expected, but as much as 40 pounds of dust per ton of steel may be generated depending on the scrap that is used. Metal dusts (consisting of iron particulate, zinc, and other metals associated with the scrap and flux (lime and/or fluorspar) not associated with the EAF). Slag. Carbon monoxide. NO, and ozone, which are generated during the melting process.</td>
</tr>
<tr>
<td>Inputs</td>
<td>Outputs</td>
</tr>
<tr>
<td>--------</td>
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</tr>
<tr>
<td><strong>Forming, cleaning, and descaling</strong></td>
<td><strong>Wastewater sludge from rolling, cooling, descaling, and rinsing operations which may contain cadmium, chromium, and lead.</strong></td>
</tr>
<tr>
<td>Carbon steel is pickled with hydrochloric acid; stainless steels are pickled with hydrochloric, nitric and hydrofluoric acids.</td>
<td>Oils and greases from hot and cold rolling.</td>
</tr>
<tr>
<td>Various organic chemicals are used in the pickling process.</td>
<td>Spent pickle liquor.</td>
</tr>
<tr>
<td>Alkaline cleaners are used to remove mineral oils and animal fats and oils from the steel surface. Common alkaline cleaning agents include caustic soda, soda ash, alkaline silicates, phosphates.</td>
<td>Spent pickle liquor rinse water sludge from cleaning operations.</td>
</tr>
<tr>
<td></td>
<td>Wastewater from the rinse baths. Rinse water from coating processes may contain zinc, lead, cadmium, or chromium.</td>
</tr>
<tr>
<td></td>
<td>Grindings from roll refinishing may be RCRA characteristic waste from chromium.</td>
</tr>
<tr>
<td></td>
<td>Zinc dross.</td>
</tr>
</tbody>
</table>

Sintering operations can emit significant dust levels of about 20 kilograms per metric ton (kg/t) of steel. Pelletizing operations can emit dust levels of about 15 kg/t of steel. Air emissions from pig iron manufacturing in a blast furnace include PM, ranging from less than 10 kg/t of steel manufactured to 40 kg/t; sulfur oxides (SO\textsubscript{2}) mostly from sintering or pelletizing operations (1.5 kg/t of steel); nitrogen oxides (NO\textsubscript{x}) mainly from sintering and heating (1.2 kg/t of steel); hydrocarbons; carbon monoxide; in some cases dioxins (mostly from sintering operations); and hydrogen fluoride.
Air emissions from steel manufacturing using the BOF may include PM (ranging from less than 15 kg/t to 30 kg/t of steel). For closed systems, emissions come from the desulfurization step between the blast furnace and the BOF; the particulate matter emissions are about 10 kg/t of steel.

In the conventional process without recirculation, wastewaters, including those from cooling operations, are generated at an average rate of 80 m³/t of steel manufactured. Major pollutants present in untreated wastewaters generated from pig iron manufacture include total organic carbon (typically 100-200 mg/l); total suspended solids (7000 mg/l, 137 kg/t); dissolved solids; cyanide (15 mg/l); fluoride (1000 mg/l); chemical oxygen demand, or COD (500 mg/l); and zinc (35 mg/l).

Major pollutants in wastewaters generated from steel manufacturing using the BOF include total suspended solids (up to 4000 mg/l, 1030 kg/t), lead (8 mg/l), chromium (5 mg/l), cadmium (0.4 mg/l), zinc (14 mg/l), fluoride (20 mg/l), and oil and grease. Mill scale may amount to 33 kg/t. The process generates effluents with high temperatures.

Process solid waste from the conventional process, including furnace slag and collected dust, is generated at an average rate ranging from 300 kg/t of steel manufactured to 500 kg/t, of which 30 kg may be considered hazardous depending on the concentration of heavy metals present. Approximately 65% of BOF slag from steel manufacturing can be recycled in various industries such as building materials and, in some cases, mineral wool.

**FATE OF SELECTED CHEMICALS**

Table 6 provides a synopsis of current scientific toxicity and fate information for the top chemicals (by weight) that steel facilities self-report as being released based upon the TRI (Toxic Release Inventory) in the United States. The descriptions provided in Table 2 are taken directly from 1993 *Toxics Release Inventory Public Data Release* (EPA, 1994), and the Hazardous Substances Data Bank (HSDB), assessed via TOXNET. TOXNET is a computer system run by the National Library of Medicine. It includes a number of toxicological databases managed by EPA, the National Cancer Institute, and the National Institute for Occupational Safety and Health. HSDB contains chemical-specific information on manufacturing and use, chemical and physical properties, safety and handling, toxicity and biomedical effects, pharmacology, environmental fate and exposure potential, exposure standards and regulations, monitoring and analysis methods, and additional references. The information contained in Table 6 is based upon
exposure assumptions that have been conducted using standard scientific procedures. The effects listed must be taken in context of these exposure assumptions, which are more fully explained within the full chemical profiles in HSDB.

Table 6. Toxicity and Environmental Fate Information

<table>
<thead>
<tr>
<th>Ammonia CAS #7644-41-7</th>
</tr>
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</table>
| **Sources.** In coke-making, ammonia is produced by the decomposition of the nitrogen-containing compounds which takes place during the secondary thermal reaction (at temperatures greater than 700°C (1296°F)). The ammonia formed during coking exists in both the water and gas that form part of the volatile products. Recovery can be accomplished by several different processes where the by-product ammonium sulfate is formed by the reaction between the ammonia and sulfuric acid.  
**Toxicity.** Anhydrous ammonia is irritating to the skin, eyes, nose, throat, and upper respiratory system. Ecologically, ammonia is a source of nitrogen (an essential element for aquatic plant growth) and may contribute to eutrophication of standing or slow-moving surface water, particularly in nitrogen-limited waters. In addition, aqueous ammonia is moderately toxic to aquatic organisms.  
**Carcinogenicity.** There is currently no evidence to suggest that this chemical is carcinogenic.  
**Environmental Fate.** Ammonia combines with sulfate ions in the atmosphere and is washed out by rainfall, resulting in rapid return of ammonia to the soil and surface waters. Ammonia is a central compound in the environmental cycling of nitrogen. Ammonia in lakes, rivers, and streams is converted to nitrate.  
**Physical Properties.** Ammonia is a corrosive and severely irritating gas with a pungent odor. |

<table>
<thead>
<tr>
<th>Hydrochloric Acid CAS #7647-01-1</th>
</tr>
</thead>
</table>
| **Sources.** During hot rolling, a hard black iron oxide is formed on the surface of the steel. This "scale" is removed chemically in the pickling process, which commonly uses hydrochloric acid.  
**Toxicity.** HCl is primarily a concern in its aerosol form. Acid aerosols have been implicated in causing and exacerbating a variety of respiratory ailments. Dermal exposure and ingestion of highly concentrated HCl can result in corrosivity. Ecologically, accidental releases of solution forms of HCl may adversely affect aquatic life by including a transient lowering of the pH (i.e., increasing the acidity) of surface waters.  
**Carcinogenicity.** There is currently no evidence to suggest carcinogenicity. |
Environmental Fate. Releases to surface waters and soils will be neutralized to an extent due to the buffering capacities of both systems. The extent of these reactions will depend on the characteristics of the specific environment. Physical Properties. Concentrated hydrochloric acid is highly corrosive.

Manganese and Manganese Compounds CAS #7439-96-5; 20-12-2

Sources. Manganese is found in the iron charge and is used as an addition agent added to alloy steel to obtain desired properties in the final product. In carbon steel, Mg is used to combine with sulfur to improve steel ductility. An alloy steel with Mg is used for applications involving relatively small sections which are subject to severe service conditions, or in larger sections where the weight saving derived from the higher strength of the alloy steels is needed. Toxicity. There is currently no evidence that human exposure to Mg at levels commonly observed in ambient atmosphere results in adverse health effects. Recent EPA review of the fuel additive MMT (methylcyclopentadienyl magnesium tricarbonyl) concluded that use of MMT in gasoline could lead to ambient exposures to Mg at a level sufficient to result in adverse neurological effects. Chronic Mg poisoning bears some similarity to chronic lead poisoning. Both occur via inhalation of dust or fumes, and primarily involve the central nervous system. Early symptoms include languor, speech disturbances, sleepiness, and cramping and weakness in legs. A stolid mask-like appearance of face, emotional disturbances such as absolute detachment broken by uncontrollable laughter, euphoria, and a spastic gait with a tendency to fall while walking are seen in more advanced cases. Chronic Mg poisoning is reversible if treated early and exposure is stopped. Populations at greatest risk of Mg toxicity are the very young and those with iron deficiencies. Ecologically, although Mg is an essential nutrient for both plants and animals, in excessive concentrations it inhibits plant growth. Carcinogenicity. There is currently no evidence to suggest that this chemical is carcinogenic. Environmental Fate. Mg is an essential nutrient for plants and animals. It accumulates in the top layers of soil or surface water sediments and cycles between the soil and living organisms. It occurs mainly as a solid under environmental conditions, though may also be transported in the atmosphere as a vapor or dust.

1,1,1-Trichloroethane CAS #71-55-6

Sources. Used for surface cleaning of steel prior to coating.
Toxicity. Repeated contact with skin may cause serious skin cracking and infection. Vapors cause a slight smarting of the eyes or respiratory system if present in high concentrations. Exposure to high concentrations of TCE causes reversible mild liver and kidney dysfunction, central nervous system depression, gait disturbances, stupor, coma, respiratory depression, and even death. Exposure to lower concentrations of TCE leads to light-headedness, throat irritation, headache, disequilibrium, impaired coordination, drowsiness, convulsions, and mild changes in perception.

Carcinogenicity. There is currently no evidence to suggest that this chemical is carcinogenic.

Environmental Fate. Releases of TCE to surface water or land will almost entirely volatilize. Releases to air may be transported long distances and may partially return to earth in rain. In the lower atmosphere, TCE degrades very slowly by photooxidation and slowly diffuses to the upper atmosphere where photodegradation is rapid. Any TCE that does not evaporate from soils leaches to groundwater. Degradation in soils and water is a very slow process. TCE does not hydrolyze in water, nor does it significantly bioconcentrate in aquatic organisms.

Zinc and Zinc Compounds CAS #7440-66-6; 20-19-9

Sources. To protect steel from rusting, it is coated with a material that will protect it from moisture and air. In the galvanizing process, steel is coated with zinc.

Toxicity. Zinc is a nutritional trace element; toxicity from ingestion is low. Severe exposure to zinc might give rise to gastritis with vomiting due to swallowing of zinc dusts. Short-term exposure to very high levels of zinc is linked to lethargy, dizziness, nausea, fever, diarrhea, and reversible pancreatic and neurological damage. Long-term zinc poisoning causes irritability, muscular stiffness and pain, loss of appetite, and nausea. Zinc chloride fumes cause injury to mucous membranes and to the skin. Ingestion of soluble zinc salts may cause nausea, vomiting, and purging.

Carcinogenicity. There is currently no evidence to suggest that this chemical is carcinogenic.

Environmental Fate. Significant zinc contamination of soil is only seen in the vicinity of industrial point sources. Zinc is a relatively stable soft metal, though it burns in air (pyrophoric). Zinc bioconcentrates in aquatic organisms.

The toxic chemical release data obtained from TRI provides detailed information on the majority of facilities in the iron and steel industry in the United States. It also allows for a comparison across years and industry sectors. Reported chemicals are limited, however, to the 316 reported chemicals. Most of the hydrocarbon emissions from iron and steel facilities are not captured by TRI. The EPA Office of Air Quality Planning and Standards has compiled air pollutant emission factors for determining the total air emissions of priority pollutants.
(e.g., total hydrocarbons, SO\(_x\), NO\(_x\), CO, particulates, etc.) from many iron and steel manufacturing sources. The Aerometric Information Retrieval System (AIRS) contains a wide range of information related to stationary sources of air pollution, including the emissions of a number of air pollutants which may be of concern within a particular industry. With the exception of VOCs, there is little overlap with the TRI chemicals reported above. By way of comparison to other industry sectors, the steel industry in the United States emits about 1.5 million short tons/year of carbon monoxide, which is more than twice as much as the next largest releasing industry, pulp and paper. The iron and steel industry also ranks as one of the top five releasers for NO\(_2\), PM\(_{10}\), and SO\(_2\). Carbon monoxide releases occur during ironmaking (in the burning of coke, CO produced reduces iron oxide ore), and during steelmaking (in either the basic oxygen furnace or the electric arc furnace). Nitrogen dioxide is generated during steelmaking. Particulate matter may be emitted from the coke-making (particularly in quenching operations), ironmaking or the basic oxygen furnace (as oxides of iron that are emitted as submicron dust) or electric arc furnace (as metal dust containing iron particulate, zinc, and other materials associated with the scrap). Sulfur dioxide can be released in ironmaking or sintering.

**POLLUTION PREVENTION PRACTICES AND OPPORTUNITIES**

Most of the pollution prevention practices have concentrated on reducing coke-making emissions, electric arc furnace (EAF) dust, and spent acids used in finishing operations. Because of the complexity, size, and age of the equipment used, projects that have the highest pollution prevention potential often require major capital investments, which make many pollution prevention projects difficult to justify. Despite this, the industry must seek ways to become more cost-competitive, which requires investing in more cost-effective, less polluting technologies. Table 7 provides a summary of P2 practices and opportunities. To supplement this list, the following discussions should be considered.

With regard to coke-making, this process is seen by industry experts as one of the steel industry's areas of greatest environmental concern, with coke oven air emissions and quenching wastewater as the major problems. In response to expanding regulatory constraints in the United States, including the Clean Air Act National Emission Standards for coke ovens, U.S. steelmakers are turning to new technologies to decrease the sources of pollution from, and their reliance on, coke. Pollution prevention in coke-making has focused on two areas: reducing coke oven emissions and developing cokeless ironmaking techniques. Although these processes have not yet been widely demonstrated on a commercial scale, they may provide important benefits, especially for the integrated segment of the
industry, by potentially lowering air emissions and wastewater discharges. Several technologies are available or are under development to reduce the emissions from coke ovens. Typically, these technologies reduce the quantity of coke needed by changing the method by which coke is added to the blast furnace or by substituting a portion of the coke with other fuels.

The reduction in the amount of coke produced proportionally reduces the coking emissions. Some of the most prevalent or promising coke-reduction technologies are listed in Table 7.

Cokeless technologies (refer to Table 7 for examples) substitute coal for coke in the blast furnace, hence eliminating the need for coke-making. Such technologies have enormous potential to reduce pollution generated during the steelmaking process. The drawbacks with these technologies are that (1) the capital investment required for retrofits is very significant, and (2) some countries whose economies are dependent upon the steel industry need to undergo significant industry rationalization and restructuring in order to justify investments into these technologies. For example, Russia and Ukraine, which have significant steel production and export capabilities, heavily depend on a labor-intensive coking industry. The elimination of the coking industry in these countries would likely result in significant social implications.

Table 7. Recommended Pollution Prevention Practices

<table>
<thead>
<tr>
<th>Area of opportunity</th>
<th>Recommended pollution prevention practice</th>
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<tbody>
<tr>
<td>Eliminating coke with coke-less technologies</td>
<td>1. The Japanese Direct Iron Ore Smelting (DIOS) process. This process produces molten iron directly with coal and sinter feed ore. A 500 ton per day pilot plant was started up in October, 1993 and the designed production rates were attained as a short-term average. Data generated are being used to determine economic feasibility on a commercial scale.</td>
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Reduction of coke oven emissions with other technologies

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<tr>
<th>Area of opportunity</th>
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<tbody>
<tr>
<td>2. HIs melt process.</td>
<td>A plant using the HIs melt process for molten iron production, developed by HIs melt Corporation of Australia, was started up in late 1993. The process, using ore fines and coal, has achieved a production rate of 8 tons per hour using ore directly in the smelter. Developers anticipate reaching the production goal of 14 tons per hour. The data generated are being used to determine economic feasibility on a commercial scale. If commercial feasibility is realized, Midrex is expected to become the U.S. engineering licensee of the HIs melt process.</td>
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<tr>
<td>3. Corex process.</td>
<td>The Corex or Cipcor process has integral coal desulfurizing, is amenable to a variety of coal types, and generates electrical power in excess of that required by an iron and steel mill which can be sold to local power grids. A Corex plant is in operation in South Africa, and other plants are expected to be operational in South Korea and India.</td>
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<tr>
<td>4. Pulverized coal injection.</td>
<td>This technology substitutes pulverized coal for a portion of the coke in the blast furnace. Use of pulverized coal injection can replace about 25 to 40% of coke in the blast furnace, substantially reducing emissions associated with coke-making operations. This reduction ultimately depends on the fuel injection rate applied to the blast furnaces which will, in turn, be dictated by the aging of existing coking facilities, fuel costs, oxygen availability, capital requirements for fuel injection, and available hot blast temperature.</td>
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<tr>
<td>5. Nonrecovery coke battery.</td>
<td>As opposed to the by-product recovery coke plant, the nonrecovery coke battery is designed to allow combustion of the gases from the coking process, thus consuming the by-products that are typically recovered. The process results in lower air emissions and substantial reductions in coking process wastewater discharges.</td>
</tr>
<tr>
<td>6. The Davy Still Auto-process.</td>
<td>In this precombustion cleaning process for coke ovens, coke oven battery process water is utilized to strip ammonia and hydrogen sulfide from coke oven emissions.</td>
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<td>Area of opportunity</td>
<td>Recommended pollution prevention practice</td>
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<td></td>
<td><strong>Reducing wastewater</strong></td>
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<td>7. <em>Alternative fuels.</em> Steel producers can inject other fuels, such as natural gas, oil, and tar/pitch, instead of coke into the blast furnace, but these fuels can only replace coke in limited amounts.</td>
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<td></td>
<td>8. In Europe, some plants have implemented technology to shift from water quenching to dry quenching in order to reduce energy costs. However, major construction changes are required for such a solution.</td>
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<td><strong>Recycling of coke by-products</strong></td>
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<td></td>
<td>9. Improvements in the in-process recycling of tar decanter sludge are common practice. Sludge can either be injected into the ovens to contribute to coke yield, or converted into a fuel that is suitable for the blast furnace.</td>
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<tr>
<td></td>
<td><strong>Electric arc furnace dust</strong></td>
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<td></td>
<td>10. EAF dust is a hazardous waste because of its high concentrations of lead and cadmium. With 550,000 tons of EAF dust generated annually in the United States, there is great potential to reduce the volume of this hazardous waste. U.S. steel companies typically pay a disposal fee of $150 to $200 per ton of dust. With an average zinc concentration of 19%, much of the EAF dust is sent off-site for zinc recovery. Most of the EAF dust recovery options are only economically viable for dust with a zinc content of at least 15 to 20 percent. Facilities that manufacture specialty steels such as stainless steel with a lower zinc content, still have opportunities to recover chromium and nickel from the EAF dust. In-process recycling of EAF dust involves pelletizing and then reusing the pellets in the furnace; however, recycling of EAF dust on-site has not proven to be technically or economically competitive for all mills. Improvements in technologies have made off-site recovery a cost-effective alternative to thermal treatment or secure landfill disposal.</td>
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<td></td>
<td><strong>Pig iron manufacturing</strong></td>
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<td>11. Improve blast furnace efficiency by using coal and other fuels (such as oil or gas) for heating instead of coke, thereby minimizing air emissions.</td>
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<td>12. Recover the thermal energy in the gas from the blast furnace before using it as a fuel.</td>
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<td>13. Increase fuel efficiency and reduce emissions by improving blast furnace charge distribution.</td>
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<td>14. Recover energy from sinter coolers and exhaust gases.</td>
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<td>Area of opportunity</td>
<td>Recommended pollution prevention practice</td>
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<td></td>
<td>15. Use dry SO(_x) removal systems such as caron absorption for sinter plants or lime spraying in flue gases.</td>
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<td>16. Recycle iron-rich materials such as iron ore fines, pollution control dust, and scale in a sinter plant.</td>
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<td>17. Use low- NO(_x) burners to reduce NO(_x) emissions from burning fuel in ancillary operations.</td>
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<td>18. Improve productivity by screening the charge and using better taphole practices.</td>
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<td>19. Reduce dust emissions at furnaces by covering iron runners when tapping the blast furnace and by using nitrogen blankets during tapping.</td>
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<td>20. Use pneumatic transport, enclosed conveyor belts, or self-closing conveyor belts, as well as wind barriers and other dust suppression measures, to reduce the formation of fugitive dust.</td>
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<tr>
<td>Steel manufacturing</td>
<td>21. Use dry dust collection and removal systems to avoid the generation of wastewater. Recycle collected dust.</td>
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<td>22. Use BOF gas as fuel.</td>
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<td></td>
<td>23. Use enclosures for BOF.</td>
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<td>24. Use a continuous process for casting steel to reduce energy consumption.</td>
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<tr>
<td>Finishing stages</td>
<td>25. Pickling acids - In finishing, pickling acids are recognized as an area where pollution prevention efforts can have a significant impact in reducing the environmental impact of the steel mill. The pickling process removes scale and cleans the surface of raw steel by dipping it into a tank of hydrochloric or sulfuric acid. If not recovered, the spent acid may be transported to deep injection wells for disposal, but as those wells continue to close, alternative disposal costs are rising.</td>
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<tr>
<td>Area of opportunity</td>
<td>Recommended pollution prevention practice</td>
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| 26. Pickling acids - Large-scale steel manufacturers recover HCl in their finishing operations, however the techniques used are not suitable for small- to medium-sized steel plants. Currently, a recovery technique for smaller steel manufacturers and galvanizing plants is in pilot-scale testing. The system removes iron chloride (a saleable product) from the HCl, reconcentrates the acid for reuse, and recondenses the water to be reused as a rinse water in the pickling process. Because the only by-product of the hydrochloric acid recovery process is a non-hazardous, marketable metal chloride, this technology generates no hazardous wastes. The manufacturer projects industry-wide HCl waste reduction of 42,000 tons/year by 2010. This technology is less expensive than transporting and disposing waste acid, plus it eliminates the associated long-term liability. The total savings for a small- to medium-sized galvanizer is projected to be $260,000 each year.  
27. Pickling acids - To reduce spent pickling liquor and simultaneously reduce fluoride in the plant effluent, one facility modified their existing treatment process to recover the fluoride ion from rinse water and spent pickling acid raw water waste streams. The fluoride is recovered as calcium fluoride (fluorspar), an input product for steelmaking. The melt shop in the same plant had been purchasing 930 tons of fluorspar annually for use as a furnace flux material in the EAF at a cost of $100 per ton. The recovered calcium fluoride is expected to be a better grade than the purchased fluorspar, which would reduce the amount of flux used by approximately 10%. Not only would the generation rate of sludge from spent pickling liquor treatment be reduced (resulting in a savings in off-site sludge disposal costs), but a savings in chemical purchases would be captured. |
<p>| Process modifications | 28. Replacing single-pass wastewater systems with closed-loop systems to minimize chemical use in wastewater treatment and to reduce water use. |</p>
<table>
<thead>
<tr>
<th>Area of opportunity</th>
<th>Recommended pollution prevention practice</th>
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<tbody>
<tr>
<td>29. Continuous casting, now used for about 90% of crude steel cast in the United States offers great improvements in process efficiency when compared to the traditional ingot teeming method. This increased efficiency also results in a considerable savings in energy and some reduction in the volume of mill wastewater.</td>
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<tr>
<td>30. Use scrap steel with low lead and cadmium content as a raw material, if possible. 31. Eliminate the generation of reactive desulfurization slag generated in foundry work by replacing calcium carbide with a less hazardous material.</td>
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<tr>
<td>32. Recycle or reuse oils and greases. 33. Recover acids by removing dissolved iron salts from spent acids. 34. Use thermal decomposition for acid recovery from spent pickle liquor. 35. Use a bipolar membrane/electrodialytic process to separate acid from metal by-products in spent NO₃-HF pickle liquor. 36. Recover sulfuric acid using low temperature separation of acid and metal crystals. 37. Use blast-furnace slag in construction materials. Slag containing free lime can be used in ironmaking.</td>
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</table>

**LEAD AND ZINC SMELTING**

**INDUSTRY DESCRIPTION AND PRACTICES**

Lead and zinc can be produced pyrometallurgically or hydrometallurgically, depending on the type of ore used as a charge. In the pyrometallurgical process, ore concentrate containing lead, zinc, or both is fed, in some cases after sintering, into a primary smelter. Lead concentrations can be 50 to 70%, and the sulfur content of sulfidic ores is in the range of 15 to 20%. Zinc concentration is in the range of 40 to 60%, with sulfur content in sulfidic ores in the range of 26 to 34%. Ores with a mixture of lead and zinc concentrate usually have lower respective metal concentrations. During sintering, a blast of hot air or oxygen is used to oxidize the sulfur present in the feed to sulfur dioxide. Blast
furnaces are used in conventional processes for reduction and refining of lead compounds to produce lead. Modern direct smelting processes include QSL, Kivcet, AUSMELT, and TBRC.

Primary Lead Processing

The conventional pyrometallurgical primary lead production process consists of four steps: sintering, smelting, drossing, and refining. A feedstock made up mainly of lead concentrate is fed into a sintering machine. Other raw materials may be added, including iron, silica, limestone flux, coke, soda, ash, pyrite, zinc, caustic, and particulates gathered from pollution-control devices. The sintering feed, along with coke, is fed into a blast furnace for reducing, where the carbon also acts as a fuel and smelts the lead-containing materials. The molten lead flows to the bottom of the furnace, where four layers form: "speiss" (the lightest material, basically arsenic and antimony), "matte" (copper sulfide and other metal sulfides), blast furnace slag (primarily silicates), and lead bullion (98% by weight). All layers are then drained off. The speiss and matte are sold to copper smelters for recovery of copper and precious metals. The blast furnace slag, which contains zinc, iron, silica, and lime, is stored in piles and is partially recycled. Sulfur oxide emissions are generated in blast furnaces from small quantities of residual lead sulfide and lead sulfates in the sinter feed.

Rough lead bullion from the blast furnace usually requires preliminary treatment in kettles before undergoing refining operations. During drossing, the bullion is agitated in a drossing kettle and cooled to just above its freezing point, 370 to 425°C (700 to 800°F). A dross composed of lead oxide, along with copper, antimony, and other elements, floats to the top and solidifies above the molten lead. The dross is removed and is fed into a dross furnace for recovery of the nonlead mineral values.

The lead bullion is refined using pyrometallurgical methods to remove any remaining nonlead materials (e.g., gold, silver, bismuth, zinc, and metal oxides such as oxides of antimony, arsenic, tin, and copper). The lead is refined in a cast-iron kettle in five stages. First, antimony, tin, and arsenic are removed. Next, gold and silver are removed by adding zinc. The lead is then refined by vacuum removal of zinc. Refining continues with the addition of calcium and magnesium, which combine with bismuth to form an insoluble compound that is skimmed from the kettle. In the final step, caustic soda, nitrates, or both may be added to remove any remaining traces of metal impurities. The refined lead will have a purity of 99.90 to 99.99%. It may be mixed with other metals to form alloys, or it may be directly cast into shapes.
Secondary Lead Processing

The secondary production of lead begins with the recovery of old scrap from worn-out, damaged, or obsolete products and with new scrap. The chief source of old scrap is lead-acid batteries; other sources include cable coverings, pipe, sheet, and other lead-bearing metals. Solder, a tin-based alloy, may be recovered from the processing of circuit boards for use as lead charge.

Prior to smelting, batteries are usually broken up and sorted into their constituent products. Fractions of cleaned plastic (such as polypropylene) case are recycled into battery cases or other products. The dilute sulfuric acid is either neutralized for disposal or recycled to the local acid market. One of the three main smelting processes is then used to reduce the lead fractions and produce lead bullion.

Most domestic battery scrap is processed in blast furnaces, rotary furnaces, or reverberatory furnaces. A reverberatory furnace is more suitable for processing fine particles and may be operated in conjunction with a blast furnace.

Blast furnaces produce hard lead from charges containing siliceous slag from previous runs (about 4.5% of the charge), scrap iron (about 4.5%), limestone (about 3%), and coke (about 5.5%). The remaining 82.5% of the charge is made up of oxides, pot furnace refining drosses, and reverberatory slag. The proportions of rerun slags, limestone, and coke vary but can run as high as 8% for slags, 10% for limestone, and 8% for coke. The processing capacity of the blast furnace ranges from 20 to 80 metric tons per day (tpd).

Newer secondary recovery plants use lead paste desulfurization to reduce sulfur dioxide emissions and generation of waste sludge during smelting. Battery paste containing lead sulfate and lead oxide is desulfurized with soda ash, yielding market-grade sodium sulfate as a by-product. The desulfurized paste is processed in a reverberatory furnace, and the lead carbonate product may then be treated in a short rotary furnace. The battery grids and posts are processed separately in a rotary smelter.

Zinc Manufacturing

In the most common hydrometallurgical process for zinc manufacturing, the ore is leached with sulfuric acid to extract the lead/zinc. These processes can operate at atmospheric pressure or as pressure leach circuits. Lead/zinc is recovered from solution by electrowinning, a process similar to electrolytic refining. The process
most commonly used for low-grade deposits is heap leaching. Imperial smelting is also used for zinc ores.

POLLUTION PREVENTION PRACTICES AND OPPORTUNITIES

The principal air pollutants emitted from the processes are particulate matter and sulfur dioxide. Fugitive emissions occur at furnace openings and from launders, casting molds, and ladles carrying molten materials, which release sulfur dioxide and volatile substances into the working environment. Additional fugitive particulate emissions occur from materials handling and transport of ores and concentrates. Some vapors are produced in hydrometallurgy and in various refining processes.

The principal constituents of the particulate matter are lead/zinc and iron oxides, but oxides of metals such as arsenic, antimony, cadmium, copper, and mercury are also present, along with metallic sulfates. Dust from raw materials handling contains metals, mainly in sulfidic form, although chlorides, fluorides, and metals in other chemical forms may be present. Off-gases contain fine dust particles and volatile impurities such as arsenic, fluorine, and mercury.

Air emissions for processes with few controls may be of the order of 30 kilograms lead or zinc per metric ton (kg/t) of lead or zinc produced. The presence of metals in vapor form is dependent on temperature. Leaching processes will generate acid vapors, while refining processes result in products of incomplete combustion (PICs). Emissions of arsine, chlorine, and hydrogen chloride vapors and acid mists are associated with electrorefining.

Wastewaters are generated by wet air scrubbers and cooling water. Scrubber effluents may contain lead/zinc, arsenic, and other metals. In the electrolytic refining process, by-products such as gold and silver are collected as slimes and are subsequently recovered. Sources of wastewater include spent electrolytic baths, slimes recovery, spent acid from hydrometallurgy processes, cooling water, air scrubbers, washdowns, and stormwater. Pollutants include dissolved and suspended solids, metals, and oil and grease.

The larger proportion of the solid waste is discarded slag from the smelter. Discarded slag may contain 0.5-0.7% lead/zinc and is frequently used as fill or for sandblasting. Slags with higher lead/zinc content, say 15% zinc, can be sent for metals recovery. Leaching processes produce residues, while effluent
treatment results in sludges that require appropriate disposal. The smelting process typically produces less than 3 tons of solid waste per ton of lead/zinc produced.

The most effective pollution prevention option is to choose a process that entails lower energy usage and lower emissions. Modern flash-smelting processes save energy, compared with the conventional sintering and blast furnace process. Process gas streams containing over 5% sulfur dioxide are usually used to manufacture sulfuric acid. The smelting furnace will generate gas streams with SO$_2$ concentrations ranging from 0.5% to 10%, depending on the method used. It is important, therefore, to select a process that uses oxygen-enriched air or pure oxygen. The aim is to save energy and raise the SO$_2$ content of the process gas stream by reducing the total volume of the stream, thus permitting efficient fixation of sulfur dioxide. Processes should be operated to maximize the concentration of the sulfur dioxide. An added benefit is the reduction (or elimination) of nitrogen oxides NO$_x$. Table 8 provides a list of pollution prevention practices and opportunities. Regarding standard treatment technologies, ESPs and baghouses are used for product recovery and for the control of particulate emissions. Dust that is captured but not recycled will need to be disposed of in a secure landfill or in another acceptable manner.

Table 8. Summary of Pollution Prevention Practices

<table>
<thead>
<tr>
<th>Practice</th>
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<tbody>
<tr>
<td>Use doghouse enclosures where appropriate; use hoods to collect fugitive emissions.</td>
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<tr>
<td>Mix strong acidic gases with weak ones to facilitate production of sulfuric acid from sulfur oxides, thereby avoiding the release of weak acidic gases.</td>
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<tr>
<td>Maximize the recovery of sulfur by operating the furnaces to increase the SO$_x$ content of the flue gas and by providing efficient sulfur conversion. Use a double-contact, double-absorption process.</td>
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<tr>
<td>Desulfurize paste with caustic soda or soda ash to reduce SO$_2$ emissions.</td>
</tr>
<tr>
<td>Use energy-efficient measures such as waste heat recovery from process gases to reduce fuel usage and associated emissions.</td>
</tr>
<tr>
<td>Recover acid, plastics, and other materials when handling battery scrap in secondary lead production.</td>
</tr>
<tr>
<td>Recycle condensates, rainwater, and excess process water for washing, for dust control, for gas scrubbing, and for other process applications where water quality is not of particular concern.</td>
</tr>
<tr>
<td>Give preference to natural gas over heavy fuel oil for use as fuel and to coke with lower sulfur content.</td>
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<tr>
<td>Use low-NO$_x$ burners.</td>
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</table>
Use suspension or fluidized bed roasters, where appropriate, to achieve high
SO\textsubscript{2} concentrations when roasting zinc sulfides.

Recover and reuse iron-bearing residues from zinc production for use in the
steel or construction industries.

Give preference to fabric filters over wet scrubbers or wet electrostatic
precipitators (ESPs) for dust control.

Good housekeeping practices are key to minimizing losses and preventing
fugitive emissions. Losses and emissions are minimized by enclosed buildings,
covered conveyors and transfer points, and dust collection equipment. Yards
should be paved and runoff water routed to settling ponds.

Arsenic trioxide or pentoxide is in vapor form because of the high gas
temperatures and must be condensed by gas cooling so that it can be removed in
fabric filters. Collection and treatment of vent gases by alkali scrubbing may be
required when sulfur dioxide is not being recovered in an acid plant.

Effluent treatment of process bleed streams, filter backwash waters, boiler
bleedown, and other streams is required to reduce suspended and dissolved
solids and heavy metals and to adjust pH. Residues that result from treatment are
recycled to other industries such as the construction industry, sent to settling
ponds (provided that groundwater and surface water contamination is not a
concern), or disposed of in a secure landfill.

Slag should be either landfilled or granulated and sold for use in building
materials.

**NICKEL ORE PROCESSING AND REFINING**

**INDUSTRY DESCRIPTION AND PRACTICES**

Primary nickel is produced from two very different ores, lateritic and sulfidic.
Lateritic ores are normally found in tropical climates where weathering, with
time, extracts and deposits the ore in layers at varying depths below the surface.
Lateritic ores are excavated using large earth-moving equipment and are screened
to remove boulders. Sulfidic ores, often found in conjunction with copper-
bearing ores, are mined from underground. Following is a description of the
processing steps used for the two types of ores.
Lateritic Ore Processing

Lateritic ores have a high percentage of free and combined moisture, which must be removed. Drying removes free moisture; chemically bound water is removed by a reduction furnace, which also reduces the nickel oxide. Lateritic ores have no significant fuel value, and an electric furnace is needed to obtain the high temperatures required to accommodate the high magnesia content of the ore. Some laterite smelters add sulfur to the furnace to produce a matte for processing. Most laterite nickel processors run the furnaces so as to reduce the iron content sufficiently to produce ferronickel products. Hydrometallurgical processes based on ammonia or sulfuric acid leach are also used. Ammonia leach is usually applied to the ore after the reduction roast step.

Sulfidic Ore Processing

Flash smelting is the most common process, but electric smelting is used for more complex raw materials when increased flexibility is needed. Both processes use dried concentrates. Electric smelting requires a roasting step before smelting to reduce sulfur content and volatiles. Older nickel-smelting processes, such as blast or reverberatory furnaces, are no longer acceptable because of low energy efficiencies and environmental concerns.

In flash smelting, dry sulfide ore containing less than 1% moisture is fed to the furnace along with preheated air, oxygen-enriched air (30-40% oxygen), or pure oxygen. Iron and sulfur are oxidized. The heat that results from exothermic reactions is adequate to smelt concentrate, producing a liquid matte (up to 45% nickel) and a fluid slag. Furnace matte still contains iron and sulfur, and these are oxidized in the converting step to sulfur dioxide and iron oxide by injecting air or oxygen into the molten bath. Oxides form a slag, which is skimmed off. Slags are processed in an electric furnace prior to discard to recover nickel. Process gases are cooled, and particulates are then removed by gas-cleaning devices.

Nickel Refining

Various processes are used to refine nickel matte. Fluid-bed roasting and chlorine-hydrogen reduction produce high-grade nickel oxides (more than 95% nickel). Vapor processes such as the carbonyl process can be used to produce high-purity nickel pellets. In this process, copper and precious metals remain as a pyrophoric residue that requires separate treatment. Use of electrical cells equipped with inert cathodes is the most common technology for nickel refining.
Electrowinning, in which nickel is removed from solution in cells equipped with inert anodes, is the more common refining process. Sulfuric acid solutions or, less commonly, chloride electrolytes are used.

**POLLUTION PREVENTION PRACTICES AND OPPORTUNITIES**

Sulfur dioxide is a major air pollutant emitted in the roasting, smelting, and converting of sulfide ores. (Nickel sulfide concentrates contain 6-20% nickel and up to 30% sulfur.) SO$_2$ releases can be as high as 4 metric tons (t) of sulfur dioxide per metric ton of nickel produced, before controls. Reverberatory furnaces and electric furnaces produce SO$_2$ concentrations of 0.5 to 2.0%, while flash furnaces produce SO$_2$ concentrations of over 10% - a distinct advantage for the conversion of the sulfur dioxide to sulfuric acid. Particulate emission loads for various process steps include 2.0 to 5.0 kilograms per metric ton (kg/t) for the multiple hearth roaster; 0.5 to 2.0 kg/t for the fluid bed roaster; 0.2 to 1.0 kg/t for the electric furnace; 1.0 to 2.0 kg/t for the Pierce-Smith converter; and 0.4 kg/t for the dryer upstream of the flash furnace. Ammonia and hydrogen sulfide are pollutants associated with the ammonia leach process; hydrogen sulfide emissions are associated with acid leaching processes. Highly toxic nickel carbonyl is a contaminant of concern in the carbonyl refining process. Various process offgases contain fine dust particles and volatilized impurities. Fugitive emissions occur at furnace openings, launders, casting molds, and ladles that carry molten product. The transport and handling of ores and concentrates produce windborne dust.

Pyrometallurgical processes for processing sulfidic ores are generally dry, and effluents are of minor importance, although wet ESPs are often used for gas treatment, and the resulting wastewater could have high metal concentrations. Process bleed streams may contain antimony, arsenic, or mercury. Large quantities of water are used for slag granulation, but most of this water should be recycled.

The smelter contributes a slag that is a dense silicate. Sludges that require disposal will result when neutralized process effluents produce a precipitate.

Pollution prevention is always preferred to the use of end-of-pipe pollution control facilities. Therefore, every attempt should be made to incorporate cleaner production processes and facilities to limit, at source, the quantity of pollutants generated. The choice of flash smelting over older technologies is the most
significant means of reducing pollution at source. Sulfur dioxide emissions can be controlled by:

- Recovery as sulfuric acid
- Recovery as liquid sulfur dioxide (absorption of clean dry off-gas in water or chemical absorption by ammonium bisulfite or dimethyl aniline)
- Recovery as elemental sulfur, using reductants, such as hydrocarbons, carbon, or hydrogen sulfide

Toxic nickel carbonyl gas is normally not emitted from the refining process because it is broken down in decomposer towers. However, very strict precautions throughout the refining process are required to prevent the escape of the nickel carbonyl into the workplace. Continuous monitoring for the gas, with automatic isolation of any area of the plant where the gas is detected, is required. Impervious clothing is used to protect workers against contact of liquid nickel carbonyl with skin.

Preventive measures for reducing emissions of particulate matter include encapsulation of furnaces and conveyors to avoid fugitive emissions. Covered storage of raw materials should be considered.

Wet scrubbing should be avoided, and cooling waters should be recirculated. Stormwaters should be collected and used in the process. Process water used to transport granulated slag should be recycled. To the extent possible, all process effluents should be returned to the process.

The discharge of particulate matter emitted during drying, screening, roasting, smelting, and converting is controlled by using cyclones followed by wet scrubbers, ESPs, or bag filters. Fabric filters may require reduction of gas temperatures by, for example, dilution with low-temperature gases from hoods used for fugitive dust control. Preference should be given to the use of fabric filters over wet scrubbers.

Liquid effluents are used to slurry tailings to the tailings ponds, which act as a reservoir for the storage and recycle of plant process water. However, there may be a need to treat bleed streams of some process effluents to prevent a buildup of various impurities. Solid wastes from nickel sulfide ores often contain other metals such as copper and precious metals, and consideration should be given to further processing for their recovery. Slag can be used as construction material after nickel recovery, as appropriate (e.g., return of converter slag to the
Sanitary sewage effluents require treatment in a separate facility or discharge to a municipal sewer.

COPPER SMELTING

INDUSTRY DESCRIPTION AND PRACTICES

Copper can be produced either pyrometallurgically or hydrometallurgically. The hydrometallurgical route is used only for a very limited amount of the world's copper production and is normally only considered in connection with in situ leaching of copper ores. From an environmental point of view, this is a questionable production route. Several different processes can be used for copper production. The traditional process is based on roasting, smelting in reverberatory furnaces (or electric furnaces for more complex ores), producing matte (copper-iron sulfide), and converting for production of blister copper, which is further refined to cathode copper. This route for production of cathode copper requires large amounts of energy per ton of copper: 30 to 40 million British thermal units (Btu) per ton cathode copper. It also produces furnace gases with low sulfur dioxide concentrations from which the production of sulfuric acid or other products is less efficient. The sulfur dioxide concentration in the exhaust gas from a reverberatory furnace is about 0.5-1.5%; that from an electric furnace is about 2 - 4%. So-called flash smelting techniques have therefore been developed that utilize the energy released during oxidation of the sulfur in the ore. The flash techniques reduce the energy demand to about 20 million Btu/ton of produced cathode copper. The SO₂ concentration in the off-gases from flash furnaces is also higher, over 30%, and is less expensive to convert to sulfuric acid. The INCO process results in 80% sulfur dioxide in the off-gas. Flash processes have been in use since the early 1950s.

In addition to the above processes, there are a number of newer processes such as Noranda, Mitsubishi, and Contop, which replace roasting, smelting, and converting, or processes such as ISA-SMELT and KIVCET, which replace roasting and smelting. For converting, the Pierce-Smith and Hoboken converters are the most common processes.

The matte from the furnace is charged to converters, where the molten material is oxidized in the presence of air to remove the iron and sulfur impurities (as converter slag) and to form blister copper. Blister copper is further refined as either fire-refined copper or anode copper (99.5% pure copper), which is used in
subsequent electrolytic refining. In fire refining, molten blister copper is placed in a fire-refining furnace, a flux may be added, and air is blown through the molten mixture to remove residual sulfur. Air blowing results in residual oxygen, which is removed by the addition of natural gas, propane, ammonia, or wood. The fire-refined copper is then cast into anodes for further refining by electrolytic processes or is cast into shapes for sale.

In the most common hydrometallurgical process, the ore is leached with ammonia or sulfuric acid to extract the copper. These processes can operate at atmospheric pressure or as pressure leach circuits. Copper is recovered from solution by electrowinning, a process similar to electrolytic refining. The process is most commonly used for leaching low-grade deposits *in situ* or as heaps.

Recovery of copper metal and alloys from copper-bearing scrap metal and smelting residues requires preparation of the scrap (e.g., removal of insulation) prior to feeding into the primary process. Electric arc furnaces using scrap as feed are also common.

**POLLUTION PREVENTION PRACTICES AND OPPORTUNITIES**

The principal air pollutants emitted from the processes are sulfur dioxide and particulate matter. The amount of sulfur dioxide released depends on the characteristics of the ore-complex ores which may contain lead, zinc, nickel, and other metals, and on whether facilities are in place for capturing and converting the sulfur dioxide. SO\(_2\) emissions may range from less than 4 kilograms per metric ton (kg/t) of copper to 2000 kg/t of copper. Particulate emissions can range from 0.1 kg/t of copper to as high as 20 kg/t of copper. Fugitive emissions occur at furnace openings and from launders, casting molds, and ladles carrying molten materials. Additional fugitive particulate emissions occur from materials handling and transport of ores and concentrates. Some vapors, such as arsine, are produced in hydrometallurgy and various refining processes. Dioxins can be formed from plastic and other organic material when scrap is melted. The principal constituents of the particulate matter are copper and iron oxides. Other copper and iron compounds, as well as sulfides, sulfates, oxides, chlorides, and fluorides of arsenic, antimony, cadmium, lead, mercury, and zinc, may also be present. Mercury can also be present in metallic form. At higher temperatures, mercury and arsenic could be present in vapor form. Leaching processes will generate acid vapors, while fire-refining processes result in copper and SO\(_2\) emissions. Emissions of arsine, hydrogen vapors, and acid mists are associated with electrorefining. Wastewater from primary copper production contains...
dissolved and suspended solids that may include concentrations of copper, lead, cadmium, zinc, arsenic, and mercury and residues from mold release agents (lime or aluminum oxides). Fluoride may also be present, and the effluent may have a low pH. Normally there is no liquid effluent from the smelter other than cooling water; wastewaters do originate in scrubbers (if used), wet electrostatic precipitators, cooling of copper cathodes, and so on. In the electrolytic refining process, by-products such as gold and silver are collected as slimes that are subsequently recovered. Sources of wastewater include spent electrolytic baths, slimes recovery, spent acid from hydrometallurgy processes, cooling water, air scrubbers, washdowns, stormwater, and sludges from wastewater treatment processes that require reuse/recovery or appropriate disposal. The main portion of the solid waste is discarded slag from the smelter. Discard slag may contain 0.5-0.7% copper and is frequently used as construction material or for sandblasting. Leaching processes produce residues, while effluent treatment results in sludges, which can be sent for metals recovery. The smelting process typically produces less than 3 tons of solid waste per ton of copper produced.

Process-gas streams containing sulfur dioxide are processed to produce sulfuric acid, liquid sulfur dioxide, or sulfur. The smelting furnace will generate process gas streams with SO₂ concentrations ranging from 0.5% to 80%, depending on the process used. It is important, therefore, that a process be selected that uses oxygen-enriched air (or pure oxygen) to raise the SO₂ content of the process gas stream and reduce the total volume of the stream, thus permitting efficient fixation of sulfur dioxide. Processes should be operated to maximize the concentration of the sulfur dioxide. An added benefit is the reduction of NOₓ. Some pollution prevention practices for this industry include the following:

- Closed-loop electrolysis plants will contribute to prevention of pollution.
- Furnaces should be enclosed to reduce fugitive emissions, and dust from dust control equipment should be returned to the process.
- Energy efficiency measures (such as waste heat recovery from process gases) should be applied to reduce fuel usage and associated emissions.
- Recycling should be practiced for cooling water, condensates, rainwater, and excess process water used for washing, dust control, gas scrubbing, and other process applications where water quality is not a concern.
- Good housekeeping practices are key to minimizing losses and preventing fugitive emissions. Such losses and emissions are minimized by enclosed buildings, covered or enclosed conveyors and transfer points, and dust collection equipment. Yards should be paved and runoff water routed to settling ponds. Regular sweeping of yards and indoor storage or coverage of concentrates and other raw materials also reduces materials losses and emissions.
Pollution control technologies acceptable for this industry are as follows. Fabric filters are used to control particulate emissions. Dust that is captured but not recycled will need to be disposed of in a secure landfill or other acceptable manner. Vapors of arsenic and mercury present at high gas temperatures are condensed by gas cooling and removed. Additional scrubbing may be required. Effluent treatment by precipitation, filtration, and so on, of process bleed streams, filter backwash waters, boiler blowdown, and other streams may be required to reduce suspended and dissolved solids and heavy metals. Residues that result from treatment are sent for metals recovery or to sedimentation basins. Stormwaters should be treated for suspended solids and heavy metals reduction. Slag should be landfilled or granulated and sold. Modern plants using good industrial practices should set as targets total dust releases of 0.5 to 1.0 kg/t of copper and SO₂ discharges of 25 kg/t of copper. A double-contact, double-absorption plant should emit no more than 0.2 kg of sulfur dioxide per ton of sulfuric acid produced (based on a conversion efficiency of 99.7%).

A SHORT REVIEW

Industry practices are shifting away from end-of-pipe treatment technologies toward pollution prevention. The transition in general is slow, because many companies face large-scale investments in more environmentally friendly technologies. Large infrastructure investments into green technologies which reduce pollution and forms of waste at the source generally are taking years of planning and implementation and are often implemented over several stages. Because these investments are not examined in terms of the four tiers of environmental costs, more conservative and lengthy transitions to greener technologies are taking place.

In the chapter to follow, the methodology behind waste minimization and pollution prevention programs is explained in greater detail. The principles of life-cycle costing and their application to assessing P2 technologies are described.