4 Environmental Leadership

Through the promotion of responsible policies that conserve energy and natural resources while sustaining a sound economic environment, the steel industry is committed to the protection of human health and the environment.

The steel industry has invested more than $7 billion in environmental controls over the past 30 years in order to meet the challenge of compliance with national health-based standards. In a typical year, iron and steel plants spend roughly 15% of their capital expenditures on environmental projects. In fact, the industry's discharge of air and water pollutants has been reduced by well over 90% since the early 1970s. Despite this significant progress, further improvements in pollution prevention technologies are needed for iron and steel plants to reduce costs, improve profitability, and facilitate compliance with changing federal regulations.

Recently promulgated and impending air and water pollution control regulations pose a daunting challenge for the U.S. steel industry. In accordance with requirements of the Clean Air Act, EPA has established Maximum Achievable Control Technology (MACT) standards for hazardous air pollutant emissions. Under this program, EPA established standards for coke oven door and topside leaks and charging emissions in 1992 and placed cokemakers on a timetable to achieve progressively more stringent standards between 1995 and 2020. In 2001, additional MACT standards are proposed for coke oven pushing and quenching operations and coke battery combustion stacks. Also in 2001, MACT standards are proposed for blast furnaces, sinter plants, basic oxygen shops, and ancillary operations.

In addition to these industry-specific regulations, EPA has also revised the ambient air quality standards for fine particulate matter (PM-2.5) and for ozone. As regulatory programs are implemented over the next few years to achieve these ambient standards, additional control requirements are possible for iron and steel industry sources emitting fine particles or gases that contribute to the formation of urban smog, including NOx, SOx, and VOCs. Also, the federal air permitting process under Title V of the Clean Air Act will require additional administrative controls and monitoring obligations.

The industry also faces substantially tighter regulations under the Clean Water Act. EPA has proposed revisions to Effluent Limitations Guidelines (ELGs) for the Iron and Steel Point Source Category that have been in place since the early 1980s. The EPA is on schedule to issue these rules in final form by April 2002. The new limits are dramatically lower than the existing ELGs and would require significant increases in recycling and more efficient treatment for the full range of iron and steel processes. Many steel plants are already required to reduce effluents below the previously established ELG limits because of the need to meet state and federal water quality standards, particularly in the Great Lakes area as a result of the Great Lakes Water Quality Initiative.

Meeting these new and changing regulations requires effective R&D efforts throughout many different aspects of the steelmaking process. To target future research, it is useful to examine the various processes and the pollutants they produce. Although the coking process has been widely considered to pose the biggest environmental challenge, environmental regulations affect all stages of the manufacturing and forming process. The following sections discuss the potential pollutant output and development needs of each of the major processes: cokemaking, ironmaking, steelmaking, refining, casting, forming, and finishing.

4.1   Cokemaking

Cokemaking represents perhaps the greatest environmental concern to the steel industry. Although much progress has been made, cokemaking emissions continue to be a target of federal environmental regulations. Continual efforts to reduce emissions are necessary to ensure the stability of U.S. cokemaking; some by-products present an additional concern. Figure 4-1 illustrates the cokemaking process with its major inputs and outputs.

Strict environmental regulations in the United States, including the Clean Air Act Amendments of 1990, threaten the economic viability of domestic coke production. While improvements to contain emissions have been incorporated into recent oven designs, many older cokemaking facilities cannot be retrofitted economically to meet current and proposed environmental standards. Tighter environmental regulations threaten to accelerate plant closures, in turn reducing domestic production capacity by approximately 30% by the year 2003. Other developed and developing nations are expected to follow the lead of the United States with tighter environmental regulations that will affect worldwide coke production. At present, no new by-product cokemaking technology is guaranteed to be environmentally compliant. In fact, new MACT standards provide an incentive for non-recovery coke ovens for new facilities. In the future, U.S. dependence on foreign sources is expected to increase.

4.1.1   Cokemaking Emissions

Typical cokemaking air emissions include ammonia, benzene-soluble organics, benzene, particulates, SOx, and VOCs. Coke plant operators have initiated significant efforts to control these emissions and have spent millions of dollars on environmental control systems, improved operating and maintenance practices, and increased personnel training. These efforts have substantially reduced cokemaking air emissions over the last three decades
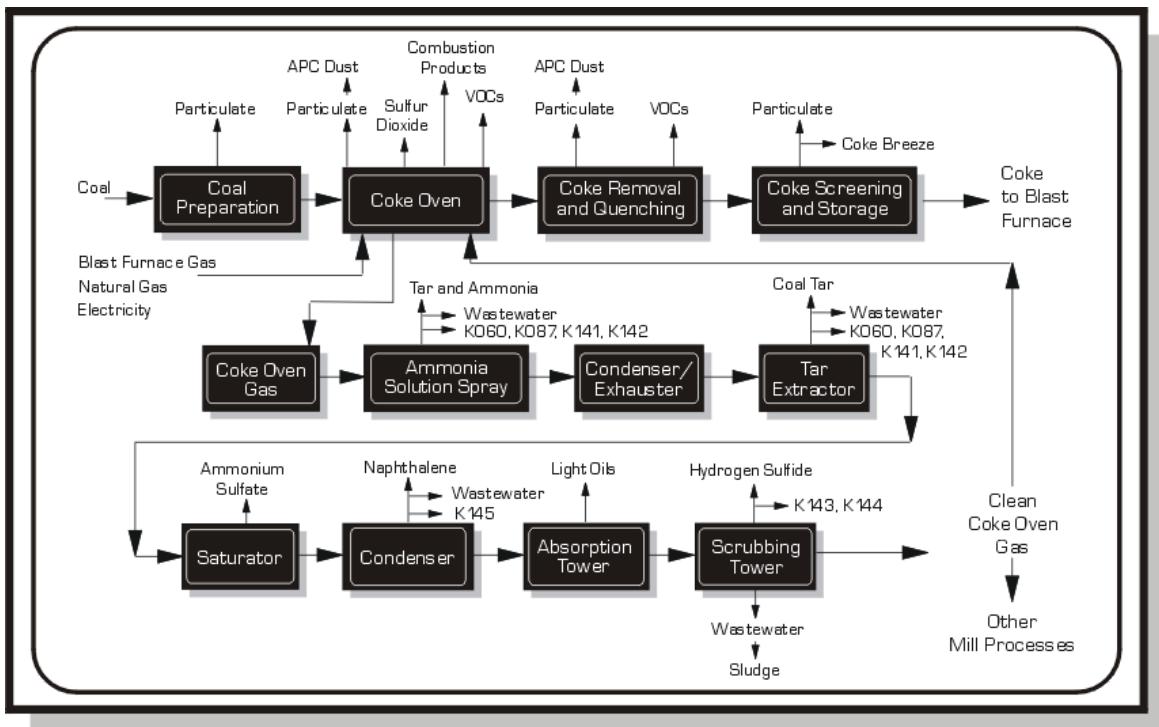
Figure 4-1. Cokemaking Flow Diagram

The industry's efforts have reduced emissions by more than 95% for benzene and VOCs from by-product sources, particulate matter emissions from charging and pushing, and SOx emissions from the combustion of "cleaned" coke oven gas. To reduce air emissions, the industry installed many types of new and improved environmental hardware. Training and, more importantly, the conscientious efforts of skilled operating personnel have also substantially reduced emissions of benzene-soluble organics from coke plant doors, lids, offtakes, and charging emissions sources.

4.1.2 Cokemaking Effluents

The typical volume of process wastewater generated at a well-controlled coke plant is approximately 150 gallons/ton of coke produced (EPA 2000). About 25 to 35 gallons/ton are generated as waste ammonia liquor from moisture contained in the charged coal. The balance is from the steam used in distilling ammonia from the waste liquor, light oil recovery, and other processes.

Cokemaking wastewaters contain significant levels of oil and grease, ammonia, nitrogen, cyanides, thiocyanates, phenols, benzenes, toluene, xylene, other aromatic volatile components, and polynuclear aromatic compounds. Wastewaters also contain trace amounts of the toxic metals antimony, arsenic, and selenium. The amount of each pollutant generated depends on the by-product process, specific facility equipment, practices, and the range of constituents in the coals used.

4.1.3 Cokemaking By-Products

In the by-product coking process, volatile components are collected as unpurified "foul" gas containing water vapor, tar, light oils, coal dust, heavy hydrocarbons, and complex carbon compounds. Condensable materials, such as tar, light oils, ammonia, and naphthalene are removed, recovered, and processed as gas and coal chemical by-products. Finally, sulfur is removed, leaving clean, desulfurized coke oven gas. The cleaned, desulfurized gas is then used as fuel for coke ovens or other plant combustion processes, or it is sold to nearby facilities.

Approximately 11,000 scf of coke oven gas (at about 500 Btu/scf) is produced/ton of coal charged (EPA 2000; AISE 1998). About 40% of the gas is used to heat the coke ovens.

4.1.4 Hazardous Cokemaking Wastes

As shown in Figure 4-1, seven listed hazardous wastes are associated with cokemaking under the Resource Conservation and Recovery Act (RCRA). These include residues from coal tar recovery, tar storage tanks, light oil processing units, wastewater sump residues, and naphthalene collection and recovery.

Process residues from coal tar recovery (K141) are generated when uncondensed gas enters a primary cooler. Condensates from the primary cooler flow into the tar collecting sump and are discharged in the flushing liquor decanter. Tar collection sump residue or sludge accumulates at the bottom of the collecting sump, and must be recycled periodically as an individual stream, through the flushing liquor decanter, or back to the coke oven. Tar storage tank residues (K142) are produced when residuals settle out of the crude coal tar collected as a coking by-product. The residues are periodically removed from the storage tanks and are recycled to the oven or landfilled.

Residues from light oil processing units (K143) collect in a light-oil scrubber and light-oil stripping still. Resin is a related waste that accumulates from cleaning wash oil used in the light-oil recovery process. Wash-oil muck, residue from a wash-oil purifier or decanter, is periodically removed and recycled to the coke oven, reclaimed off-site, or used as blast furnace or boiler fuel.

Wastewater sump residues (K144) accumulate in the bottom of a sump used to provide sufficient quiescent residence time for oil and water to separate during light oil recovery. These settled solids are removed periodically and either recycled to the oven or landfilled off-site. Residues from naphthalene collection and recovery (K145) accumulate at the bottom of a skimmer sump where naphthalene is mechanically skimmed off the surface. Residues also accumulate in the hot and cold sumps used as collection or surge vessels and on cooling tower surfaces. K145 is recycled to the decanter or sometimes the oven.

4.1.5 Cokemaking Environmental Trends and Drivers

Meeting the constantly changing environmental regulations is important to ensure the stability of U.S. cokemaking. The federal government has already promulgated coke plant air emission regulations for doors, offtakes, lids, coal charging, and collection mains that call for significantly more stringent emission requirements. In addition, standards are also being proposed for pushing, quenching and battery combustion stack emissions. Moreover, tighter effluent requirements are being proposed for cokemaking wastewaters.

These regulatory requirements challenge operating management and employees as they deal with aging batteries. Even the installation of new batteries as greenfield sites or increased capacity at conventional existing coke oven by-product plants will present environmental challenges because of new EPA regulations. On start-up, new-source by-product batteries with novel designs (e.g., jumbo ovens), pad-up rebuilds, or replacement batteries at the same plant site will be subject to 2010 limits.

4.1.6   New and Emerging Cokemaking Technologies

Non-recovery batteries have been implemented at two sites. The newest project, a joint venture between a steel plant and power company, produces coke and electricity without by-product chemicals.

4.1.7   Cokemaking Research and Development
Needs and Opportunities

Keeping the cokemaking process environmentally sustainable will require significant R&D. Some needs can be met by incremental improvements to the current cokemaking process. One example is the need for new sealing methods, compounds, devices, or mechanisms to effectively reduce emissions from leaking doors, lids, and offtakes. Improved cars and capture devices are additional cokemaking development needs.

R & D Needs

Cokemaking

- ‣ New ways to reduce emissions from leaking doors, lids, and offtakes
- ‣ Improved quench cars
- ‣ Improved capture devices or quenching methods
- ‣ Improved refractories for walls or better ways to seal existing leaks through walls
- ‣ Refractories or oven designs to accommodate operation as negative-pressure batteries
- ‣ New, more environmentally friendly cokemaking technologies
- ‣ Improved or higher valued chemicals from coke oven gas and by-products

Alternative cokemaking technologies that incorporate enhanced emission containment, capture, and/or control capabilities also need to be developed.   Such technologies are needed to ensure the long term environmental viability of cokemaking. Development of negative pressure ovens and closed bar ovens is needed.

4.2   Ironmaking

This section focuses on the sintering and blast furnace ironmaking processes. Although sintering plants offer significant benefits, environmental concerns have stymied greater use of traditional plants. NOx, VOC, and CO_2 control are the major areas requiring further R&D. Figures 4-2 and 4-3 illustrate the sintering and blast furnace processes, respectively, with their major inputs and outputs.

4.2.1   Ironmaking Emissions

Sinter Plant

Sinter plant emissions are generated from raw material handling, wind-box exhaust, sinter discharge (associated sinter crushers and hot screens), and the cooler and cold screen. Wind-box exhaust is the primary source of particulate emissions - mainly iron oxides, sulfur oxides, carbonaceous compounds, and chlorides. Fluorides, ammonia, and various metal compounds may also be present (Steiner 1976). At the discharge end, emissions are mainly iron and calcium oxides.

Sinter strand wind-box emissions are commonly controlled by cyclone cleaners followed by a dry or wet electrostatic precipitator, high-pressure drop wet scrubber, or baghouse. Crusher and hot screen emissions, the next largest emission source, are controlled by a hood and baghouse or scrubber.
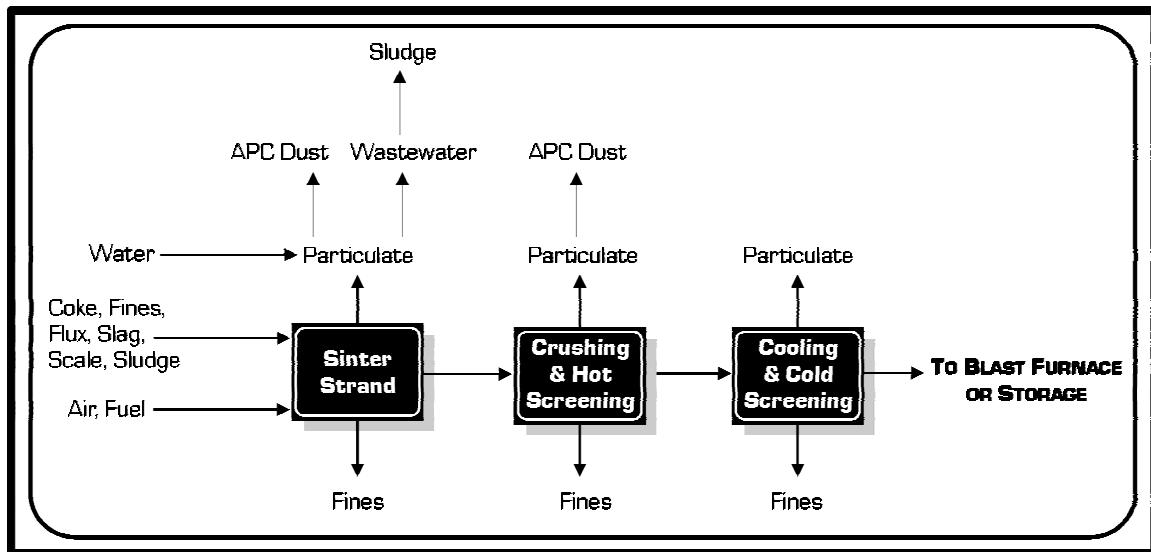
Figure 4-2. Sintering Flow Diagram

Other material-handling operations also generate emissions. Baghouses are used to capture particulate matter generated during conveyor transport and loading or unloading of sinter plant feedstocks and product. This dust is either recycled as feedstock to the sinter plant or landfilled as solid waste (EPA 1995; Baker Environmental 1992). Although the chemical composition of the dust is highly dependent upon the sintering practice, typical components include Fe, C, S, Fe_2O_3, SiO_2, Al_2O_3, CaO, and MgO (Steiner 1976).

The EPA, which reported a total of 2 million tons of CO_2 emitted from sinter plant windboxes in 1998, is gathering data to update some of its emission factors (AISI 1999). For example, its unreleased data suggest that some venturi scrubber emission factors may be significantly lower (in the range of 0.18 to 0.20 lb/ton) than the 0.47 lb/ton of sinter statistic reported in its AIRS database (Mulrine 1995).

Sinter plants have also been identified as potential sources of small concentrations of dioxin emissions. However, the sources and formation of dioxins is not well understood and more study is needed.
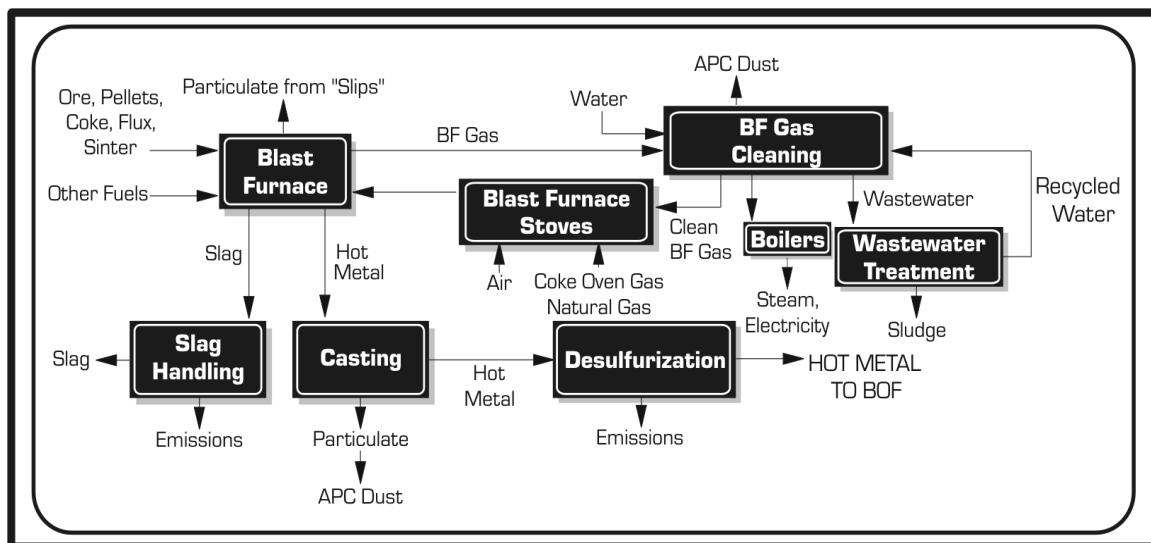

Figure 4-3. Blast Furnace Flow Diagram

Blast Furnace

Particulate emissions are primarily generated during the casting of molten iron and slag from the blast furnace. During casting, molten iron and slag flow out of a taphole at the base of the furnace into runners that lead to transport ladles. When the molten iron and slag contact air, particulate emissions are generated. Emissions also are generated by drilling and plugging the taphole, and by using an oxygen lance to open a clogged taphole.

During the casting operation, iron oxides, magnesium oxide, and kish are generated as particulate matter. Casting emissions are captured in a high canopy or local hood and exhausted to a cleaning device, generally a baghouse. Flame suppression techniques can minimize the amount of fume generated.

Dust captured from casting emissions is much less than that collected by a blast furnace gas cleaning system. (EPA 1995; Baker Environmental 1992)

If hot metal desulfurization is used to remove or alter the sulfur compounds in the hot metal, emissions are controlled by hoods and the exhaust gases are discharged through a baghouse to control particulate matter. This operation usually occurs at a facility located between the blast furnace and BOF facilities.

4.2.2 Ironmaking Effluents

Sintering

Wastewaters are generated from the use of wet air pollution control scrubbers to clean the wind-box and discharge ends of sinter machines. Typical flows for wet air pollution control devices are 1,000 gallons/ton, with discharge (blowdown) rates of 50 to 100 gallons/ton for the better controlled water treatment plants (EPA 2000).

Wet-scrubber wastewater treatment includes removal of heavy solids by sedimentation, recycle of clarifier or thickener water overflows, and metals precipitation treatment for blowdowns. Some sinter plants are operated with once-through water in the wet-scrubber wastewater treatment plants. The principal constituents can include suspended solids, oil and grease, ammonia-nitrogen, cyanide, phenolic compounds, and heavy metals, such as lead, zinc, arsenic, cadmium, copper, chromium, and selenium (EPA 2000).

Blast Furnace

Nearly all of the wastewater generated from blast furnace operations is direct contact water used in the gas coolers and high-energy wet scrubbers that clean the blast furnace gas. Typical water requirements are 6,000 gallons/ton of iron, which is recycled (EPA 2000). These waters are typically treated by clarifiers or thickeners to remove suspended solids, and the overflows are recycled to the gas scrubbers. The final blowdown from the recirculated system is then treated to remove additional heavy metals and other non-solid pollutants, such as cyanide and, typically less than 100 gallons/ton, ammonia.

4.2.3 Ironmaking By-Products

The primary by-products generated during the production of molten iron include blast furnace gas, slag, air pollution control dust (flue dust), and blast furnace filter cake (wastewater treatment-plant sludge). Between 2 and 3 tons of blast furnace gas, containing up to 100 pounds of dust, are generated for each ton of iron (AISI 1999). Blast furnace gas contains up to 40% CO and 6% H. The main solid components of the flue dust include Fe, C, SiO_2, Al_2O_3, CaO, and MgO (Steiner 1976). Blast furnace flue gas is emitted at the top of the furnace as particulate-laden combustion gases composed primarily of CO. About 60% of the particulate matter is removed from the gas stream by cyclonic vortex separation (i.e., dust catcher) of the heavy particles (flue dust). Fine

particulate matter is subsequently removed in a two-stage cleaning process with a wet scrubber and a high-energy venturi impact scrubber or electrostatic precipitator. This two-stage cleaning process produces a gas containing less than 0.05 grams/m^3 of particulate matter (EPA 1995b). The cleaned gas is used as a fuel to pre-heat the blast air for the furnace or to generate steam in an adjacent boiler house.

Dust and Sludge

Blast furnace dust is often recycled through the sinter plant. At steelmaking operations without sintering plants, blast furnace dust is sometimes mixed with other by-product residues, briquetted, and recycled into the blast furnace. In other steelmaking operations, the dust and sludge are landfilled, stockpiled, or sold.

Slag

The blast furnace also yields a slag that contains oxides of silicon, aluminum, calcium, and magnesium, along with other trace elements. Blast furnace slag amounts to 20 to 40% of molten iron production by weight. In 1997, a total of 14 million tons of blast furnace slag was produced. Virtually all blast furnace slag is processed and sold commercially for a variety of material applications.

4.2.4   Hazardous Ironmaking Wastes

None have been identified.

4.2.5   Ironmaking Environmental Trends and Drivers

Traditional sintering capacity is not expected to increase in coming years, but it will remain a major method of recycling and recovery of iron-bearing waste oxides and secondary materials. Although the technology exists for efficient particulate matter collection systems, opportunities exist for improving capture and collection systems, wastewater treatment, and reducing water use.

Sintering poses a unique environmental challenge. Sintering is the traditional and proven method for recycling iron-bearing secondary materials produced by ironmaking and steelmaking facilities. It can also produce a material that replaces iron pellets and adds stability to blast furnace operation. Japanese blast furnaces, and at least one U.S. plant, for example, operate on virtually 100% sinter feed. As more emphasis is placed on recycling and recovering waste or secondary iron-bearing materials, plants with sintering operations will have an advantage over those that do not.

Most sinter plants are equipped with high-energy wet scrubbers, fabric filters, or wet electrostatic precipitators for collection of wind-box emissions. However, some of these devices have not always performed well across the range of feed materials that operators would like to introduce into sintering. Therefore, opportunities exist for developing new environmental control technologies. New emphasis on fine particles and NOx emissions will place further pressures on the ability of traditional air pollution control devices. Concern over potential dioxin emissions and restrictions on oily sinter plant feed materials are also relevant issues.

4.2.6   New and Emerging Ironmaking Technologies

The demand for sintering or other agglomeration processes that can produce iron pellet replacement material remains high. However, environmental concerns and high capital and operating costs have led to a decline in traditional sinter plants, leading to the development of other waste oxide agglomeration processes that serve as a substitute for sintering. For example, AISI's waste oxide smelting technology has been demonstrated, and may be licensed in several installations.

New technologies for ironmaking are covered in detail in Chapter 2 of this document.

4.2.7   Ironmaking Research and Development
         Needs and Opportunities

Fundamental research is needed to provide more information on the formation and mitigation of CO from sintering, reduction of NOx (see section 4.9) and sulfur emissions, and formation and control of organic and inorganic toxic air pollutants.

When conducting R&D on new and emerging ironmaking technologies, information on environmental aspects and energy consumption must be an integral part of that work in order to assess alternative technologies on the basis of environmental issues, operating costs, capital costs, and productivity. Data on particulate and gaseous air pollutant generation, wastewater generation and treatability, solid and hazardous wastes, and energy consumption, including CO_2 emissions, should all be considered.

R & D Needs

Ironmaking

- ‣ Improved capture and collection systems and improved wastewater treatment for sintering
- ‣ Understanding of NOx and toxic air pollutants emissions, formation, and control
- ‣ Alternative cost-competitive agglomeration processes
- ‣ Coke substitutes
- ‣ Greater understanding of formation and mitigation of NOx emissions in stoves
- ‣ Methods of reducing total sulfur emissions
- ‣ Improved methods of cast house emission controls
- ‣ Improved methods of slag quenching, including collection and treatment of excess slag quenching water
- ‣ Methods for de-oiling sinter plant feed materials

Specific environmental control R&D opportunities in ironmaking include:
- •   NOx and VOC control
- •   Energy Use and CO_2 Emission Reduction

NOx and VOC control

NOx and VOC controls have grown in importance as ozone control strategies have been developed for ozone non-attainment areas and ozone transport regions. Because NOx is a precursor for fine particles, new fine particle standards are likely to place even greater emphasis on sinter plants as a source of potential NOx. Although a lower flame temperature makes NOx formation less problematic for blast furnace gas than for other fuels, increased concern over NOx emissions presents challenges for combustion practices and devices that reduce NOx emissions in boilers. A comprehensive study of NOx control at sinter plants is needed to develop ways of reducing these emissions. The emission, formation, and control of NOx and organic and inorganic toxic air pollutants, including dioxins, need to be understood.

As a result of the interest in ozone strategies, sinter plants may have to limit VOC components in feed materials or increase the efficiency of air pollution control systems. A study of VOC components, including dioxins, is also needed.

Energy Use and CO$_2$ Emission Reduction

Energy consumption and CO$_2$ emissions in existing and emerging agglomeration and ironmaking technologies pose opportunities for reductions. Government concern over greenhouse gas emissions, particularly CO$_2$, and the related impetus for reducing energy consumption, suggest the need for developing ways to reduce energy consumption and CO$_2$ generation in existing and emerging agglomeration and ironmaking technologies.

4.3   Steelmaking - Basic Oxygen Furnace

Environmental standards for air and water emissions, including those for BOF's, are becoming more stringent. Consequently, current environmental controls may not be adequate in the future. In particular, better air-cleaning and in-shop work environments are needed. Figure 4-4 illustrates BOF steelmaking with its major inputs and outputs.

4.3.1   BOF Emissions

Sources

Emissions are generated during each of the five major BOF steelmaking and refining operations: charging, melting, refining, tapping, and slag handling. The most significant emissions from BOF steelmaking occur during the oxygen blow period. The principal compounds generated are iron oxides and lime.

Control Systems

The particulate-laden combustion gases and fume (a very fine iron oxide) created during oxygen blow periods are removed from the furnace by evacuation through a large collection main. These hot gases are typically treated by one of three air pollution control methods:

- *Semi-Wet*. Water is added to condition furnace off-gas temperature and humidity prior to processing the gas in electrostatic precipitators or baghouses.

- *Wet-Open Combustion*. Excess air is drawn into the hood of the off-gas exhaust system, allowing CO to combust prior to high-energy wet scrubbing for air pollution particulate control.

- *Wet-Suppressed Combustion*. Excess air is excluded from the off-gas collection system prior to high-energy wet scrubbing for air pollution particulate control, thus suppressing the combustion of CO until after scrubbing (EPA 1995a).

Charging and tapping emissions are controlled by a variety of evacuation systems and operating practices. Charging hoods, tapside enclosures, and full furnace enclosures are used to capture these emissions. The particulate emissions are then exhausted to a primary gas cleaner or a second gas cleaner.

As in the case of the blast furnace, most trace hazardous air pollutants generated in the BOF are heavy metals, including cadmium, chromium, lead, manganese, and nickel. Zinc compounds are also present in BOF fume in varying amounts depending on the zinc content of the scrap used in the process. Other factors affecting HAP emissions from the BOF include the degree of oxidation of the molten steel and the amount of time required to process the melt.

4.3.2   BOF Effluents

The gases and fumes released during BOF steelmaking are quenched with water to reduce their temperature prior to being treated in air pollution control systems. The three major types of off-gas control systems generate wastewater streams containing total suspended solids and metals (primarily lead and zinc, but also trace amounts of arsenic, cadmium, copper, chromium, and selenium).

Suppressed-combustion and open-combustion systems use, respectively, about 1,000 and 1,100 gallons of water/ton of steel, but typically less than 100 gallons/ton is discharged (EPA 2000). Standard treatment consists of sedimentation in clarifiers or thickeners. Blowdown treatment consists of metals precipitation.
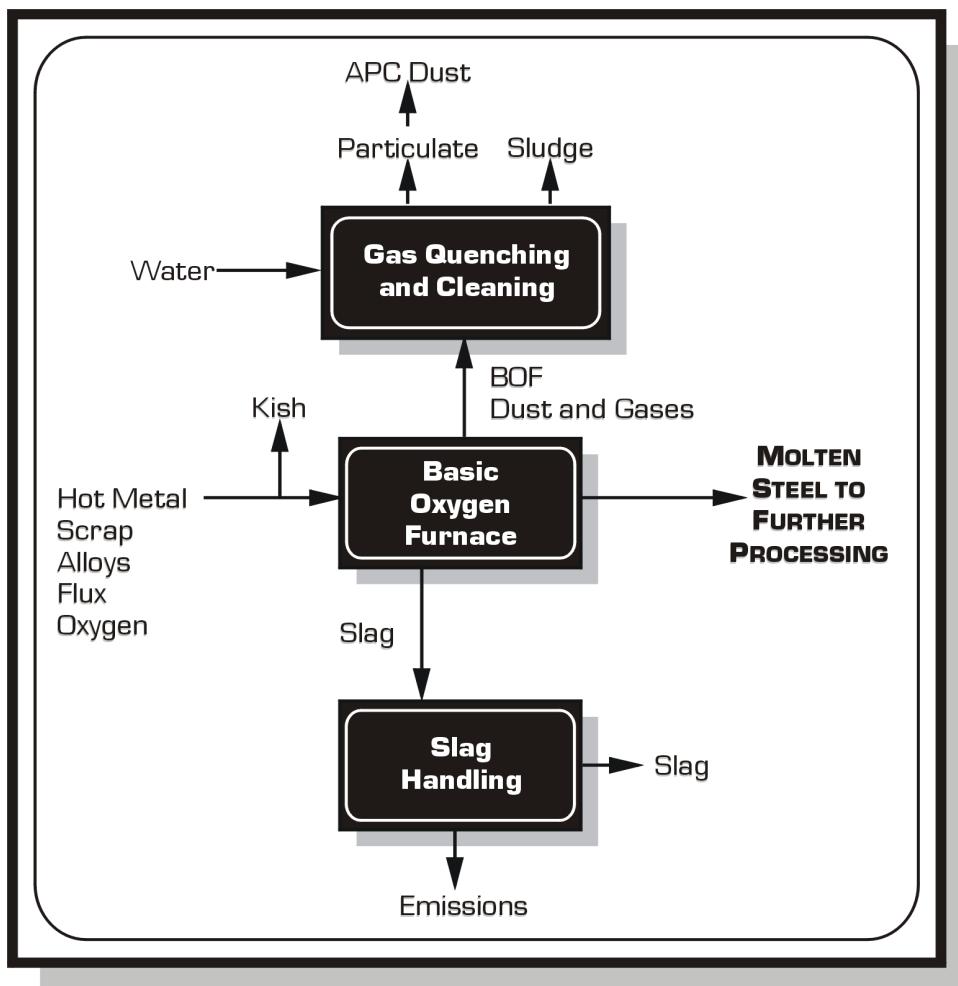

Figure 4-4. BOF Steelmaking Flow Diagram

4.3.3 BOF By-Products

BOF steelmaking by-products include BOF slag, air pollution control dust, and water treatment plant sludge.

Slag

BOF slag is composed of calcium silicates and ferrites combined with fused oxides of iron, aluminum, manganese, calcium, and magnesium. After molten BOF slag is removed from the furnace, it is cooled and processed to recover the high metallic portions (iron and manganese) for use in the sinter plant or as a flux in blast furnaces. Some slag may also be recycled to steelmaking under certain conditions. The remaining non-ferrous fraction is then crushed and sized for reuse either within the steel works or as a by-product.

BOF slag differs from blast furnace slag in composition (hydration of up to 10% can occur because of calcium oxide and other oxides are present in BOF slag); therefore, its uses are more limited than blast furnace slag. The lower metallic aggregate is typically used in construction applications such as railroad ballast or unconfined highway base or shoulders, where its expansion will not create a problem. It is also used as an additive in cement kilns.

Dust and Sludge

The BOF dust and sludge collected in the air pollution control system represent two of the three largest-volume wastes typically land-disposed by iron and steel plants. Together with slag and water treatment plant sludge, these wastes represent more than 93% of all wastes stored, recycled, or disposed (Baker Environmental 1992).

Particulate matter is separated from combustion gases generated during BOF steelmaking by one of the three means described in Section 4.3.1. Cleaned gases from suppressed combustion systems are ignited before release to the atmosphere to prevent CO emissions in the uncombusted gas. These gases can also be recovered for heating value.

4.3.4 Hazardous BOF Wastes

There are no RCRA-listed hazardous wastes associated with BOF steelmaking. However, BOF dusts or slags may need to be evaluated for hazardous constituents such as lead and other heavy metals.

4.3.5 BOF Steelmaking Environmental Trends and Drivers

Air Emissions

Regulatory pressures to reduce releases of toxic and hazardous substances in all media, including air, water, and solid wastes, will continue. The issue of global warming may lead to increased requirements to reduce emissions of greenhouse gases from fossil-fuel combustion. This increased pressure on CO_2 emissions affects the steel industry because the BOF steelmaking process inherently generates CO_2.

During BOF steelmaking, carbon in the hot metal is oxidized and emitted from the process as CO_2. This carbon oxidation provides the heat that converts the iron into steel and is the basis for BOF steelmaking. Until another method of steelmaking is developed, BOF steelmaking will continue to emit CO_2.

Fugitive Emissions

Fugitive emissions from a BOF come from the following:

*   Scrap handling
*   Ore and flux handling
*   Hot metal transfer operations
*   Hot metal charging operations
*   Tapping
*   Teeming operations

Each state has regulations governing fugitive emissions; it is anticipated that there will be continued regulatory pressure to minimize these emissions.

Water Discharges

Stringent EPA and state water quality standards will likely reduce the allowable discharge limits for the discharges from BOF steelmaking facilities in the near future. Such a reduction will probably be directed at the discharge of metals such as lead and zinc. Reducing metal-laden wastewater discharges may require additional water pollution control facilities and water recycling for some BOF steelmaking operations.

Waste Discharges

The primary wastes collected from a BOF are slag dust and fumes collected either by wet scrubbers or dry electrostatic precipitators or baghouses. Baghouse dust is also collected from operations such as hot metal reladling, hot metal desulfurization, and slag skimming.

By current EPA definitions and test protocols, these wastes are not hazardous and can be disposed of in non-hazardous landfills. However, with increasing government emphasis on pollution prevention and waste minimization programs, and with the increasing scarcity of landfill space, steelmakers will have to reduce the volume of these wastes, increase recycling, or develop additional processing to increase their use as products. Many steelmakers will be looking at ways to include these wastes in their pollution prevention and waste minimization programs.

4.3.6   New and Emerging BOF Steelmaking Technologies

No new and emerging air or water pollution control technologies for BOF steelmaking operations are anticipated. In waste management, developing technologies will increase the amount of BOF slag, BOF fume, and other steelmaking revert materials that are recycled or used as other products.

Some companies are processing BOF fumes with other steel plant wastes for recycle to the BOF. Others are recycling BOF fumes with low zinc content to the blast furnace via the sintering plant. Over the years, a number of processes have been studied to remove the zinc from the BOF fume so more of it can be recycled to the blast furnace via the sinter plant, and some of these processes may be viable in the future.

4.3.7 BOF Steelmaking Research and Development Needs and Opportunities

BOF Slag

As discussed in Chapter 3, research is needed to find either alternate uses of BOF slag (with the calcium oxide content and hydration effects) or an economical way to remove the calcium oxide. Research is also needed to remove phosphorous from BOF slag because phosphorus content is a limiting factor to increased use of this material. Removing phosphorus from the blast furnace pig iron prior to steelmaking would help increase the amount of this slag that can be recycled to the iron and steelmaking process. Some companies recycle a portion of their BOF slag to the blast furnace in order to supply calcium oxide flux and reclaim the iron oxide content of the slag.

Zinc Content

Research into the mechanisms of zinc ferrite formation during the steelmaking process to prevent its formation is needed, making it much easier to remove the zinc from fume. BOF fumes contain varying amounts of zinc, lead and other metals. The primary source of these metals is the scrap used in the steelmaking process. If the scrap contains a large amount of zinc, as does much of galvanized steel scrap, the zinc content of the fume can be high enough to prevent its recycle to the blast furnace. The presence of zinc in the feed materials of a blast furnace can cause serious damage to blast furnace refractories, which will shorten the life of a blast furnace.

Continued research is needed to develop economical ways to remove zinc from scrap since zinc is a commercial product. This would help decrease the amount of zinc in BOF fumes and thus promote increased recycling of these fumes.

Research to determine the distribution of zinc throughout the recycle system could lead to a better understanding of the chemical mechanisms at work, which would improve understanding of this recycling technique. Some companies recycle BOF fume directly to steelmaking after mixing and agglomerating it with other iron oxide materials, such as mill scale. When recycling zinc-bearing fumes directly to steelmaking, the zinc content of the fume, slag, or steel will increase substantially unless a bleed stream is provided to keep the zinc build-up in the system at manageable levels. In facilities using this recycling practice, zinc build-up has not occurred.

R & D Needs

BOF Steelmaking

- ‣ Methods of removing phosphorus from the blast furnace pig iron prior to steelmaking
- ‣ Economical ways to remove zinc from scrap
- ‣ Understanding of zinc ferrite formation mechanism
- ‣ Determination of zinc distribution throughout the recycle system
- ‣ Determination of zinc's effect on the properties of steel

Research will likely be conducted to determine the effect of zinc on the physical, chemical and metallurgical properties of steel. When zinc-bearing scrap is used in steelmaking, or when zinc-bearing fumes are recycled to steelmaking, the zinc concentration in the steel produced also increases. Analysis has shown that some steel samples from these systems contain several hundred parts per million of zinc.

4.4   Steelmaking - Electric Arc Furnace

Over the past 30 years, electric arc furnace fume systems have evolved considerably from simple systems aimed at improving the ambient work environment around the furnace to sophisticated systems aimed at controlling not only particulate emissions, but also toxic gases. Environmental regulations have stimulated progress in primary and secondary fume control technology from side draft hoods, furnace roof hoods, and rudimentary fourth hole extraction systems to today's sophisticated direct evacuation systems and fugitive emission control systems. Modern fume systems are now designed to minimize the formation of gaseous pollutants and ensure that others are destroyed before exiting the system. Figure 4-5 illustrates electric arc furnace steelmaking with its major inputs and outputs.

4.4.1   EAF Emissions

Sources

Emissions are generated during each of the five major EAF processes: charging, melting, refining, tapping, and slag handling. During the EAF process, oxide and other metal forms are volatilized in the presence of intense heat and turbulence inside the furnace. Also, carbon from the addition of coal, iron, and steel scrap and graphite electrodes react with injected air or oxygen. Consequently, the primary constituents in EAF emissions are particulate matter and gases (specifically CO_2, CO, and NOx). Note that use of EAF for steel production provides the single most effective means of reducing CO_2 emissions due to the significantly lower energy requirements of melting scrap compared to smelting ore.
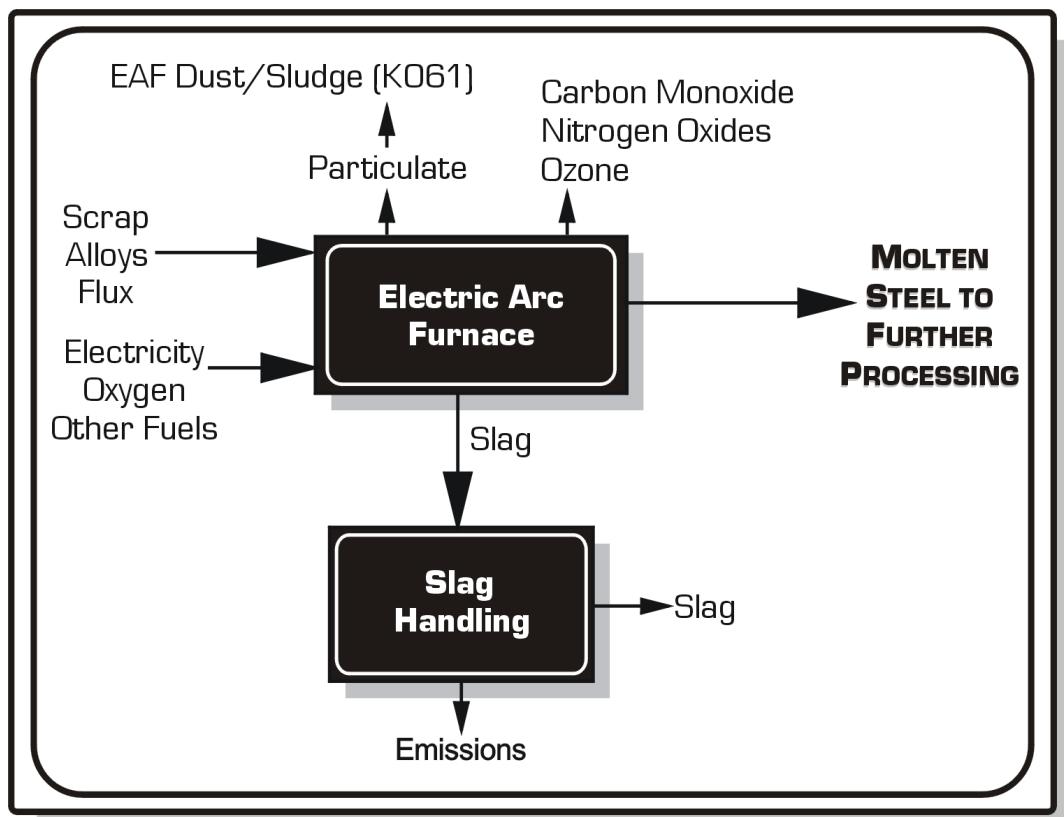

Figure 4-5. Electric Arc Furnace Steelmaking Flow Diagram

Dioxins and furans have become a major concern over the past few years. Dioxins and furans are combustion by-products and the prevention of these emissions depends strongly on control of the combustion process. Some concern has been expressed over possible dioxin formation in EAFs.

Iron oxide is the predominant constituent of the particulate matter emitted during melting. In addition, small amounts of NOx and ozone are generated during melting. During refining, the primary particulate compound emitted is calcium oxide from the slag. These particulate emissions from melting and refining account for about 90% of total EAF emissions. The remaining 10% of emissions are generated during charging and tapping.

Emissions from charging scrap are difficult to quantify because they depend on the grade of scrap utilized. Scrap emissions usually contain iron and other metallic oxides from alloys in the scrap metal. Iron oxides and oxides from the fluxes are the primary constituents of slag handling emissions. During tapping, iron oxide is the major particulate compound emitted. (EPA 1995; Baker Environmental 1992)

4.4.2   EAF Effluents

Most electric arc furnaces are operated with dry gas cleaning systems, which have no process wastewater discharges. A small number of wet and semi-wet systems also exist. The water flows and pollutants of concern for EAFs with wet and semi-wet air cleaning systems are similar to those of wet BOFs, but the metal content (primarily lead, zinc, arsenic, cadmium, copper, chromium, and selenium) is higher because of the 100% scrap charge and higher use of post-consumer scrap. EAF wastewater treatment operations are similar to those for the wet BOFs, including sedimentation in clarifiers or thickeners and water recycling. (EPA 2000)

4.4.3   EAF By-Products

Slag

The major non-hazardous by-product generated during EAF steelmaking is slag. The primary components in EAF slag are CaO, SiO_2, FeO, MgO and Al_2O_3. EAF slag is managed similar to BOF slag. Cooled, solidified slag is crushed and screened to recover metallics for recycle or reuse, and the lower metallic aggregate is used in construction applications (Baker Environmental 1992). Worldwide, about 77% of the slag produced in EAFs is reused; the remainder is landfilled (Szekely 1995).

4.4.4   Hazardous EAF Wastes

Dust and Sludge

EAF dust consists of particulate matter and gases produced during the EAF process and subsequently conveyed into a gas cleaning system. The particulate matter that is removed from emissions in a dry system is called EAF dust. Particulate matter removed from emissions in a wet system is called EAF sludge.

TABLE 4-1. COMPARATIVE CHEMICAL COMPOSITION OF DUST FROM ELECTRIC ARC FURNACES		
CHEMICAL	Stainless Steel Dust (% by weight)	Carbon Steel Dust (% by weight)
Iron	31.7	28.5
Zinc	1.0	19.0
Cadmium	0.16	<0.1
Lead	1.1	2.1
Chromium	10.2	0.39
Calcium Oxide	3.1	10.7[a]

[a]Calcium oxide and magnesium oxide combined
Source: *Electric Arc Furnace Dust - 1993 Overview*, prepared by A.D. Little for the EPRI Center for Materials Production, July 1993.

The dust (or sludge) removed from EAF emissions is designated by EPA as a listed hazardous waste - K061. Since most of the dusts are collected dry, associated pollution issues generally fall into a non-wastewater category (A.D. Little 1993). The primary hazardous constituents of EAF emission control dust/sludge are lead, cadmium, and chromium.

EAF dust can vary greatly in composition depending on both the composition of the scrap charge and the furnace additives used. Table 4-1 shows the typical composition of EAF dust generated during production of stainless and carbon steels. The primary components are iron or iron oxides; typical EAF dust contains 24% iron by weight (Kolarik 1996). As shown in Table 4-1, carbon steel dusts are richer in zinc and lead than stainless steel dusts because of the greater use of galvanized scrap.

Over the past four decades oxygen usage in the EAF has increased by an order of magnitude (1970: 96 ft^3/ton, 1980: 352 ft^3/ton, 1990: 769 ft^3/ton, 1999: 961 ft^3/ton). This trend is expected to continue. With increased oxygen use, the generation of fumes occurs at a greater rate. However, this rate increase is offset by the reduction in average heat time and better scrap preparation. As a result, the generation of dust/ton of steel is expected to decrease by 35 to 30 lbs/ton by 2010.

4.4.5   EAF Steelmaking Environmental Trends and Drivers

There will continue to be regulatory pressures to reduce releases of toxic and hazardous substances in all media, including air, water, and wastes. EPA has concluded that the amount of toxic pollutants for which MACT standards should be developed as part of Title III of the Clean Air Act. However, if EAFs are located in integrated mills where the total amount of toxic air pollutants exceeds the applicability threshold for plantwide toxic air pollutants, EAFs could be subject to case-by-case MACT standards. In addition, modifications to existing EAF facilities shops can also trigger case-by-case MACT determinations. Regulatory requirements in such instances can be expected to focus on lead, cadmium, chromium, nickel and other heavy metals listed as toxic air pollutants. As in the case of other iron and steel MACT standards being developed, regulators are expected to require state-of-the-art particulate matter controls to serve as a surrogate for MACT for these pollutants.

As noted in the discussion on BOF steelmaking, new ambient air quality standards for fine particulate matter (PM-2.5) may also lead to tighter requirements for emissions associated with EAF steelmaking and related fugitive emissions, and Title V permits and compliance assurance monitoring rules may require new continuous process and emission monitoring facilities and practices. New ambient air standards for ozone will also lead to increase regulatory attention of NOx, which contribute to the ozone formation in the atmosphere. EPA and state agencies are expected to continue to apply pressure to reduce emissions of NOx from industrial processes and EAFs could be a target for such reductions.

Increased national and international emphasis on climate change and the relationship between CO_2 emissions and global warming potential may also lead to increase regulatory pressure to reduce CO_2 associated with EAF production.

The EPA will also likely review the New Source Performance Standard for EAFs in the coming years. Because New Source Performance Standard's are technology-based and technology continues to improve, tighter particulate emission standards, monitoring requirements, and CO or NOx emission limitations are all possible considerations during that review.

Dusts and sludges from EAF air pollution control facilities have been a designated hazardous waste (K061) under RCRA for many years, and standards exist for the acceptable treatment and disposal of these wastes and their treatment residuals. Nevertheless, the high costs of treatment and disposal of K061 continue to present challenges for more cost-effective means of treatment and recovery. Although tighter requirements are not anticipated in the near future, the presence of hazardous constituents in EAF dust will continue to draw close scrutiny of treatment and disposal practices. For example, an exemption from RCRA rules for EAF dust in fertilizers has recently been granted by EPA, and new technology-base treatment standards for "non-nutritive" metals (such as arsenic, cadmium, lead, chromium, mercury, and nickel) have been proposed and will likely be finalized in 2002 for any zinc micro-nutrient fertilizers derived from hazardous waste. EPA is also expected to continue to examine other practices involving disposition of EAF dust for commercial purposes and to raise questions about other EAF waste materials deemed to be similar to K061, such as material collected in drop-out boxes and ductwork of air pollution control systems.

Slag from EAF steelmaking has also historically not been environmentally regulated. However, EPA has recently suggested that in some cases and applications, hazardous constituents in steelmaking slag may be cause for reporting as part of EPA's Toxic Release Inventory.

4.4.6 New and Emerging EAF Steelmaking Technologies

None have been identified.

4.4.7 EAF Steelmaking Research and Development Needs and Opportunities

Modern fume systems are now designed to minimize the formation of gaseous pollutants and ensure that others are destroyed before exiting the system. Thus, gas cleaning in the modern day fume system entails much more than trapping and collecting particulates. With tighter environmental restrictions expected in the future, it is expected that electric furnace operations will have to look at environmental concerns in conjunction with furnace operations. The key areas where additional R&D are required are outlined below.

Raw Materials Related Issues

Better control of feed material quality is needed because many of the undesirable components contained in EAF dust are contained in the scrap feed to the furnace. Though scrap selection is primarily an economic consideration, treatment of scrap to eliminate the transfer of undesirable materials into the EAF will likely become necessary in the future. The use of lower grade fluxes and additives containing sulfur is also a concern if the sulfur is not tied up in the slag and instead reports to the offgas stream.

Process Related Issues

A better understanding of the interactions between EAF process and environmental operations should be developed. The EAF operation is extremely dynamic, and furnace feed materials can vary substantially from one heat to the next. Thus the offgas system is typically designed for the worst case scenario, resulting in greater costs. Future EAF operations will be based on a more holistic approach and it will be necessary to integrate furnace process control with environmental control.

R & D Needs

EAF Steelmaking

- Better control of feed quality
- Real time offgas analysis method
- Real time offgas chemistry adjustment method
- Understanding interactions between EAF process and environmental operations
- Effect of closing up the furnace on process control
- Improved oxygen injection system to decrease peak loads to the offgas system
- Acceleration of tap-to-tap times to reduce energy use and emissions
- Offgas cleaning system to produce low BTU gas, recovering more of the off-gas heat content
- Improved off-gas system reliability, maintenance practices, and design
- Optimized operating cycles to reduce peak conditions
- Improved gas cooling techniques
- Reduction of gas cleaning operating costs
- Cost effective, environmentally friendly gas cleaning alternatives

Although proven technology for the measurement of offgas chemistry on a continuous basis is currently available, few installations of on-line, offgas chemistry for EAF process optimization exist. In order to better understand the complexity of the melting and environmental parameters, more fundamental R&D must be completed. It is likely that offgas systems will move to a more closed operation with controlled addition of combustion air via injectors. The juncture of the furnace elbow and water cooled duct may include an adjustable sleeve, which will allow for minimization of air infiltration without impairing furnace roof movement. The successful EAF operations of the future will be based on real-time measurements of off-gas chemistry to control both the EAF steelmaking process and the EAF fume control system.

Research into major process changes of steelmaking are needed. The feasibility of hydrogen-based steelmaking, which generates H_2O rather than CO and CO_2, may be researched. The potential for sealing the furnace will likely be investigated and developed further. It is already becoming apparent that future furnace designs will use multiple injection points for both gases and solids. This is beneficial for process operations and will allow for greater control of furnace operations.

Offgas system research and a more complete understanding of the combustion chemistry process may help decrease the environmental effects of steelmaking. Furnace offgas systems are typically designed for peak volumes and heat content, which only occur for a small portion of the tap-to-tap cycle. Thus, the offgas system fluctuates between "peaks and valleys" depending on the phase of the cycle. Oxygen injection frequently results in peak conditions due to the high levels of CO generated. If O_2 injection is spread out over the full cycle time using submerged injectors, the CO generation over the entire heat can be smoothed out, allowing for improved post-combustion operations and decreased peak energy loads to the offgas system.

Research is also needed to discover means to minimize the quantity of EAF fume generated by the steelmaking process and to recover the iron, zinc, and other metallics contained in the fume. Periodic additions of carbons and fluxes can exacerbate the emission problem. Tap-to-tap times could also be accelerated so that furnace energy losses are decreased and fume emissions are reduced per ton of steel production. The implementation of post-combustion research could also improve EAF performance.

Some modern EAF operations use such high levels of alternative iron in their operations that CO generation rates are similar to those encountered in BOF operations. In such cases, using the CO outside of the EAF may be more efficient. If scrap pre-heating is incorporated on a closed furnace, the resulting cool offgas stream will contain primarily CO, VOCs and CO_2. Attempting to burn such large quantities of CO in the furnace will likely result in poor heat recovery and potential equipment damage. By cleaning the gas following scrap pre-heat, the resulting low Btu gas could be used for various heating applications within the plant. This would result in maximum utilization of the heat content contained in the offgas.

System Design Issues

System reliability, maintenance, and optimized design are all concerns for future offgas control systems. Given that environmental legislation is becoming more stringent, offgas system availability may become a major issue.

Gas collection and cleaning equipment can account for up to 25% of the capital cost for a new meltshop facility. This is a growing concern as this equipment does not contribute to meltshop productivity and hence reduces profitability. Greater emphasis needs to be placed on providing more robust, lower cost systems. Offgas systems are designed for peak operating conditions which may exist for only 10 to 20% of the operating cycle. Optimization of operating cycles with a view to reducing the magnitude of peak conditions within the system could result in lower cost facilities which are better utilized. Improved gas cooling techniques are also needed.

Typically, fume system electrical power requirements equate to 10 to 20% of those required for EAF scrap melting. This represents a substantial operating cost. In addition to the cost issue, the availability of electrical power could also become an issue. Some facilities are already experimenting with variable speed fans, although the effect these might have on system performance still needs to be thoroughly evaluated.

Retrofitted environmental systems in melting facilities have become commonplace as more and more furnaces increase the use of chemical power input for scrap melting. In the future, greater care will likely be taken to provide modular systems, which are easily expanded as the meltshop steel output grows.

Alternatives to baghouse dust removal need to be developed. Current legislation makes it difficult to apply gas cleaning technologies other than baghouse cleaning. Further investigation of other gas cleaning technologies is needed. Economic factors coupled with environmental requirements may result in more appealing alternatives.

4.5   Refining and Casting

The SO_2 and VOC emissions are of particular concern in refining and casting operations. Effluent from the vacuum degassing process also requires better control technology. Figure 4-6 illustrates the refining and casting processes with their major inputs and outputs.

Ladle refining is a process for final adjustment of the chemistry and temperature of the steel. It can encompass the following techniques:

•   Addition of alloys to the ladle following tapping of the steel from the furnace
•   Electric-arc or plasma-torch heated ladle refining
•   Degassing of the steel in a separate degassing facility or reheating in the ladle or stirring

4.5.1   Refining and Casting Emissions

Continuous casting is the most prevalent casting method. During ingot casting, particulate emissions are generated when molten steel is poured (teemed) into the molds. The major emissions, including iron and other oxides (FeO, Fe_2O_3, SiO_2, CaO, and MgO), are controlled by collection devices. Operational changes in ingot casting, such as bottom pouring instead of top pouring, can reduce emissions. Bottom pouring exposes much less of the molten steel to the atmosphere than top pouring, thereby reducing the formation of particulate matter (Marsosudiro 1994).

Certain refining processes, including ladle metallurgy, generate particulate (and SOx if sulfur bearing compounds are used) emissions. These emissions are typically collected in baghouses as air pollution control dust. The EPA does not list any particulate emissions factors for continuous casting operations.
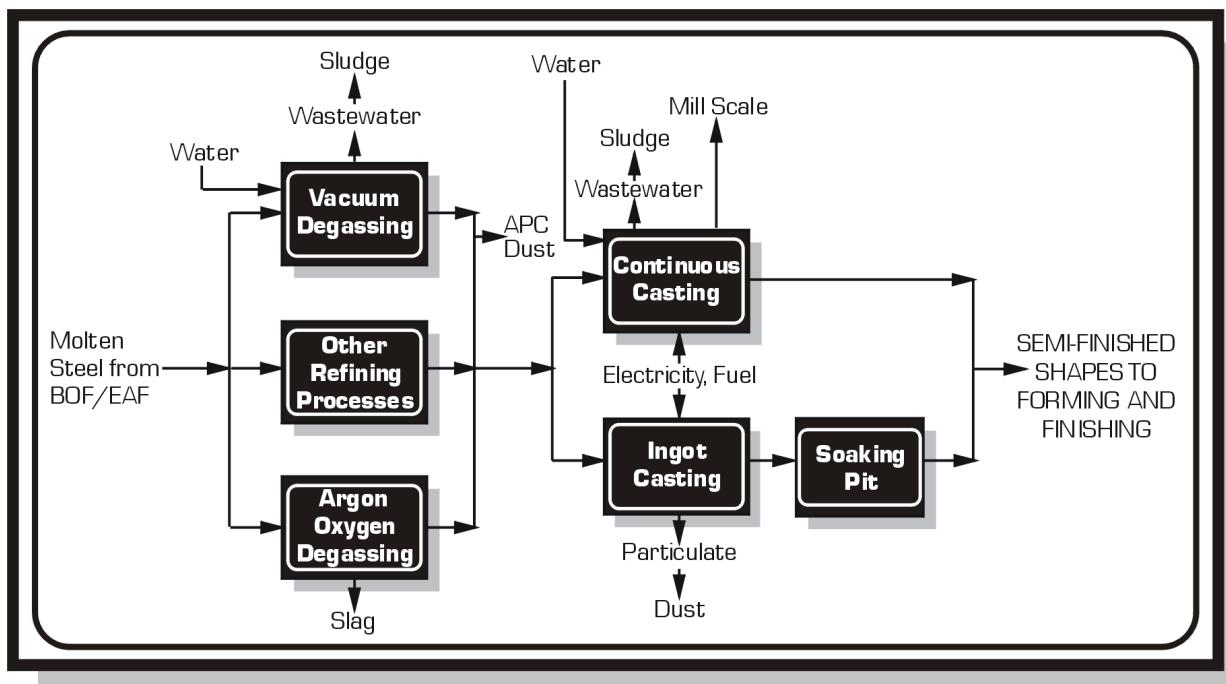

Figure 4-6. Refining and Casting Flow Diagram

4.5.2   Refining and Casting Effluents

Refining

Of all the refining processes, only vacuum degassing uses process water and generates effluent. Vacuum degassing involves direct contact between gases removed from the steel and condenser water. Principal pollutants contained in the effluent include low levels of total suspended solids (TSS) and metals (particularly lead and zinc, but also chromium, copper, and selenium) that volatilize from the steel.

Applied water rates for vacuum degassing are typically around 1,250 gallons/ton of steel, with discharge rates of 25 gallons/ton achieved through high-rate recycle (EPA 2000). Standard treatment includes processing the total recirculating flow, or a portion of the flow, in clarifiers for TSS removal; cooling with mechanical draft cooling towers; and high-rate recycle. Blowdowns are usually co-treated with steelmaking and/or continuous casting wastewaters for metals removal. Vacuum degassing plants are often operated as part of ladle metallurgy stations where additional steel refining is conducted (EPA 2000).

Casting

Continuous casters usually include two separate closed-loop, non-contact cooling water systems for spray and mist cooling. The mold cooling water system is used to cool the mold, while the machine cooling water system is used to cool all other mechanical equipment. Direct-contact water systems are used for spray cooling of the steel as it exits the mold; at the gas cutting torches to control fume generation; and for flushing mill scale down the flume beneath the runout table.

Applied water rates for the contact systems are typically about 3,600 gallons/ton of cast product; discharge rates for the better controlled casters are less than 25 gallons/ton (EPA 2000). The principal pollutants are total suspended solids, oil and grease, and low levels of particulate metals. As with vacuum degassing, chromium, copper, and selenium may be found in continuous casting wastewater. Wastewater treatment includes scale pits for mill scale recovery and oil removal, mixed- or single-media filtration, and high-rate recycle (EPA 2000).

4.5.3   Refining and Casting By-Products

Refining By-products

Wastes resulting from refining processes are very small in comparison to the wastes generated from ironmaking and steelmaking. The more common solid wastes generated include the following:

*   Ladle metallurgy facility and capped argon bubbling APC dust
*   Nozzle block sludges (Baker Environmental 1992)

Air pollution control dusts from refining are non-hazardous and are either processed and recycled or landfilled.

Casting By-products

The major by-products of continuous casting are scale and sludge. Scale generated during casting, which is subsequently washed off of the steel, is periodically removed from the bottoms of scale-collection settling basins. Fine-grained solids that do not settle in the pits are typically removed by flocculation and clarification or by filtration, depending on the level of water treatment required and the degree of water recycle practiced.

The scale is usually recycled within the steelmaking facility at integrated mills that operate sinter plants. Scale may also be landfilled (particularly by stainless steel producers) or even charged to an electric arc furnace (Burke and Liebman 1993). Sludge generated during continuous casting is either processed and recycled on-site or landfilled.

4.5.4   Hazardous Refining and Casting Wastes

There are no RCRA-listed hazardous wastes associated with refining or casting processes.

4.5.5   Refining and Casting Environmental Trends and Drivers

Ladle Refining – Air Emissions

Emissions from these sources vary depending on the operations. Emissions from these operations include:

- Particulate emissions from alloy addition practice
- Particulate and SOx emissions from ladle refining processes
- Particulate emissions from degassing, ladle reheating and ladle stirring facilities

Increased control of the particulate emissions from these sources may be required as part of the overall effort to reduce fine particulate emissions.

Ladle Refining – Water Discharges

Ladle refining air emissions are controlled by dry collection devices (typically baghouses); therefore, process water is not normally discharged from these facilities. The exception is vacuum degassing. The vacuum for this process is normally generated by steam or water ejectors. The exhaust steam and water is condensed with water and processed to remove the suspended solids from the vacuum degassing operation.

Most steel contains low concentrations of zinc and lead. These elements are removed from the steel during the degassing process and end up in the ejector or quench water. To comply with NPDES permit effluent limitations for these operations, these suspended solids and metal discharges must be reduced to extremely low levels.

Ladle Refining – Waste Discharges

Baghouse dusts collected from the electric arc or plasma-heated ladle refining furnaces contain mostly dusts from flux, ore and slags used in the process, and some metal oxides. Normally these dusts are not hazardous and can be disposed of in a conventional landfill. However, particulate wastes collected from a vacuum degassing operation may contain enough lead to be characterized as hazardous, and, if so, must be disposed of or recycled as such.

The industry anticipates continued pressure from regulatory agencies to minimize the generation and disposal of hazardous waste. This pressure, along with shortages of landfill space and the additional cost of disposing of hazardous wastes, will serve as incentives for companies to reduce hazardous waste generation and recycle more of these wastes.

Casting – Air Emissions

Emissions from continuous casting operations consist of steam from the quenching/cooling section of the continuous caster, NOx from the fuel torches used to cut the steel sections to length, and dusts from tundish heating and repair. At some continuous casting facilities, the steam emissions from the quenching and oiling sections of the caster contain VOCs from the leakage of lubrication systems used in the cooling sections.

The NOx emissions, although minor, are the primary emissions of concern from fuel cutting torches. Particulate emissions are minimal at continuous caster operations. For facilities located in ozone non-attainment areas, additional controls may be needed to reduce emissions of NOx and VOCs.

Casting – Water Discharges

The EPA is currently revising the water effluent guideline limitations for the iron and steelmaking industries, which may result in a reduction in the allowable limits for discharges from the continuous caster water treatment facilities. Such a reduction will probably be directed at reducing the discharge of metals such as nickel, chromium, lead, and zinc, and could well require additional water pollution control facilities for continuous casting operations.

Casting – Waste Discharges

The primary wastes collected in a continuous caster are spent casting mold flux and coarse scale and sludges from the continuous caster wastewater treatment process. The coarse scales and cutting swarf, which are normally dredged from the caster's mill scale pit, are relatively coarse particulates of essentially pure iron oxide. They are not hazardous wastes and contain small amounts of water and grease. These scales are good candidates for recycling to the iron and steelmaking process, particularly for steelmaking facilities with sinter plants.

The fine particulate mill sludges collected from the caster wastewater treatment system are also not hazardous wastes, but contain larger amounts of water, oils, and greases. These sludge are normally landfilled. Drivers to increase the use of these caster wastes include the following:

- Increased pressure for waste minimization and pollution prevention programs
- Scarcity of landfill space and increasing cost of landfill disposal

4.5.6   New and Emerging Refining and Casting Technologies

None have been identified.

4.5.7   Refining and Casting Research and Development Needs and Opportunities

Ladle Refining

Small amounts of SO_2 are emitted during electric-arc heated ladle refining. For new installations, these additional emissions could require controls in order to meet Prevention of Significant Deterioration requirements. Research into the mechanism of SO_2 formation during this ladle refining process may lead to ways to prevent these emissions.

Casting

The VOC emissions from lubrication oils and greases are transplanted in the steam that is vented to the atmosphere from the quenching and cooling section of the caster. Research is needed to develop oils and greases or alternative lubrication practices to reduce or eliminate such VOC emissions, if found to be significant.

R & D Needs	*Refining and Casting*
	‣ Understanding of SO_2 formation mechanisms during the ladle refining process
	‣ Oils and greases or alternative lubrication practices to reduce VOC emissions

4.6   Forming and Finishing

Figure 4-7 illustrates the forming and finishing processes with their major inputs and outputs for steel sheet, and typical of long product rolling.

4.6.1   Forming and Finishing Emissions

Significant emissions from forming and finishing are limited to a few operations, including reheating, scarfing, and pickling. Emissions from reheat furnaces are limited to products of combustion. Hand- or machine-scarfing of semi-finished steel to remove surface defects generates particulate and gaseous emissions. Those from hand-scarfing are localized and generally minor in comparison to those from machine scarfing, which are typically controlled with local exhaust hoods and wet or dry cleaning systems. The scarfing process volatilizes the steel at the surface of the slab or other shape, creating a fine iron oxide fume. Major pollutants emitted during scarfing include iron and other oxides (FeO, Fe_2O_3, SiO_2, CaO, and MgO). Machine-scarfing operations generally use an electrostatic precipitator, scrubber, or water spray chamber for particulate control; most hand-scarfing operations are uncontrolled (EPA 1995b).

4.6.2   Forming and Finishing Effluents

Hot Forming

In hot rolling operations, clean recirculated water is used for direct cooling and descaling. Water use and discharge rates from hot rolling operations vary greatly depending upon the type of mill and the shapes produced. Applied process water rates typically range from 1,500 gallons/ton for specialty plate mills to more than 6,000 gallons/ton for hot strip mills, although most is recycled.

Descaling

Salt-bath descaling wastewaters originate from quenching and rinsing operations conducted after processing sheet steel in molten salt baths. The principal pollutants in these wastewaters are total suspended solids, cyanides, dissolved iron, hexavalent and trivalent chromium, and nickel. Wastewater flows normally range from 300 to 1,800 gallons/ton, depending upon the product and process. Descaling wastewaters are usually co-treated with wastewaters from other finishing operations, such as combination acid pickling or cold rolling (EPA 2000).
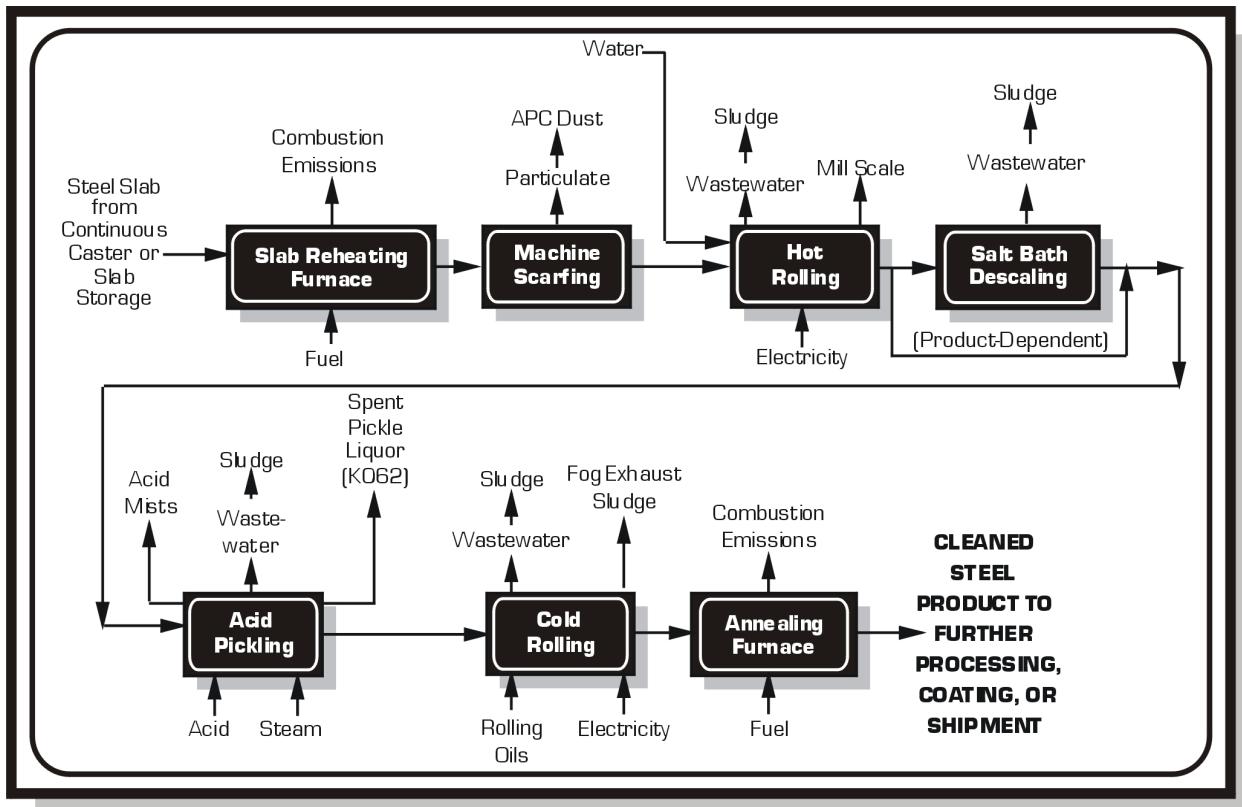
Figure 4-7. Forming and Finishing Flow Diagram

Acid Pickling

Acid pickling wastewaters include spent pickling acids, rinse waters, and pickling line fume scrubber wastewaters. Spent pickle liquor is listed as a hazardous waste (K062) because it contains considerable residual acidity and high concentrations of dissolved iron salts. Pickling performed prior to coating may use a mildly acidic bath, which is not a listed hazardous waste.

Process water and wastewater flows vary greatly depending upon the product and process. Waste pickle liquor flows typically range between 10 and 20 gallons/ton of pickled product. Rinse water flows range from less than 70 gallons/ton for bar products to more than 1,000 gallons/ton for certain flat-rolled products. The typical pollutants in rinse water include total suspended solids, dissolved iron, and other metals. For carbon steel operations, the principal metals are lead and zinc; for specialty and stainless steels, the metals are chromium and nickel (EPA 2000).

Cold Rolling

Process wastewaters from cold forming operations result from rolling operations that use synthetic or animal-fat based rolling solutions, many of which are proprietary. The rolling solutions may be treated and recycled at the mill, used on a once-through basis, and discharged to a wastewater treatment system, or handled as some combination of the two.

The principal pollutants are suspended solids, oil and grease (emulsified), and metals (lead and zinc for carbon steels, and chromium and nickel for specialty and stainless steels). Trace chromium may also be a contaminant from cold rolling of carbon steels caused by wear on chromium-plated work rolls. Toxic organic pollutants, including naphthalene, other polynuclear aromatic compounds, and chlorinated solvents, have also been found in cold rolling wastewaters (EPA 2000).

Process wastewater discharge rates range from less than 10 gallons/ton for mills with recirculated rolling solutions to more than 400 gallons/ton for mills with direct application of rolling solutions (EPA 2000). Conventional treatment of cold rolling wastewaters includes chemical emulsion breaking, dissolved gas flotation for gross oil removal, and co-treatment with other finishing wastewaters for removal of toxic metals.

4.6.3 Forming and Finishing By-Products

The main by-products associated with forming and finishing are mill scale (typically iron oxides), an oily sludge that results from lubricating the rolls (water treatment plant sludges), and air pollution control dusts associated with treating effluents and cleaning exhaust gases.

Mill Scale

Coarse mill scale is separated from the sludge and collected in scale pits. The quantities of mill scale generated vary but range from 10 and 80 lbs/ton for non-oily scale, averaging around 55 lbs/ton, and 4 to 60 lbs/ton for oily scale, averaging about 10 to 15 lbs/ton (Szekely 1995; IISI 1994). In 1994, approximately 3.7 million tons of scale were produced in the United States (Hamling 1996; Kolarik 1996).

Dust

Hot rolling mills have air pollution control equipment that collects iron oxide fumes, dust and particulate. The dust and fume are generated during scarfing, a method of surface treatment in which the surface layer of steel is burned off to remove imperfections. The dust and fumes are typically recycled, sold to sinter plants, or landfilled.

Sludge

Sludge from hot forming operations is produced from the treatment of mill scale pit effluent. The sludge consists of oils, greases, and fine-grained solids that are collected in settling basins or other solid or liquid separation equipment.

Unlike hot rolling, no scale is formed in cold rolling mills or reduction operations. However, much greater rolling pressures are required to form the metal, which generates considerable heat that must be dissipated by a system of flood lubrication. Lubricants applied to rolled products must serve the dual purpose of lubricating and cooling.

Another by-product associated with cold rolling is the fog-exhaust sludge generated from the mist or fog produced during cold rolling. Fog-exhaust systems are used primarily to allow continuous observation of the strip during processing. Particulate matter also combines with steam and oil mist generated during cold rolling and is discharged to a settling chamber. The settled material is a sludge that is generally landfilled (Baker Environmental 1992).

4.6.4   Hazardous Forming and Finishing Wastes

Spent Pickle Liquor

Spent pickle liquor is an EPA-listed hazardous waste (K062) because it contains considerable residual heavy metals and acidity. The hazardous constituents in K062 are nickel and hexavalent chromium. Waste pickle liquor sludge generated by lime stabilization of spent pickle liquor is not considered hazardous unless it exhibits one or more of the characteristics of hazardous waste.

Spent pickle liquor is discussed further in Section 3.1.3 (part of the Recycling Chapter).

4.6.5   Forming and Finishing Trends and Drivers

A hazardous air pollutant standard was promulgated for HCl pickling in June 1999 and no additional requirements are anticipated for that source category in the foreseeable future. New ambient air quality standards for fine particulate matter (PM-2.5) may also lead to tighter requirements for emissions associated with forming and finishing operations such as scarfing, and Title V permits and compliance assurance monitoring rules may require new continuous process and emission monitoring facilities and practices. New ambient air standards for ozone will also lead to increased regulatory attention of NOx, which contribute to ozone formation in the atmosphere. The EPA and state agencies are also expected to apply pressure to reduce NOx emissions from industrial processes, reheat furnaces, or other forming and finishing combustion-based processes.

Revised federal Effluent Limitation Guidelines, including requirements for numerous forming and finishing subcategories, have been proposed and will be promulgated as final rules in 2002. Because these standards are required to be based on best available technology, tighter standards can be expected for many forming and finishing subcategories.

A few companies still use deep well injection for disposal of waste pickle liquor, but requirements to continue this practice continue to be made more rigorous. Acid regeneration and recovery processes are the challenges for more cost-effective means of treatment and recovery. In addition, some attention has been given by the regulatory and environmental community to possible alternative process for pickling. This interest is driven by the prospect of eliminating pickling waste waters altogether and to the possibility of eliminating HCl pickling because of general concern for chlorinated compounds in the environment.

The general disposal, reuse, recovery, and recycling of dusts and sludges, many of which derive from forming and finishing operations, continues to be a challenge for the industry, particularly when they contain oily residues, which can limit alternatives for recycling or reuse. Although waste oils are not considered to be hazardous under federal law, some states classify them as such, and the potential for comparable federal action exists. Thus, waste oils represent both a processing and environmental challenge.

4.7   Coating

Figure 4-8 illustrates the coating processes with their major inputs and outputs for various steel products (e.g., strip, sheet, and other shapes). For tonnage mass production, there are many coating processes; these can mainly be classified as hot-dip metallic coatings (e.g., galvanizing, aluminizing, terne, etc.,), electrocoating (e.g., electrogalvanizing, tin plating, tin-free coating, and other metallic coatings) and non-metallic coatings (e.g., ceramic, conversion coatings, and organic coatings such as paint and polymers). Vacuum and controlled-atmosphere coating processes are used for specialized, niche applications.
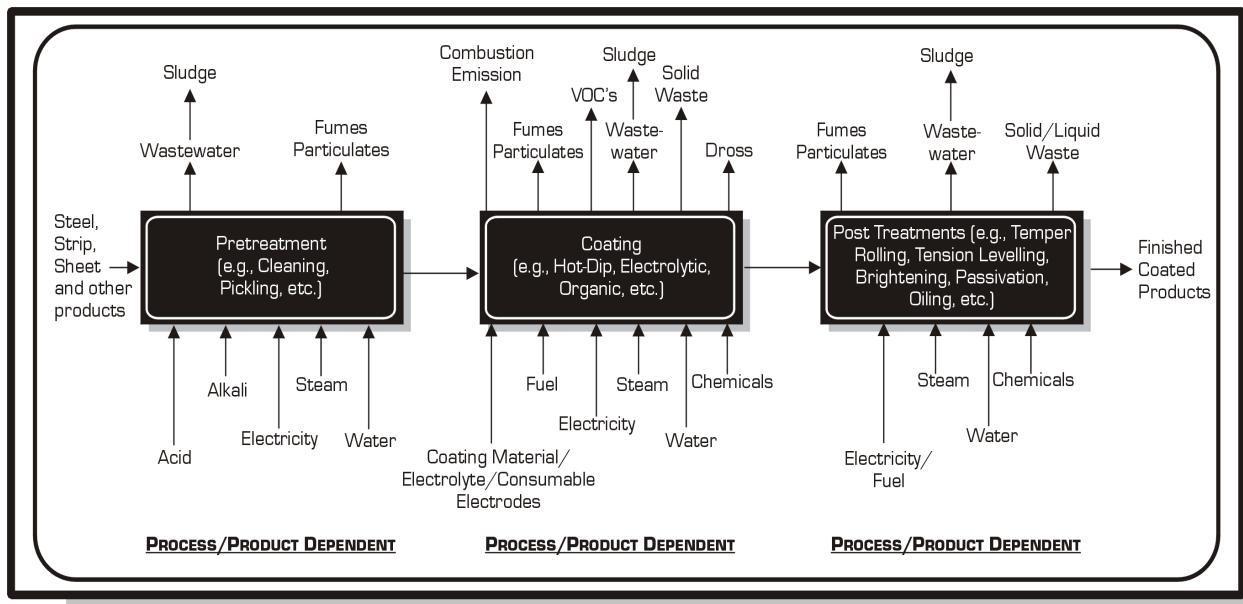
Figure 4-8. Coating Flow Diagram

Coating processes can be continuous or batch type. However, all coating processes have three distinct steps or stages as shown in Figure 4-8. In the pretreatment stage or step, the steel surface is prepared for the coating operation. This is generally accomplished by surface cleaning techniques (e.g., alkaline cleaning, acid pickling, mechanical cleaning, or combination of these techniques), followed by rinsing at each sub- stage. In organic coating lines, the pretreatment stage may also include application of some conversion coating to improve coating adhesion at the subsequent coating stage.

There are many coating processes, dependent on the type of coating or the final product. After the coating has been applied, the steel product generally goes through some post-treatments, such as skin passing and/or tension leveling to improve flatness or shape, reflowing to improve surface brightness (for tin plates), surface passivation to improve aging or storage characteristics, and oiling to impart lubricity.

4.7.1 Coating Emissions

Significant emissions can occur in coating lines at each major stage or step–pretreatment, coating, and post-treatment–depending upon the product or process. At the pretreatment stage, emissions are limited to alkali mist/fume, acid mist/fume, dust, and sometimes VOCs depending upon the cleaning process (alkaline cleaning, acid pickling, mechanical cleaning such as brushing, abrasive blast cleaning and buffing, or combinations thereof), special cleaning reagents (solvent cleaners, emulsion cleaners, etc.) and other processes used (such as conversion coating). These emissions are collected by local exhaust fume extraction systems and scrubber cleaning systems.

At the coating stage, emissions are limited to products of combustion, metal/metal oxide mists, fumes and powders (from molten metals in hot-dip pots), VOCs and product of combustion (from organic coating lines with baking ovens), as well as acid/electrolyte mists/fumes (from electroplating lines). Products of combustion are carried away with the flue gas and are typically well controlled. VOCs and mists/fumes are collected by local exhaust fume extraction systems and scrubber cleaning systems. Metal/metal oxide mist/fume/powders from molten metal hot-dip pots may be collected with local exhaust fume extraction systems and baghouses.

At the post-treatment stage, the emissions are limited to fumes and dust. These are generally collected by local exhaust fume extraction systems, together with scrubber cleaning systems, if required.

The control techniques for removing pollutants and maintaining EPA standards include packed towers and wet scrubbers, as well as baghouse dust collectors. Removal effectiveness in excess of 95% is common. In general, available technologies are quire sufficient to control emissions from various coating operations.

4.7.2   Coating Effluents

At the pretreatment stage, wastewaters include rinse waters from various sub-stages (e.g., alkaline cleaning, acid pickling, mechanical cleaning, solvent cleaning), overflow and spills from various sub-stages, and various fume scrubber wastewaters. At the coating stage, wastewaters come from:

- quench tanks (in hot-dip metallizing and organic coating lines)
- rinse tanks (in all coating lines)
- over-flow, drag-out and recirculating tanks (mainly from electroplating lines)
- scrubbers

At the post-treatment stage, wastewater comes from various rinse tanks, make-up water tanks, spills and overflow as well as fume scrubbers. Process water and wastewater flow at each stage and sub-stage are dependent on the product and process used. Rinse water flow may range from 50 to 1,000 gallons/ton. The typical pollutants are TSSs, oil and grease, and heavy metals such as Fe, Pb, Zn, Cr, Cd, Ni, and Ba, depending on the coating, base metal, and process.

Acidic alkaline rinse waters are generally neutralized separately before being mixed with other rinse water effluents. These are then sent to a central water treatment plant. The available technologies are adequate in meeting the effluent discharge regulations for existing plants. All large steel companies have their own central and localized wastewater treatment plants. Small coating operators, new installations with one or two coating lines, and large installations such as integrated plants, try to avoid the cost of central water treatment plants. They would prefer to recirculate and reuse the wastewaters, if such cost-effective technologies are available. An ultra-filtering water treatment technology is available but is cost-prohibitive.

4.7.3   Coating By-Products

The main by-products associated with coating operations are dross (from hot-dip coating lines), sludge (mainly from the pretreatment stage and from all electroplating tanks), and dust (associated with treating effluents and cleaning exhaust gases, as well as baghouses).

Dross

Dross is a by-product generated in hot-dip metallizing processes (e.g., hot-dip galvanizing, aluminizing, terne coating, and so forth). Top dross is the scum that forms on the surface of the molten metal bath, consisting mainly of oxides. Bottom dross is the solid waste that forms by the reaction of iron in the steel product with the metals in the molten bath and sinks to the bottom of the hot-dip pot. The amount of dross formed in a hot-dip pot depends on many factors, such as temperature, composition of the molten bath, and composition of the steel product. Hot-dip galvanizing lines produce the vast majority of the dross since more than 20 million tons of galvanized products are produced in the United States. Dross is always sent to outside processors for reclaiming the metals for reuse.

Sludge

For coating operations, the sludge can be defined as the insoluble materials and reaction products that collect in cleaning, processing and electroplating lines. The sludge from the cleaning and processing tanks consists mainly of oils, greases, and fine grained solids (mainly iron oxides). Oil and grease may be recovered for subsequent reuse or recycle. The remaining part can be further dewatered by mechanical filtration or by use of sludge drying beds, and can be reused as iron feed material in ironmaking and steelmaking operations. Untreated sludge is also landfilled.

The vast majority of the sludge from coating operations comes from electroplating lines (from the electroplating tanks). These types of sludges are generated by the reaction of the steel product with the electrolyte and other additives and are complex in nature. This sludge, which contains valuable metals, is separated out from the electrolyte by filtering or even by dredging in many cases, and is always sent to outside processors to reclaim the valuable metals.

Dust

The dust and fumes associated with treating effluents and cleaning exhaust gases at the coating operation plant are typically landfilled. Metal oxides or powders collected at the baghouse are generally sold or reused.

4.7.4   Hazardous Coating Wastes

Pickling performed in the pretreatment stage in coating operations generally uses a mildly acidic bath, which is not a listed hazardous waste. Where strong acidic bath is used, as in the case of incoming steel products with heavy scale (e.g., hot bands, wire rods, shapes as the incoming materials in hot-dip galvanizing lines or conversion coating lines), the spent liquor is a hazardous waste. Spent liquor is discussed in section 3.1.3 and 4.6.4.

As indicated in section 4.6.4, the hazardous constituents of K062 are generally heavy metals. Thus, the sludge formed in the plating of heavy metals such as Cr, Ni, and Cd, and even for some tin plating operations, are hazardous. Some of the effluents from passivation treatments (containing hexavalent Cr^{+6}) are also hazardous.

4.7.5   Coating Environmental Trends and Drivers

Federal, state, and local environmental regulations are driving coating environmental trends. In some cases, state or local regulations are more stringent than federal regulations. There are at least three major federal acts that govern the environmental requirements for coating operations. The federal Clean Air Act (CAA) states that coating operations must undertake the following tasks:

- Reduce emissions of NOx and SOx (product of combustion)
- Reduce or eliminate the use of VOCs
- Control, reduce, or eliminate chemicals identified as HAPs
- Phase out ozone-depleting substances

National Ambient Air Quality Standards specify the requirements for VOCs and HAPs. RCRA is the primary law that governs the management of solid and hazardous wastes. The Clean Water Act dictates the water quality standards for wastewaters, including the effluent limitations for hot coating operations (e.g., hot-dip galvanizing, terne coating, and other coatings). The limitations are spelled out for existing and new installations under the best practicable control technology currently available (BPT), the best available technology (BAT) economically achievable, and the best conventional technology (BCT).

4.7.6   New and Emerging Coating Technologies

None have been identified.

4.7.7   Coating Research and Development Needs and Opportunities

In general, the environmental R&D needs in the coating area are the same as in the industry as a whole: reduce or eliminate emissions, water pollutants and solid wastes, especially hazardous waste.

Research needs to reduce NOx and CO_2 from combustion processes have been identified in the previous sections. Elimination or reduction of VOCs requires research in process development and in coating types.

In water treatment area, the major need is in developing cost-effective water treatment methods so that rinse and overflow waters can be reused or recirculated at the point of origin. This research should include alternatives to ultra filtration to remove heavy metals since ultra filtration is very costly, especially for small coating operations.

In the area of solid wastes (including hazardous), the emphasis will likely be on the development of coating processes that eliminate or reduce these wastes. Some of these needs are described below.

Direct Environmental R&D Needs

Two direct needs exist for coating research. First, methods or processes need to be developed to treat wastewater (to cost effectively remove heavy metals) from various rinse/overflow operations for complete reuse or recirculation at the point of origin. Second, the ability to selectively extract environmentally damaging compounds in effluents, electrolytes and spent liquors (e.g., spent acid, spent alkali, spent electrolyte, etc.) could be developed.

Indirect R&D Needs

Indirect R&D needs are focused on coating and process improvements. Environmentally-friendly, flexible, economical and shorter routes are needed for surface treatments and coatings, as well as substitute electrolytes for electroplating (e.g., phenol-free electrolyte for tin plating). Chromium-free, especially hexavalent chromium-free, electrolytes and/or solutions for surface passivation treatments, primers and plating are also needed.

R & D Needs

Coatings

- ‣ Methods to treat wastewater from various rinse/overflow operations
- ‣ Processes for selective extraction of toxic compounds in effluents, electrolytes and spent liquors
- ‣ Environmentally-friendly solutions for pickling and cleaning treatments
- ‣ Improved routes for surface treatments and coatings
- ‣ Chromium-free electrolytes and/or solutions for surface passivation treatments, primers and electroplating
- ‣ Elimination of VOCs in the coating process through new curing techniques
- ‣ Organic coating products in order to avoid any organic compound solvent emissions
- ‣ "Dry" coating techniques for a wide range of coated product applications
- ‣ Cost-effective metallic/alloy coating techniques to avoid the use of electrolytes

VOCs may also be eliminated in the coating process through the development of new cost-effective curing techniques, possibly using radiation, to avoid any organic compound solvent emissions. Research is needed into new organic coating products (e.g., paint in powder form) which avoid organic compound solvent emissions.

4.8   Refractory Recycling

The annual production of the U.S. refractory industry is in excess of 3.3 million tons, worth more than $2 billion. Refractory production data for 1995 (as reported by the U.S. Bureau of Census) are summarized in Table 4-2. The single largest consumer of these materials is the steel industry, which typically purchases about 50% by weight of the refractories produced annually. Most of these refractories are high-value, non-clay refractories that are used as linings for various steelmaking vessels.

When vessel linings can no longer be used, the spent lining is demolished and discarded, and a new one is put in place. Depending on the particular application, refractory material may last only a few hours or as long as several years. Spent refractory materials are disposed of in a landfill or are recycled.

TABLE 4-2. QUANTITY AND VALUE OF UNITED STATES REFRACTORY PRODUCTION IN 1995		
PRODUCT DESCRIPTION	Quantity (tons)	VALUE ($1,000)
Clay Refractories		
Brick and shapes	957,559	565,186
Unshaped clay refractories	661,673	320,080
Lump or ground materials	191,423	22,522
Unspecified	NR	21,452
Non-clay Refractories		
Brick and shapes	482,234	718,079
Mortars	26,106	21,921
Plastics and ramming mixes	158,750	121,785
Other castables and plastics	15,397	20,855
Basic gunning mixes	221,384	91,191
Ceramic fibers	44,978	152,813
Lump or ground materials	386,094	146,736
Unspecified	NR	15,605
Dead burned dolomite	362,775	22,125

NR - Not reported
Source: U.S. Census Bureau

Many issues must be considered for the successful recycling and reuse of spent refractory material. These include the type and quantity of spent refractories, the location of users and producers of refractories; local, state, and federal regulations; health concerns; contamination; value of materials (including worth of components and cost associated with disposal); and economics of separation or beneficiation. In general, refractory recycling may fit into a company's overall recycling program and may follow the same progression as all other recycling.

4.8.1 Refractory Environmental Trends and Drivers

Many factors are driving the interest in recycling and reuse of spent refractory materials. Foremost is the need to develop pollution prevention technologies for the iron and steel industry that will improve efficiency, reduce costs, and ensure compliance with environmental regulations.

Refractory recycling is complicated by the presence of varying amounts and types of impurities within the used refractories, problems with sorting and removing unwanted refractories, and problems with foreign objects being included with the refractories of interest.

4.8.2 New and Emerging Refractory Technologies

It is possible that the technology necessary for recycling spent refractory materials exists. Technologies customarily used by the minerals processing industry have been recently applied to spent refractories in isolated instances. Although these processing techniques are not new, such economically viable and proven technologies merit further study in their application to recycling spent refractory materials.

Previous efforts to recycle spent refractory materials have resulted in some high-value refractory components, such as natural flake graphite, being reused in steelmaking refractories. Entire or partial ladle linings may be reused many times by mechanically removing surface slag or metal, then applying a new surface by vibration casting or hot gunning. New techniques such as slag splashing and monolithic linings have also helped reduce refractory wear and costs in BOF vessels.

4.8.3 Refractory Research and Development Needs and Opportunities

In general, opportunities in refractory recycling are in developing highly efficient in-process separation of useful materials from components of the refractory waste stream and reusing the separated products within the steelmaking facility where they were generated. This development would dramatically reduce the amount of waste generated for disposal, eliminate the need for expensive material transport, and increase economic feasibility.

A comprehensive refractory recycling program would include the following:

R & D Needs

Refractory Recycling

‣ Highly efficient, in-process separation of useful materials from components of the refractory waste stream
‣ Methods of reusing recycled refractory products within the steelmaking facility where they were generated
‣ Characterization of spent refractories
‣ Microscopic analysis of crushed/ground spent refractories
‣ Uses of reclaimed refractory materials, including any process that uses oxide materials

•   Collection of data on the types of quantities of refractories used throughout the steel industry
•   Characterization of representative samples of spent refractories
•   Separation/beneficiation and post characterization of the reclaimed material

Subsequent research will likely focus on investigating the manufacture of products from these materials and maximizing efforts to develop in-house recycling. In addition, research into ways to minimize refractory consumption or replacement would decrease the amount of spent refractories that are generated.

Surveying and Sampling

Information is needed on refractory types, quantities used, disposal techniques and frequency based on variations in the type of refractory and demolition technique. The most important issue is to establish a systematic sampling procedure that will produce representative samples. In addition to sampling current spent refractories, outdoor stockpiles need to be sampled to obtain information on refractory materials that tend to age or hydrate.

Characterization of Spent Refractories

Characterization of spent refractories is an essential part of a comprehensive refractory recycling and reuse program. The objectives of characterization are to accomplish the following:

- Identify changes that have occurred in the refractories as a result of extended, high-temperature operation in a corrosive environment
- Provide insight as to possible separation, beneficiation, and recycling techniques

The characterization procedures and devices necessary include the following techniques commonly used by geologists and mineral engineers in their surveys of potential sources of raw materials:

- Visual examination
- Reflected light
- Transmitted light
- Cathodoluminescence microscopy with energy dispersive spectroscopy, chemical analysis, and x-ray powder diffraction

Beneficiation of Spent Refractories

Another area of research may focus on crushing and grinding using various crushers and mills and then performing microscopic analysis of the ground materials to determine whether there has been effective liberation of the reusable refractory particles from the impurities.

In addition, appropriate separation techniques need to be identified. If steel is the principal contaminant, magnetic separation could be used to remove the iron material which could then be recycled using ordinary methods. If other metals are present, such as lead contamination at the bottom brick of steelmaking furnaces, density separation may be required. Density separation techniques can also be used to separate brick materials in which a density change has occurred. When magnetic or density separation are not adequate, froth flotation may allow separation of desirable components from contaminated materials.

Characterization of Reclaimed Refractory Materials

Reclaimed refractory materials would likely be equivalent to other beneficiated refractory raw materials and as such, the reclaimed materials could be characterized using the standard techniques that are applied to refractory raw materials. These data should provide potential consumers the information necessary to incorporate reclaimed materials into a variety of products.

Standard characterization techniques used by raw material suppliers include chemical and phase analysis and bulk properties. Additional properties are included when raw materials are sold predominantly to a single industry. For example, the refractory industry might be especially interested in the pyrometric cone equivalent of a material, while the petroleum industry might be interested in acid resistance. Specific data could be provided if an individual industry were identified as a potential consumer of the reclaimed materials.

Potential Uses of Reclaimed Refractory Materials

Any process that uses oxide materials is a potential consumer of reclaimed refractory materials, as long as sufficient characterization of the beneficiated material is available. Some examples of applications include the following:

- Desulfurizers
- Slag conditioners
- Slag splashing additives
- Raw materials for calcia-alumina cement manufacture
- Aggregates for refractory concretes

Alternate uses for spent refractory materials include ferro-alloys, portland cements, and construction concrete aggregates. Once reclaimed aggregates have been characterized, they can be listed with similar aggregates, based on virgin raw materials, and can be sold into the same markets.

4.9   NOx and Steelmaking

The iron and steel industry annually emits 138,985 tons of NOx routinely reported as NO_2 (EPA 1995). NOx contributes to the production of smog and acid rain. NOx reacts with VOCs in a complex sequence of reactions to produce ozone, commonly referred to as smog. NOx also reacts with other atmospheric constituents to form particulate matter, which generally is in the fine respirable range.

The quantity of NOx produced depends on the specific combustion process. Cokemaking, for instance, typically emits 0.98 lbs NOx/ton of product, with sintering emitting 0.3 lbs NOx/ton, blast furnaces 0.41 lbs NOx/ton, and steel reheat furnaces 0.8 lbs/ton.

4.9.1 NOx Environmental Trends and Drivers

EPA has identified NOx as a primary pollutant subject to control under the Clean Air Act and its amendments. Ozone or smog is regulated by ambient standards, and EPA recently proposed tightened ambient standards for ozone and fine particulate matter (PM 2.5), both of which can be formed from NOx emissions. Many populated areas of the United States have been designated as ozone non-attainment areas. One of these, the Great Lakes region in and around Chicago and northern Indiana, has been designated as a severe ozone non-attainment area and is subject to stringent source NOx controls on new source equipment. This region includes a number of steel mills.

Operating and capital costs, including the cost of emission control, are important to the steel industry. Burners represent a low-cost route for NOx control and several manufacturers now sell low-NOx burners designed for boilers and furnaces used by the steel industry. Emission levels of these burners are a small fraction of those of conventional burners. However, these low-NOx burners are not always acceptable to older furnace designs because of heat-transfer limitations.

The source of nitrogen in NOx is derived from either molecular nitrogen in combustion air or chemically bound nitrogen in the fuel. Three NOx mechanisms are associated with nitrogen source and chemical reactions leading to formation of nitrogen oxide: thermal, prompt, and fuel. Thermal NOx production is dependent on flame temperature, and the high temperatures used in steel production favor high levels of NOx formation. Prompt NOx is usually produced in fuel rich flames through a mechanism involving carbon-hydrogen fragments, while fuel NOx refers to the oxides produced from the nitrogen associated with the fuel. Techniques used to control NOx emissions address these mechanisms singly or in combination.

4.9.2   NOx Technological Challenges

Production of NOx, especially the combustion route, is a critical factor in steelmaking because of the high temperatures required to produce iron and steel. Both traditional and newer iron and steelmaking processes produce NOx.

The final mill product is often cooled and subsequently reheated. Steel reheating is a process that not only generates NOx but also raises operating costs because of increased fuel use.

In the drive to increase electric arc furnace productivity by reducing tap-to-tap time, EAF operators are supplementing electrical energy with energy from the combustion of fuels, a process that produces NOx. For example, some electric arc furnaces use the oxy-fuel combustion of natural gas to provide additional heat for scrap melting. Another growing trend is to capture and burn CO offgas to supplement electrical energy. Both processes, while increasing the productivity of the EAF, increase NOx emissions.

Coke oven gas, a by-product of cokemaking, is burned in integrated mills as a fuel to produce steam in boilers and generate heat in furnaces. Although the gas is scrubbed, nitrogen-containing components, primarily ammonia, generally remain. When combusted, these nitrogen-containing compounds are converted into NOx, producing an unusually high NOx level for a fuel with a relatively low BTU content.

4.9.3   New and Emerging NOx Technologies

New steel melting facilities are being built and processes are being modified that will comply with regulations and reduce the cost of steel production. The Department of Energy is sponsoring several R&D projects to assist the steel industry in reducing its NOx emissions and reduce its fuel costs:

• Dilute oxygen combustion
• NOx formation and control
• Low-NOx burners
• Oscillating combustion
• Oxygen-enriched air staging

Dilute oxygen combustion (DOC) is a novel technique in which gaseous fuel is combusted with the least possible amount of oxidant, thereby reducing flame temperature and NOx emissions. In DOC, the combustion of natural gas proceeds via a high velocity turbulent jet reacting with hot surrounding furnace gas as a dilute oxygen source. High oxygen jet velocity promotes sufficient in-furnace recirculation for dilution of the oxidant. A key advantage of DOC is its mechanical design and installation simplicity. The technology is expected to reduce emissions of NOx by about 10% of current levels, while improving furnace efficiency.

The NOx emissions are often found to be higher in steel mills where by-product fuels are used in the steel plant to save on supplemental fuel costs. These by-product fuels usually contain nitrogen-containing species that are converted to NOx. The University of Utah is currently identifying the NOx formation issues, defining the controlling mechanisms, and evaluating low-cost NOx control concepts.

Three extremely low-NOx burner projects are being pursued for boilers in steel mills. Each of these projects has the goal of achieving NOx levels of 9 ppm and CO levels of 50 ppm or lower at 3% excess oxygen without a decrease in combustion efficiency or production rate. A different low cost combustion approach is used in each project to reach this goal. These include combinations of staging, internal (within the boiler) combustion gas recirculation, and conversion of natural gas to CO and H, and flux-enhanced radiant combustion. All three projects are in various stages of development and demonstration, with a small model of one project (Radiation Stabilized Burner) commercially available.

Oscillating combustion is a potentially low-cost route to realizing current state-of-the-art NOx levels without burner replacement. Oscillating combustion involves the creation of successive fuel-rich and fuel-lean zones within the flame through forced oscillation of fuel flow rate. Heat is removed from the zones before the rich and lean fuel mix to reduce peak flame temperature, thus reducing NOx formation. Heat transfer to the load increases due to the more luminous fuel-rich zones and the break-up of the thermal boundary layer. Typically, NOx emissions are reduced by 60 to 90%, and heat transfer is increased by up to 10%.

Oxygen-enriched air-staging is being pursued as a low-cost NOx-reduction technique by avoiding the high cost of 100% oxygen use. Tested on a glass furnace, NOx levels were reduced by 40% under optimum conditions. Currently on the market for glass manufacturing, this approach should also be applicable to steel furnaces.

4.9.4   NOx Research and Development Needs and Opportunities

<table>
<tr><td rowspan="2">R & D Needs</td><td>

Nitrogen Oxides

- Improved scheduling in the manufacturing process
- Advanced combustion control systems coupled with low-NOx burners
- Improved furnace heat transfer
- Reduced cost of low-NOx systems
- Direct flame reading sensors for continuous control of pollutants

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R&D needs for reducing NOx generation and emission primarily include operational and equipment issues. One practice development, improved scheduling in steel manufacturing process, would improve product flow and eliminate cool-down between processes and thereby the requirement for reheating.

Combustion and furnace research needs are key to improving NOx performance. For example, advanced combustion-control systems coupled with advanced-generation, low-NOx burners may significantly lower emissions. Improved furnace heat transfer would also minimize fuel consumption and consequently, NOx emissions. Direct flame reading sensors for continuous control of NOx and other pollutants are an additional development need. Continued reductions in the cost of these low-NOx combustion systems and equipment are needed to ensure financial, as well as environmental, motivation for implementation.