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POLLUTION PREVENTION AND ABATEMENT GUIDELINES FOR THE IRON AND STEEL INDUSTRY*

prepared by

the UNIDO Secretariat

*This document is one of the chapters prepared for a forthcoming set of pollution guidelines jointly prepared by the World Bank, UNIDO and UNEP. This document has not been edited.

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1. EXECUTIVE SUMMARY

Most steel products are made through one of the sequence of steps shown in Figure 1-1. This document addresses various environmental aspects of the following segments of the iron and steel industry: ore mining and preparation; 'coke preparation; pig iron production in the blast furnace; direct reduction; steelmaking in basic oxygen, open hearth, and electric arc furnaces; and finishing operations including continuous casting, hot rolling, cold rolling, wire drawing, and acid pickling. (Smelting reduction is not described since there is only one commercially operating plant in the world using this technology. The main benefits of this process compared with the others are energy savings and elimination of the coking and sintering stages)

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Each process uniquely affects air and water quality and creates particular solid waste disposal problems. This guideline will address the environmental concerns of the iron and steel industry and propose waste minimization opportunities, material handling procedures, and treatment technologies that can reduce its impact on the environment. This section of the guideline will review the general environmental issues for the industry as a whole. In later sections, each industry segment will be separately addressed with additional detail and with respect to environmental issues unique to the segment.

Air Emissions - For many operations within the steelmaking complex, air comes in direct contact with toxic or otherwise harmful materials. Discharges of contaminated air must be kept to a minimum through source reduction measures and employment of the proper pollution control equipment. Given local concerns that acid rain may contribute to damage of inland water systems and forests, acid-forming emissions from the iron and steel industry are of current interest and the extent of control required is a matter of controversy. Globally, the large carbon dioxide emissions from iron and steel making operations adds an environmental dimension 'o the continuing development of less energy consuming steel making routes.

Water Pollution - For many operations within the steelmaking complex, waters are used in direct contact with toxic or otherwise harmful materials. For example, cooling and purification of coke vent gas can allow pollutants such as tar, oil, ammonia, phenols, cyanides, thiocyanates, and thiosulfates to enter the water system. The water requires extensive purification before it can be recycled or discharged to the environment or to local sewage treatment stations.

Since water is used extensively in the iron and steel industry, proper technologies must be used to keep water pollution to a minimum. According to average data obtained from Eastern and Western European countries and the United States (U.S.), about 200 m' of water are used per ton of steel. Total water use at a large steelworks carrying out all steelmaking operations exceeds 2 billion m' per year divided among the various branches of production as follows in Table 1-1. Most of this water is not consumed during a single use at a modern steel mill but recirculated many times before treatment and discharge.





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Process	Percent of Total Water Us		
Sintering	3		
Coke by-product manufacturing	7,		
Blast furnace production	24		
Steelmaking	23		
Rolling mill production	42		

Table 1-1 Water Use in the Iron and Steel Industry

Water is used primarily to remove and dissipate heat at an iron and steel works. Minimum quality requirements for water at an integrated iron and steel works are shown below in Table 1-2.

 Table 1-2
 Water Quality Required at an Integrated Steelworks for Influent Process

 Water
 Water

Type of Water	Quality Parameters	Primary Use
Potable	physically, chemically, and biologically wholesome	drinking, amenity,air conditioning
High-grade industrial	low total dissolved solids, low organic matter	steam raising
General industrial	low suspended solids, non corrosive, non scale-forming	cooling condensers, furnacus, rolling mills, gases
Low-grade industrial	absence of gross pollution	coke and slag quenching

Solid Wastes - Iron and steel making generates large volumes of slag. Also, considerable amounts of refractory wastes are accumulated during the relining of blast furnaces, hot blast stoves, mixers, converters, open hearth and electric furnaces, ladles, soaking pits, and reheating furnaces. Furthermore, substantial amounts of dust are produced from sintering plants, coke wharfs, and baghouses that must be properly disposed. Where options do not exist for recycling and reuse of these materials, landfilling must be practiced with care and where markets do not exist for sale of solid wastes, they must be developed.

Noise - Sources of noise pollution from iron and steelmaking operations include sinter plant fans, the snort valve in the blast furnace, ultra high power electric arc furnaces, rotary saws, and certain burners. Also, excessive noise results from crushing, grinding, and mining activities such as explosive blasting and drilling operations. Noises of metal rubbing against metal in mills and on processing lines as well as noise from truck and rail movements can be quite loud.

Pollution Prevention - before the implementation of control technologies, with their associated high costs, measures to reduce the volume of waste generated should be investigated. Iron and steelmaking processes generate large quantities of by-products and it is of interest to reuse or recycle as much as possible provided this is economically feasible and markets are available. Improving operational techniques will minimize consumption of raw materials and power by introducing energy-efficient iron and steelmaking and processing technologies in existing plants. Recovering exhaust energy by installing cost effective energy recovery equipment result in lower fuel consumption and associated emissions.

From an environmental and energy point of view it is also desirable to maximize the manufacture of market steel products from scrap steel, thus avoiding the energy intensive reduction stage, see Table 1-3. Making steel from steel scrap also avoids the ore mining and coke production stages and associated environmental impacts.

Production route	Reduction (GJ/t)	<u>Melting</u> (GJ/t)	Forming (GJ/t)	<u>Total</u> (GJ/t)
Steel from iron ore	14	2	6	22
Steel from scrap in electric arc furnace, EAF	-	6	6	12
Steel from scrap in basic oxygen furnace		3	6	9

Table 1-3 Energy consumption in steelmaking

Adapted from: Kazushige Umezawa, "Scrap Melting Process - Current Status and Future Prospect." <u>Tetsu to Hagane (Iron and Steel</u>, in Japanese), pp.12-18, Vol.4 1992.

Hazardous Materials Management - Hazardous components of some wastes, such as lead, zinc, chromium, cadmium, mercury, arsenic, and copper, have potential adverse effects on human health and the environment and must be handled carefully. Acids used in finishing operations should also be managed with care. Documentation of shipments of hazardous materials into a facility, their movement within a facility, and their ultimate disposal must be maintained.

Treatment Technologies - Technologies for environmental control of iron and steel industry pollution sources have been well developed and are readily available. However, the appropriate technology to suit the specific conditions must be selected and operated as an integrated part of the production facilities.

The problems of air and water pollution from the iron and steel industry become intertwined once effective solutions for control are considered. For example, the dust that was formerly an air pollution problem becomes part of a water pollution problem when removed from the air by means of a scrubber. The ammonia and phenol contaminants of the coke plant effluent become potential air pollutants when this effluent is redirected to the sinter plant to moisten and bind the sinter.

Costs - According to the American Iron and Steel Institute, the United States Steel Industry spent \$US 103.9 million on air and water pollution controls and solid waste disposal facilities in 1988 (\$US 49.3 million for water pollution control equipment, \$US 46.7 million for air pollution control equipment, and \$US 7.9 for solid waste disposal facilities). If waste minimization measures are employed, some costs of pollution control equipment may be defrayed. Costs for incorporating pollution prevention and control at the design stage will be less than retrofitting existing facilities with such equipment.

Health and Safety - Many environmental problems are linked with concerns for the health of the workforce. To address health and safety hazards, management should have a sound policy regarding the protection of workers' health and safety and of the environment. This policy should integrate all activities and the whole workforce with an appropriate allocation of resources and be monitored periodically. Satisfactory environmental and health and safety control can only be achieved through the correct operation and good maintenance of production and pollution control facilities. Disciplined behavior of the workforce is also an essential element. Continuous education and training of staff and workers, and the consistent use of protective clothing and shoes, ear plugs, etc., is therefore indispensable to establish and maintain these standards.

For example, noise in the workplace implies that personnel should: undergo testing for hearing quality before commencing work in such areas; should be given protective equipment such as ear plugs; and should regularly be tested for the effects of exposure. Similar provisions apply to hazards such as toxic gases, lead, asbestos, solvents, heat stress, and equipment associated with repetitive strain injury. Great care should be taken to protect workers from such health hazards as coke oven fumes that contain carcinogenic polycyclic organic compounds.

Guidelines - Effluent and ambient guidelines are addressed in this document for each segment of the iron and steel industry. Although there are many different contaminants in the waste streams from each process, only those parameters that typically cause gross pollution to air and water and are most common throughout the manufacturing processes are listed.

There are certain problems that arise in attempting to regulate air and water discharges. For example, the relationship of air emissions to ambient air conditions, and the relationship of wastewater discharges to quantity of stream flow must be considered in establishing and interpreting guidelines.

Standards for environmental control should be developed jointly by the government or other responsible authority with senior management of the local industry according to the characteristics of the production process and specific local environmental conditions of the plant. These standards should be site specific. In developing countries, effluent guidelines should first be developed and enforced for the main pollutants from the industry. In iron and steel production, the key water pollutants to be regulated include suspended solids, BOD, COD, pH, and oil and grease. The key air pollutants include dusts, sulfur oxides, nitrogen oxides, carbon monoxide, and benzene from coke production.

Environmental guidelines for iron and steel have been established by Brazil, Canada, France, Germany (Federal Republic), Italy, Japan, Mexico, Spain, Sweden, the United Kingdom, and the United States, as well as by the World Health Organization (WHO), the United Nations Environment Programme (UNEP), and the Organization of Economic Cooperation and Development (OECD). There are significant differences between the standards employed by each country and organization as noted in the guideline tables throughout this document. For instance, besides standards for existing sources, Spain and the U.S. Environmental Protection Agency (EPA) have standards for new sources that are more stringent and therefore more costly. Also, the U.S. regulates water discharges from iron and steel manufacturing operations based on defined categories of operations and levels of production. However, most other guidelines employ concentration standards or ambient/receiving air and water quality standards. Table 1-3 lists the industry subcategories used by the EPA and relates them to the six subcategories identified in this guideline document. Although U.S. iron and steel water effluent standards are extensively detailed and production level based, they may not always be appropriate for use in other countries. This document has assumed that the EPA Best Practicable Control Technology (BPT) effluent limitations for water are the most appropriate for developing nations to consider as these limitations are the least stringent and most economically achievable.

Iron and Steel Document	EPA Subcategory
Ore Mining and Preparation	Sintering
Coke Production	Coking
Pig Iron Production	Ironmaking
Direct Reduction	Ironmaking
Steel Production	Steelmaking Vacuum Degassing
Rolling and Finishing Operations	Continuous Casting Hot Forming Cold Forming Salt Bath Descaling Acid Pickling Hot Coating

Table 1-4 EPA Subcategories for Effluent Guidelines

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Note: The EPA regulates ore mining operations independent of the iron and steel industry.

2. ORE MINING AND PREPARATION

2.1 Summary

See Section 1, Executive Summary.

2.2 Introduction

The mining component of the iron and steel industry involves major mining operations for iron ore and coal. It also involves minor mining activities for silica, manganese, and nickel and chromium ores, and the winning of limestone and industrial minerals for the manufacture of fluxes and refractories.

2.3 Manufacturing Process

The two common types of mining operations are open-pit mining and underground mining. Open-pit mining is accomplished by drilling and blasting the ore or coal into sizes that can be handled by mining equipment and beneficiation facilities. Underground mining involves drilling, blasting, transporting the ore or coal within the mine, and hoisting or hauling the ore or coal to the surface. The use of rail cars or buckets connected to a hoisting system are generally used in transportation of underground materials to the surface. Once the materials are transported to the site, conveyors and/or earth moving equipment are used for on-site transportation. After reaching the site, the ore or coal is usually stockpiled before it is used.

Preparation of raw materials for use in the iron and steel industry involves transportation operations, stockpiling, coal washing, ore beneficiation, coke making, manufacture of pellels and sinter, the burning of limestone, fabrication and firing of refractories, and the recovery of scrap. Ore beneficiation encompasses all of the methods used to improve the chemical or physical characteristics of the ore. The most commonly used methods include crushing, screening, blending, concentrating, and agglomerating. Crushing, screening, and blending reduce the ore by physical processes to a desired size.

Historically, concentrating was considered a washing procedure. With the recent trend in mining low-grade ore, concentrating has developed extensively. It is now considered to encompass comminution (size reduction), washing (removal of clays and suspended particles), jigging (stratification of ore particles), heavy-media separation, magnetic separation and, electrostatic separation.

Agglomeration processes include sintering, pelletizing, briquetting, and nodulizing. The agglomerate should contain at least 60 percent iron, a minimum of undesirable constituents, and a minimum of material less than 6 millimeters and greater than 25 millimeters. Briquetting and nodulizing have become very insignificant with the advances and popularity of sintering and pelletizing.

Sintering was developed to make use of iron ore fines and recovered blast furnace flue dust and involves burning a fuel mixed with ore under controlled conditions. The sintering process produces a clinker-like aggregate from naturally fine ores, ore fines from flue dust, and ore concentrates. Sintering agglomerates iron ore fines and recycled metallurgical dusts into a porous mass for charging to the blast furnace. The iron-bearing materials are moistened, mixed with coke fines (breeze) and limestone (flux), and subjected to high heat. The effect of sinter is to increase blast furnace efficiency by decreasing the weight of the blast furnace charge by decreasing the dust loss, coke requirements, and the weight of flux required. Sintering has made it possible to use ores containing high concentrations of impurities such as sulfur.

Pelletizing differs from sintering in that a damp unbaked pellet is formed and then hardened by heating. This improves burden permeability, lowers dust loss, and increases furnace productivity. Sulfur is converted to sulfur dioxide in the process. Transportation of the pellets has generally been accomplished by rail and water, and the pellets do not suffer degradation in transit.

Another operation, smelting, separates metal from the impurities with which it may be chemically combined or physically mixed by fusion. Fluxes are used to fuse the metal from the impurities. They can enhance an element or compound combining in a preferred way with the metal. The primary acid flux is silica and is readily available in sand, gravel, and quartz. The primary basic fluxes are limestone and dolomite. Limestone is preferred as it can remove large amounts of sulfur.

2.4 Waste Sources and Characterization

Air Emissions

Granular particulates are generated in mining, crushing, screening, and cooling operations. They are spread during transportation, released at points of belt transfer, or blown from storage heaps and blending beds. Significant quantities of dust are also generated from the sintering process as are NO, emissions. Sintering emits impurities into the atmosphere, such as sulfur, and poses a particulate emission problem of collecting the gas from the sinter machine. Presence of oil in any mill scale that is returned to sinter plants can result in heavy visible emissions.

Water Pollution

Water pollution from ore mining results from the subsurface extraction of the ore. This has many effects as it causes upheaval of the hydraulic gradient, depletion of aquifers, leaching of mine sludge into the ground water and allows other contaminants to come into direct contact with water. Ore preparation contribut s to water pollution as water is used to control wind erosion of stockpiles or is used in pollution control equipment in sintering and pelletizing processes. Tremendous amounts of water are used for the actual beneficiation operations.

Solid Wastes

Solid wastes associated with ore mining and preparation are composed of materials rejected from coal washeries, dusts recovered from the cleaning of gaseous effluents, oil and grease residues, tailings, and discarded tools and equipment.

Where these cannot be sold or recycled, they must be landfilled. Considerable quantities of material are involved in this component of the iron and steel industry and the establishment and maintenance of land disposal areas can create problems. There are also the possible dangers of leaching of hydrocarbon residues, soluble salts, sulfur compounds, and toxic heavy metals to local water supplies.

Contaminants of Concern

Contaminants of concern from ore mining and preparation activities include the following compounds:

Air Contaminants	Water Contaminants
fugitive dust particles fines (usually recycled) gaseous fluorine compounds sulfurous and nitrogenous oxide gases	fines (usually recycled)

Environmental Impacts

The primary impact of mining, transportation, and charging operations on air is the release of dust. Sintering and pelletizing operations release undesirable gases into the air. Surface waters are used in process flows for beneficiation operations, for transporting materials, and as receptacles for process discharges. Mining operations can affect ground water when process waters are discharged to the ground water aquifer and ground water is used for process flow. Mining operations disturb the land by their very nature and uncontrolled landfilling of fines and scalings may add to the negative environmental impact.

2.5 Pollution Prevention and Control

<u>Raw Materials Handling</u>

Unloading, storage, and transportation of dry, fine raw materials generate fugitive dusts. Various methods are available to control these dusts:

- enclosures at belt transfer points and evacuation to a bag filter.
- spraying of the stockpiles with water,
- use of a water curtain or dedusting by evacuation to a bag filter while unloading,
- enclosure of the receiving hopper,
- design of unloading equipment with a minimum fall height,
- building walls to serve as wind-breaks, and

Sintering and Pelletizing

Fugitive dust from sintering and pelletizing operations can be recovered by the installation of suction hoods and bag filters. Particulates in stack gases are generally removed with electrostatic precipitators.

Wet scrubbing of stack gases with alkaline liquids can reduce SO₂ emissions with 90 percent efficiency. Removal of NO₂ from stack gases is expensive but required in some areas to preserve local air quality.

Because dust and sludges from sintering plants contain iron oxide and calcium compounds, they may be used as ironmaking material, provided the alkali content is low.

Energy recovery in sinter plants focuses on two areas: heat recovery from product sinter for air preheating, and steam and electricity generation; and heat recovery from stack gas emissions.

Other measures to minimize waste include preheating of the sinter mix, modifying the ignition hood, improving sealing systems, and increasing sinter bed height.

Treatment Technologies

Applicable technologies to treat air and water pollution from ore mining and preparation activities include:

- baghouses to capture fugitive dusts,
- cyclones to capture fugitive dusts,
- electrostatic precipitators to remove dusts from air streams,
- filters to remove solids from wastewater, and
- oil/water separators to remove oil from wastewater.

Hazardous Materials Handling, Management, and Disposal

All materials associated with ore mining and preparation must be handled with great care to prevent unnecessary injuries. Most of these operations require the use of heavy equipment, conveyors, or other mechanical process. Special care must be taken when handling explosives and detonating materials. Underground mining poses many considerations when blasting the ore, mining the ore, and transporting the ore to the surface. Every possibility to reduce the dust problems that arise from the storage and on-site transfer of large quantities of material should be considered. As sintering and pelletizing require heat in producing the desired products, care must be maintained in handling heated products.

<u>Costs</u>

Relative costs of some waste minimization measures and treatment technologies are included in Table 2-1.

item	Capital Costs	O & M Costs*	
Spraying	Low	Low	
Wind breaks	Low	Low	
Baghouse	Moderate(\$U.S. 10.00 per ACFM)*	High(15% of capital costs annually)*	
Cyclone	Moderate	Moderate	
Suction hoods	Moderate	Moderate	
Wet scrubber	Moderate	Moderate	
Electrostatic precipitator	High	High	
Oil/water separator	Moderate	Moderate	
Filter	Moderate	Moderate	

 Table 2-1
 Ore Mining and Preparation Pollution Control Costs

2.6 Occupational Health and Safety Issues

Ore mining and preparation operations create health hazards through exposure to dust, coal carcinogens, metal fumes, carbon monoxide, noise, and heat. Safety hazards include injuries from operating heavy machinery, using explosives and detonating equipment, underground mining operations, falling of heavy objects, obstruction of passageways, movement of locomotives, strains from lifting and pulling, burns, and eye injuries. These hazards may be reduced or eliminated through implementation of good management practices and worker training.

The occupational health and safety issues for ore mining and preparation are described in detail in the World Bank document <u>Occupational Health and Safety</u> <u>Guidelines</u> dated September 1988.

2.7 Global Overview of Discharge Requirements

Guidelines for air and water emissions from ore mining and preparation activities are listed in Tables 2-2 and 2-3, respectively. In establishing such guidelines there are many factors that must be considered beyond the allowed levels of contaminants. For instance, guidelines for the condition of mined land must be considered in order to promote reclamation projects and prevent strip mining. Such projects should be focused to prevent acid drainage and to promote future use of the exploited land.

		Spain								-
Contaminant	Existing	New	Forecast (1980)	Brazil	France	Japan ^r	UK•	Sweden	UNEP	US*
Solid Particles	400°	250	150*	80 ⁴	0.150	0.40 ^x	115	1 ^k	3	150*
	200x	150c	120°	240*	0.5g	0.30i		U.St		50°

Table 2-2Ore Mining and Preparation Air Guidelines

*All values reported in mg/m³,

* Associated with the agglomeration of minerals (sintering and pelletizing)

"Associated with the preparation of coal (grinding, etc.)

⁴ Average annual geometric concentration reported in µg/m²,

* Maximum daily concentration reported in µg/m, not to be exceeded more than once per year

^f All values reported in g/Nm³,

*Allowed for exceptional circumstances, not for more than 200 hours per year

^b For air flow less than 40,000 Nm³, per hour

'For air flow greater than 40,000 Nm', per hour

¹ All values reported in kg/ton

* Associated with existing plants

¹Associated with new plants

^a All ambient values reported in μ/m^{1} of PM-10 (particulate matter 10 μ or smaller in diameter)

*24-hour average

* Annual arithmetic mean

Table 2-3 Ore Mining and Preparation Water Effluent Guidelines

Contaminant	U.S. •Maximum Daily	U.S. "30 Day Average	Mexico Daily Average	Mexico Immediate	UNEP
pH Total	6 - 9 0.0751	6 - 9 0.0250	6 - 9 30	6 - 9 36	0.28
Suspended Solids (TSS)					
Oil and Grease Oxygen Demand	0.0150	0.00501	50	70	0.05

*All values except pH reported in kg/1000 kg of product

^bAll values except pH reported in mg/l

"All values reported in kg/tonne of product

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3. COKE PRODUCTION

3.1 Summary

See Section 1, Executive Summary.

3.2 Introduction

Coking involves heating coal in the absence of air. This results in the separation of part of the non-carbon constituents of the coal. Coke is principally carbon, ash, and sulfur and is used as a fuel and carbon monoxide source in the blast furnace. Volatiles, water, and sulfur are released in a gas stream from coke combustion. The off-gas is processed to remove salable by-products and contaminants of environmental concern.

Coke production is maybe the most polluting process in iron and steel making. It should therefore play a central role in any effort to rehabilitate old plants, especially in developing countries.

3.3 Manufacturing Process

Of the three types of coking practices, beehive, continuous, and by-product, only by-product coking is described here since the beehive process is considered outdated and the continuous processes have not been demonstrated to be economically feasible.

By-product coke ovens are those designed and operated to allow collection of the volatile material evolved from the coal during the coking process. The by-product coking process involves the pyrolysis (heating) of coal in the absence of air. Pyrolysis is a process in which the coal bakes rather than burns. The lump coke product is used in the blast furnace after being cooled and screened to a uniform size. In the by-product method, air is excluded from the coking chambers. The necessary heat for the distillation is supplied from external combustion of some of the gas recovered from the coking process. With modern equipment all volatile products are recovered as gas and coal chemicals.

By-product coking involves blending coals of different makeups to obtain a product with desired physical and chemical properties. Coals with a low ash and sulfur content are the most desired types of coal. Coal preparation is the most important step in the coke-making process in terms of quality and uniformity. There are several processes that are used to prepare the coal for charging into the oven. Preheating the coal helps to improve the strength and hardness of coke, and therefore reduces coking time by increasing oven throughput. Drying and preheating of coal in a flash dryer or fluidized bed is more efficient than in a battery oven and therefore reduces fuel requirements, reduces thermal shock to the refractory brickwork, and eliminates emissions during the coal charging phase.

Screening and crushing operations are performed to ensure the coke is of the desired size. The fines that are too small, called coke breeze, are used in coke

plants as boiler fuel, in sintering plants as sinter fuel, or screened for use in chemical or metallurgical processes.

Stamp charging is another process used in Germany and Poland because of the poor quality coals found in these regions. In stamp charging, the entire coal charge to the coke oven is stamped or compressed and then pushed into the oven for coking. The major advantage is the increase in bulk density. The addition of coke breeze is used to avoid excessive coking pressure.

The coking process is comprised of three primary steps:

- At temperatures up to 700°C, primary breakdown of coal occurs yielding water, oxides of carbon, hydrogen sulfide, hydroaromatic compounds, paraffins, olefins, and phenolic and nitrogen containing compounds.
- Secondary thermal reactions result in the evolution of hydrogen and the formation of aromatic hydrocarbons and methane. Production of ammonia, hydrogen cyanide, pyridine bases, and nitrogen result from the decomposition of nitrogen containing compounds.
- Finally, hard coke is produced through the removal of hydrogen from the oven residue.

The coke oven consists of coking chambers, heating flues, and regenerative chambers, all constructed of refractory brick. Coking starts in the coals at the walls and moves toward the oven center.

High grade silica brick having a high coefficient of thermal expansion at lower than oven operating temperatures are used in the construction of coke ovens. Coke oven doors are usually self sealing doors that have developed into a spring loaded door that depends upon metal to metal contact. Door lining is constructed of clay-brick shapes or monolithic lining of lumnite cement. All these considerations in the design of the oven prevent coke gas from leaking and reduce the amount of heat convected.

The gas collection system consists of vertical or ascension pipes connected via a duct in the oven roof. The purpose of the pipes is to collect the gas, and route it to a collecting main, with flow to the collecting main controlled by a damper valve. Between the damper valve and the oven is a cap valve that vents to the atmosphere. The damper valve is usually a liquid-sealed valve designed so that the cooling spray furnishes the seal in the closed position. Gas from the ascension pipe to the collection main is shock cooled producing precipitation of tar from the gas and cooling to a desired temperature.

Upon exiting the coke ovens, the coke is cooled from 980 to 1100°C to 90 to 260°C by a process known as quenching. The purpose of quenching is to rapidly cool the coke to prevent any further combustion. Wet and dry quenching are the two types of quenching operations practiced.

Wet quenching is accomplished by receiving the hot coke charge from the oven into the quenching car, moving the car to the quenching station, and quenching the coke with water. An immense cloud of steam and water containing coke fines is produced. The water is settled to allow the fines to settle and be removed. The water is then recycled to the quenching tower. Coke is then discharged from the car to its next destination.

The quenching car is designed with a sloping bottom to catch the coke in a uniform bed of about 2 feet and to prevent any of the quenching water that does not evaporate from escaping from the car. Water is drained from the bottom of the quenching car and collected in a settling basin where the coke fines will settle out. The clean water is then re-used in the quenching process. Baffles have been installed near the top of some chenching station stacks to minimize the escape of dust entrained in the steam.

In dry quenching the heat is recovered and used for the generation of steam and electricity. In the process, the coke is pushed from the oven into a hot-coke bucket. The bucket is then boisted to the top of the quenching tower, hot coke is discharged from the bucket into the chamber, and the chamber is then covered. Recirculating inert gases that pass upward through the chamber cool the coke as it descends through the refractory-lined chamber. The cooled coke is then discharged and carried to a screening station. The inert gas flows from the top of the chamber through a drop-out chamber to remove coke particles. Then it enters the waste-heat boiler that serves as a steam generator.

Once the coke has been quenched, it is transported to a coke wharf where it is spread in a thin bed for quick drying and visual inspection. A coke wharf is a long, narrow, inclined platform sloping away from the quenching car track toward a conveyor belt. The coke is retained by a series of gates that, when opened, allow the coke to slide down the wharf and onto the conveyor. The conveyor delivers the coke to the screening station. As the coke leaves on the belt, temperature indicators monitor the coke temperature and spray it with water if necessary.

3.4 Waste Sources and Characterization

<u>Air Emissions</u>

The coke oven is a major source of fugitive air emissions. Releases to air from the coking process occur during charging, coking, pushing, quenching, screening and crushing, and transportation operations. During charging, dusts can escape as the coal is loaded into the ovens. Emissions from the coke oven consist of particulate matter, gases, and liquids. Coke pushing emissions have been singled out as the main source of air pollution. Pushing the coke can result in coarse grit being emitted to the atmosphere. If the charge is not fully coked, high quantities of dense smoke and volatile organic compounds may be generated during pushing. Wet, quenching of coke leads to high emissions of steam and entrained particulates. Unless efficient grit arrestors are placed in the quench tower, the operation is also accompanied by dispersal of relatively coarse dusts. Also, the residuals in the liquid waste stream from quenching can be vaporized and possibly oxidized to become atmospheric discharges.

Water Pollution

Coke-plant wastewater is comprised of blowdown from off-gas controls such as the flushing-liquor systems, discharges from primary and final coolers, decanted water from light-oil decanters, discharges from tar-recovery and chemical-recovery operations, and other miscellaneous discharges throughout the plant. The main source of water pollution from coke production arises from wet quenching. Quenching water is generally high in particulates and contains pollutants such as tar, oil, ammonia, phenols, cyanides, thiocyanates, and thiosulfates from the cooling and purification of coke vent gas. The water requires extensive purification before it can be recycled or discharged to the environment or to local sewage treatment stations.

Solid Wastes

Solid wastes associated with the coking process include dusts and sludges recovered from cleaning gaseous effluents, oil and grease residues, waste by-products from coking, used refractories, and discarded tools and equipment.

Contaminants of Concern

Contaminants of concern from coke production include the following compounds:

Air Contaminants	Water Contaminants
unsaturated hydrocarbons	ammonia liquor
hydrogen	cyanide
carbon monoxide	ter
nitrogen oxides	thiocyanates
sulfur/hydrogen sulfide	paraffins
naphthalene	dusts
thiosulfates	benzo-alpha-pyreae
benzo-alpha-pyrene	unsaturated hydrocarbons
carbon dioxide	light oil
methane	phenol
benzene	olefins
ethane	
dusts	

Environmental Impacts

Environmental impacts to air from coke production include releases of dust, gaseous constituents, and vapors from screening and crushing, charging, coking, pushing, quenching, and transportation operations. Surface waters are used in process flows for quenching operations, for transporting materials, and as receptacles for process discharges. Discharge of process waters to the ground water aquifer and use of ground water as process flow can negatively affect subsurface waters. Disposal of fines or scalings to landfills and land application of process discharges may cause deleterious impacts to land.

3.5 **Pollution Prevention and Control**

Source Reduction

Under certain circumstances, direct reduction steelmaking may replace conventional processes and thereby avoid coke production and its associated pollution problems. Direct reduction is addressed in Section 5.0 of this guideline.

Measures that can be taken to reduce the amount of emissions associated with coke production include coal preheating, use of high grade coals, sealing of the coke battery, marketing waste products, and combustion control. Also, wet and dry quenching each have unique advantages and disadvantages with respect to waste minimization.

Coal preheating reduces coking time by increasing oven throughput and therefore reduces the time available for emissions to be generated. It also reduces fuel consumption (drying and preheating of coal in a flash dryer or fluidized bed is more efficient than in a coke oven), and thermal shock to the refractory brickwork that can lead to leaks from the oven. Closed oven charging via pipeline or chain conveyors has a potential of eliminating emissions during the coal charging phase.

Wet quenching is more commonly practiced than dry quenching and recycling treated quench water can reduce the amount of water that will come in direct contact with the coke. Dry quenching does not use water to cool the coke and therefore eliminates the contact between coke and water. Although dry quenching does not emit visible releases of steam, it is a source of dust. Dry coke quenching in the coke oven allows for energy recovery.

High grade coals can be made available by more intense studies of the material before mining. Desired coals are low in sulfur and ash content. The quality of the coal can be improved as discussed in Section 2.0 of this document.

Some waste products from the coking process have commercial value and may be used in other components of the iron and steel industry. For example, coke breeze recovered from the quench towers can be recycled or sold. Dust from the coke oven is a good source of carbon for use in sintering or pelletizing operations. To the greatest extent possible, opportunities for marketing waste products should be explored and exploited.

Enhancing combustion control helps to alleviate dust generation. Reducing fluctuations in the coking condition and improving the flue temperature distribution are two ways of controlling combustion.

Other measures to minimize wastes from coke ovens include improving moisture control, increasing bed height, reducing side leaks to reduce energy use, and patching oven walls. Regular door cleaning improves carbon monoxide gas yield due to better sealing and extends the life of the coke battery. Use of high grade silica brick and self-sealing coke oven doors prevent gaseous and thermal emissions from the oven. Various methods have been adopted to repair coke oven walls and hence reduce oven leaks, reduce heat loss, and increase oven efficiency. Flame gunning repair methods have become the most effective solution to repairing oven walls. These methods involve melting refractory powder in a high-temperature combustion flame and injecting the molten refractory onto damaged wall areas.

Recycling and By-Product Recovery

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Recovery of Crude Coal Tar from Coke Oven Gas

Crude coal tar can be recovered by passing the contaminated liquid condensates through a flushing-liquor tank. It separates the tar and the liquor by using differences in specific gravity. The non-condensed gas and vapors leaving the collecting and suction mains are further cooled to remove additional tar. This is conducted by passing the stream through a primary cooler which is a cylindrical scrubbing tower. The gas leaving the primary cooler is then passed through an electrostatic precipitator designed to remove any entrained tar.

Recovery of Ammonia from Coke Oven Gas

Ammonia is found in the coke oven gas and its condensed liquor. There are several different methods used to achieve this recovery. The semi-direct process uses distillation and alkali treatment to remove the ammonia from the condensed liquor. Once the ammonia has been removed from the liquor, it is added to the gas stream. This gas stream is then passed through an absorber containing an ammonia absorbing solution. The indirect process involves scrubbing the waste stream with water and removing the ammonia from the water by distillation and alkali treatment. The ammonia and steam are then passed through the absorber. The ammonia absorber is usually executed by spraying the waste stream with sulfuric acid which reacts with the ammonia to produce ammonium sulfate. An additional process produces anhydrous ammonia from the coke oven gas, a valuable by-product.

Recovery of Phenol from Coke Oven Gas

The weak ammonia liquor recovered with coal carbonization processes contains phenol. The phenol is recoverable through a solvent extraction process based on the principle that phenols are more soluble in benzene or light oil than in water and that the phenols can be extracted from benzene or light oils with caustic soda.

Recovery of Coke Oven Light Oil from Coke Oven Gas

There are three methods commonly employed in recovering light oil. These methods include refrigeration and compression, adsorption by solid adsorbents, and absorption with solvents. Refrigeration and compression use reduced temperatures and increased pressure to separate the oil from the gas. Adsorption employs passing the oil contaminated gas stream through a bed of activated carbon and recovering the light oil by heating. Absorption with solvents involves washing the gas with an absorbent, such as petroleum wash oil, and recovering the oil by steam distillation.

Removal of Hydrogen Sulfide from Coke Oven Gas

Commercial desulfurization processes are divided into those using wet oxidation to produce sulfur and those which absorb and strip the hydrogen sulfide for conversion into sulfur or sulfuric acid. Wet oxidation processes use an oxidation-reduction catalyst to facilitate oxidation. The wet oxidation processes efficiently remove sulfur, however they produce highly contaminated waste products.

Treatment Technologies

Modern technologies exist to reduce undesirable materials and compounds from plant discharges. Many waste products of treatment technologies can be recovered, sold, or recycled whereas others must be properly disposed. Driving forces behind each technology are economical considerations and effluent limits. Following are descriptions of the treatment technologies commonly used for coke plant emissions.

Coke Charging

Dust is collected from the charging car through a suction hood. The suction hood is connected via a duct to a fixed duct and dust is collected by a dust collector on the ground. Venturi scrubbers are most commonly used for cleaning the dust-laden air. Wet-type electrostatic precipitators and bag filters have also been used.

Hoods and dust collectors are used to prevent fume leakage from the charging car. When dust is collected from the charging car, it is important to prevent the leakage of emissions from the hood.

New techniques, such as preheated coal charging, have been developed to solve problems in the coke industry, such as the shortage of high-quality coking coal. Under the pre-carbon method, for example, wet coal is preheated to about 200°C in a drying tower and is then transported by a chain conveyor installed to the coking chamber after the recovery of coal dust by a cyclone.

Some emissions created during charging are sucked by the ascension pipe ejector. In recent years, high-pressure gas liquor has been used in this system, though traditionally steam has been used. To prevent gas leakage, water sealing has been adopted with good results.

Discharging the coal from the charging-car hoppers in a predetermined sequence and at specific times will prevent blockages of the gas passageways from the oven. This can be accomplished through double collector mains or jumper pipe systems.

Coke Pushing

The best methods to control emissions from the pushing operations are sheds and enclosed cars that can capture approximately 90% of the emissions from this source. Traveling hoods and wet spray control systems are other means of controlling emissions from pushing operations.

Sheds can completely capture all of the emissions generated during a pushing cycle, as well as smoke emitted from coke oven doors. The shed has enough cubic capacity to hold all the emissions for a single push. These emissions are held until the exhaust fans have had enough time to direct all captured gas through an appropriate cleaning system. Wet scrubbers and baghouses are being used to clean the captured emissions and also the gases evolved from the oven doors. Enclosed cars surround the hot coke from the time the oven is pushed until the coke is quenched. The emissions are captured within the car until they are diverted to the selected gas cleaning device.

Traveling hoods are movable hoods incorporated into a large hood over the hot car from which the fumes generated during pushing are trapped and conducted to the selected gas cleaning system. Wet-spray systems are designed to prevent the escape of emissions during pushing. For instance, spray headers have a series of spray nozzles which are directed at the coke as it is pushed from the oven. This technology has not been proven successful.

Coke Quenching

During wet quenching operations, small releases of steam will be generated that contain coke dust and must therefore be controlled. Methods to aid in this process include increasing the area where the steam rises and therefore lowering the ascending speed of the steam, dust collection using inertial forces produced by baffle plates, and high-pressure spray nozzles that increase the effect of collision, coagulation, and washing. Particulate matter entrained with steam can be controlled with the use of mist suppressors installed in the quench station stacks.

Coke Plant Wastewater Treatment

Many contaminants present in coke plant wastewaters can be removed by conventional water treatment technologies. Grit and heavy solids are removed by using bar screens and settling tanks. Oil and tar removal is achieved by using differences in specific gravity. In a tank, oil is generally skimmed from the surface of the water while tar settles and is collected and removed from the bottom of the tank. Steam stripping is usually employed to remove ammonia, hydrogen sulfide, and hydrogen cyanide. Biological treatment is then used to remove the nitrogenous and carbonaceous compounds. The biological processes are usually aerobic and therefore require oxygen. The biologically treated water is then sent to a filtration system or a settling pond as a final polishing step before discharge.

Hazardous Materials Handling, Management, and Disposal

Coking is the most environmentally problematic operation in the iron and steel industry. However, proper handling, management, and disposal of the materials used in the production of coke can reduce the effect of emissions on the environment. In several areas of the coke production operation, e.g, charging, pushing, and quenching, proper handling and management of materials must be practiced to ensure a safe working environment and controlled emissions.

<u>Costs</u>

Relative costs of some waste minimization measures and treatment technologies are included in Table 3-1.

ltem	Capital Costs	O & M Costs
Regular door cleaning	None	Low
High grade coals	Low	Low
Sale of scrap	None	•
Coal preheating	Moderate	Moderate
Wet quenching pollution controls	Low	Moderate
Dry quenching pollution controls	High	Moderate
Recovery of crude tar from coke oven gas	High	High-4
Recovery of coke oven light oil from coke oven gas	Moderate	Low
Recovery of ammonia from coke oven gas	High	High
Recovery of phenol from coke	Moderate	Moderate
Removal of hydrogen sulfide	High	High
Wastewater treatment plant	High	High

 Table 3-1
 Coke Production Pollution Control Costs

Costs of high grade coals as compared to low grade coals

• Net savings

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* Cost of electrostatic precipitation included in estimate

⁴ Cost recovery not considered

3.6 Occupational Health and Safety Issues

Coke production creates health hazards through exposure to dust, coal carcinogens, metal fumes, carbon monoxide, noise, and heat. Safety hazards include injuries from operating heavy machinery, operating coke ovens, handling of hot coke, falling of heavy objects, obstruction of passageways, movement of locomotives, strains from lifting and pulling, burns, and eye injuries. These hazard: may be reduced or eliminated through implementation of good management practices and worker training.

The occupational health and safety issues for coke production are described in detail in the World Bank document <u>Occupational Health and Safety Guidelines</u> dated September 1988.

3.7 Global Overview of Discharge Requirements

Guidelines for air and water emissions from coke production are listed in Tables 3-2 and 3-3, respectively.

			Spain*							
Contaminant	France	Existing	New	Forecast (1980)	Brazil ⁴	Mexico	Canada ⁱ	Germany (Federal Republic)	UNEP	US
Solid Particles	5 - 100*				80 240*	4.24 - 6.74 ^s 100 ^h	100 ⁴ 50 ^k	90*	1	0.070° 0.040° 9
Sulfur Oxides (SO _x)	800	1000	500	500	80 365*	57 - 95* 10 ⁶		0.5 ¹	0.3	0.140 ^r 0.03'
Nitrogen Oxides (NO _x)	350 - 1300°					6.6 - 8ª 2250 - 9000			0.2	0.053'
Carbon Monoxide					10,000 ⁺ 40,000 ⁴	0.6 - 0.66* >)0 - 640*			0.3	9" 35"
Hydrogen Sulfide (H ₂ S) Benzene		2500	2000	2000				1.5'		500- 10,000*

Table	3-2	Coke	Prvdi	iction a	Air (Guidel	ines

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All values reported in mg/m³

Values associated with Cupola Furnaces

Values vary depending upon the fuel used

⁴ All values reported in $\mu g/m^3$ and are annual averages, except where noted

Maximum d.u/ concentration not to be exceeded more than once per year

Maximum hourly concentration not to be exceeded more than once per year

⁴ Values associated with combustion processes of fuel oil; values expressed as kg/m³

Values associated with combustion processes of natural gas; expressed as kg/10⁶m³

- All values reported in g/metric ton of coke
- Values associated with charging operations
- * Values associated with quenching operations
- ¹ All values reported in g/m³
- " All values reported in percent to be removed
- * All values reported in kg/tonne of product
- Value reported in g/dscm; indicates limit for particulate matter from thermal dryer gases for coal preparation plants; source also shall not exhibit 20% opacity or greater

Value reported in g/dscm; indicates limit for particulate matter from pneumatic coal cleaning equipment for coal preparation plants; source also shall not exhibit 10% opacity or greater

- ¹ Gases from coal processing and conveying equipment, coal storage systems, or coal transfer and loading systems processing coal shall not exhibit 20% opacity or greater
- ' Value in ppm; 24 hour average
- Value in ppm; simual arithmetic mean
- ¹ Value in ppm; annual arithmetic mean
- * Value in ppm; 8 hour average
- * Value in ppm; 1 hour average
- Fugitive emissions reported as ppm above background levels; equipment leaks resulting in concentrations above these levels must be repaired within approximately 15 calendar days; more detailed requirements in 40 CFR Part 61

Contaminant	U. S. [•] Maximum Daily	U. S.* 30 Day Average	Mexico ⁴ Daily Average	Mexico ^e Immediate	UNEP
pН	6 - 9	6 - 9	6 - 9	6-9	
Total Suspended Solids (TSS)	0.253	0.131	30	36	0. 06
Oil and Grease	0.0327	0.0109	50	70	
Ammonia-N	0.274	0.0912			0.03
Phenois	0.00451	0.00150			0.005
Oxygen					0.08
Demand					2.00
Benzene ^b	0.0000319				

Table 3-3 Coke Production Water Effluent Guidelines

All values except pH reported in kg/1000 kg of product
Also for Naphthalene and Benzo(a)pyrene
All values except pH reported in mg/l
All values reported in kg/tonne of product

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4. PIG IRON PRODUCTION IN THE BLAST FURNACE

4.1 Summary

See Section 1, Executive Summary.

4.2 Introduction

Pig iron refers to the metallic product of the blast furnace when it contains over ninety percent iron.

4.3 Manufacturing Process

Most of the iron produced in blast furnaces is transported to the steelmaking shop while it is still liquid and is then used directly for the manufacture of steel. The blast furnace is a large refractory lined chamber. It has a vertical stack superimposed over a crucible-like hearth. Iron-bearing materials (iron ore, sinter, pellets, mill scale, steelmaking slag, scrap, etc.), coke, and flux (limestone and dolomite) are charged into the top of the shaft. These materials react with large amounts of hot air introduced through openings at the shaft base to produce molten iron. The heated air burns the injected fuel and most of the coke charged in from the top to produce the heat required by the process and to provide reducing gas that removes oxygen from the ore. The molten iron and slag collect in the hearth at the base of the furnace and are cast from the furnace periodically by drilling a taphole in the clay-filled, iron notch at the base of the hearth. The molten iron flows into runners that lead to transport ladles. Slag flows through separate runners that lead to a slag pit or cinder pot.

4.4 Waste Sources and Characterization

Air Emissions

Significant air emissions result from boilers that generate power for blast furnace operation and from turbo blowers that compress the blast air.

Emissions from blast furnaces occur at several other points in the process. The major source of particulate emissions is the charging process. As the blast furnace gas leaves the top of the furnace, it contains dust particles varying in size from about 6 millimeters to a few microns. When the burden slips in the furnace, there are some relatively large lumps of coke and burden material blown out with the gas. The dust that is carried out of the top of the furnace, the flue dust, is made up of fine particles of coke and burden material and extremely fine particles of chemical compounds that are formed from reactions within the blast furnace and are condensed from the vapor phase. Before the blast furnace gas can be burned as a fuel in either the hot-blast stoves or the boiler house, it must be cleaned to remove most of the flue dust to prevent plugging and damaging of the cherers or burners and to keep the dust from being discharged into the atmosphere during combustion. Emissions may also occur if the facility uses a hot metal desulfurization process to remove sulfur from the molten pig iron. Finally, large

quantities of toxic carbon monoxide gas are produced in the processes of combusting carbon with oxygen to refine pig iron into steel.

Water Pollution

Cooling and cleaning waters in contact with gases containing the materials mentioned above can become laden with cyanides, fluorides, lead and zinc compounds, and dust particles.

Solid Wastes

For every metric ton of iron, the blast furnace produces 200 to 400 kilograms of slag, 25 to 50 kilograms of flue dust, and 2.0 to 3.0 metric tons of blast furnace gas. (United States Steel, page 541) The slag goes to a water-spray granulator, a dry slag pit, or a slag dump.

Blast furnace slag is handled in many different ways, depending upon space available around the furnace and on the type of product that is to be made from the slag. At most of the older blast furnaces, the slag was run into cinder pots, unlined, thimble-shaped, cast-iron or steel castings mounted on railroad cars. At other blast furnaces, the slag is run into pits next to the casthouse. There are usually two pits so that one can be excavated while the other is being filled.

Contaminants of Concern

Contaminants of concern from pig iron production in the blast furnace include the following compounds:

Air Contaminants	Water Contaminants
carbon monoxide	suspended solids
particulates	dissolved solids
ammonia	ammonia
sulfur	cyanide
	phenois

Environmental Impacts

The blast furnace gas is a valuable resource to the steel plant. However, before the gas can be used as fuel or emitted to the atmosphere, it must be cleaned. This gas can cause indoor and regional air pollution problems. When using water to clean the air, water contamination results. If this water is discharged to surface water or ground water without treatment, the solids and other contaminants may negatively affect aquatic life and drinking water sources.

4.5 Pollution Prevention and Control

Wastes from pig iron production can be minimized through techniques to improve blast furnace operating performance and increase efficiency. High hot-blast temperatures, accomplished by better stove-firing techniques and better stove-changing equipment, allow for decreases in the average coke rate and improvements in burden materials. The use of tuyere-injected fuels (pulverized coal) and the control of blast moisture make it possible for the blast furnaces to accept the higher hot-blast temperatures. With the development of techniques for increasing hot-blast temperatures to 1000°C to 1100°C and the need for controlling the flame temperature because of the type of burden materials in use, it was discovered that hydrocarbon fuels could be injected into the blast furnace through the tuyeres to control the flame temperature, increase the reducing power of the bosh gas and at the same time, replace some of the coke. The use of natural gas also reduces the air emissions from the burning of fuel.

Before the blast air is delivered to the blast furnace tuyeres, it is preheated by passing it through regenerative stoves that are heated primarily by combustion of the blast furnace off gas. In this way, some of the energy of the off gas that would otherwise have been lost from the process is returned to the blast furnace, thus decreasing the amount of fuel that has to be burned for each unit of hot metal. An additional benefit resulting from the lower fuel requirement is an increase in the hot-metal production rate.

Efficiency of the blast furnace is also increased when limestone and dolomite are mixed with the iron-bearing material to be sintered or pelletized. Oxygen may be used to enrich the blast and to increase hot metal production rates.

High-pressure operation through the use of a septum valve permits more air to be blown and therefore increases furnace production rates. Improved burden distribution in the furnace increases the fuel efficiency.

Depending on the manner in which molten blast furnace slag is cooled and solidified, four distinct types of by-products can result: air-cooled, expanded, granulated, and pelletized. Air-cooled slag has been used extensively as an aggregate in all types of concreting operations including pavements, bridges, railroad ballast, and other concrete products. On remelting and blowing with minor additions of other materials, slag can be converted into mineral wool with high insulating value. Expanded slag is used for manufacture of light weight concrete for structures, precast and prestressed shapes, and for manufacture of cement. Pelletized slag is used as a raw material in the manufacture of portland cement. The granulated slag is used in large tonnages in cement manufacture, highway construction, aggregate for concrete products, and conditioner to neutralize acid soils.

Improved productivity also may be achieved through screening of the charge before skip, better tap-hole practices, mud guns, and through continuous furnace casting. Self-fluxing pellets are a dramatic recent gain in blast furnace operating technology.

Treatment Technologies

Hoods and other dust catchers over the furnace and in the roof of the building are used to collect air emissions from blast furnace operation. The gas collected from the top of the furnace goes through the gas-cleaning system, and then a portion goes to fire the hot-blast stoves with the balance being used in other parts of the plant, for example, in the reheating furnace. Several stages are involved in cleaning the collected gas, including cyclones, to eliminate coarse dust, followed by high energy scrubbing and electrostatic precipitation. The use of dry electrostatic precipitators or bag filters, followed by a so called top pressure recovery turbine, is a recent development. Dry dust can be recycled to sintering and pelletizing plants, if the zinc, lead, and alkali contents are low.

High variations can occur in the level of pollutants in blast furnace wastewaters because of sudden changes in operating conditions within the furnace. In general, treatments for the water used to clean the blast furnace gas include settling tanks, filters, chemical treatment, clarifiers, chlorination, and carbon adsorption. Biological treatment is not appropriate due to low organic concentrations of the wastewater and the slow recovery from upsets.

Hazardous Materials Handling, Management, and Disposal

Molten iron must be managed properly to avoid contact with workers, the environment, and equipment. The coke used in the blast furnace also requires proper handling and management.

<u>Costs</u>

Relative costs of some waste minimization measures and treatment technologies are included in Table 4-1.

Item	Capital Costs	O & M Costs
Recycling of dry dust to sintering plants	None	2
Slag use in cement industry	None	8
High hot-blast temperatures	Moderate	Low
Settling tank	Moderate	Low
Filter	Moderate	Moderate
Cyclone	Moderate	Moderate
Wet scrubbing	Moderate	Moderate
Baghouse	Moderate(\$U.S. 10.09 per ACFM) ⁶	Moderate to High(5% to 15% of capital costs annually) ^b
Electrostatic precipitator	High	High

Table 4-1 Pig Iron Production Follution Control Costs

4.6 Occupational Health and Safety Issues

Health hazards related to pig iron production in the blast furnace include exposure to dust, coal carcinogens, metal fumes, carbon monoxide, noise, and heat. Safety hazards include injuries from falling heavy objects, obstruction of passageways and floors, movement of locomotives, wagons, bogies, furnace chargers, cranes and ladles and the loads suspended from them, strains from lifting and pulling, burns, and eye injuries. These hazards may be reduced or eliminated through implementation of good management practices and worker training. The occupational health and safety issues for pig iron production in the blast furnace are described in detail in the World Bank document <u>Occupational Health</u> and <u>Safety Guidelines</u> dated September 1988.

4.7 Global Overview of Discharge Requirements

Guidelines for air and water emissions from pig iron production are listed in Tables 4-2 and 4-3, respectively.

			Spain ⁴				Germany					
Contaminant Fran	France	Existing	New	Forecast (1980)	Brazil	Mexico	(Federal Republic) ^d	UK4	Japan*	Sweden*	UNEP*	US
Solid Particles ^b	0.120 °	200	100	100	80 240 ⁴	4.24 - 6.74° 100'	20 50	460	0.10	0.3	2	150° 50°
Sulfur Oxides (SO _x)	800*	1000	500	500	80 365 ^r	57 - 95° 10'					0.2	0.140° 0.03°
Nitrogen Oxides(NO ₂)	350 - 1300°					6.6 - 8º 2250 - 9000'					0.2	0.053*
Carbon Monoxide					10,000 ⁴ 40,000*	0.6 - 0.66 ^k 500 - 640 ⁱ					5	9" 35"
Hydrogen Sulfide (H ₂ S)		2500	2000	2000								

Table 4-2 Pig Iron Production Air Guidelines

- Values reported in g/Nm³
- Values are associated with blast furnaces; values expressed as mg/m³
- ⁶ Values vary depending upon the fuel used; values expressed as mg/m³
- ⁴ Ail values reported in mg/m³
- [•] All values reported in μ g/m³ and are annual averages, except where noted
- ¹ Maximum daily concentration not to be exceeded more than once per year
- ⁴ Maximum hourly concentration not to be exceeded more than once per year
- * Values associated with combustion processes of fuel oil; values expressed as kg/m3 fuel oil
- ¹ Values associated with combustion processes of natural gas; expressed as kg/10⁴m³ natural gas
- ¹ Values associated with blast furnaces and basic oxygen furnaces
- ^k All values reported in kg/ton
- ¹ All values reported if gases flared
- * Ambient values reported in µg/m³ of PM-10 (particulate matter 10 microns or smaller in diameter); 24 hour average
- Ambient values reported in µg/m³ PM-10 (particulate matter 10 microns or smaller in diameter); annual arithmetic mean
- Value in ppm; 24 hour average
- * Value in ppm; annual arithmetic mean
- * Value in ppm; annual arithmetic mean
- ^r Value in ppm; 8 hour average
- Value in ppm; 1 hour average

	U. S. •	U. S. •	Mexico	Mexico	
Contaminant	Maximum Daily	30 Day Average	Daily Average	Immediate	UNEP
рH	6 - 9	6 - 9	6 - 9	6 - 9	
Total Suspended	0.0782	0.0260	30	36	0.24
Solids (TSS)					
Oil and Grease			50	70	
Ammonia-N	0.161	0.0537			0.08
Phenols	0.00626	0.00210			
Lead	0.000263	0.0000876			
Zinc	0.000394	0.000131			
Oxygen Demand					0.16

Table 4-3 Pig Iron Production Water Effluent Guidelines

All values except p:1 reported in kg/1000 kg of product
All values except pH reported in mg/l
All values reported in kg/tonne of product

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5. DIRECT REDUCTION

5.1 Summary

See Section 1, Executive Summary.

5.2 Introduction

In direct reduction (DR), iron ore is reduced in the solid state by a reducing agent such as methane. The product is known as sponge iron. The success of this process has been made possible by two technological developments of recent years: post-combustion, which speeds up the reaction process in steelmaking furnaces; and ladle metallurgy, which makes it possible to tailor molten steel to end-use specifications outside of the melting furnace. DR's share of world iron production was in 1991 about 4%.

5.3 Manufacturing Process

There are gas-based and coal-based DR. The coal-based process has low productivity and is only applied at small scale. Gas-based direct reduction needs secure supplies of inexpensive natural gas and high quality iron-bearing material to be economically viable. Therefore, predominant steel production route most likely will remain the coke oven, blast furnace, basic oxygen furnace, and scrap-based electric arc furnace, unless advances in smelting reduction can change that scenario.

Advantages of direct reduction include the elimination of coke ovens and blast furnaces, the reduction in necessary plant size, and the possibility of using local energy_sources. Direct reduction permits flexibility in steelmaking with the use of scrap and direct reduced iron. Sponge iron is virtually free of the unwanted residual alloys or tramp elements inherent in scrap.

Coal-based DR is usually achieved by the rotary kiln process. Although there are many variations within both coal and gas-based DR they all employ the same basic idea of reducing the iron ore charge by a countercurrent flowing reducing gas.

Gas-based DR uses variations of the shaft furnace process. Each process has its own unique features, however the general scheme is as follows. The ore is charged at the top of the furnace where it is heated and reduced. This is known as the reduction zone in which an ascending stream of hot reducing gas introduced at the bottom of the reduction zone reacts with the descending iron oxides. The direct reduced iron is cooled by a recirculating, non-oxidizing gas mixture in the lower portion of the shaft known as the cooling zone. The reducing gas is produced from a mixture of natural gas and clean off-gas from the reduction process.

In the coal-based rotary kiln process, a blend of pelletized or lumped iron ore and limestone is charged into a refractory-lined, rotary kiln. The charge passes through the kiln while reducing gas is passed in a countercurrent direction. The kiln contains a preheat zone, a reduction zone, and a cooler. Once the iron has been reduced, it can be shipped in its present state or it can be melted into liquid steel with an electric arc furnace. The electric arc furnace is described in Section 6.0. In converting the iron to liquid steel, the content of various impurities is reduced or removed, depending on quality requirements.

5.4 Waste Sources and Characterization

Air Emissions

The main air pollutants from direct reduction include dust, sulfur oxides, nitrogen oxides, and possibly fluorides. Dust is generated from the charging and discharging of raw materials and from the flue gases from the heat recuperators. Sulfur is introduced by the ore to be reduced, by the reducing agent (natural gas or coal), and the heating agent. Nitrogen oxides are emitted in all combustion processes. Fluorides can become a problem if initially present in the raw iron oxides.

Water Pollution

There are two principal sources of water pollution from the direct reduction process; indirect contact cooling water and water used in scrubbing operations.

<u>Solid Wastes</u>

Solid wastes arise at various points in the direct reduction process. Fume and water treatment systems produce solid wastes containing dust, sludges, sulfates from the desulfurization processes, and carbon and dolomite wastes from the rotary kiln process. The process also creates iron ore dusts, pellet dust, screenings, and broken refractory parts.

Contaminants of Concern

Contaminants of concern from direct reduction steelmaking include the following compounds:

Air Contaminants	Water Contaminants
fugitive dust particles potassium and sodium sulfates (if oil is used as a fuel) lead sulfur dioxides nitrogen oxides gaseous fluorine compounds temperature	fines (usually recycled) phenol temperature pH oil and grease cyanide tar tin
	zinc

Environmental Impacts

The impacts on air from direct reduction include the release of dust from charging operations and from charge and product transportation. Surface waters are used in process flows, as routes for transporting materials and as receptacles for process discharges. Discharge of process waters to the ground water aquifer and use of ground water as process flow can greatly affect ground water. Leachate from solid wastes can impact ground water. Impacts on land result from disposal of fines or scalings to landfills and from land application of process discharges.

5.5 Pollution Prevention and Control

Direct reduction reduces many of the environmental concerns associated with traditional steelmaking processes. The size of the direct reduction plant is usually smaller than the traditional steel mill and the discharge of pollutants to air or water is reduced. Coke production ovens are not a prerequisite for direct reduction steelmaking and, therefore, the wastes associated with coke oven operations are eliminated. The number of by-products in the form of solid, liquid, or gas is greatly reduced. Solid wastes are either iron ores and products or desulfurization products. Iron ores and products can be easily recycled while desulfurization products are inert and can be safely disposed. Natural gas is the fuel sources, and it is economical to desulfurize the gas before use.

Treatment Technologies

Wastes are produced during direct reduction that must be treated prior to ultimate disposal. The treatment technologies most commonly applied to direct reduction processes are described below.

Gas-based Processes

Wet scrubbing is used for gaseous emissions. The scrubbers are usually located at the exits of the reduction furnace stack. Dedusting systems are employed to capture and control particulate emissions. Contact wastewater is usually cleaned by a gravity filter. Sanitary water uses biological treatment to reduce any contamination. Surface water is usually cleaned by a rail buffer bin and sand filtration. Thickeners and neutralization are also commonly employed.

Rotary Kiln Processes

Scrubbing, electrostatic precipitation, bag houses, or cyclones can be employed in dust emission problems. Oxidation of combustibles under controlled conditions is often practiced. Thickeners and neutralization can be used to treat water streams.

Hazardous Materials Handling, Management, and Disposal

Proper management of large volumes of natural gas must be considered to prevent explosion and fire. Proper materials of construction should be implemented in the design of the plant to achieve safe operating conditions.

Handling of the charging materials to minimize dust emissions should be practiced. Practices to handle the iron must incorporate the elevated temperatures that exist in the material. Proper lining of the direct reduction units must be designed to minimize gaseous emissions and temperature radiation.

<u>Costs</u>

Relative costs of some waste minimization measures and treatment technologies are included in Table 5-1.

ltem	Capital Costs	O & M Costs
Eliminated need for coke ovens	None	1
Water sprays	Low	Low
Gravity filtration	Moderate	Moderate
Biological treatment	Moderate	Moderate
Cyclone	Moderate	Moderate
Baghouse	Moderate	High
Wet scrubbing	High	High
Electrostatic precipitation	High	High

 Table 5-1
 Direct Reduction Pollution Control Costs

5.6 Occupational Health and Safety Issues

Health hazards related to the direct reduction process include exposure to dust, metal fumes, carbon monoxide, noise, and heat. Safety hazards include injuries from operating heavy machinery, falling heavy objects, obstruction of passageways, movement of locomotives, strains from lifting and pulling, burns, and eye injuries. These hazards may be reduced or eliminated through implementation of good management practices and worker training.

The occupational health and safety issues for direct reduction are described in detail in the World Bank document <u>Occupational Health and Safety Guidelines</u> dated September 1988.

5.7 Global Overview of Discharge Requirements

Guidelines for air and water emissions from direct reduction are listed in Tables 5-2 and 5-3, respectively.

		Spain*								
Contaminant	Existing	New	Forecast 1980	Brazil	Mexico	Canada ^b	Japan	Sweden	UNEP	US*
Solid Particles				80 240	4.24 - 6.74c 100 ^r	120* 70*	200 ⁴ 100 ⁴	0.6k 0.3'	0.5	150* 60 ⁴
Sulfur Oxides (SO ₂)	1000	500	500	80 365°	57 - 95° 10 ⁴	300* 60 ⁴	.226 ¹ 106 [#]		0.2	365* 80*
Nitrogen Oxides (NO,)					6.6 - 8ª 2250 - 9000	200* 100*	80 - 110 ⁱ		0. i	100*
Carbon Monoxide				10,000 ^c 40,000 ^c	0.6 - 0.66 ^e 500 - 640 ^f				15	

 Table 5-2
 Direct Reduction Air Guidelines

* All values reported in mg/m³

^b Ali values reported in $\mu g/m^3$ and are annual averages, except where noted

⁶ Maximum daily concentration not to be exceeded more than once per year

Maximum hourly concentration not to be exceeded more than once per year

* Values associated with combustion processes of fuel oil; values expressed as kg/m³

^f Values associated with combustion processes of natural gas; expressed as kg/10⁶m³

4 hour average

Annual arithmetic mean

1 hour average

¹ All values reported in kg/ton

^k Values associated with existing plants

¹ Values associated with new plants

Table 5-3 Direct Reduction Water Effluent Guidelines

Contaminant	Mexico ^e Daily Average	Mexico ^a Immediate	UNEP
рН	6 - 9	6 - 9	
Total Suspended Solids (TSS)	30	36	0.07
Oil and Grease	50	70	
Oxygen Demand			0.20

All values except pH reported in mg/l

All values reported in kg/tonne of product

⁶ There are no discharge limitations for direct reduction operations in the U.S.

6. STEEL PRODUCTION

6.1 Summary

See Section 1, Executive Summary.

6.2 Introduction

Steel manufacturing can be performed in an electric arc furnace, a basic oxygen furnace, or an open hearth furnace.

6.3 Manufacturing Process

The electric arc furnace is a shallow depth, large diameter cylindrical refractory-lined shell with a removable cover. Electric arc furnaces receive iron, scrap metal, and fluxing materials. The electric arc furnace can be adapted to use molten iron in the charge. It uses essentially all cold metal, i.e., all scrap and directly reduced iron, as inputs. The economic advantages or disadvantages of the electric arc furnace over other furnaces are determined largely by the relative cost of fuels and scrap. The electric arc furnace does not require supporting coke oven, sinter strand, and blast furnace facilities.

In the electric arc furnace, electric power is the main source of heat, with graphite electrodes positioned above the cold charge to produce an arc that melts the scrap. Refining is carried out by a combination of the heat developed by the electrical resistance of the molten metal and the heat radiated from the arc. Either oxygen injection or an ore charge may be used as the principal source of refining oxygen.

The process of making steel in the basic-lined electric arc furnace can be divided into: 1) the melt-down period; 2) the oxidizing period; 3) the composition and temperature adjustment period; and 4) the tapping period. The first step in metal melting is to clean all organic compounds from the metal with solvents or through burning. After the metal is cleaned, it is placed in the electric arc furnace for melting. The metal is melted by heat generated by the electric current flowing among the electrodes and through the metal. The furnaces are charged by removing the lid or by using a door on the side of the furnace. During the melting process, the furnace remains closed. More metal and possibly some alloys may be added in a step termed back charging. This step also helps to adjust the carbon content. Oxygen is injected through an oxygen lance to dislodge slag and to adjust the chemistry and temperature of the metal. The metal and slag are then tapped by releasing the metal through the bottom of the furnace.

A basic oxygen process furnace is a large, open-mouthed vessel lined with a basic refractory material. The furnace is mounted on trunnions that allow it to be rotated through 360° in either direction. A typical vessel can have an opening 12 to 14 feet in diameter and be 20 to 30 feet high. Two types of basic oxygen furnaces are in general use. The most common type is the "top blown" furnace, in which oxygen is blown into the vessel through a lance inserted through the mouth of the furnace. The second type of furnace is "bottom blown". Oxygen in these furnaces is added through tuyeres (nozzles) in the furnace bottom.

The basic oxygen furnace is filled with scrap and molten iron that it converts to molten steel. This is accomplished through the introduction of high-purity oxygen that reacts with the carbon and silicon in the molten iron, removes these products, and provides heat for melting the scrap. After the oxygen blow is started, lime may be added to the vessel to provide a slag of the desired basicity. Fluorspar may also be added to achieve the desired slag fluid ty.

After the oxygen has been introduced, the furnace is turned down or tilted tc one side so hot metal samples and temperature readings can be taken. If the samples taken during the turndown show the need, oxygen can again be blown into the furnace. This additional oxygen is usually only added for a very brief period. The next step is to pour the molten steel out of the furnace into the teeming ladle that is used to pour the molten steel into the ingot molds. The last step is to pour the residual slag out of the furnace into a slag pot, after which the furnace is ready to begin the cycle again.

An open hearth furnace is a shallow, refractory-lined basin in which scrap and molten iron are melted and refined into steel. Scrap is charged to the furnace through doors in the furnace front and molten metal is charged by pouring from a lad!e through a trough positioned in the door. Melting heat is provided via gas burners above and at the sides of the furnace. Refining of the metal is accomplished by oxidation of the carbon in the metal and generation of a limestone slag that removes impurities. Most furnaces are equipped with oxygen lances to reduce the melting and refining times. Steel is removed from the furnace by opening a hole in the base with an explosive charge. Processing with an open hearth furnace typically requires 4 to 10 hours for each heating period. Open hearth steelmaking is almost an obsolete process. It is doubtful that another open hearth furnace will ever be built.

6.4 Waste Sources and Characterization

Air Emissions

During steelmaking, large quantities of air pollutants are generated. Emissions from the furnaces are particulates, dusts, fumes, carbon monoxide, organic compounds, sulfur dioxide, nitrogen oxide, small quantities of chlorides and fluorides, chromium, cadmium, zinc, lead, and other toxic metals. The highest concentrations of furnace emissions occur during charging, back charging, oxygen lancing, slag and molten metal removal, and when the furnace lid and doors are open. Emissions are also generated from raw material handling operations, e.g., particulates generated from the moving and storage of raw materials, and from metal cleaning operations. The presence of oil in scrap material fed to electric arc furnaces can result in heavy visible emissions.

Emissions are produced at the mouth of the basic oxygen furnace during the refining process. Emissions are also produced during the transfer of the hot metal to the teeming ladle, from charging the furnace with scrap and hot metal, and during the dumping of the residual slag and molten steel into the ingot molds.

Emissions from open hearth steel production vary considerably. Oxygen lancing increases emissions of dust and fumes. Exhaust gas drawn from the furnace passes through a slag pocket and a regenerative checker chamber. These emissions, mostly iron oxides, are then ducted to an electrostatic precipitator or wet scrubber. Other furnace processes produce fugitive emissions that are usually uncontrolled.

Water Pollution

Steelmaking wastewaters may be generated as a result of some of the gas cleaning operations. Pollutants in these wastewaters may include biological oxygen demand (BOD), chemical oxygen demand (COD), total suspended solids (TSS), oil and grease, and toxics.

Waters used for cooling and cleaning in steelmaking furnaces may have high solid concentrations, elevated temperatures, and may carry particulates, fluorides, and zinc compounds.

Solid Wastes

Slags are the primary source of solid waste from steelmaking operations. Specific output of slags from furnaces at different steel works varies between 70 and 170 kilograms per ton of liquid steel. Estimated production of steelmaking slags in the world in 1986 was 76 million tons. (Singhal, 1990) Baghouse dusts and oil sludges are also generated from steelmaking facilities.

Contaminants of Concern

Contaminants of concern from steelmaking include the following compounds:

Air Contaminants	Water Contaminants
particulates sulfur oxides lead and other heavy, toxic metals nitrogen oxides carbon monoxide	particulates lead and other neavy, toxic metals oil and grease

Environmental Impacts

Steelmaking activities may negatively impact ambient air quality through the escape of untreated and fugitive emissions from the furnaces and their control equipment. If the water used in wet gas cleaning systems is not treated properly, it may negatively affect the environment. Slag from steelmaking operations is a major source of solid waste and must be managed properly to prevent contamination to land.

6.5 **Pollution Prevention and Control**

Energy savings may be realized from recovering furnace off-gases and use of this gas for combustion purposes throughout the plant. Slags from basic oxygen and open hearth furnaces containing less than 4 percent free lime are used for on-site land filling and land reclamation, road building or ballast for railway tracks, and for construction of harbors, dams, and embankments. Slags with more than 4 percent free lime are recycled for iron-making or sintering or in the production of fertilizer where slag is ground and swelling is of no significance. Steelmaking slags are also used in acid soil as a conditioner. On a global scale, 65 percent of steelmaking slags are reused. (Singhal, 1990) Major international sources of basic oxygen and open hearth furnace slags in order of volume are the U.S., Japan, and France.

Treatment Technologies

While primary collection systems can handle most of the fumes and dust generated in steelmaking, small portions escape as fugitive emissions, particularly during intermittent operations such as charging and tapping, and these have to be controlled.

Before emission of furnace gases to the atmosphere, they are treated to remove particulates and waste gases. Various forms of energy recovery from the furnace gases are described below. Particulate emissions from raw material handling operations are also controlled by enclosing the major emission points and passing the air to baghouses.

Electric Arc Furnace

The cover of the electric arc furnace may be mounted with emission capture devices and ducts for conveyance to baghouses. Decarburization, dephosphorization, and desulfurization can all be achieved in the electric arc furnace. Gases such as hydrogen, oxygen and nitrogen may also be removed. Residual elements such as copper and tin can also be controlled. Emissions escaping from the furnace body are collected either by point source hoods, in large roof canopies, or in both. In most electric arc steel works, there is a need to collect both primary and fugitive emissions. Because the volume of gas that must be treated is so large, high intensity scrubbers are inappropriate and baghouses are generally used. Before treating the furnace exhaust gas it is advantageous to use it for preheating the scrap steel.

Electric arc furnace dust with a high zinc content (greater that 15 percent total zinc) comprises approximately 75 percent of all electric arc furnace dust and may be thermally treated for zinc recovery. Low zinc electric arc furnace dust may be treated through chemical solidification followed by landfill disposal.

Basic Oxygen Furnace

Recent technological developments have enabled increased recovery of the energyrich furnace exhaust gas for use in downstream processes. The new closed-type system involves tight hooding of the mouth of the vessel during the blowing period. The exhaust gas is first cleaned and then the CO gas is extracted. The removed dust contains appreciable amounts of steel and can be recycled to the sinter or pelletizing plants. In the older open-type system the gas was burned directly and then treated and discharged.

In open or closed combustion, the waste gases may be washed through high intensity scrubbers. Raw wastewaters from the scrubbers must then be treated. High efficiency electrostatic precipitators have been installed to allow greater energy recovery and improved dust recycling.

Open Hearth Furnace

Since open hearth furnaces are, for the most part, no longer constructed, they must be retrofitted to achieve pollution control. The use of electrostatic precipitators and roof monitors are appropriate.

Hazardous Materials Handling, Management, and Disposal

Electric arc furnace dust has been classified as a hazardous material under the United States Resource Conservation and Recovery Act (RCRA) because it may contain toxic levels of lead, zinc, cadmium, and hexavalent chromium. The zinc may be reclaimed. This material may be stabilized according to strict guidelines and landfilled.

<u>Costs</u>

Relative costs of some waste minimization measures and treatment technologies are included in Table 6-1.

ltem	Capital Costs	O&M Costs
Hooding	Moderate	Moderate
Baghouse	Moderate(\$US 10.00 per ACFM)*	High(10% to 15% of capital costs annually)
High intensity scrubber	High	High
Electrostatic precipitator	High	High

 Table 6-1
 Steel Production Pollution Control Costs

6.6 Occupational Health and Safety Issues

Health hazards related to steelmaking include exposure to dust, coal carcinogens, metal fumes, carbon monoxide, noise, and heat. Safety hazards include injuries from falling heavy objects, obstruction of passageways and floors, movement of locomotives, wagons, bogies, furnace chargers, cranes and ladles and the loads suspended from them, strains from lifting and pulling, burns, and eye injuries. These hazards may be reduced or eliminated through implementation of good management practices and worker training.

The occupational health and safety issues for steelmaking are described in detail in the World Bank document <u>Occupational Health and Safety Guidelines</u> dated September 1988.

6.7 Global Overview of Discharge Requirements

Guidelines for air and water emissions from steelmaking operations are listed in Tables 6-2 and 6-3, resp-ctively.

		Spain*							
Contaminant	Existing	New	Forecast (1980)	- Brazil*	Mexico	Germany (Federal Republic) [*]	Sweden	UNEP	US
Solid Particles	2 50 *	150	12 0*	80 240 ^r	4.24 - 6.74 ^b 100 ^c	150	0.3 ^k 0.6 ^l	0.5	m
Solid									
Particles:"									
Capacity 1 - 5 tonnes/hr	800	600	250						
Capacity > 5 tonnes/hr	600	300	150						
Solid Particles ⁴	200	150	120						
Sulfur Oxides (SO ₁)	1000	500	500	80 365'	57 - 95° 10'			0.2	
Carbon				10,000	0.6 -			0.1	
Monoxide				40,000ª	0.66 ⁶				
					500 -				
					640				
Nitrogen					6.6 - 8 ⁶			15	
Oxides (NO _x)					2250 -				
					9000'				

 Table 6-2
 Steel Production Air Guidelines

All values reported in mg/m³

• Values are associated with the manufacture of steel

Values are associated with electric arc furnaces

⁴ Values are associated with open hearth furnaces

* All values reported in $\mu g/m^3$ and are annual averages, except where noted

Maximum daily concentration not to be exceeded more than once per year

⁴ Maximum hourly concentration not to be exceeded more than once per year

Values associated with combustion processes of fuel oil; values expressed as kg/m³ fuel oil

Values associated with combustion processes of natural gas; expressed as kg/10⁴m³ natural gas

¹ All values reported in kg/ton

* Values associated with new electric arc, blast and basic oxygen furnaces

¹ Values associated with existing electric arc furnaces

 Reference 40CFR Part 60, Subparts N and AA for standards of performance for basic oxygen furnace emissions and electric arc furnace emissions, respectively

Mexico Immediate	UNEP
6.9	
36	0.07
50	0.07
70	
36	
20	
	0.20
	Mexico ^b Immediate 6 - 9 36 70 36

 Table 6-3
 Steel Production Water Effluent Guidelines

7. ROLLING AND FINISHING OPERATIONS

7.1 Summary

See Section 1, Executive Summary.

7.2 Introduction

Rolling and finishing operations include a variety of processes which can produce a wide range of pollutants. Continuous casting, hot rolling, cold rolling, wire drawing, and acid pickling are discussed in this section. Continuous casting is normally considered belonging to steel making operations. This document has, however, chosen to follow the categorization adopted by the USEPA, see Table 1-4. Plating operations are not covered although these activities often take place at the same site.

7.3 Manufacturing Process

Continuous Casting

The continuous casting process is used to produce semi-finished steel directly from molten steel. Molten steel from the steelmaking operation is ladled into a tundish from where it is continuously cast. The semi-solidified steel is sprayed with water for further cooling and solidification.

Continuous casting has had a dramatic impact on steel production throughout the world. Of all the technologies developed and applied in the steel industry, continuous casting has had the greatest effect on improving the efficiency of material utilization. Smaller continuous billet casters, with ultra-high powered electric arc furnaces, were the critical technology development that created the phenomenon of the mini-mill – a small capacity plant (about a few hundred thousand tons per year) serving local markets.

Hot Rolling

Hot rolling is the steel forming process in which hot steel is transformed in size and shape through a series of forming steps to ultimately produce semi-finished and finished steel products. Four different types of hot forming mills (primary, section, flat, and pipe and tube) are used to produce the many types of hot formed steel products. Feed materials to the hot rolling process may be ingots, billets, blooms, or slabs. Fuel and water are also inputs to the operation.

Generally, the hot rolling mill process consists of slab-heating furnaces and the rolling mill. The rolling mill includes the following components:

- scale breakers which, through a combination of roll pressure and high pressure water jets, break up and remove surface scale before the size reductions begin;
- the rolling train, in which the required size reduction is achieved -- water is used as the coolant and lubricant during this process;

• the cooling area or run-out table in which the strip is cooled to a temperature suitable for handling and transfer.

Primary advantages of hot rolling result from the plasticity of the hot steel. This plasticity allows for high rolling speeds and large thickness reductions per set of rolls. Hot rolling is limited, however, in the thickness to which the steel can be rolled and in the quality of the surface produced.

<u>Cold Rolling</u>

For the requirements of very thin strip, or strip with a high quality finish, cold rolling must follow the hot rolling operations. The cold rolling process reduces the thickness of the hot rolled material by relatively large amounts with each stand in the mill. Electricity is required to run the cold mill and lubricant is necessary to achieve high surface quality and to prevent overheating of the product. Lubricants are comprised of water and different combinations of oils and additives. Products of cold rolling mills include rolled sheets.

Wire Drawing

After rods are properly heat treated, if required, cleaned, and coated, they are delivered to the wire-drawing equipment. Most wire that is drawn for three or more drafts is produced on continuous machines. Wire that is to be drawn for one or two drafts is produced on single of double-deck motor blocks. Wire with a diameter of 15.9 mm and coarser is drawn on horizontal bull blocks. However, there is still a considerable amount of wire produced on what are called wire drawing frames. The frame supports a single die, the power-driven block for drawing the rod through the die, and a drawbar for drawing the first few feet of the rod. One end of the rod becomes pointed, or tapered, so that it may be threaded through the die hole, which is somewhat smaller than the rod in section. Next, the die holder on the entering side of the die is filled with a lubricant so that in passing through the die the rod must first pass through the lubricant. The pointed end of the rod is now inserted through the proper die hole, where it is grasped by tongs attached to the drawbar, and drawn through far enough to be attached to the draw block. When this block revolves, it coils the wire about itself and thus continuously draws the rod through the die, thereby causing a fixed decrease in its sectional area and a proportional increase in its length.

Wet drawing is used for copper or tin coated wire. After coating, the wire is usually kept under water to protect it from the influence of the atmosphere. In subsequent wet drawing, the pay-off reel containing the wire is placed in a tub of water to which a special type of soap is usually added as a lubricant.

Acid Pickling

To prepare the steel for cold rolling or drawing, acid pickling is performed to chemically remove oxides and scale from the surface of the steel through use of water solutions of inorganic acids. While pickling is only one of several methods of removing undesirable surface oxides, this process is used most widely in the manufacture of wire and sheet and in mill products, due to comparatively low operating costs and ease of operation. Considerable variation in type of pickling solution, operation, and equipment is found in the industry. Types of pickling equipment may include batch, modified batch, semi-continuous, and continuous picklers.

Most carbon steels are pickled in sulfuric or hydrochloric acids. Most stainless and alloy steels are pickled in a mixture of nitric and hydrofluoric acids. Wastewater characteristics are dependent on the acid used and the operations employed.

When steel or iron materials are immersed in dilute inorganic acid solution, the reaction produces a solution of metal as a salt of the acid and the evolution of hydrogen. For instance, steel pickled in dilute sulfuric acid solution will produce reaction end products of ferrous sulfate and hydrogen.

7.4 Waste Sources and Characterization

Continuous Casting

Elevated ambient air temperatures result from continuous casting operations. Also, the direct contact cooling water vaporizes and carries particulates and hydrocarbons to the air.

Iron oxide in wastewaters arising from continuous casting, as well as from soaking, reheating, and rolling operations is termed mill scale and is relatively pure iron oxide with few contaminants other than oil. This mill scale, containing lubricating oil, and hydraulic fluids, can contaminate the water from continuous casting operations. The water that directly cools the steel and guide rollers contains particulates and roller lubricating oils. It must be cooled and cleaned before reuse or discharge.

Contaminants of concern from continuous casting include the following compounds:

Water Contaminants	
mill scale	
lubricating oil	
hydraulic fluids	

Hot Rolling

Elevated ambient air temperatures result from hot rolling operations. Also, the direct contact cooling water vaporizes and carries particulates and hydrocarbons to the air.

The predominant contaminants in contact wastewater from the hot rolling process are suspended solids, such as iron oxides, mill scale, hydraulic fluids, and oil and grease. Heat, transferred to the wastewater during cooling operations, may also be considered a contaminant. Indirect cooling waters require treatment to prevent fungal or bacterial growths, and corrosion in water circuits. The chemicals used must be removed before the waters are released to the environment.

Contaminants of concern from hot rolling operations include the following compounds:

Air Contaminants	Water Contaminants
sulfur dioxide	particulates
particulates	suspended solids
	oil and grease

<u>Cold Rolling</u>

Lubricants can volatilize from the product surface and from sprays during cold rolling liberating hydrocarbons to the air.

Scale and lubricating oil and hydraulic fluids can contaminate process water from cold rolling mills.

Contaminants of concern from cold rolling operations include the following compounds:

Air Contaminants	Water Contaminants
airborne organic compounds	mill scale
	hydraulic fluids
	lubricating oil
	oil and grease

Wire Drawing

Significant wastes are created from the steps required to prepare wire for drawing, heating, coating, pickling, not from the drawing operations themselves. For instance, elevated air temperatures are created during the heating of the wire. Acids enter the wastewater stream during the rinsing of rods after the scale removal and before the wire drawing process. As lime may be used to coat the rods before drawing, a high pH of the wastewater may result. Oil and grease are commonly found in wastewaters from operations to prepare wire for drawing. As mentioned above, wastewater characteristics are dependent on the acid used and the pickling operations employed.

Contaminants of concern from wire drawing operations include the following compounds:

Water Containments oil and grease acids Acid Pickling

Acid fumes are released to the air from pickling lines and may require some type of scrubbing.

Besides the wastewater used to scrub these acid vapors and mists, other major wastewater sources associated with acid pickling operations are spent pickle liquor and rinse waters. These wastewaters contain free acids and ferrous salts and other organic and inorganic impurities. Oil and grease are also commonly found in wastewaters from acid pickling operations.

Contaminants of concern from acid pickling operations include the following compounds:

Air Contaminants	Water Contaminants
acid fumes	acids oil and greases salts

Environmental Impacts

Environmental impacts to air from rolling and finishing operations result primarily from airborne particulates, from the volatilization of lubricants, and from acids. These compounds present an air pollution problem from both a nuisance and toxicological point of view.

If plant wastewaters are discharged to local waterways without adequate treatment, the mill scale, pickle liquor, and other contaminants will damage aquatic life and drinking water sources.

Mill scale and oils collected from settling ponds require disposal. If materials are not able to be recycled back into the steelmaking process, they must be landfilled properly to prevent leaching.

7.5 Pollution Prevention and Control

Continuous Casting

Continuous casting reduces pollution through the elimination of ingot-processing facilities such as soaking pits. Specifically, continuous casting has eliminated pollutant emissions and heat exposure to workers during casting, stripping, charging, and discharging in and out of soaking pits, primary rolling, and mold preparation. Moreover, the achievement of relatively high yields from crude steel to semi-finished products and greatly reduced energy consumption are an indirect contribution to environmental control in steelmaking. This technology is a good example of how environmental improvements could be achieved while, at the same time, reducing cost.

Hot Rolling

Ensuring the most efficient use of cooling water will both conserve water and limit the amount of pollutants able to be entrained in the air with the water vapor. This involves the proper design of spray nozzles and cooling water collection systems. Regulating the amount of oil used, i.e. lowering the oil-water ratio, also minimizes the entrainment of unnecessary oil to the wastewater stream. Segregation of sumps can prevent oil from mixing with large volumes of wastewater. Finally, positioning of oil collection sumps at locations to capture the maximum amount of oil should reduce uncollected oil and therefore reduce oil volatilizing and entering the plant wastewater.

Recycling of mill scale to the sinter plant reduces waste generation. Globally, approximately 90 percent of mill scale is directly recycled within the steel industry. Some mill scale is sold to cement manufacturers and some scale, typically the small size fraction as oil contaminated sludge, is landfilled.

Cold Rolling

Water used for lubrication and rinsing during cold rolling can be minimized through careful control and monitoring to ensure that only the necessary water is expended.

Wire Drawing

As mentioned in Section 7.2.4, significant wastes are not created from wire drawing operations, per se, but from processes used to prepare wire for drawing. These wastes may be minimized through carefully controlled coating and acid pickling processes.

Acid Pickling

The most efficient use of the acid is achieved when the pickling process is arranged for counter current flow, with several connected tanks of increasingly fresh acid. The strip first enters the tank with the mos^{*} spent acid and proceeds toward the tank with the fresh acid.

Sulfuric acid and hydroflouric acid can be recovered from the spent pickle liquor, thereby reducing purchase costs for acid and decreasing the amount of acid to be neutralized. Iron oxide can be recovered from the pickling sludge.

Treatment Technologies

Treatment technologies for wastewater from rolling and finishing operations may generally be classified as separation processes. Oil-water separation may be achieved mechanically through sedimentation basins or parallel plate separators. Oils collected from routine lubricant changes and leaks and oils of the same type recovered through skimming can be treated in a central purification plant. They may be subjected to settling, centrifugation, pressure filtration, or vacuum dehydration. Oil thus recovered can be reused as a lubricant with suitable additives or as fuel if it has suitable purity. Chemical flocculation-sedimentation, floatation, and filtration are also well known separation processes used in industrial waste treatment and may be used to remove mill scales, lubricating oils, and hydraulic fluids from wastewater.

Spent sulfuric acid can be treated chemically resulting in acid and metallic oxide recovery. The recovered free acid can be recycled to the pickling baths. For hydrochloric acid, treatment may involve controlled neutralization plus filtration to recover ferrite which is a valuable by-product. The remaining water with high solids may be further treated to recover fresh acid for recirculation to the pickling baths. Controlled neutralization of the spent liquor discharge is most important.

Hazardous Materials Handling, Management, and Disposal

Acids are the primary hazardous material used in rolling and finishing operations. Contact with these materials as well as inhalation of acid vapors should be avoided.

<u>Costs</u>

Relative costs of some wastes minimization measures and treatment technologies are included in Table 7-1.

ltem	Capital Costs	O & M Costs
Mill scale recycle	Low	Low
Sedimentation basins/scale pits	Low	Low
Oil skimming	Moderate	Low
Parallel plate separators	High	Moderate
Flotation	Moderate	Moderate
Chemical precipitation	Low	Moderate
Filters	Moderate	Moderate
Biological processes	Moderate	Moderate
Carbon adsorption	Moderate	High

Table 7-1 Rolling and Finishing Pollution Control Costs

7.6 Occupational Health and Safety Issues

Occupational health and safety issues related to rolling and finishing operations arise primarily from indoor air pollution problems. Inhalation of acid fumes and water vapor laden with contaminants can cause health problems. Respirators can serve to minimize exposure to these materials. During the rolling of steel slabs at high speeds, accidents can occur if the steel is misfed through the mills.

7.7 Global Overview of Discharge Requirements

Guidelines for air and water emission from rolling and finishing operations are listed in Tables 7-2 and 7-3, respectively.

		Spain					
Contaminant	Existing	New	Forecast (1980)	Brazil*	Mexico	UNEP	US
Solid Particles	200	150	150	80 240°	4.24 - 6.74 ^r 100*	0.6	
Sulfur Oxides (SO ₂)	1000	500	500	80 365'	57 - 95 ^r 10 ⁴	2	
Nitrogen Oxides(NO,)					6.6 - 8' 2250 - 9000*	0.5	
Volatile Organic Compounds							0.28 ⁹ 0.14k
Carbon Monoxide				10,000c 40,000 ⁴	0.6 - 0.66 ¹ 500 - 640 [#]	0.3	

 Table 7-2
 Rolling and Finishing Air Guidelines

• All values reported in mg/m³

All values reported in µg/m³ and are annual averages, except where noted

" Maximum daily concentration not to be exceeded more than once per year

⁴ Maximum hourly concentration not to be exceeded more than once per year

Maximum concentration over 8 hours not to be exceeded more than once per year

^f Values associated with combustion processes of fuel oil; values expressed as kg/m³ fuel oil

⁴ Values associated with combustion processes of natural gas; expressed as kg/10⁴m³ natural gas

All values reported in kg/tonne of product

All values reported in kg VOC/liter of coating solids applied for each calendar month

ⁱ For facility that does not use a pollution control device(s)

^b For facility that continuously uses an emissions control device(s) operated at the most recently demonstrated overall efficiency; guideline could also be 10 percent of the VOC's applied for each calendar month (90 percent emission reduction) for each affected facility that continuously uses an emission control device(s) operated at the most recently demonstrated overall efficiency; or a value between 0.14 (or a 90-percent emission reduction) and 0.28 kg VOC/liter of coating solids applied for each calendar month for each affected facility that intermittently uses an emission control device operated at the most recently demonstrated overall efficiency; or a value between 0.14 (or a 90-percent emission reduction) and 0.28 kg VOC/liter of coating solids applied for each calendar month for each affected facility that intermittently uses an emission control device operated at the most recently demonstrated overall efficiency

	Ū. S. *	U. S. *	Mexico	Mexicos
Contaminant	Maximum Daily	Maximum 30 Day	Daily Average	Immediate
pН	6 - 9	6 - 9	6 - 9	6 - 9
Total	0.0818*	0.0350°	30	36
Suspended	0.001254	0.000626d		
Solids (TSS)	0.0730 *	0.0313*		
	0.175 ^r	0.0751		
Oil and Grease	0.0350	0.0117*	50	70
	0.0005224	0.000209 ⁴		
	0.0313*	0.0104 ^e		
	0.0751 ^r	0.0250		
Zinc	0.000701*	0.000234°		
	0.0000634	0.00000214		
	0.00150	0.0005 ^r		
Lead	0.000526*	0.000175		
	0.0000094 ⁴	0.00000314		
	0.00113 ^r	0.000376		
Chromium	0.00292 ⁶	0.00117		
	0.0000209 ⁴	0.00000844		
	0.00015 ^r	0.0000501 ²		
Nickel	0.00263 ^b	0.000876		
	0.00001884	0.00000634		
N ammoniacal			30	36
as NH ₄				
Naphthalene	0.00000214			
Tetra	0.00000314			
chloroethylene				

 Table 7-3
 Rolling and Finishing Water Effluent Guidelines

* All values reported in kg/1000 kg of product

* Values associated with salt bath descaling

* Values associated with acid pickling operations

⁴ Values associated with cold forming operations

* Values associated with alkaline cleaning operations

^f Values associated with hot coating operations

* All values reported in mg/l

8. BIBLIOGRAPHY

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9. GLOSSARY

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Baghouse: Air pollution control device consisting of several fabric filters in parallel that can remove dry particles from a gas stream.

BOD: Biochemical Oxygen Demand is the quantity of oxygen used in aerobic stabilization of wastewaters and polluted waters and is often used to define the strength of the wastewater.

Calcination: Conversion of high flux containing materials such as limestone and dolomite into basic oxides of CaO and MgO to remove moisture and unwanted volatiles and to densify the material.

COD: Chemical Oxygen Demand is a measure of the oxygen equivalent of the organic matter susceptible to oxidation by a strong chemical oxidant.

Coke: The primary fuel in the blast furnace produced from the destructive distillation of coal.

Communition: Size reduction step in beneficiation operations designed to produce particles of a uniform size distribution by physical processes.

Cyclone: Air pollution control device in which a particulate-laden gas stream enters at the top and is forced downward into a downward spiral that uses centrifugal forces and inertia to remove the particles from the gas stream.

Electrostatic precipitator: Air pollution control device that uses a high intensity electric field created by electrodes of different surface areas to charge particles and then to collect them on the electrode of greater surface area.

Electrostatic separation: Process that uses high voltage to impose a surface charge on dry iron oxides passing over an electrically grounded drum causing the charged particles to conduct their charge to the drum and forcing the particles to fall into a collection basin at the bottom of the drum.

EPA: United States Environmental Protection Agency

Flocculation - sedimentation: Processes used to treat wastewaters. Flocculation is agitation of chemically treated water to force particles to collide and agglomerate into larger, heavier particles. Sedimentation is the removal of these solid floc particles from suspension by gravity.

Flotation separation: Process that uses the fact that, when certain reagents are added to water, suspensions of finely ground iron ore will exhibit an affinity to air and therefore will remain at the surface of the solution in a froth solution where the particles can be recovered by collectors.

Fluorspar: Slag fluidizer that has the chief function to aid in promoting rapid lime solution and to lower the melting point of the slag.

Flux: Substances used to form desired reactions with the impurities found in the metal-bearing material that would otherwise retard smelting.

Heavy-media separation: Process that uses the "sink-float" principle by which a mixture of particles of different specific gravities will separate when placed in a material having an intermediate specific gravity.

Jigging: Stratification of ore particles by alternating upward and downward pulsations of water.

Magnetic separation: Process that uses the magnetic characteristic of magnetite materials by passing these materials over a magnetic field to promote particle separation.

NOx: Nitrogen Oxides include Nitrogen Oxide (NO) and Nitrogen Dioxide (NO.) which are major air pollutants.

OECD: Organization of Economic Cooperation and Development

Ore beneficiation: All methods used to improve the chemical and physical characteristics of the ore (i.e., crushing, screening, blending, concentrating, and agglomerating)

Oxygen lance: Equipment used in oxygen steelmaking processes that provide pure oxygen at an elevated pressure to the furnace.

pH: Term used to express the hydrogen ion activity of a solution and is equal to the - $\log \{H^*\}$.

RCRA: Resources Conservation and Recovery Act, first passed into law in 1976.

Scrubber: Any wet collection device for fumes, mist, and suspended dusts.

Smelting: Any metallurgical operation in which metal is separated by fusion from the impurities with which it may be chemically combined or physically mixed as in ores.

SOx: Sulfur Oxides include Sulfur Dioxide (SO₂) and Sulfur Trioxide (SO₃) which are major air pollutants.

Suction hoods: Air pollution control device in which gas streams or particulates are encaptured by vacuum forces.

Trunions: Mechanical device upon which the electric arc furnace is mounted that enable the furnace to be rotated through 360 degrees.

TSS: Total Suspended Solids are any solid materials that can be settled out of solution.

Tundish: Large, shallow containers, located between the ladle and the continuous caster, for molten steel that provide a stable flow of metal into the mold by maintaining a constant ferrostatic head.

Tuyeres: Water-cooled openings located at the top of the furnace through which air enters the furnace.

UNEP: United Nations Environmental Programme

Venturi scrubber: Air pollution control device that uses the Venturi Effect by passing the contaminated gas through a chamber with a decreasing cross-sectional area to increase its velocity. The gas is then sprayed with high velocity water streams to help collect the dust in the water stream.

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WHO: World Health Organization.