

Pollution Reduction and No-Regrets Options in the Iron/Steel and Pulp/Paper Manufacturing Sectors

by

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Submitted to the Technology and Policy Program
in partial fulfillment of the requirements for the degree of

Master of Science in Technology and Policy

at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

June 1998

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Abstract

The existence of *No-Regrets* options, in terms of a trade-off between economic growth and pollution reduction, has been established. The investigation has been conducted for the manufacturing industry in the United States of America, specifically concentrating on the iron/steel and pulp/paper sectors.

A detailed description of the technology that is currently in widespread use in each sector has been provided. The emission points in the industrial processes have been identified. Effort has also been devoted towards a concise enumeration of the pollutants generated by each industry. In order to further establish the context, the current regulatory atmosphere in the U.S. has been described.

Proof of existence of no-regrets options is then provided by citing several examples of novel technologies in each industry that have been implemented world-wide on an industrial or pilot-scale. The pollution reduction achieved during *practical* implementation of these technologies, their energy consumption, and their operating/maintenance costs have been compared with those for the conventional technologies. This comparison has been used to demonstrate the existence of no-regrets options that can enable manufacturing processes to operate more efficiently, reduce pollutant emissions, and environmental compliance costs, while improving profitability and competitiveness.

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Acknowledgements

I take this opportunity to extend my sincere gratitude towards my advisor, Prof. Uday B. Pal. He has been a constant source of encouragement all through my three years at M.I.T. The advice he has provided will be invaluable to me in my future career. I am especially thankful to him for understanding my time constraints during the last semester. Receiving this second masters would not have been possible without his support.

I would also like to thank Dr. Richard Tabors for advising me through my tumultuous last semester in Technology and Policy. But for his help, I would have found it difficult to graduate in time.

I am thankful to my officemates, Ashish Agarwal, Dr. David Woolley and Dr. Stephen Britten for making my stay at M.I.T all the more exciting and enjoyable. I consider myself extremely fortunate to have met David and hope our relationship only gets better.

Finally, I would like to acknowledge the financial support received from the National Institute of Standards and Technology.

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1 Introduction

The environment has emerged as the issue of the 1990's with global warming, acid rain, and ozone depletion to name a few common topics. Over the years, the government and citizens have pressured companies to become environmentally responsible. The American manufacturing industry has been faced with an unrelenting wave of environmental laws and regulations. The Clean Air Act of 1970 and its amendments of 1977 and 1990, the Clean Water Act of 1972 and its 1987 amendments, the Resource Conservation and Recovery Act, the Superfund law and numerous lesser-known statutes have spawned thousands of environmental regulations. The U.S. congress has passed legislation requiring many companies to develop plans to reduce the effects of industrial activity on the environment.

The manufacturing industry has devoted substantial resources toward compliance with environmental laws and regulations. The passage of additional environmental legislation represents the potential for more costs and difficult environmental challenges. Industry perceives environmental restriction as strictly a further financial drain and there is great concern that policy measures aimed at reducing pollution could constrain future prosperity. However, one need not choose between economic growth and pollution reduction. A host of new technologies offer the means to simultaneously boost the economy and reduce emissions of environmentally harmful substances. Such technologies may offer industry the opportunity to evaluate projects that both have positive environmental effects and reduce costs. The present work shows examples of how pollutant reductions can be a beneficial side effect of profitable, cost-saving business choices.

Pollution reduction technologies in two different manufacturing industries have been examined, including the pulp/paper and iron/steel (as an example for the primary metals sector) industries. Figure 1-1 compares *total releases* across manufacturing groups that are significant polluters. Under the U.S. Environmental Protection Agency's (EPA) Toxic Release Inventory Program (TRI), total releases are defined as on-site discharges of a toxic chemical¹ to the environment. This includes emissions to the air, discharges to bodies of water, releases at the manufacturing facility to land, as well as disposal into underground injection wells. It can be seen that both the pulp/paper and primary metals industries are significant polluters, contributing 14% and 22%, respectively, of the releases shown in Figure 1-1. In addition, both these industries are important

contributors to the nation's economy (see Figure 1-2). Employing 1.3 million people, with the value of industry shipments at 353 billion dollars, the two industries together rank among the nation's top ten manufacturing industries.

The thesis has been divided into two major sections. The first section deals with the pulp and paper industry, followed by a discussion of pollution reduction options in the iron and steel industry. For each industry, first the technology that is in widespread use presently in the sector is analyzed. This includes a description of the materials and equipment used, and the processes employed. This provides a general understanding of the industry and also helps establish an inter-relationship between the industrial processes and the pollution-reduction technologies described in subsequent chapters.

Next, effort is devoted towards a concise enumeration of the pollutants generated by the industry. The emission points in the industrial processes, where pollutants may be produced, are also discussed. This enables identification of the process steps where significant pollution reduction opportunities exist, and therefore focuses attention on technologies that may provide the maximum benefit. The major environmental statutes and regulations that apply to each industry are also highlighted, in order to gauge the significance of compliance requirements for both the industries.

Finally, several examples of novel technical advances that offer the potential of reducing pollutant emissions in each industry are provided. For each technology, a detailed description of the pollution reduction achieved during practical implementation of the process has been provided. Data on modifications in industrial energy consumption through utilization of the new technologies are presented. The above, in combination with economic information on operating costs, prove the case that, for the industries studied, no-regrets options exist that enable manufacturing processes to operate more efficiently, reduce pollutant emissions and environmental compliance costs, while improving profitability and competitiveness.

¹ The TRI system includes over 600 pollutants.

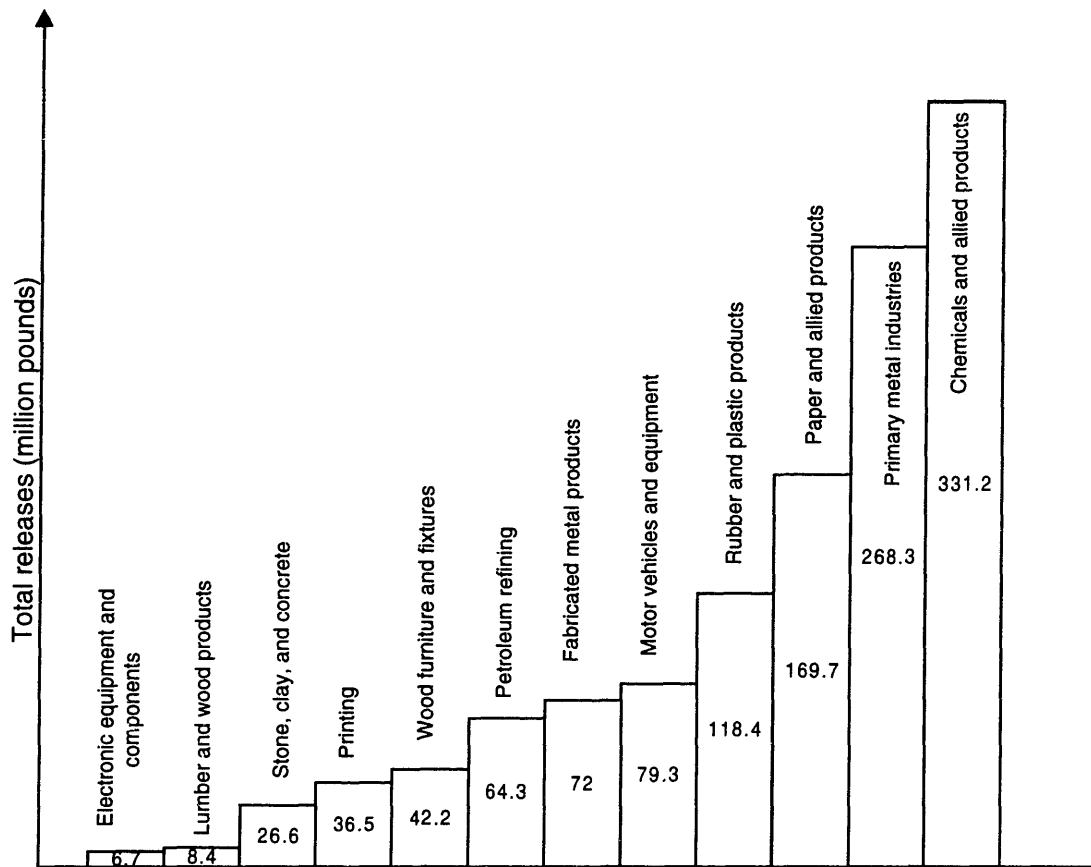


Figure 1-1 Total releases of toxic chemicals by the U.S. manufacturing industry (summary of 1993 TRI data) [1].

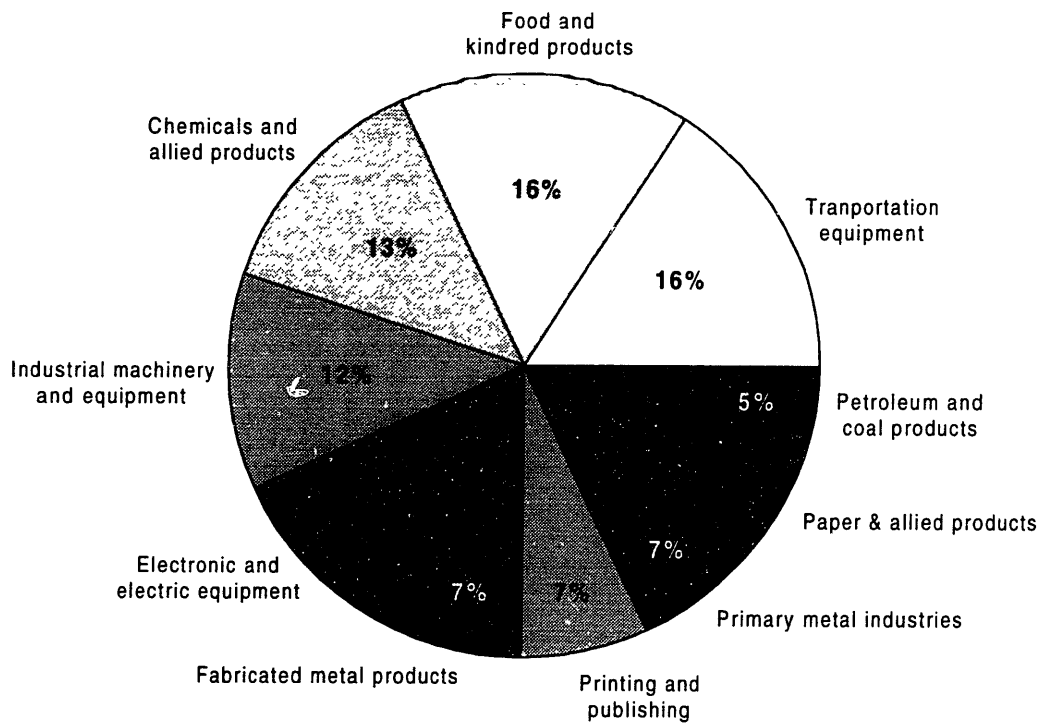


Figure 1-2 Manufacturing industry shipments for the top ten manufacturing industries, total industry shipments are 2821 billion dollars [2].

2 Conventional Technology: Pulp/Paper

2.1 Introduction and Role in the U.S. Economy

The United States has the world's largest installed pulp, paper, and paperboard production capacity, approximately 86 million air-dry² metric tons (ADMT) per year in 1994, or 30% of world capacity [3]. Based upon responses to the Environmental Protection Agency's 1990 National Census of the pulp and paper industry, the Agency estimates that there are approximately 565 manufacturing facilities located in 42 states [4]. The Bureau of the Census estimates that in 1995, 629,500 people were employed in the paper and allied products sector, with a payroll of \$22 billion [2].

The paper and allied products sector is described under Standard Industrial Classification (SIC) code 26. Manufacturing facilities in this sector can be classified as market pulp facilities that produce pulp only, non-integrated facilities that only manufacture primary paper products from pulp, and integrated facilities that produce the pulp they use for primary paper manufacture on-site.

Paper is manufactured by applying a watery suspension of cellulose fibers to a screen which allows the water to drain and leaves the fibrous particles in the form of a sheet. The watery fibrous substrate which is formed into paper sheets is called *pulp*. A pulp mixture is produced by digesting a material into its fibrous constituents via chemical, mechanical or a combination of chemical or mechanical means. The pulp is then transferred to a plant complex for manufacture into paper products. On a tonnage basis, chemical pulping methods produced approximately 85% of the pulp manufactured domestically in 1991, mechanical pulp 10% and semi-chemical (i.e. combined chemical and mechanical) 5% [5]. Due to its dominance, the present study concentrates on paper manufacture via chemical pulping means. In order to place the environmental profile of the industry in perspective, this chapter describes the manufacturing processes used in chemical pulping and subsequently, paper manufacture.

Figure 2-1 illustrates the primary processes used at a typical chemical integrated paper mill. The pulp manufacturing system includes fiber furnish preparation and handling, pulping, pulp

² Air-dry is a term applied to any pulp or paper sample whose moisture content is in equilibrium with the surrounding atmospheric conditions. In the industry, air-dry pulps are assumed to contain 10% moisture.

processing, chemical recovery, bleaching and stock preparation. Paper-making processes consist of wet-end operations, dry-end operations, paper drying, and finishing. All of these processes are briefly discussed in the following sections (details can be found in [5]).

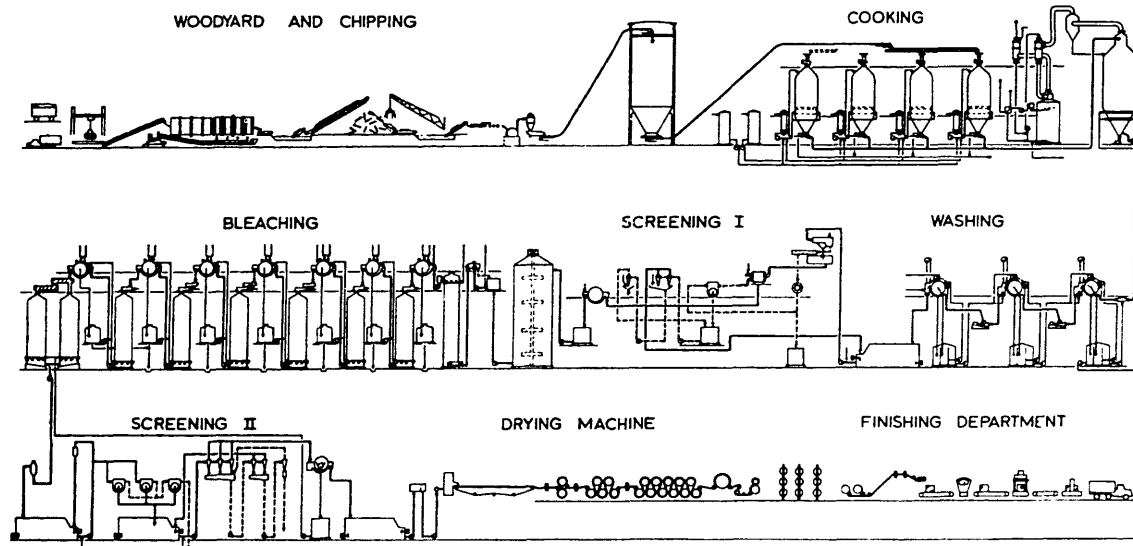


Figure 2-1 Simplified flow diagram of an integrated mill (chemical pulping, bleaching, and paper production).

2.2 Fiber Furnish Preparation and Handling

Furnish is the blend of fibrous materials used to make pulp. A wide variety of fiber furnish types are used in the industry, but the most widely used is wood. According to the 1990 EPA Census, wood furnish averages approximately 50% of pulp content industry-wide. Wood preparation entails converting wood into a form amenable to pulping. Tree-length logs are generally cut to manageable lengths using a slasher, followed by log washing and debarking. Debarked logs are generally chipped using blades mounted on a rotating disk. After chipping, wood chips are passed over vibratory screens to remove oversized chips and fines (the process is known as chip refining). After screening, chips are moved to subsequent operations via conveyors. Chip bins or silos may also be used to facilitate metering and blending of chips prior to pulping.

2.3 Pulping

2.3.1 Chemical Pulping

Pulping processes convert raw materials into fibers that can be formed into a sheet. In the case of wood furnish, the fibrous particles used to make paper are made of cellulose, a primary component of the cell walls of vascular plant tissues. The objective of chemical pulping is to degrade and dissolve away the lignin that binds the cellulose fibers together. In chemical pulping, the wood chips are cooked with the appropriate chemicals in an aqueous solution at elevated temperature (115 to 170°C) and pressure. The two principal methods are the kraft process and the sulfite process. Annual pulp production in the U.S. by each major process is shown in Table 2-1. Kraft pulping processes produced approximately 80% of all U.S. pulp tonnage during 1993 according to the American Forest and Paper Association (AFPA). The kraft process has come to occupy the dominant position because of advantages in recovery of pulping chemicals, pulp strength and is described below.

Table 2-1 Pulp production in the U.S. (1990) [5].

Pulping method	Production (million short tons)
Total sulfite	1,416
Total kraft	45,143
Semi-mechanical	3,828
Mechanical	5,854

The sequential steps in the kraft pulping process are shown schematically in Figure 2-2. The kraft process uses a sodium-based alkaline pulping solution (*white liquor*) consisting of Na_2S and NaOH . The white liquor is mixed with wood chips in a reaction pressure vessel known as a digester. The *digester process* is called cooking and can be either batch or continuous. In *batch* cooking, the digester vessel is filled with chips and enough liquor is added to cover the chips. A

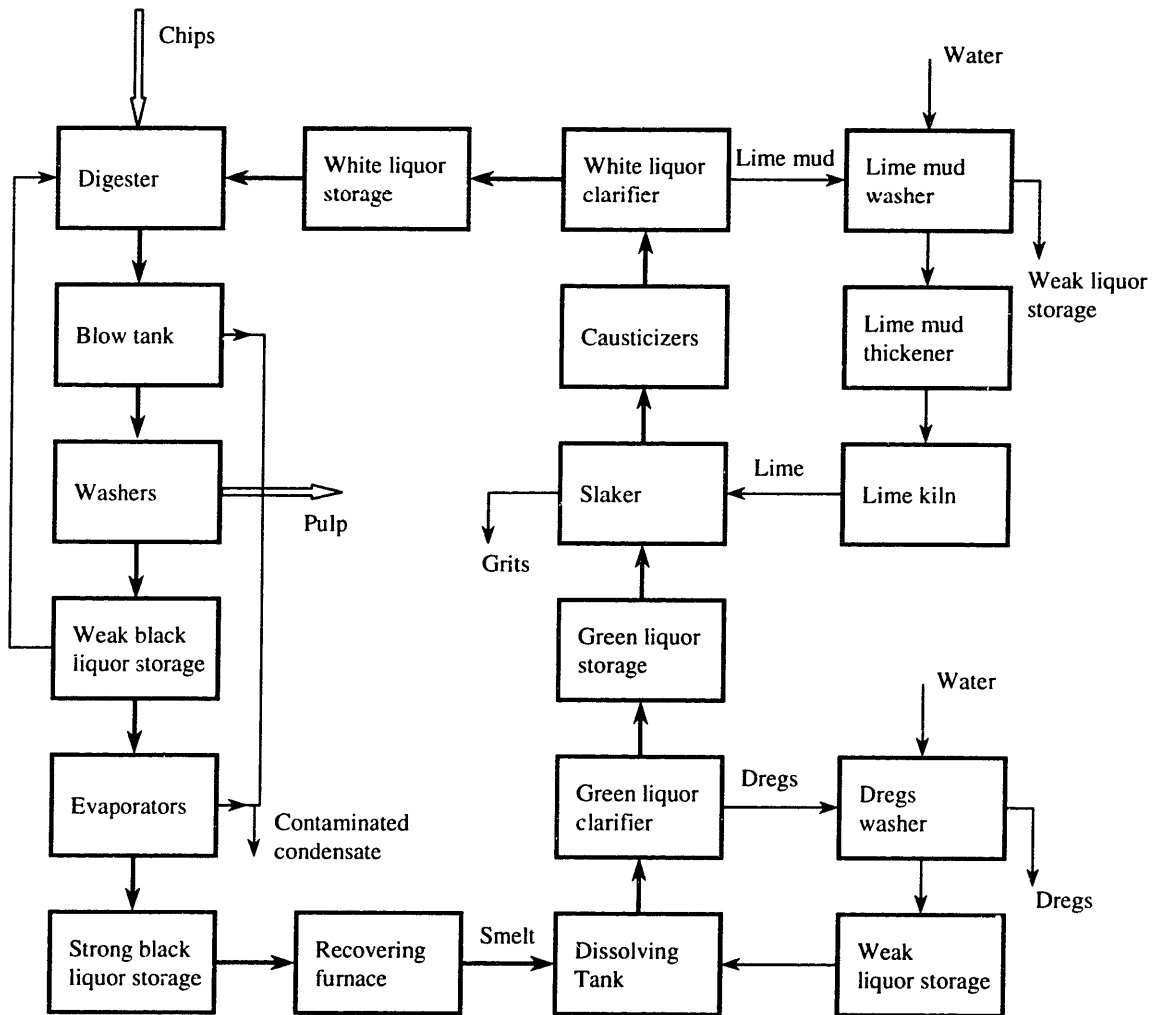


Figure 2-2 Schematic of the Kraft pulping process.

modern batch digester is provided with a circulation system and heat exchanger for bringing the contents to pulping temperature. A common circulation design draws liquor from the midpoint of the digester, through a heat exchanger, and distributes the return flow to the top and bottom of the digester vessel. Air and other non-condensable gases are relieved through a pressure control valve at the top of the vessel. The output products are separated fibers and residual *black liquor* that contains the dissolved lignin solids in a solution of reacted and unreacted pulping chemicals. After digestion, the contents are discharged into a blow³ tank. Steam released during the blow flashes⁴ from the liquor, while the cook spontaneously cools. A blow heat recovery system is used to recover the heat from the flash steam in a usable form. The flash steam from the liquor carries over to the top of the blow-tank accumulator, where it enters a direct-contact condenser along with cool water pumped from the bottom of the tank. The steam condenses, producing hot “contaminated” water. This “dirty” water is pumped through a heat exchanger to heat fresh, clean water for pulp washing; after which it is returned in a cold condition to the bottom of the accumulator.

The most widely utilized continuous digester is the Kamyr vertical downflow type. In *continuous* cooking, the chips are preheated in a steaming vessel before entering the digester to remove air and other non-condensibles. The preheated chips are soaked in the cooking liquor and are then deposited inside the continuous reaction vessel. The chip mass travels downward through the digester via gravity. After entering the digester, the mixture of chips and white liquor is heated as in batch digesters. The pulping reaction is stopped by extracting the hot residual liquor into a flash tank that supplies steam to the steaming vessel. The hot liquor is displaced by upward-flowing brown stock washer filtrate (see Section 2.3.2) which is injected near the bottom of the vessel and moves countercurrent to the chip flow to provide “diffusion washing”.

2.3.2 Pulp Processing

The primary pulp processing operations include defibering, deknottting, brown stock washing, pulp screening, and centrifugal cleaning. Defibering is akin to chip refining and is used to separate the fibers. Knots are generally defined as the fraction of pulp that is retained (as wood chips or fiber bundles) on a 3/8" perforated plate. Knots are removed prior to pulp washing. The cooked pulp from the digesters is then washed with the objective to:

³ Blow stands for discharge under pressure from a digester.

1. remove residual liquor that would contaminate the pulp during subsequent bleaching, and
2. maximize return of spent cooking liquor to chemical recovery.

The most common washing technology is rotary vacuum washing. The vacuum washer is a wire- or cloth-covered cylinder that rotates in a vat containing the pulp slurry. By means of internal valving, a vacuum is applied as the rotating drum enters the stock. A thick layer of pulp builds up and adheres to the wire surface as it emerges from the vat. Wash water is applied to displace the black liquor in the sheet as the drum continues to rotate. Finally, the vacuum is cut off and the washed pulp is removed from the mold.

In most pulp and paper processes, a pulp screening operation is required to remove oversized or unwanted particles from good papermaking fibers. Many types of screens are available, but they all depend on some form of perforated barrier to pass acceptable fiber and reject the unwanted material. All screens are equipped with a mechanism to continuously or intermittently clean the openings in the perforated barrier. In open screen rooms, wastewater from the screening process goes to wastewater treatment prior to discharge. In closed-loop screen rooms, wastewater from the process is reused in other pulping operations and ultimately enters the mill's chemical recovery system. Rejects from the screening process are either repulped or disposed of as solid waste. Centrifugal cleaning is used after screening to remove high specific gravity contaminants such as sand and dirt. Following low-consistency⁵ operations such as cleaning and screening, the stock is thickened, i.e. its consistency is increased, prior to the next process operation (bleaching).

2.3.3 Kraft Chemical Recovery System

The recovery of chemicals from the spent cooking liquor and the reconstitution of these chemicals to form fresh cooking liquor is necessary for viable economic operation of chemical pulp mills. These objectives are achieved through a series of steps, starting with the weak black liquor recovered from brown stock washing, screening, and de-knotting (see Figure 2-2). Residual weak black liquor is concentrated by *evaporation* to form “strong black liquor”. Water removal is usually carried out in multiple-effect evaporators, a series of evaporators operated at

⁴ Flashing is defined as the spontaneous boiling or cooling of a liquid caused by reduction of pressure below the vapor pressure of the liquid.

⁵ Consistency is defined as the weight percent of pulp in a pulp and water mixture.

different pressures so that the vapor from one evaporator body becomes the steam supply to the next evaporator. The strong black liquor from the evaporators is burned in a Tomlinson *recovery boiler*. Combustion air in the recovery furnace is used to evaporate residual moisture from the liquor solids and to burn the organic constituents in the liquor with maximum combustion efficiency. Carbon and carbon monoxide generated act as reducing agents to convert oxidized sulfur compounds to sulfides. The heat released during combustion of the organic fuel is used for steam generation and is also sufficient to melt the sodium salts. The product of the recovery furnace is a molten inorganic process *smelt*, consisting of Na_2S and Na_2CO_3 . The smelt flows by gravity through water-cooled spouts to a dissolving tank.

Recausticizing starts with the dissolving of furnace smelt in “weak wash” to form green liquor. The green liquor is then clarified to remove unburned carbon and inorganic impurities (dregs). The clarifying operation essentially consists of settling and decantation. The dregs are mixed with wash water and settled again in a dregs washer. The clear liquor containing the recovered soda chemical is known as weak wash. The clarified green liquor is subsequently reacted with CaO to form $\text{Ca}(\text{OH})_2$, which in turn reacts with Na_2CO_3 precipitating CaCO_3 and leaving an aqueous solution of NaOH and Na_2S (fresh white liquor). The white liquor is clarified to remove precipitated lime mud (CaCO_3), and is then ready to be used for cooking. The lime mud is converted to quick lime via *calcination* in a lime kiln for reuse in the recausticizing cycle.

2.3.4 Bleaching

Bleaching is defined as any process that chemically alters pulp to increase its brightness. Bleached pulps create papers that are whiter, brighter, softer, and more absorbent than unbleached pulps. Of the approximately 72 million tons of pulp used in paper production in the U.S. in 1993, 50% was bleached [6]. A bleach plant consists of multiple alternating stages of chemical bleaching and washing with water (see Figure 2-3). Typically, the chemical bleaching stages alternate acid and alkaline conditions. Cellulose is inherently white and does not contribute to color. It is generally agreed that lignin is principally responsible for imparting color to paper.

The early stages of bleaching may be considered as a continuation of the delignification⁶ process started by cooking. The later stages employ oxidizing agents to scavenge and destroy the residual color. The most common bleaching chemicals used are elemental chlorine, chlorine dioxide,

⁶ Delignification is the process of dissolving lignin that binds the cellulose fibers together.

sodium hydroxide, sodium or calcium hypochlorite, hydrogen peroxide, and oxygen. Table 2-2 lists the chemicals used and their abbreviations. Bleaching is usually carried out in five or six stages (e.g. C_DEDED). This sequence includes first-stage bleaching with elemental chlorine and chlorine dioxide, second-stage extraction with sodium hydroxide, third-stage bleaching with chlorine dioxide, fourth-stage extraction with sodium hydroxide, and fifth-stage bleaching with chlorine dioxide.

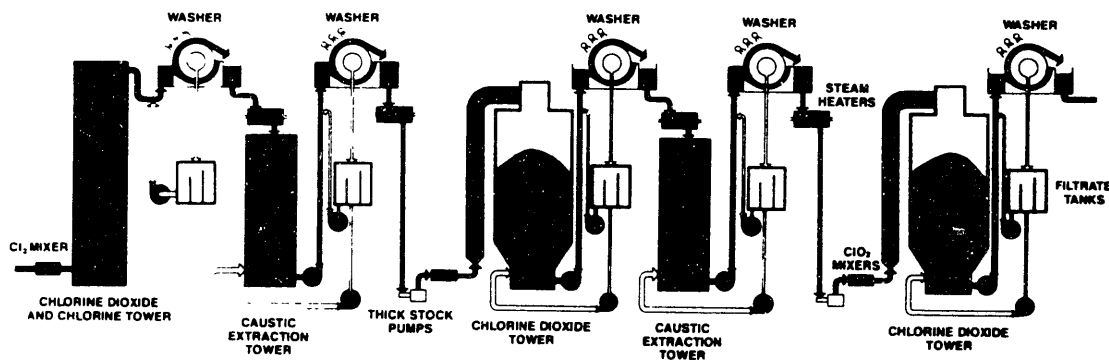


Figure 2-3 Flow diagram of a typical bleach plant.

Table 2-2 Chemicals used in pulp bleaching.

Chemical/Treatment	Short hand notation	Description
Chlorination	C	Reaction with elemental chlorine in an acidic medium
Alkaline extraction	E	Dissolution of reaction products with NaOH
Hypochlorite	H	Reaction with hypochlorite in alkaline solution
Chlorine Dioxide	D	Reaction with ClO ₂ in acidic medium
Peroxide	P	Reaction with peroxides in acidic medium
Oxygen	O	Reaction with elemental oxygen at high pressure in alkaline medium
-	C _D	Admixtures of chlorine and chlorine dioxide

Chlorination and caustic extraction are commonly employed as the first two stages in a pulp bleaching sequence. Their function is to delignify and purify the pulp. Chlorine reacts readily with lignin, rendering it water-soluble or soluble in alkaline media. Since the 1970's, the use of chlorine dioxide in the first chlorination stage has increased rapidly. This trend can be attributed to the high selectivity of chlorine dioxide in destroying lignin, without significantly degrading

cellulose. Efficient washing following the chlorination stage is important to minimize carry-over of acid effluent to the next stage. In the alkaline extraction stage, removal of chlorinated and oxidized lignin is accomplished by solubilization. The purpose of the latter acidic stages is to remove the color imparting groups on any remaining lignin. Caustic extraction in the later stages serves to remove the colored products. A significant bleaching development of the past decade is the oxygen-enriched extraction stage. This refers to the use of elemental oxygen in the first alkaline extraction stage of a conventional bleaching sequence. The oxygen selectively reacts with residual lignin on the pulp, thereby enhancing the removal of lignin and providing additional bleaching power. When oxygen is used in extraction, the bleaching stage is denoted as E_O .

Pulp bleaching is generally conducted in upflow or downflow bleach towers to provide retention time for the bleaching reactions, followed by vacuum washers to remove residual chemicals. Major auxiliary equipment includes various types of pumps for moving the stock and mixers for blending in steam and chemicals.

2.4 Stock Preparation

Stock preparation is the interface between the pulp mill and the paper machine. The basic objectives in stock preparation are to take the required fibrous raw materials (pulp) and non-fibrous additives, treat and modify each constituent as required, and then combine all the ingredients continuously and uniformly into the papermaking stock. The first step in stock preparation is *repulping* and it refers to any mechanical action that disperses pulp fibers into a water suspension. Typical devices for this purpose are called fiberizers, or deflakers. The pulp fibers are further “developed” or modified for formation into paper by a mechanical treatment called *refining*. Refining makes the finished paper stronger, more uniform, dense, opaque, and less porous. Refining refers to the mechanical action of rotating bars, opposing a stationary bedplate, on a circulating fiber suspension. The most common stock preparation refiners are those equipped with a two-sided rotating disc sandwiched between two stationary refiner plates. The gap between the plate surfaces determines the amount of work done on the pulp.

A wide variety of mineral and chemical agents are added to the stock, either to impart specific properties to the paper product or to facilitate the papermaking process. Most paper manufactured is *sized* to resist penetration by fluids. The action of a sizing agent is to provide the fiber surfaces with a hydrophobic coating. Rosin, a resin obtained from pines, is the traditional sizing agent applied. Starches, gums, and latexes are admixed with the stock to reinforce the fiber-to-fiber bonds and thereby improve the paper strength. Wet-strength resins (e.g. urea-formaldehyde) can

be added for making papers that must retain strength when wet, such as paper towels. Finely-divided white mineral fillers are added to papermaking furnishes to fill in the crevices between fibers, thus producing a denser, softer, brighter, smoother and more opaque sheet. The common papermaking fillers are clay, calcium carbonate, talc and titanium dioxide. Many papers are colored by the addition of inorganic and organic synthetic dyes and pigments.

2.5 Paper Making

Paper making consists of *wet end* operations, including the formation of paper sheet from wet pulp, and *dry end* operations, including the drying of paper product, application of surface treatments, and spooling for storage.

2.5.1 Wet End Operations

The processed pulp is converted into a paper product via a paper production machine, the most common of which is the Fourdrinier paper machine (see Figure 2-4). Wet end operations begin with the approach system, wherein, a fan pump serves to mix the stock with white water (white water is the drainage from wet stock, in pulping and papermaking operations) and deliver the blend to the flowspreader. The flowspreader takes the incoming flow from the fan pump and distributes it evenly across the width of the headbox. The function of the headbox is to discharge a jet of papermaking stock equal in width to the paper machine and at uniform velocity on to the moving forming fabric. A design of a modern headbox is illustrated in Figure 2-5. Shear forces applied through hollow perforated rolls (rectifier rolls) in the headbox are used to even out flow irregularities and to create turbulence to break up the fiber network. The headbox slice is a nozzle with an adjustable opening to give the desired rate of flow. A paper machine forming fabric is basically a cloth woven from polyester filaments. The meshes of the fabric permit the drainage of water while retaining the fibers. The fabric travels between two large rolls (see Figure 2-6), and various elements between the rolls (hydrofoils, vacuum rolls and vacuum boxes) serve the dual functions of wire support and water removal. Drainage, shear forces and turbulence along the fourdrinier wire form the fibers into a continuous matted web.

The paper web is transferred from the forming wire section and conveyed on specially constructed felts through a series of roll press nips and into the dryer section. The pressing operation may be considered as an extension of the water-removal process that was started on the wire. It is here that the fibers are forced into intimate contact so that fiber-to-fiber bonding develops during drying.

2.5.2 Dry End Operations

After pressing, the sheet is conveyed through the dryer section where the residual water is removed by evaporation. The wet web from the press section is passed over a series of rotating steam-heated cylinders where water is evaporated and carried away by ventilation air (see Figure 2-7). The wet web is held tightly against the cylinders by a synthetic, permeable fabric called a dryer felt. Paper drying can be viewed as a repetitive two-phase process. In the first phase, the sheet picks up sensible heat while in contact with the steam cylinder. In the second phase, the sheet flashes off steam in the open draw between the top and bottom cylinders, causing the sheet to spontaneously cool and become ready to pick up sensible heat again. Most paper machines have three to five independently-felted dryer sections, making this massive dryer section the most expensive part of a paper machine in terms of capital cost.

In the calendering section, the dry paper is passed through one or more two-roll nips, with the objective being to reduce paper thickness and obtain a smooth surface. The paper is pressed against the smooth roll surfaces with sufficient force to deform the paper plastically and replicate the calendar roll surface on to the paper. After drying and calendering, the paper is wound on to a reel for intermediate storage.

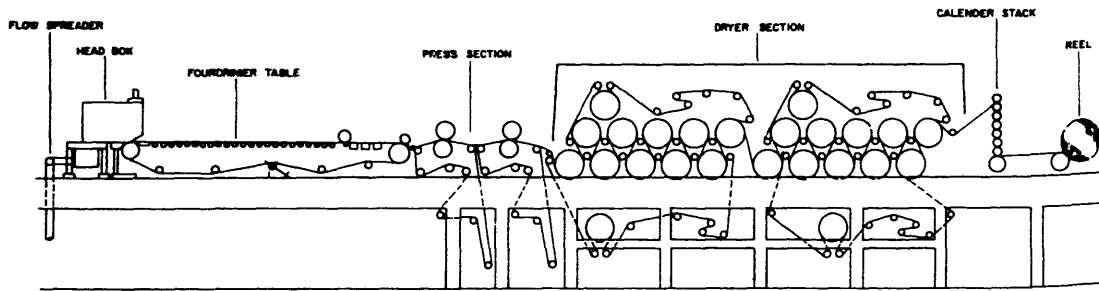


Figure 2-4 Fourdrinier paper machine.

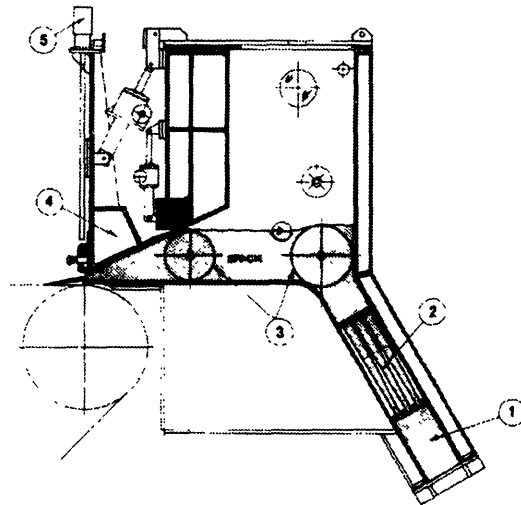


Figure 2-5 Schematic of a headbox illustrating (1) flow spreader with (2) tapered laterals, (3) rectifier rolls, (4) slice assembly, and (5) slice profile adjustment.

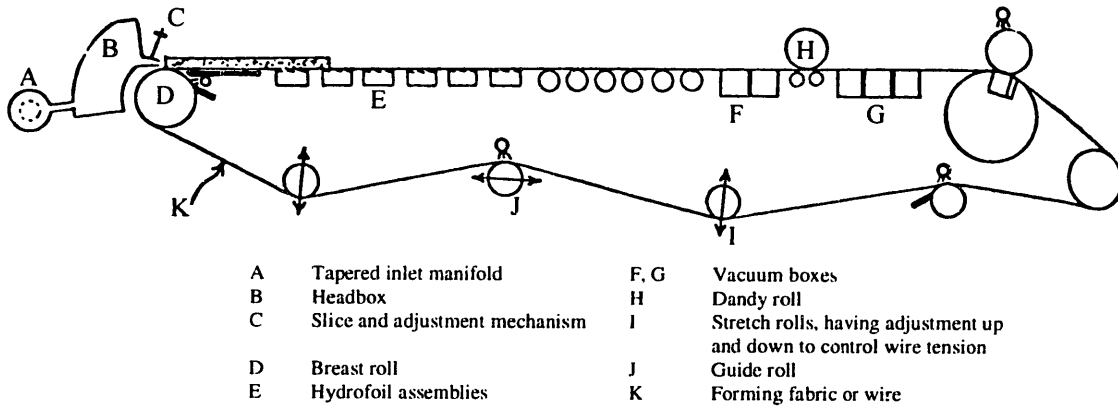


Figure 2-6 Diagram of fourdrinier wet end.

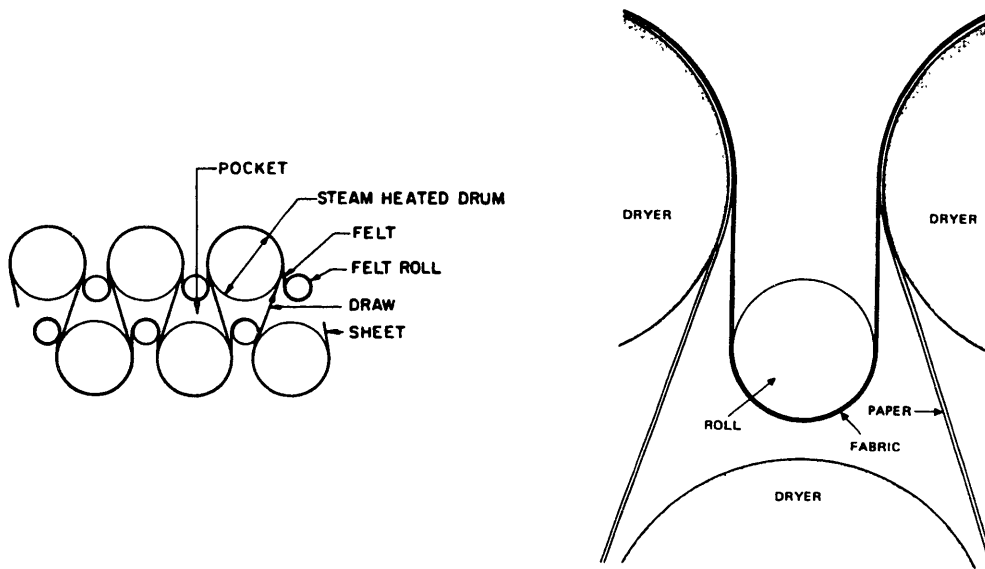


Figure 2-7 Schematic of a cylinder-drying configuration.

3 Pollution Profile and Regulations

Having described the essentials of pulp and papermaking technology, this chapter concentrates on the pollutants released and the major sources of pollution in the manufacturing sequence. This discussion, coupled with the technology description above, facilitates the identification of pollution prevention opportunities. The major statutes and proposed regulations for the pulp and paper industry, including limitations guidelines and standards for the control of water and air pollution have also been described.

3.1 Water Pollution

3.1.1 Water Use and Sources of Wastewater

The pulp and paper industry is the largest industrial process water user in the U.S.. In 1988, a typical pulp and paper mill used 61 to 64 m³ of water per ton of pulp produced [6]. Approximately 16 million m³ of wastewater are discharged daily by pulp and paper manufacturers [4]. It is important to note that pulping/bleaching operations and papermaking processes are the most significant dischargers of wastewater. Table 3-1 describes the production-normalized flow discharged to treatment by process area for kraft mills.

Table 3-1 Production normalized flow discharged to treatment (m³/metric ton of final product) [4].

Process area	Bleached kraft
Wood preparation	1.8 (2%)
Pulping	16.4 (18%)
Chemical recovery	8.8 (10%)
Bleaching	27.3 (30%)
Pulp drying	2.8 (3%)
Power operation	5.7 (6%)
Pulp handling	4.9 (5%)
Paper-making	23.2 (25%)

In case of chemical pulping, water is used as a solvent for cooking chemicals, as the pulp cooking medium, as pulp wash water, and as a diluent for screening, cleaning, and subsequent pulp processing. Wastewater sources from chemical pulping include digester relief and blow condensates, wastewater from the screen room, cleaners, thickeners, and spills from the digester area. Excess evaporator condensates and weak wash generated during recovery of kraft pulping chemicals are discharged to wastewater treatment. Primary water use in bleaching is for inter-stage pulp washing. The high chloride content of bleaching wastewaters (from mills that practice chlorine-based bleaching) makes them incompatible with pulping chemical recovery processes, resulting in discharge to wastewater treatment. White water from paper making is reused in stock preparation, on the paper machine, in the woodyard, brown stock washers and bleach line washers. Excess white water constitutes the discharge from paper making. Water reuse and recycle are common practices in most pulp and papermaking processes and Table 3-2 summarizes the important recycling paths for kraft chemical pulping mills.

Table 3-2 Wastewater sources and recycling paths for kraft chemical pulping mills.

	Wastewater sources	Water recycle (use)	Water recycle (source)
Wood preparation	Log conveyance, log washing and wet debarking	Wet debarking, chip washing	Screen room, white water, treated final effluent, evaporator condensates
Chemical pulping	Digester condensates, wastewater from screen room, cleaners, and digester area spills	Pulp washing	Screen room
Kraft chemical recovery	Evaporator condensates, weak wash	Recovery cycle to dissolve furnace smelt, final pulp washing	Weak wash, evaporator condensates
Bleaching	Inter-stage pulp washing, air emission control equipment	Bleaching washwater	Later bleaching stages, white water
Papermaking	White water from wet-end operations	Fiber recovery, machine showers, vacuum pumps	White water

3.1.2 Wastewater Characterization: Conventional Pollutants

Conventional pollutants have been defined under the Clean Water Act (CWA) of 1977. EPA has identified the conventional pollutants, 5-day *biochemical oxygen demand* (BOD_5) and *total suspended solids* (TSS), to be of concern in the pulp and paper industry [4].

BOD_5 is a measure of the tendency of an effluent to consume dissolved oxygen from receiving waters. High levels of BOD_5 in the effluent stream can deprive non-photosynthetic organisms of the oxygen they need to survive. High BOD_5 effluent is produced at many stages including: debarking, washing, cooking, condensing of spent liquors, and bleaching.

TSS consist of the non-filterable residue retained by a glass fiber filter. In a conventional integrated kraft mill, the solids load in untreated effluent consists mainly of: (1) dirt, grit, and fiber from wood preparation stages, (2) screen rejects and spills from the pulping area, (3) fiber and dissolved lignin solids from the pulp bleaching stages, and (4) fiber and additives washed from the early stages of papermaking.

The estimated industry wide discharge of conventional pollutants in 1990 is shown in Table 3-3.

Table 3-3 Industry-wide discharge of conventional pollutants (billion kg/yr.) [4].

	Direct discharging mills ⁷	Indirect discharging mills ⁸
BOD_5	0.18	0.91
TSS	0.27	1.37
Total	0.45	2.28

3.1.3 Wastewater Characterization: Priority and Nonconventional Pollutants

The Clean Water Act also identifies 126 toxic pollutants, commonly known as priority pollutants. Additional compounds not designated as priority pollutants, but that exhibit toxic effects to

⁷ Mills where effluent stream is discharged to the receiving water body.

⁸ Effluent stream is discharged to Publicly-Owned Treatment Works (POTWs), which are municipal wastewater treatment plants.

aquatic life and the environment are considered as nonconventional pollutants. Priority and nonconventional pollutants of concern in the pulp and paper industry include 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD), 2,3,7,8-tetrachlorodibenzofuran (2,3,7,8-TCDF), chlorinated phenolic compounds, volatile organic compounds (VOCs), adsorbable organic halides (AOX), chemical oxygen demand (COD), and color [4].

Chlorinated dibenzo-p-dioxins (CDDs) and chlorinated dibenzofurans (CDFs) are families of highly toxic and persistent chlorinated organic chemicals. In the pulp and paper industry, CDDs and CDFs are formed during pulp bleaching where chlorine and chlorine derivatives are used. 2,3,7,8-TCDD and 2,3,7,8-TCDF are CDDs and CDFs with chlorine substituted at the 2,3,7, and 8 positions and are considered more biologically active and more toxic than other CDDs and CDFs. VOCs are organic species that participate in the formation of photochemical oxidants. Derived from lignin and carbohydrates in the pulp, typical VOC emissions include terpenes, alcohols, phenols, acetone, and chloroform. Certain VOCs, including acetone and methyl ethyl ketone (MEK), are attributable to chemical pulping operations, while others, such as chloroform, are associated with bleach plant operations.

AOX is a measure of the total amount of halogens bound to dissolved or suspended organic matter in a wastewater sample. For pulp and paper mills bleaching with chlorine or chlorine-containing compounds, virtually all of the AOX present can be attributed to bleach plant operations. COD is a measure of the oxygen equivalent of the organic matter in a sample, as measured through sample oxidation using strong chemical oxidants. For chemical pulp and paper mills, COD is associated with pulping and bleaching operations. Color interferes with aquatic life by limiting light transmittance. For kraft pulp and paper mills, most of the effluent color is attributable to losses of black liquor and bleach plant extraction stage filtrates.

Table 3-4 summarizes total discharges (1992 levels) for the priority and nonconventional pollutants that EPA has selected for regulation.

3.2 Effluent Limitations Guidelines (Clean Water Act)

Existing effluent guidelines for different subcategories within the pulp and paper industry were promulgated by the EPA in 1982 and 1986. These regulations mainly focused on reducing conventional pollutants and are covered by 40 CFR⁹ Part 430. As part of a consent decree with

⁹ CFR – Code of Federal Regulations.

the Environmental Defense Fund and the National Wildlife Federation, EPA was to review the need for revised rulemaking applicable to dioxins and furans for the pulp and paper industry. The revised effluent guidelines are a key follow-up effort to implement this decree and have been summarized in this section. Reference [4] describes the guidelines in detail.

3.2.1 Best Practicable Control Technology Currently Available

Best Practicable Control Technology Currently Available (BPT) effluent limitations guidelines are based upon the average of the best existing performance, in terms of treated effluent discharged by facilities in an industry. BPT focuses on end-of-pipe treatment technology and such process changes and internal controls that are common industry practice. In establishing BPT, EPA considers the cost of achieving effluent reductions in relation to the effluent reduction benefits. The proposed BPT effluent guidelines apply to dischargers of conventional pollutants from existing sources to waters of the United States and are based on the average performance level of the best 50% of mills in an industry. Table 3-5 presents the BPT effluent limitations that EPA is proposing for the bleached kraft subcategory.

3.2.2 Best Available Technology Economically Achievable (BAT)

BAT effluent limitations guidelines represent the best existing economically achievable performance of plants in the industry. The factors considered in assessing BAT are the same as for BPT. However, BAT may include process changes or internal controls, even when these technologies are not common industry practice. The CWA establishes BAT as the principal national means of controlling the direct discharge of priority and nonconventional pollutants. Table 3-6 presents the BAT effluent limitations guidelines that the Agency is proposing for the bleached kraft industry. BAT limitations for 2,3,7,8-TCDD, 2,3,7,8-TCDF, VOCs, and chlorinated phenolics will be applied at the effluent from the bleach plant, whereas guidelines for AOX, COD, and color are applicable to the final end-of-pipe effluent.

Table 3-4 Total discharges for priority and nonconventional pollutants (as of 1992).

Pollutant	EPA estimated discharges
AOX (from chemical pulp mills that bleach)	51,100 kkg ¹⁰ /yr.
2,3,7,8-TCDD and 2,3,7,8-TCDF	410 g/yr.
Acetone, chloroform, methylene chloride, MEK	1530 kkg/yr.
Chlorinated phenolic compounds	282 kkg/yr.

Table 3-5 Proposed BPT effluent limitations guidelines (kg/kkg of product).

	BOD ₅	TSS
Continuous dischargers (Monthly Average)	2.19	3.89
Non-continuous dischargers (Annual Average)	1.57	2.72

Table 3-6 Proposed BAT limitations for papergrade kraft subcategory.

Pollutant	Bleach plant effluent		Final effluent
	Maximum for one day	Monthly average	Monthly average
2,3,7,8-TCDD	ND ¹¹	NA ¹²	NA
2,3,7,8-TCDF	359 ng/kkg	NA	NA
Chloroform	5.06 g/kkg	2.01 g/kkg	NA
Acetone	43.0 g/kkg	21.9 g/kkg	NA
Methyl ethyl ketone	3.81 g/kkg	1.75 g/kkg	NA
Methylene chloride	1.33 g/kkg	0.518 g/kkg	NA
Chlorinated phenolics	ND	NA	NA
AOX	NA	NA	0.156 kg/kkg
COD	NA	NA	25.4 kg/kkg
Color	NA	NA	76.3 kg/kkg

¹⁰ kkg – 1000 kg¹¹ ND – Non-detect value (a measurement below the level that can be reliably measured by the analytical method for the pollutant).¹² NA – Not applicable.

3.2.3 New Source Performance Standards (NSPS)

Industry has the opportunity to design and install the best and most efficient processes and wastewater treatment facilities at new mills. Accordingly, EPA has considered the best demonstrated alternative processes (for priority and non-conventional pollutants) and end-of-pipe treatment technologies (for control of conventional pollutants and additional control of certain priority and nonconventional pollutants) in proposing revised NSPS for pulp and paper mills. EPA considers best demonstrated processes to be those that result in the minimum generation of pollutants of concern in this industry, that can be used to produce the full range of products currently produced by existing facilities in the industry. Table 3-7 presents the Agency's selection of NSPS for bleached kraft mills.

Table 3-7 Proposed NSPS for bleached kraft subcategory.

Pollutant	Bleach plant effluent		Final effluent
	Maximum for one day	Monthly average	Monthly average
2,3,7,8-TCDD	ND	NA	NA
2,3,7,8-TCDF	329 ng/kkg	NA	NA
Acetone	12.0 g/kkg	6.09 g/kkg	NA
Methylene chloride	ND	NA	NA
Chlorinated phenolics	ND	NA	NA
BOD ₅	NA	NA	0.365 kg/kkg
TSS	NA	NA	0.383 kg/kkg

3.3 Air Pollution

This section provides a discussion of air emissions and its sources in the kraft pulp and paper industry. Major sources of air pollutant releases are at the pulping and bleaching stages. Major pollutants include reduced sulfur compounds, particulates, hazardous air pollutants (HAPs, see Section 3.4.2), and VOCs. SO_x, SO₂, and NO_x are also a concern. Table 3-8 presents the emissions for the various emission points during the pulping process.

Digester blow gases (source IDs 1 and 2) and digester relief gases (source ID 3) are a source of VOCs and reduced sulfur compound emissions. In addition to HAP emissions from process vents,

the wastewater produced by the digestion process (source ID 6) is a source of HAP emissions. Emissions also occur from brownstock washing (ID 4) as compounds entrained in the pulp and black liquor slurry volatilize. Pollutants are emitted from the evaporation process in the recovery of cooking chemicals by two basic mechanisms. Noncondensable gases containing pollutants that have been vaporized during the process of concentrating the cooking liquor are emitted from the evaporator vents (ID 5). Emissions also occur from the evaporator condensate streams due to the partitioning of certain compounds to the air from the liquid phase (ID 7).

Table 3-8 Typical emissions for kraft pulping facilities [7].

Emission point ID	Emission point	Emissions (g/Mg pulp, except where noted)				
		Total HAP	Total VOC (kg/Mg pulp)	Methanol	Acetone	TRS ¹³ (kg/Mg pulp)
1	Batch digester blow gas	100	2.4-4.4	6.2-91	1.5	2.37-4.02
2	Continuous digester blow gas	0.35-0.39	4-4.9	0.24-3	0.04-0.2	2.4-4.0
3	Digester relief gas	4	2.6-2.7	3	0.06	2.6-2.7
4	Brownstock washing ¹⁴	229-555	3.41-9.223	184-343	15.5-80	1.62-2.32
5	Evaporator	2-20	3.1-5.4	1.4-20	0.007-2	3.5
6	Digester blow condensate	100-620	0.34-1.2	100-590	1.2-4.3	0.33
7	Evaporator condensates	170-3040	0.17-3.04	150-3000	3.9-10	0.52

In addition to the sources outlined above, boilers and chip digesters are generic pulp and paper mill sources of air pollutants such as particulate matter and nitrogen oxides. Besides evaporators, the recovery boiler in the chemical recovery process is a source of fine particulate emissions, sulfur oxides, and total reduced sulfur. Table 3-9 further illustrates the process inputs and air-pollutant outputs for the chemical recovery system in a pulp and paper mill using kraft chemical pulping.

¹³ Four reduced sulfur gases are together called Total Reduced Sulfur (TRS) and include hydrogen sulfide, methyl mercaptan, dimethyl sulfide, and dimethyl disulfide.

Traditional chlorine-based bleaching generates significant air pollution. While the use of traditional chlorine bleaching is in decline, a significant proportion of kraft mills currently use the process, and this merits a discussion of the emissions involved. During bleaching, side reactions produce chloroform, chlorinated phenolics, and other chlorinated organics. These byproduct emissions, as well as unreacted chlorine, may be vented from the C- and D-stages. The hypochlorite stage has been identified as one of the most significant sources of chloroform emissions. Table 3-10 provides emissions data for typical bleaching sequence components.

Table 3-9 Air pollution outputs from chemical recovery in a kraft pulp mill [6].

Process step	Materials inputs	Process outputs	Major pollutant outputs
Evaporators	Black liquor	Strong black liquor	Evaporator noncondensibles (TRS, VOC's, alcohols, terpenes, phenols)
Recovery boiler	Strong black liquor	Smelt, energy	Fine particulates, TRS, sulfur dioxide
Calcining (lime kiln)	Lime mud	Lime	Fine and coarse particulates

Table 3-10 Summary of typical air emissions for kraft bleach plant facilities [7].

Emission source	Emission range (kg/Mg pulp, except where noted)				
	Total HAP	Total VOC	Chloroform (g/Mg pulp)	Chlorine	Methanol
C-stage	0.12-1.22	0.099-0.8	1.85-22	0.1-0.42	0.016-0.755
E-stage	0.057-0.295	0.078-0.278	2.89-20.5	0-0.006	0.009-0.112
D-stage	0.02-0.116	0.0002-0.08	0.063-41	0.0203	0-0.0052
H-stage	0.312-0.844	0.282-0.345	83-93	0.0203	0.16
Acid sewer	0.12-0.52	0.12-0.53	0.8-5	0	0.05-0.5
Caustic sewer	0.042-0.32	0.04-0.32	0.2-2.3	0	0.03-0.3

¹⁴ Includes washing and subsequent screening emissions.

3.4 Clean Air Act

3.4.1 New Source Performance Standards

Kraft pulp mills that have been constructed or modified after September 24, 1976 are subject to NSPS emission limitations at 40CFR60 Subpart BB. The NSPS establish emission limits for TRS compounds and particulate matter from sources that include digester systems, multiple-effect evaporators, brownstock washers, recovery furnaces, smelt dissolving tanks, lime kilns, and condensate strippers (a condensate stripper system means a column used to strip, with air or steam, TRS compounds from condensate streams from various processes within a kraft pulp mill). Table 3-11 summarizes the Federal regulations for these emission sources. In addition to the NSPS, which applies to new and modified sources, many States have adopted similar limits for existing sources.

Table 3-11 Summary of NSPS regulations for emissions from kraft pulping facilities [7].

Process unit	NSPS emission limits	
	Total reduced sulfur	Particulate matter
Digester, brownstock washer, multiple-effect evaporator, condensate stripper system	5 ppmv ¹⁵	NA
Lime kiln	8 ppmv	0.15-0.30 g/dscm
Smelt dissolving tank	0.016 g/kg black liquor solids as H ₂ S	0.1 g/kg black liquor solids
Recovery furnace	5-25 ppmv	0.1 g/dscm

¹⁵ ppmv – parts per million by volume.

3.4.2 Pending and Proposed Regulations

Title III of the Clean Air Act Amendments (CAAA) lists a minimum of 189 Hazardous Air Pollutants (HAPs) (now known as air toxics) that will be subject to technology-based emission limitations, commonly known as National Emission Standards for Hazardous Pollutants, or NESHAPs. NESHAPs are based on the use of Maximum Achievable Control Technology (MACT), which is defined as the technology achieving the maximum degree of reduction in the emission of HAPs, taking into account cost and other factors [6]. MACT is intended to reduce the 1991 estimated 2 billion pounds of total industrial toxic air pollutant emissions by as much as 90% by 2003. Proposed NESHAPs for the pulp and paper industry will control emissions of the HAPs identified in Table A-1, from all significant emission points in the pulping, bleaching, wastewater collection/treatment systems.

4 No Regrets Pollution Prevention: Pulp/Paper

Having discussed the state-of-the-art for the chemical pulping industry and the relevant environmental legislation, technical innovations that can help combat pollution have been described in the present chapter. Reference [8] provides a good overview of the technology involved.

4.1 *Extended Delignification*

The amount of bleaching chemicals required in the bleach plant to bring the pulp to the target brightness level is directly related to the kappa number¹⁶ of the brownstock pulp i.e. the amount of lignin that remains in the pulp following chemical cooking. The mill can reduce bleaching chemical demands and subsequent environmental effects by adopting techniques that reduce the brownstock kappa number. Extended delignification or extended cooking is a method developed over the last decade that allows the pulp cooking time to be extended, enabling further delignification to occur before the pulp moves on to the bleach plant. Longer residence times in conventional pulping will similarly increase bleachability, but will also lead to a loss in pulp yield and strength, as the pulping chemicals become less selective and begin to attack the cellulose material. However, extended cooking protects the pulp from detrimental effects that would normally accompany increased cooking time.

The technique involves charging the cooking chemicals at several points throughout the cook. Improved selectivity is also obtained by minimizing the concentration of dissolved lignin at the end of the cooking process and by maintaining low temperatures at the beginning and end of the cook. The alkali profile in the pulp is leveled out, permitting more lignin to be dissolved in the latter stages of the process. The lignin content of the brownstock pulp is reduced by 20-50% compared to conventional digesters.

For batch pulping, the cook can be extended using the Rapid Displacement Heating (RDH) process [5]. The basic RDH cycle is illustrated in Figure 4-1 and includes the following stages:

1. Chips are fed into the digester.

¹⁶ Test result which indicates the lignin content of a pulp sample based on its consumption of permanganate.

2. Warm black liquor is used to impregnate the chips.
3. The warm liquor is displaced with hot black and hot white liquor. The digester is brought up to temperature by adding steam.
4. After time at temperature, the hot spent cooking liquor is displaced using brownstock washer filtrate, thereby ending the cook and cooling the chip mass. The displaced hot and warm liquor is stored and used in subsequent cooks.
5. The cooled chip mass is pumped or air blown out of the digester vessel.

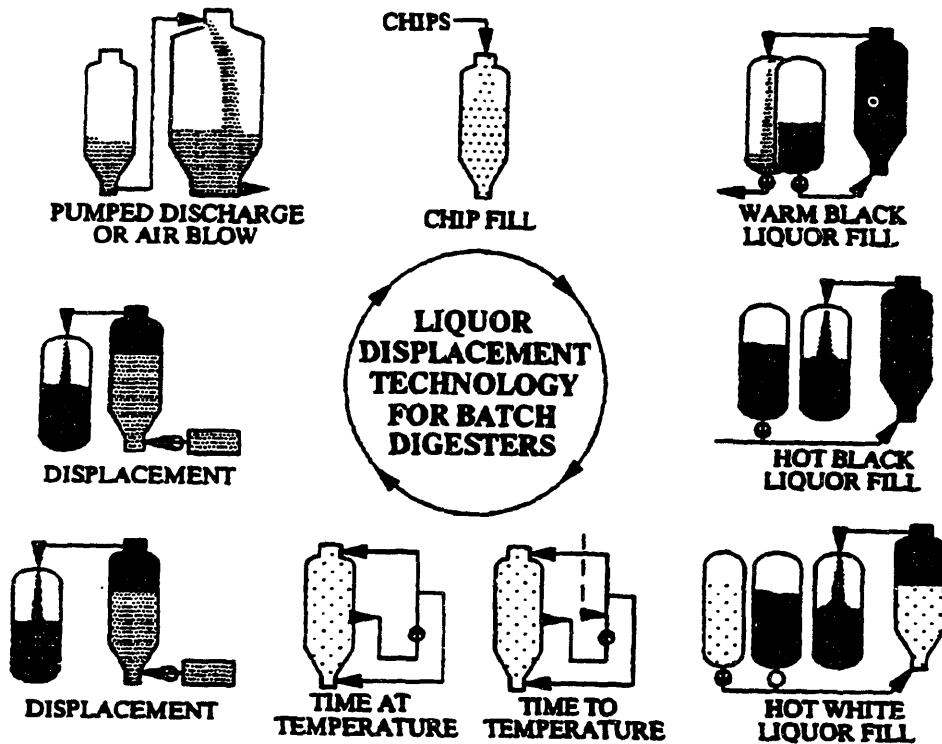


Figure 4-1 Rapid displacement heating cycle for batch digester systems.

6. Hot black liquor is passed through a heat exchanger and is used to heat white liquor.

Application of extended delignification to the continuous digester has led to the development of Extended Modified Continuous Cooking (MCC)[5]. In MCC, the normal continuous cooking process is altered as follows:

1. White liquor is added at three different points in the process.
2. 20-25% of the white liquor is added to the washer filtrate in the diffusion washing stage. The final stage is therefore carried out in a countercurrent mode.

AOX and chlorinated phenols will be reduced in approximate proportion to reductions in the brownstock kappa number. Data in Table 4-1 show the pollution reduction potential of extended delignification, as compared with conventional cooking. Modified continuous cooking can reduce kappa by 22%, while BOD₅ and color are reduced by 29 and 31%, respectively. Pulping with RDH has been shown to decrease the AOX level by 55-59%.

Both the conventional batch and continuous processes generate a comparable quantity of flash steam. However, in the continuous system, the flash steam is utilized continuously to presteam the chips, and therefore it uses half as much heat as the conventional batch process. RDH utilizes the high grade heat in the spent pulping liquor to preheat white liquor and wood chips, thus effecting a large reduction in steam demand. Digester steam consumption is typically 3.5-4 GJ/ADMT in the conventional batch process and 1.7-2.5 GJ/ADMT in a modern batch or continuous process[3]. The greatest energy impacts are expected to be observed through reductions in bleaching chemical demands. The manufacture of most bleaching agents consumes a large amount of electricity (see Table 4-2). Conversion of a 1000 tons-per-day (tpd) C_DEDED mill to extended delignification has been estimated to reduce the offsite electricity requirements (through decreased chemical use) by 800 kWh/ADMT while resulting in no net increase in onsite power requirements.

Table 4-1 Characteristics of conventional vs. MCC and RDH pulping [8].

Conventional vs. MCC			Conventional vs. RDH		
Parameter	Conventional	MCC	Parameter	Conventional	RDH
Kappa number	32	25	Kappa number	34	23
BOD, mg/dm ³	675	480	BOD, kg/ton	14	10
COD, mg/dm ³	4,618	3,931	COD, kg/ton	78	50
Color ¹⁷ , Pt mg/dm ³	10,202	7,065	Color, kg/ton	120	60
			AOX, kg/ton	3.13	1.40

¹⁷ Color is determined by spectrophotometric comparison of the effluent sample with known concentrations of colored solutions. The unit of color is that produced by 1 mg/l Platinum, in the form of chloroplatinate ion.

It has been suggested that costs for a retrofit of a model 1320 tpd continuous digester average \$4.9 million. Annualized over 20 years at an 8% discount rate, the incremental annual capital costs per ton are \$1.08, which are more than offset by operating cost savings of \$6.19 per ton. Beloit, the vendor of the RDH system has reported that the expected payback period on an RDH retrofit is approximately 18 months. This discussion shows that extended delignification can effectively reduce pollution, while leading to energy savings, bleaching chemical cost savings and delivering better pulp quality.

According to EPA, world capacity for extended cooking was about 11 million tons per year in 1993, representing 20% of bleached kraft capacity. Modified continuous cooking represented 25% of U.S. bleached chemical pulp capacity and the RDH system had been installed at four U.S. mills [6].

Table 4-2 Electricity use in the manufacture of major bleaching chemicals [3].

Chemical	Electricity consumption (kWh/kg)
Chlorine	1.7
Sodium hydroxide	1.7
Chlorine dioxide	5.0
Hypochlorite (NaOCl)	3.4

4.2 Oxygen Delignification

Oxygen delignification provides an additional way to extend the pulp cooking process. The technique involves the addition of an oxygen reactor between the kraft pulping stages and the bleach plant. The brownstock pulp from the digester is first washed and then mixed with sodium hydroxide or oxidized white liquor. The pulp is deposited in the oxygen reactor, steam heated, and injected with gaseous oxygen wherein it undergoes oxidative delignification. The pulp is then washed again to remove the dissolved lignin before moving to the bleaching plant. There are two generally accepted oxygen delignification processes, high consistency (HC) and medium consistency (MC). In HC systems, pulp is handled in the 25-28% consistency range and a press is used to raise the consistency of the feed pulp from the brownstock washers. MC systems operate at a lower solids concentration of approximately 10-14%, which can be delivered directly from the brownstock washers, thereby eliminating the need for the pulp press. Magnesium salts

(MgSO₄) are used in both systems to protect the cellulose fibers from degradation that may occur in pockets of high oxygen concentration.

From an environmental standpoint, oxygen delignification offers the following advantages:

1. Installation of an oxygen delignification stage can reduce the kappa number of brownstock pulp from a range of 30-35 to 16-17, a 50% reduction. Reductions in the amount of lignin entering the bleach plant translate directly into reductions in BOD₅, color and organochlorines.
2. In addition, reduction in discharge of pollutants is achieved by washing the dissolved solids from the oxygen-delignified pulp and recycling them to the pulp mill recovery system. Unlike the alkaline effluent from oxygen delignification, conventional bleach plant filtrate cannot be recycled through the pulp mill recovery cycle because post-chlorination effluents are corrosive to process equipment.
3. At kappa numbers achievable through oxygen delignification, a range of innovative bleaching options become available. First, by allowing the mill to cut back on the application of chlorine, oxygen delignification enables the mill to essentially increase the substitution rate of chlorine dioxide for chlorine. A second possibility is “short sequence” bleaching, in which oxygen delignification is followed by three rather than five stages.

Table 4-3 shows the typical effluent properties for the common C_DE_ODED bleach sequence and for the short sequence, OC_DE_OD.

Table 4-3 Effluent summary for kraft softwood [9].

Parameter	C _D E _O DED	OC _D E _O D	Reduction, %
BOD ₅ , kg/metric ton	15-21	8-11	40-50
COD, kg/metric ton	65-75	30-40	45-55
Color, kg Pt/metric ton	200-300	80-120	60-75
TOCl ¹⁸ , kg/metric ton	5-8	3-4	35-50
Flow, 10 ³ l/metric ton	20-25	15-20	25-30

¹⁸ TOCl – Total Organic Chlorine. TOCl is a measure of all organically bound chlorine in an effluent sample.

A comparison of the estimated net energy requirements for the C_DE_ODED and high-consistency OC_DE_OD bleaching of kraft softwood¹⁹ is provided in Table 4-4. With oxygen delignification, the total solids load to the recovery boiler will increase as a result of recovering and recycling solids from the oxygen stage. In a new fiber line with oxygen bleaching, the solids load to the recovery boiler will be approximately 4% greater with softwoods and 3% with hardwoods. The higher level of solids leads to additional steam and electricity generation through the recovery boiler. The use of oxidized white liquor in the oxygen stage will increase the load on the causticizing plant and lime kiln, leading to an increase in kiln fuel usage. Additional steam may be required in the evaporation plant because of recovery of the steam and white liquor or caustic added to the oxygen stage. Table 4-4 shows that the overall energy consumption is lower for the oxygen delignification sequence.

Table 4-4 Comparison of energy consumption for a high consistency oxygen reactor using softwood kraft pulp at 50% oxygen delignification [9].

	C _D E _O DED	OC _D E _O D
<i>Steam usage, kg/metric ton</i>		
Bleach plant	500	600
Chemical preparation	370	250
Evaporator, increase	0	40
Recovery boiler, increase	0	-100
Total	870	790
<i>Power usage, kWh/metric ton</i>		
Bleach plant and chemical preparation	160	170
Turbine increase	0	-10
Total	160	160
Kiln fuel, increase in L oil/metric ton		2

¹⁹ Botanically, woods are classified into two main groups. Conifers or evergreens are commonly called softwoods. Deciduous or broad-leaved trees are called hardwoods.

Investment in an oxygen reaction tower and related equipment has been estimated at \$8-\$16 million. The high end in the estimate corresponds to a mill that would require a considerable upgrade in pulp washing equipment (successful implementation of oxygen delignification requires effective pulp washing). At the low end of this range, the savings in chemical costs alone may favor the switch to oxygen. Table 4-5 compares the chemical consumption for the C_DE₀DED and OC_DE₀D sequences for softwood pulp. The largest reductions occur in chlorine and caustic usage. Based on chemical costs published in early 1987, the chemical reductions with oxygen delignification correspond to savings of approximately \$9/metric ton for softwood pulps.

Table 4-5 Typical chemical consumption for bleaching to 90% ISO brightness²⁰ [9].

Chemical, kg/metric ton	C _D E ₀ DED	OC _D E ₀ D
Oxygen	5	28
Chlorine	70	31
NaOH	50	20
Chlorine dioxide	19	13
Oxidized white liquor, as NaOH		22
Magnesium ion		0.5

Idner [10] has reported on the total costs of installing an oxygen delignification stage in a kraft pulp mill. The variable operational costs divided into wood, chemicals, and energy for MC systems in relation to a conventional system are given in Table 4-6. Idner's analysis suggests that the variable operational costs will be lowered by \$3.4 to \$9 per metric ton, depending on the wood species. When annualized capital costs are added to operating and maintenance costs (see Table 4-7), the change in net annual costs compared to conventional bleaching range from a decrease of \$2.9 to \$4.1 per ton for softwood pulping to an increase of \$1.5-\$2.7 per ton for

²⁰ Brightness of pulp is measured by its ability to reflect light in the blue region of the visible spectrum, relative to a magnesium oxide standard.

hardwood pulping. It is important to note that Idner's analysis does not include credits for avoided investment in C or D-stage equipment. In addition, the analysis has been carried out for a five stage bleaching sequence, irrespective of the inclusion of the oxygen delignification stage. Consideration of chemical savings inherent in the incorporation of a three stage bleaching sequence can be expected to make installation of the oxygen stage economically favorable for hardwood pulps also.

Table 4-6 Differences in variable operational costs in \$/metric ton (in relation to a conventional system, a 600-metric ton/day mill) [10].

	Softwood	Hardwood
Wood	+1.3	+0.5
Electricity and steam	+6.3	+6.3
Chemicals	-11.1	-6.8
Steam from recirculated organic substance	-5.5	-3.4
Total	-9.0	-3.4

Table 4-7 Difference in total costs for oxygen bleaching in a kraft mill in relation to a conventional system, a 600-metric ton/day mill (\$/ton, except where noted) [10].

	Softwood	Hardwood
Investment, 10 ⁶ \$	6.5-8.1	6.5-8.1
Variable costs	-9.0	-3.4
Maintenance	0.9-1.1	0.9-1.1
Capital costs	4.0-5.0	4.0-5.0
Total costs	(-4.1)-(-2.9)	1.5-2.7

As of 1993, there were 155 mills worldwide operating oxygen delignification systems, representing 34% of the total world kraft output. Oxygen delignification projects had been

installed or were planned for 27 U.S. mills, accounting for more than 40% of U.S. bleach kraft pulp production.

4.3 Ozone Delignification

Ozone is an extremely powerful oxidant whose potential as a pulp bleaching agent has been extensively studied in laboratory and pilot plant operations. Until recently, the poor selectivity of ozone, which produces inferior strength pulp has prevented the development of a commercial ozone bleaching system. Considerable research has been devoted towards determining the optimum conditions for ozone bleaching. In addition, developments in extended and oxygen delignification have reduced the amount of work that must be done in the ozone stage. As a result of these efforts, ozone bleaching is now being used in full-scale mills (1000 tpd or more) in the pulp and paper industry. The ozone bleaching process under greatest scrutiny is a high consistency process, which is performed using techniques and equipment similar to that used in high-consistency oxygen bleaching. A major distinction is that ozone bleaching is carried out under acidic conditions, and therefore, the pulp to be bleached is pretreated with sulfuric acid prior to feeding in the reactor [5].

The movement towards ozone bleaching has also been achieved through advances in ozone generation equipment. Ozone is unstable and will decompose to molecular oxygen; thus ozone must be generated on-site and fed immediately to the pulp reactor. Ozone is produced by the corona discharge method. In this process, a high voltage is applied across a discharge gap through which an oxygen-containing gas is passed. The oxygen carrier gas used to deliver ozone to the pulp is recycled back to the ozone generator.

The major impetus for the development of ozone bleaching has been the elimination or reduction of chlorine-containing chemicals in the effluent. Ozone is a non-chlorine containing compound that is also a powerful lignin dissolver. When used in combination with oxygen and/or extended delignification, the two processes can result in a high quality bright pulp that eliminates the use of elemental chlorine in bleaching. In September 1992, Union Camp began production on the world's first high-consistency ozone bleach plant at its mill in Franklin, VA [11]. The mill has been able to modify the state-of-the-art $OC_D E_0 D$ bleach sequence and uses only oxygen, ozone and chlorine dioxide to produce elemental chlorine-free (ECF) pulp. Table 4-8 compares the emissions from the $OZE_0 D$ (Z stands for ozone) line at the Franklin mill with conventional bleaching sequences. Elimination of elemental chlorine is responsible for the reduction in chlorinated organics (TOCl and chloroform). The ability to recycle all of the O, Z, and E_0 stage

effluents leads to lower effluent flows, and reduced color, BOD₅, COD levels. The mill has been unable to detect TCDD in the pulp or filtrate, while TCDF has been measured in the effluent at a low level of 5.6 ppq (parts per quadrillion).

In terms of energy requirements, ozone generation is twice as energy intensive as chlorine dioxide. However, the greater electricity demand is offset by the fact that ozone is also twice as powerful a bleaching agent. Figure 4-2 compares the electricity demands for the production of chlorine, chlorine dioxide and ozone. Energy consumed onsite in the generation of ozone (13 kWh per kg of ozone) replaces energy used offsite to produce chlorine and chlorine dioxide.

Table 4-8 Percent reduction in emissions for OZE₀D bleaching of kraft pulp [12].

	OZE ₀ D vs. CEDED	OZE ₀ D vs. OC ₀ ED
TOX	98	95
Chloroform	99	99
BOD ₅	89	72
COD	91	75
Color	99	98
Volume of effluent	86	47

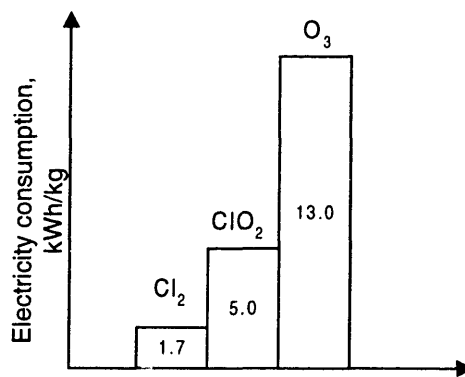


Figure 4-2 Electricity consumption for ozone production [3].

The OZE₀D line at the Franklin mill is able to achieve very low bleaching chemical doses. Table 4-9 compares the chemical usage for the conventional CEDED and the ECF bleach line. Using

the raw material costs in Table 4-10, Nutt et al. have compared operating costs of the OZE₀D line at the Franklin mill with the CEDED bleaching sequence, and against other contemporary bleaching processes with 100% chlorine dioxide substitution. Table 4-10 indicates that the operating costs for ozone bleaching, *including* ozone generation, are lower than for conventional sequences.

Table 4-9 Chemical usage for CEDED and OZE₀D bleaching [11].

Chemical, %	CEDED	OZE ₀ D
Chlorine	7.11	-
Caustic	5.89	0.22
Chlorine dioxide	2.17	0.65
Oxygen	-	3.33
Magnesium sulfate	-	0.25
Oxidized white liquor as NaOH	-	4.00
Sulfuric acid	-	1.25

Table 4-10 Bleaching chemical costs of ozone versus conventional sequences at Union Camp's Franklin Virginia mill [8].

Sequence	Relative costs
CEDED	100
OZE ₀ D	48
DEDED	100
ODED	56
OZE ₀ D	32
Assumptions	Chlorine:\$153/ton, Chlorine dioxide:\$0.32/lb, Oxygen:\$53/ton, Magnesium sulfate: \$485/ton, Caustic: \$340/ton, Oxidized white liquor: \$29/ton, Sulfuric acid: \$68/ton, Ozone: \$0.29/lb

Capital costs for an ozone-based bleach plant are estimated to be approximately 25% greater than for a state-of-the-art OC_DE_OD sequence. However, there may be substantial off-sets in capital costs. Ozone bleaching benefits from the ability to use cheaper construction materials, as corrosion problems are less severe compared to chlorine bleaching. It is expected that due to dioxin and total chlorinated organic considerations, the only viable way to operate present day CEDED and OC_DE_OD systems in the future will be with 100% chlorine dioxide substitution. By eliminating the need for additional chlorine dioxide generating capacity, the OZE_OD process will reduce new chlorine dioxide capital costs substantially. It is also important to note that with a high-consistency oxygen stage prior to the ozone stage, the mill can forego the investment in additional process equipment associated with ozone bleaching (pulp press, high shear mixers).

4.4 Improved Brownstock Washing

In recent years, substantial progress has been made in improving brownstock pulp washing systems. These advances have been aimed at reducing effluent flows, improving energy efficiency, and achieving better removal of dissolved lignin solids and spent liquor from the pulp. Efficient washing is also a prerequisite for successful operation of an oxygen delignification system. Alternative methods to rotary vacuum washing include the following [5]:

1. Diffusion washers.
2. Rotary pressure washers.
3. Horizontal belt washers.

The different types of washers mentioned are illustrated in Figure 4-3. *Diffusion washing* is characterized by a relatively long period of contact between the pulp and the moving wash liquor, which allows time for the liquor solids to diffuse from the fiber structure. In a pressure diffusion washer, the pulp is introduced at the top and is caused to flow downward through an annulus formed by a cylindrical screen and a central liquor chamber. The wash liquor is injected from the central chamber and is forced to flow to the screen, where it is extracted. *Rotary pressure* washers are similar in operation to rotary vacuum washers. The pulp mat formed on the cylinder surface is dewatered by applying pressure outside the cylinder, as opposed to inside it. The *horizontal belt* washer resembles the fourdrinier section of a paper machine.

In diffusion systems, the pulp is introduced at blow line consistency and washing takes place without dilution to low consistency, thereby avoiding the large flows of recycled filtrate required

in conventional washing systems. In case of vacuum washing, a certain amount of air is continuously pulled through the pulp sheet and entrained with the liquor, leading to undesirable foaming in the liquor. Diffusion washing takes place in a submerged environment, which excludes the possibility of air entrainment and foaming. Because the driving force for washing in a rotary pressure system is outside the cylinder, the interior of the washer drum can be utilized for a sophisticated filtrate collection and recirculation system. The higher pressure also greatly reduces foaming and a closed vapor circulation system facilitates collection and treatment of odorous vapors.

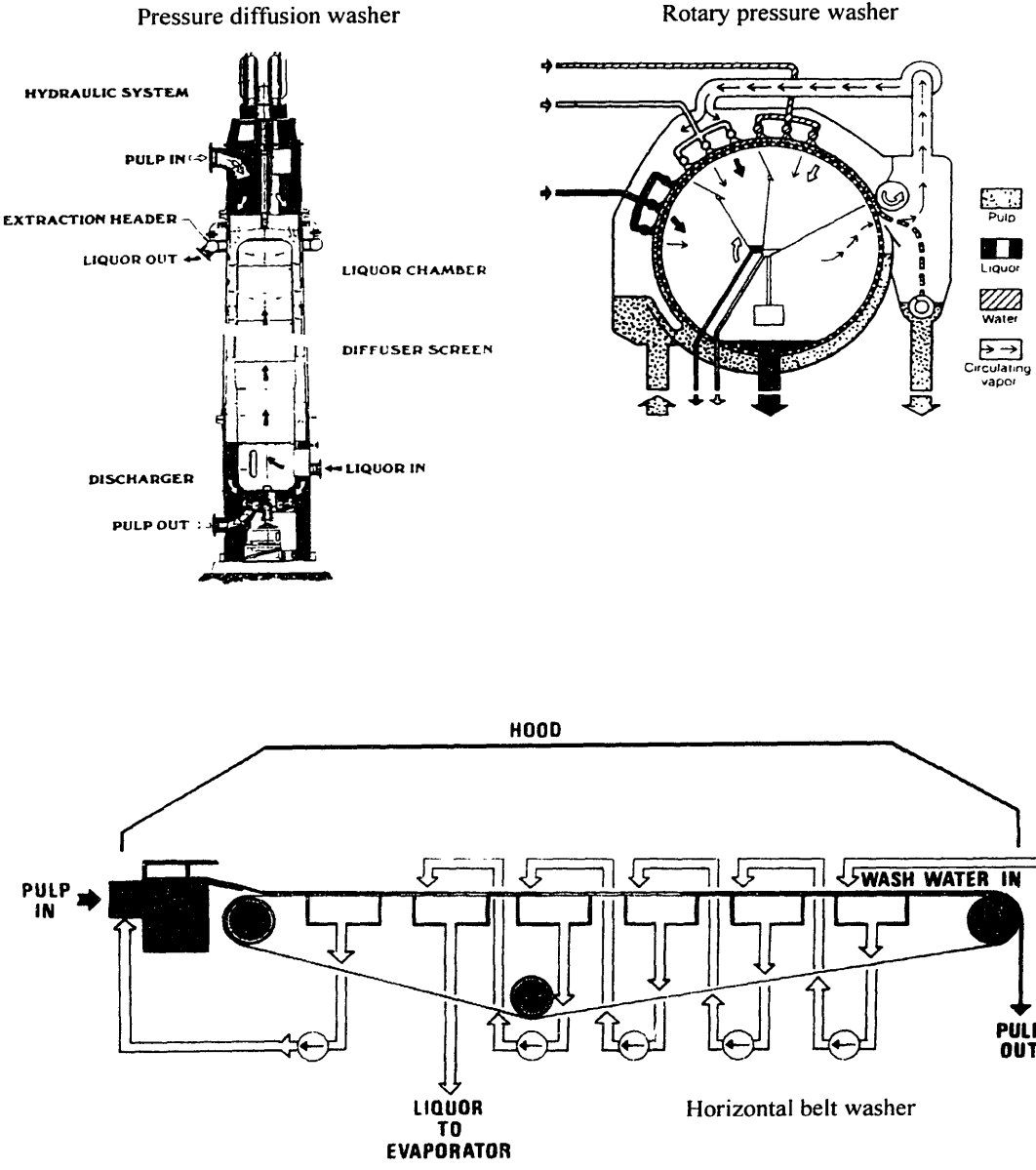


Figure 4-3 Alternative methods to rotary vacuum washing [5].

Improved brownstock pulp washing will reduce the amount of dissolved organic lignin solids carried through to the bleaching stages, thereby reducing the potential for formation of chlorinated organic compounds such as dioxins, furans, and chlorinated phenolics. Hise et al. [13] have conducted studies to characterize organic carry-over from brownstock washers and to determine the effect of carry-over on the formation of chlorinated organics in the bleach plant. In their study, COD in filtrate samples squeezed from brownstock pulp was used as a measure of the organic carry-over. Figure 4-4 shows that as COD in the pulp squeezings increased the amount of 2,3,7,8-TCDF, tetrachlorinated phenolics and AOX in bleaching stage filtrates also increased. Mill trials were conducted at Westvaco Corporation to study the effects of black liquor carry-over. Table 4-11 presents the impact of brownstock washing on the formation of 2,3,7,8-TCDD at Westvaco. The chlorinated and extracted pulps and final bleached pulp were reported to have lower TCDD levels during “good” washing.

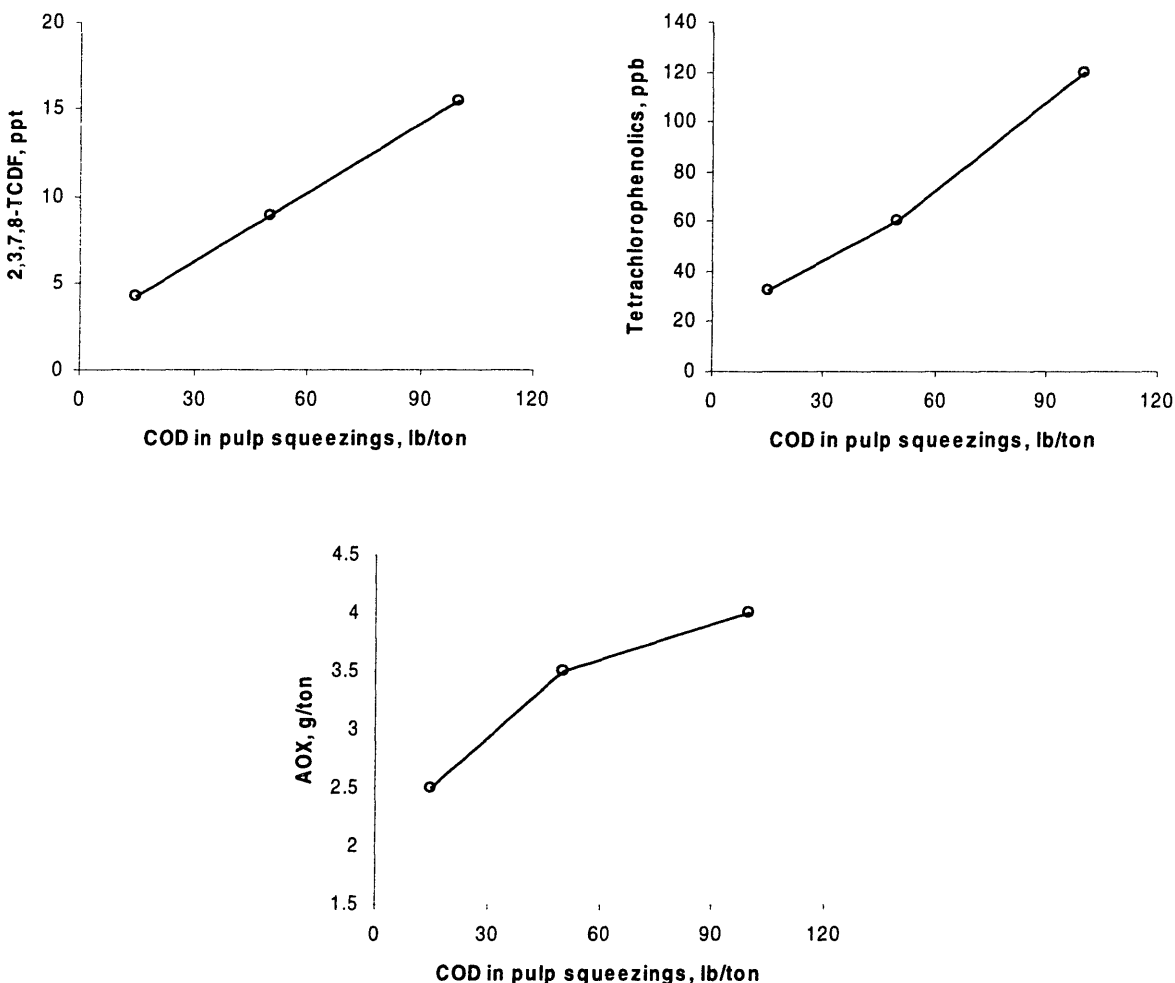


Figure 4-4 Effect of organic carry-over on formation of 2,3,7,8-TCDF, tetrachlorinated phenolics, and AOX in C- and E-stage filtrates [13].

Table 4-11 Impacts of improved washing practices on formation of 2,3,7,8-TCDD (concentration in ppt) [8].

Bleaching stage	Good washing	Poor washing
C-stage pulp	3.3	7.3
E-stage pulp	2.1	6.3
D ₁ -stage pulp	2.5	8.1
D ₂ -stage pulp	4.2	9.3

Costs for improved washing can range from negligible in the case of relatively simple optimization of existing equipment to \approx \$20 million to completely upgrade the wash system in a 1000 tpd mill. Ricketts [14] has examined the relative capital and operating costs of replacing conventional rotary vacuum washers at a hypothetical U.S. mill with each of three advanced brownstock washing systems. The capital costs for all three ranged from approximately \$10 million to \$12 million.

The installation of the new washing systems is expected to result in significant operating cost savings. Some of the key operating parameters for the three proposed systems and the existing washer line are shown in Table 4-12. The dilution factor is a direct measure of the water being added to the liquor wash system and, as shown in Table 4-12, process water use would be reduced in all cases due to the lower dilution factors. The washwater requirement could drop from 1560 gpm to 960 gpm, leading to a decreased load on the evaporator in the chemical recovery system, and therefore, a reduced steam consumption. In addition, upgraded brownstock washing increases the quantity of solids recovered from the pulping effluent and the recovery of additional solids through the boiler results in an increase in boiler energy output. Table 4-13 lists the significant factors impacting the operating cost of each washing system. Table 4-14 shows the estimated annual operating costs for the three washing systems compared with the existing line. Besides the fact that each system offers operating cost savings, Table 4-14 also demonstrates that the newer systems are more energy efficient. In Ricketts' analysis, the mill produces unbleached paper and, therefore, the cost savings that will result from reduced bleaching chemical requirement have not been included. Hise et al. provide an estimate of the impact that carry-over

to the bleach plant has on bleaching chemical costs. Figure 4-5 shows the effect of increased carry-over on relative chemical costs for their analysis.

Table 4-12 Key operating parameters for three proposed washing systems and the existing line at case study linerboard mill [14].

	Existing line	Chemi-washer ²¹	CB filters ²²	Drum displacer ²³
Feed consistency, %	1-1.25	2-2.5	2-2.5	2-2.5
Dilution factor, lb. water/lb. pulp	3.5	1.0	2.5	3.3
Wash water flow, gpm	1560	960	1080	1330

Table 4-13 Operating cost items for existing washing line vs. three modern systems [14].

	Existing line	Chemi-washer	CB filters	Drum displacer
Horsepower, hp	870	820	910	270
Net steam savings, 1000 lb/hr	0	39.3	12.6	3.0
Defoamer usage, lb./ton	3.0	2.0	1.0	0.5

²¹ A belt-type, horizontal washer

²² A compaction baffle filter that uses a baffle to press the pulp mat to expel strong liquor, followed by a displacement wash

²³ A drum washer

Table 4-14 Annual operating cost savings ($\times 1,000\$$) for each proposed washer system vs. the mill's existing washer line [14].

	Chemi-washer	CB filters	Drum displacer
Power	\$12	(\$12)	\$158
Steam	\$1,155	\$370	\$88
Defoamer	\$118	\$236	\$297
Maintenance	(\$60)	\$15	\$15
Total annual cost	\$1,225	\$609	\$558
Cost per ton	\$4.67	\$2.32	\$2.13

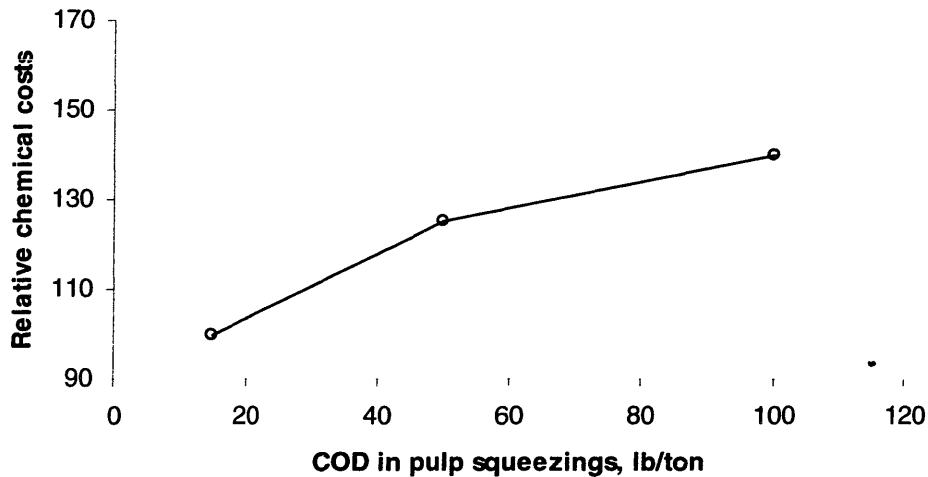


Figure 4-5 Effect of carry-over on relative bleaching costs in C and E stages [13].

EPA has reported that the importance of efficient brownstock washing is now well recognized throughout the North American pulp and paper industry. However, the multitude of ways in which washing system improvements can be made has made it difficult to estimate the extent to which the industry has adopted the various upgrade options. According to Ricketts, there were

approximately five Chemi-Washers operating on softwood pulps in the U.S. in 1991. In addition, IMPCO had more than 60 Compaction Baffle Filters operating successfully worldwide.

4.5 Peroxide-Enhanced Extraction

As with oxidative extraction, the use of hydrogen peroxide has been found to promote additional removal of lignin during the first extraction stage. Peroxide and oxygen can be used together in the E_1 (first extraction) stage, i.e. E_{OP} . The most popular method of addition utilizes a medium-consistency mixer which fluidizes the stock and injected chemicals. The oxidative power of peroxide can also be used in subsequent extraction stages to perform bleaching.

Webster has described a strategy to achieve significant environmental and economic benefit from the use of peroxide (see Table 4-15). Using a $C_D E_0 D E D$ mill as an example, the first step is to add peroxide to the last extraction stage to do some of the bleaching work of the final D-stage. For each chemical equivalent of peroxide used, a greater chemical equivalency of chlorine dioxide is saved in the subsequent stage. Then, peroxide is added to the first E-stage to assist in delignification, allowing the mill to cut the chlorine charge upstream and maintain the same kappa number after the E_1 stage (chlorination-extraction kappa number or CE kappa number). Finally, the chlorine dioxide saved in the final D-stage can be shifted forward to raise the chlorine dioxide substitution in the C_D stage to a higher level. This will accomplish the goal of lowering elemental chlorine without the need for expensive increases in chlorine dioxide capacity and without sacrificing pulp quality.

Table 4-15 Implementing peroxide extraction [15].

Step 1	Add H_2O_2 to last E stage $C_D E_0 D E D$ to $C_D E_0 D E_P D$ Cut ClO_2 in D stages to maintain goal brightness
Step 2	Add H_2O_2 to first E stage for delignification $C_D E_0 D E_P D$ to $C_D E_{OP} D E_P D$ Cut Cl_2 charge to maintain CE kappa
Step 3	Shift ClO_2 cut in Step 1 to the C stage to raise substitution $C_D E_{OP} D E_P D$ to $C/D E_{OP} D E_P D$

Hydrogen peroxide can also effectively replace the use of hypochlorite in bleaching of kraft pulps. Because hypochlorite tends to attack both lignin and cellulose, pulp quality can be improved when peroxide is used as a replacement. Hypochlorite is also a major source of chloroform emissions.

Reductions in bleaching chemical use, particularly in the first chlorination stage, are directly associated with reduced levels of chlorinated organics. Webster has summarized recent mill trials using peroxide at various locations in the bleaching sequence, and the results are shown in Figure 4-6. The most significant reductions, over 80% , were for dioxin. There were also up to 35% lower AOX levels and 60% lower chloroform emissions. The net effect for mill A was to increase chlorine dioxide substitution from 7% to 27% .

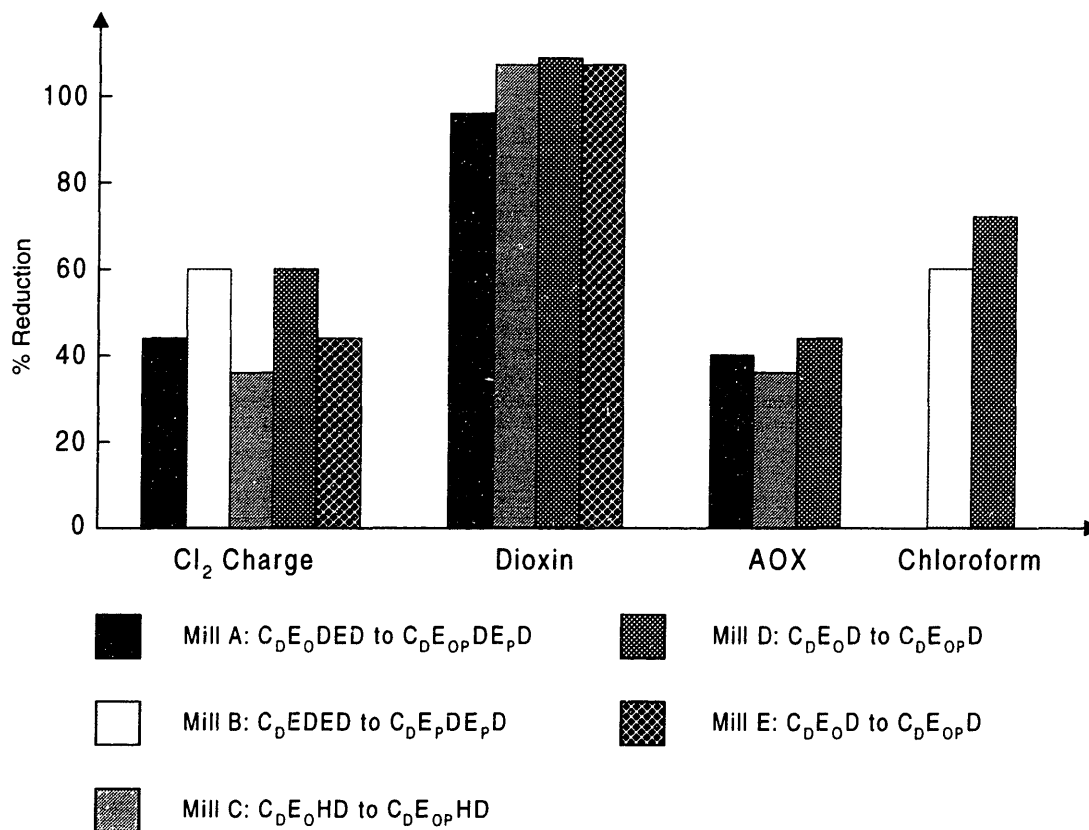


Figure 4-6 Results using hydrogen peroxide enhanced extraction – bleaching strategy [15].

In a case reported by Walsh [16], conversion of a C_DE_HD sequence to C_DE_PD sequence reduced the CE kappa number from 3.1 to 2.4 (23%), and the chlorine dioxide charge in the final D-stage

was reduced by 7.2 lb./ton. Hydrogen peroxide replaced hypochlorite at a ratio of 1:3.5. The final brightness increased 1.4 points. In another study, conversion of a CEHD sequence to CE_pHD sequence led to AOX and chloroform reductions of 27.5% and 49.4%, respectively.

Webster notes that compared to other options, such as modifying chlorine stage operations or increasing chlorine dioxide generating capacity, hydrogen peroxide substitution presents a low capital option. Permanent installations, including the storage tank, mix tank, and process piping, typically cost less than \$100,000, and no major construction or significant modification of existing facilities is needed. In terms of operating costs, the main impact is the change in overall chemical consumption. Helmling et al. [17] have reported on the benefits of replacing the E₀ stage of a C_DE₀HD sequence with hydrogen peroxide at a U.S. kraft pulp mill. While maintaining the D-stage washer brightness, the hypochlorite and the chlorine dioxide charges could be reduced by 20% and 35%, respectively. These reductions led to a savings in bleaching costs of approximately \$2/ton of pulp.

A mill can also apply hydrogen peroxide economically in the E₀ stage of a shortened bleaching sequence. Helmling et al. [17] report on attempts to reduce a five-step bleach sequence, C_DE₀DED, into a three-step C_DE₀PD sequence. Bleaching steps require steam in order to reach desired reaction temperatures in the bleach towers. Most of the bleach plant electricity use is for pumping and mixing. Fewer steps result in lower electricity and steam demands. Althouse [18] reported that shortening the bleach sequence enabled a pulp mill to realize the following savings:

1. Electrical Costs: \$1 to \$3 per ton of pulp or \$175,000 to \$525,000 per year.
2. Steam Costs: \$3 to \$5 per ton of pulp or \$525,000 to \$875,000 per year.
3. Maintenance Costs: \$2 to \$5 per ton of pulp or \$375,000 to \$875,000 per year.

The percentage of all bleach lines in North America using hydrogen peroxide in the extraction stage was estimated in 1987 to be 25%. Walsh reported a 30% increase in peroxide use in the pulp and paper industry between 1989 and 1990 and about half of the U.S. consumption was accounted for by kraft bleaching.

Iron and Steel

This section follows the same general outline as the discussion for the pulp/paper industry. Chapter 5 describes conventional iron and steelmaking technology. Emphasis has been placed on process steps that are of most concern to the industry from the standpoint of environmental regulations. Sources of air and water pollution have also been identified. This is followed by Chapter 6, that provides an introduction to environmental legislation relevant to the iron/steel sector. Finally, in Chapter 7, novel technical advances that offer economic benefits along with pollution reduction have been described.

5 Conventional Technology: Iron and Steel

Steel is an important material of any modern economy. Its versatile range of physical properties and chemical resistance make it the main structural and engineering material today. It is an indispensable component in the manufacture of cars, trucks, ships, oil and gas installations, electrical and mechanical machines, environmental control equipment, household appliances, buildings, factories, roads and bridges.

The iron and steel industry is categorized by the Bureau of the Census under the SIC code 33, primary metal industries. SIC 3312 is the most significant class under SIC code 33, and includes blast furnaces, steel works, and rolling mills [1]. The 1995 Census data reported 247 establishments under SIC 3312, with an estimated 153,000 employees, a payroll of \$7.5 billion, and a value of shipments totaling \$54 billion [2].

Currently, there are two process routes that dominate steel manufacture. These are the *integrated* and the electric arc furnace or EAF routes, the latter sometimes referred to as the *mini-mill* route. The key difference between the two is the type of iron bearing feedstock they consume. In an integrated works, this is predominantly iron ore, with a smaller quantity of scrap, while the EAF works use mainly scrap, or other sources of metallic iron such as directly reduced iron. Figure 5-1 is a flowsheet for the production of molten steel via the integrated and mini-mill routes.

The production of steel in an integrated works involves the processes of cokemaking, ironmaking and finally, steelmaking. Coke, which functions as the fuel and the reducing agent for iron ore, is produced by heating coal in coke ovens. Pig iron is then produced by heating the coke, iron ore and limestone in a blast furnace. Finally, iron from the blast furnace is converted to steel in the Basic Oxygen Furnace (BOF). Molten iron from the blast furnace, flux, alloying materials, and scrap are placed in the BOF, melted and refined by injecting high purity oxygen. Reaction of oxygen with carbon and silica in the iron generates the heat necessary to melt the scrap. The oxidized impurities are captured in the slag formed from the flux. The alloying elements are used to achieve the desired steel composition.

About one-quarter of the world's steel is produced by the electric-arc method, which uses high-current electric arcs to melt steel scrap and convert it into liquid steel. During melting, oxidation of impurities occurs and a slag is formed on top of the molten metal. Since scrap metal is used

instead of molten iron, there are no cokemaking or ironmaking operations associated with steel production that uses an EAF. However, electric-arc steelmaking is not as oxidizing, and therefore, undesirable residuals (i.e. copper, chromium, nickel, molybdenum, and tin) that are present in scrap do not get oxidized during steelmaking. Instead, they accumulate and increase in recycled scrap. EAF shops therefore augment their scrap charges with Direct Reduced Iron (DRI), which does not contain residuals. Direct reduction is a process in which iron is extracted from ore at a temperature below the melting point of the iron produced. In the most successful of these, known as the Midrex process, a gas reformer converts methane to a mixture of carbon monoxide and hydrogen and feeds these gases to the top half of a small shaft furnace. There descending pellets of ore are chemically reduced at a temperature of 850°C. The metallized charge is cooled in the bottom half of the shaft before being discharged.

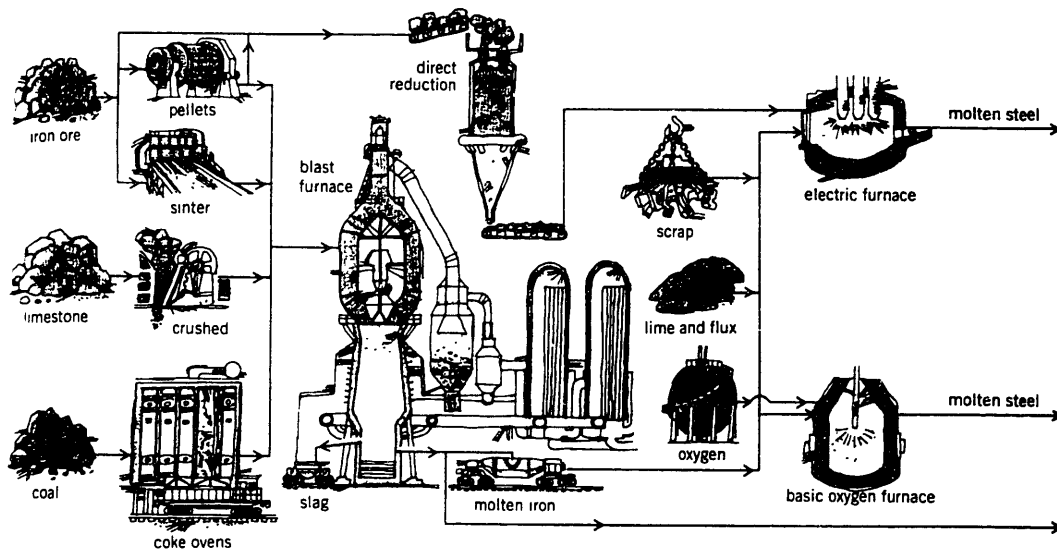


Figure 5-1 Schematic process flowsheet for integrated and mini-mill steel production.

The cokemaking process is seen by industry experts as one of the steel industry's areas of greatest environmental concerns, with coke oven air emissions and waste water as the major problems [1]. Most of the pollution prevention activities in the iron and steel industry have therefore concentrated on reducing cokemaking emissions or developing coke-less ironmaking techniques. This chapter concentrates on the production of coke in coke ovens and its utilization in blast furnaces. An in-depth description of these and other processes in the iron and steel industry can be found in [19].

5.1 Cokemaking

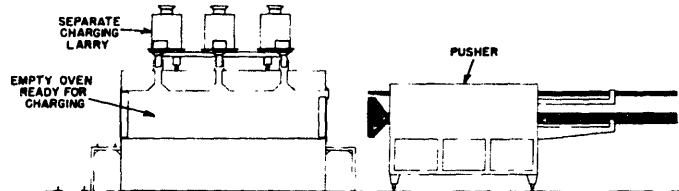
The primary function of coke in the blast furnace is to provide carbon that is required to chemically reduce iron oxide to iron metal. Coke also provides physical support for the furnace burden and allows the free flow of gases through the furnace. Coal is converted to coke by heating to $\approx 1300^{\circ}\text{C}$ in an oxygen-free atmosphere. Coal is a complex mixture of organic compounds, the principal elements of which are carbon and hydrogen, with smaller amounts of oxygen, nitrogen, and sulfur. It also contains some non-combustible, inorganic compounds, collectively called ash. When heated to high temperatures, in the absence of air, the complex organic molecules break down to yield gases, together with liquid and solid organic compounds of lower molecular weight and a non-volatile residue primarily made up of carbon. The process is called coal carbonization and the carbonaceous residue left behind is coke. Structurally, coke is a cellular, porous substance and the most important physical property of metallurgical coke is its strength to withstand abrasion and breakage during handling and use in the blast furnace. Only certain coals, for example coking or bituminous coals, with the right plastic properties, can be converted to coke. Modern cokemaking operations are carried out in by-product coke ovens.

The by-product coking process involves the use of retort ovens that essentially consist of three main parts: the coking chambers, the heating chambers, and the regenerative chambers, all constructed of refractory brick. Ovens are constructed in batteries of 40 or more coking chambers interspaced with heating chambers. The regenerative chambers are underneath the heating and coking chambers. Hot waste gases from the heating chambers are used to preheat combustion air in the regenerative chambers. Each coking chamber is fitted at both ends with removable full height doors. Coal is charged through holes above each coking chamber from a special car that runs along the top of the battery. Once charged, the coal is leveled, the doors and charge lids are sealed, and heating commences (see Figure 5-2). The heating chambers consist of a large number of flues which permit uniform heating of the coking chamber (Figure 5-3). The necessary heat for coal carbonization is supplied from combustion of coke-oven gas (COG)²⁴ or a mixture of coke-oven and blast furnace gas (see Section 5.2). The combustion of fuel with air in the heating chambers is known as underfiring.

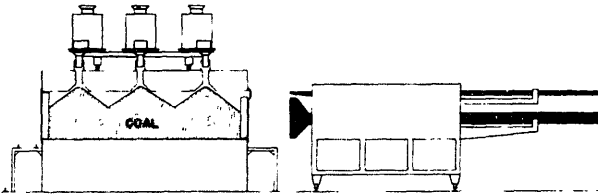
Besides the production of coke, coal carbonization results in the evolution of mixed gases and vapors. These volatile products (foul gas) pass through ducts in the oven top and enter a

²⁴ COG is the gas recovered from the coking process.

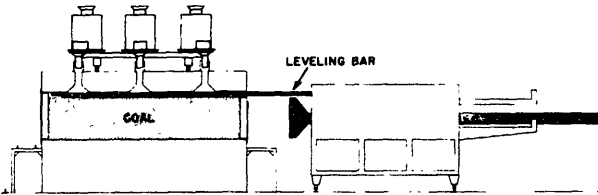
**CHARGING, LEVELING AND PUSHING OPERATIONS
IN ONE COKING CYCLE OF A BY-PRODUCT COKE OVEN**



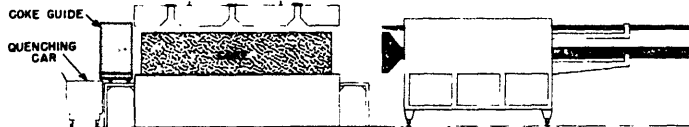
A. THE CHARGING LARRY, WITH HOPPERS CONTAINING MEASURED AMOUNTS OF COAL, IS IN POSITION OVER CHARGING HOLES FROM WHICH COVERS HAVE BEEN REMOVED. THE PUSHER HAS BEEN MOVED INTO POSITION.



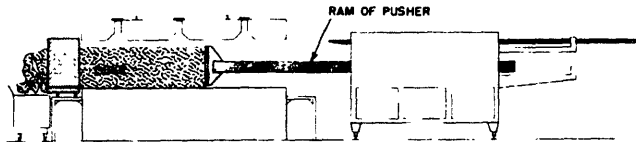
B. THE COAL FROM THE LARRY HOPPERS HAS DROPPED INTO THE OVEN CHAMBER, FORMING PEAKED PILES.



C. THE LEVELING DOOR AT THE TOP OF THE OVEN DOOR ON THE PUSHER SIDE HAS BEEN OPENED, AND THE LEVELING BAR ON THE PUSHER HAS BEEN MOVED BACK AND FORTH ACROSS THE PEAKED COAL PILES TO LEVEL THEM. THE BAR NEXT IS WITHDRAWN FROM THE OVEN, THE LEVELING DOOR AND CHARGING HOLES ARE CLOSED, AND THE COKING OPERATION BEGINS.



D. COKING OF THE COAL ORIGINALLY CHARGED INTO THE OVEN HAS BEEN COMPLETED (IN ABOUT 18 HOURS) AND THE OVEN IS READY TO BE "PUSHED." THE OVEN DOORS ARE REMOVED FROM EACH END, AND THE PUSHER, COKE GUIDE AND QUENCHING CAR ARE MOVED INTO POSITION.



E. THE RAM OF THE PUSHER ADVANCES TO PUSH THE INCANDESCENT COKE OUT OF THE OVEN, THROUGH THE COKE GUIDE AND INTO THE QUENCHING CAR.

Figure 5-2 Sequence of operations involved in charging, leveling and pushing of a byproduct coke oven.

refractory lined pipe (ascension pipe), which in turn is connected to a collecting main. The condensate from the volatile products driven off in the coking process is known as *flushing liquor*. The flushing liquor serves as a carrying medium for the condensable compounds formed in the cokemaking operations and is delivered to a collecting unit customarily called a flushing liquor decanter tank. The decanter tank functions as a settling basin to permit separation of tar, carbonaceous and other finely divided material that is carried along with liquor from the collecting main. The liquor from the decanter is recirculated back to the collector main and the tar is pumped to storage. The gas passing from the ascension pipe to the collecting main is shock-cooled with the recirculated flushing liquor spray to precipitate tar from the gas and to cool the gas to the desired temperature. The virgin tar as it comes from the coke-ovens contains valuable oils which can be extracted and the residue used as a fuel.

When the heating cycle is complete, the oven is isolated from the collecting main, the end doors are removed and solid coke is pushed into a coke car (Figure 5-2). The coke car travels to the quench tower where fresh or recycled water is sprayed on the hot coke to reduce its temperature to $\approx 200^{\circ}\text{C}$.

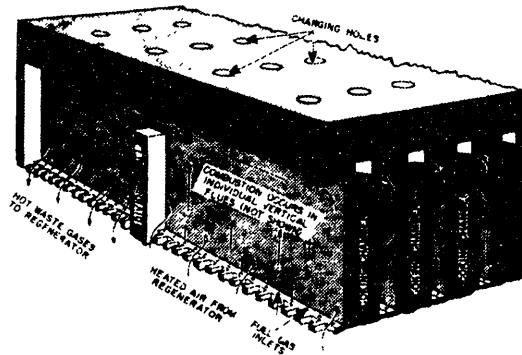


Figure 5-3 Firing method employed in byproduct coke ovens.

The non-condensed gas and vapors leaving the collecting main are further cooled in a primary cooler. This results in the formation of ammonia liquor²⁵ and condenses additional tar. The functioning of a primary cooler is shown in Figure 5-4. The gas enters the bottom of the tower and the cooling water (or cooling liquor) is pumped into the top of the tower through a spray system. This provides a downward flow of cooling liquor in countercurrent flow to the gas

²⁵ Ammonia liquor is the water condensate from the gas cooled in the primary cooler.

stream. The direct contact results in the transfer of heat from the hot gas to the cold liquor. The gas leaving the primary coolers still contains small amounts of tar, which is removed by passing

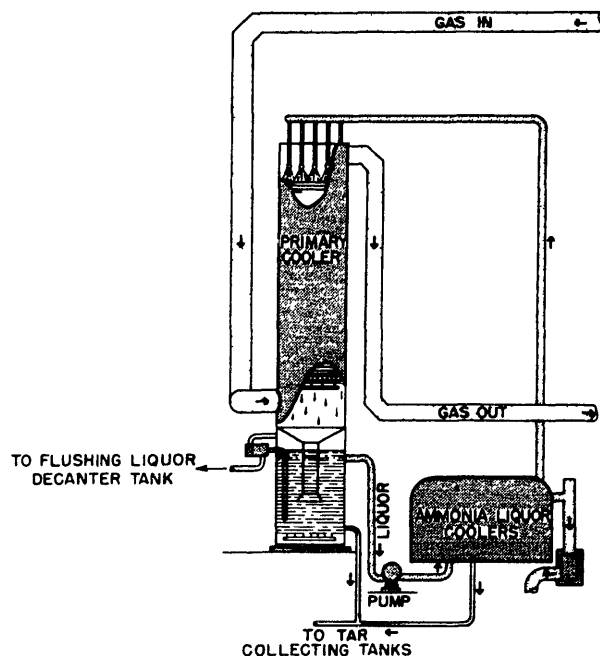


Figure 5-4 Schematic diagram of a primary cooler.

the gas through an electrostatic precipitator²⁶.

Ammonia liquor is an aqueous solution of ammonium salts. The ammonia present in the ammonia liquor is in two forms, classified as free and fixed. The free ammonia is readily dissociated by heat (steam) while the fixed ammonia requires the presence of a strong alkali (calcium hydroxide) to effect the displacement of the ammonia from the compound in which it is present. The operation to recover ammonia from the liquor is carried out in an ammonia still (Figure 5-5). The ammonia vapors leaving the still are added to the gas stream and all of the ammonia is recovered in ammonia absorbers.

The gas leaving the ammonia absorbers contains light oil. It contains varying amounts of coal-gas products with boiling points from about 40°C to 200°C. The principle usable products are benzene, toluene, xylene and solvent naphthas. The first step in light oil recovery is that of cooling the gas leaving the ammonia absorbers by direct contact with water in a tower scrubber

called a final cooler. This removes naphthalene from the gas, which then comes in contact with petroleum wash oil. Wash oil adsorbs 90-95% of the light-oil content of the gas. This is followed by the debenzolization step, where light oil is separated from the wash oil by steam distillation.

Debenzolization is followed by removal of hydrogen sulfide from the gas by wet oxidation processes. An example is the Holmes-Stretford process. Crude coke-oven gas is scrubbed with an alkaline solution of a reduction-oxidation catalyst, which oxidizes H_2S in the gas to elemental sulfur. Sulfur is recovered as a froth and the reduced solution is re-oxidized with air to regenerate

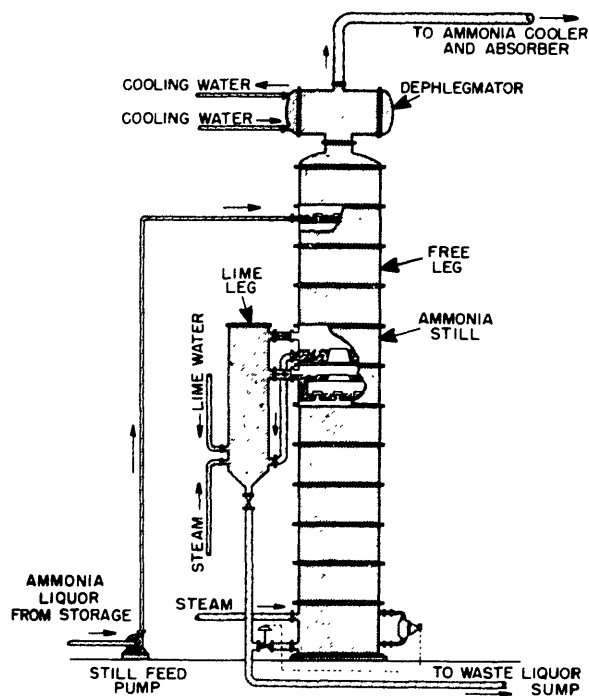


Figure 5-5 Essential parts and operation of an ammonia still.

the catalyst.

Sources of air pollution in cokemaking may be defined as either continuous or fugitive [20]. The main sources of continuous emissions are those that originate from combustion processes such as underfiring, and steam production. Fugitive emissions may be subdivided into three categories. First, the discontinuous emissions that are linked to specific operational processes such as the

²⁶ In the electrostatic precipitator, removal of tar from gas is achieved by passing the gas between electrodes having a high electrical potential. The electrical field ionizes the suspended particles, which are then transferred to the collecting electrode.

charging and pushing of ovens and the wet quenching of hot coke. Second, the diffuse emissions that arise from leakage at the charging holes, ascension pipes and oven doors, or from vents on storage tanks in the byproducts plant. The final category includes the fugitive emissions that occur from open sources, such as stockpiles, under windy conditions. The main pollutants present in the underfiring gases are SO₂, NO_x, and particulates (PM₁₀)²⁷. Particulate matter in stack emissions is mainly soot arising from incomplete combustion. Particulate emissions arise from underfiring, charging, pushing, and quenching operations. Fugitive emissions from the battery operations contain polycyclic aromatic hydrocarbons (PAHs), benzene, toluene, and xylene (BTX), and odoriferous substances such as H₂S.

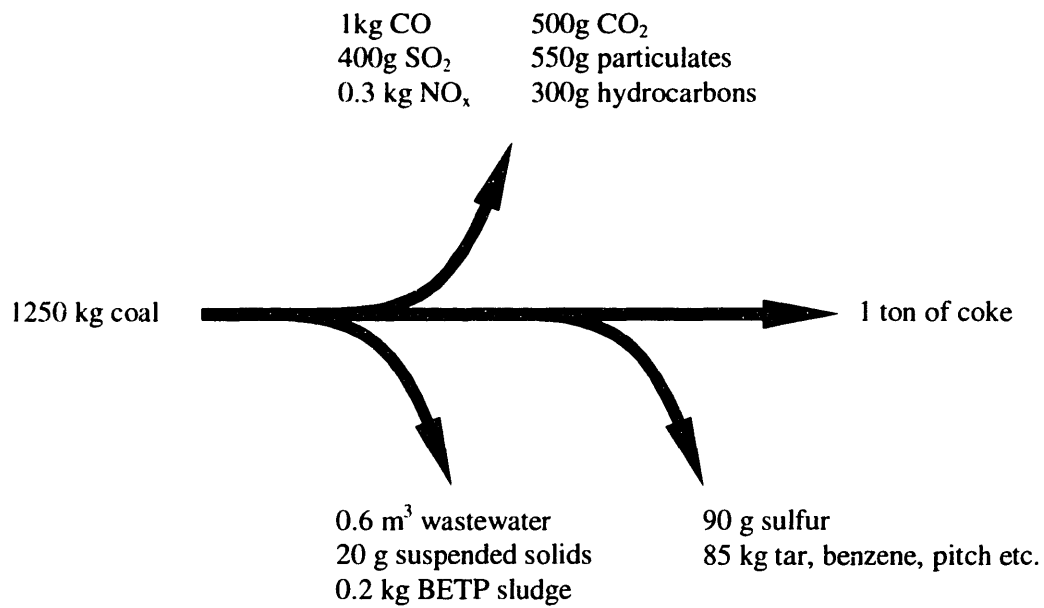
Coke-plant waste water is made up of discharges from the flushing liquor system, from the primary and final coolers, decanted water from the light-oil decanters, and discharges from the tar-recovery/chemicals-recovery operations [19]. The treatment of coke-oven waste water is a three stage process, involving pretreatment for separation of oils and tar, steam stripping for the removal of ammonia, H₂S, and HCN, and finally biological oxidation in a biological effluent treatment plant (BETP) for the destruction of phenols, thiocyanates, cyanides, and thiosulphates that contribute to the chemical oxygen demand of the effluent. Table 5-1 gives the typical composition of the waste water stream from a coke plant following the treatment steps outlined above.

Table 5-1 Typical composition of coke-plant waste water after treatment [19].

Constituent	Concentration
Ammonia	< 10 ml/m ³ (ppm)
Phenol	< 0.1 ml/m ³ (ppm)
Thiocyanate	< 1.0 ml/m ³ (ppm)
Total Cyanide	< 1.0 ml/m ³ (ppm)
Oil	< 15 ml/m ³ (ppm)
Total Suspended Solids	< 25 ml/m ³ (ppm)

Figure 5-6 presents an energy/material balance for the coke oven works.

²⁷ PM₁₀ is a designation for particulate matter with an aerodynamic diameter less than or equal to 10µm.



Emissions of concern	PAHs, benzene, PM ₁₀ , H ₂ S, CH ₄
Waste water constituents of concern	Suspended solids, oil, cyanide, phenol, ammonia
Input energy breakdown	485 MJ electrical; 41.1 GJ coal; 0.5 GJ steam; 3.2 GJ underfire gas
Output energy breakdown	29.8 GJ coke; 8.2 GJ COG; 1.9 GJ coal tar; 0.7 GJ benzene; 0.9 GJ electrical; 33 MJ steam

Figure 5-6 Energy/materials balance for the coke oven works [21].

5.2 Ironmaking in the Blast Furnace

The blast furnace is a tall shaft-type furnace with a vertical stack superimposed over a crucible-like hearth. In an integrated steel mill, the blast furnace performs the function of converting iron ore to liquid iron, which is then used to produce steel. A schematic view of a typical blast-furnace plant is presented in Figure 5-7. The material inputs to a blast furnace include the following:

1. **Iron-bearing materials:** The function of the iron-bearing materials is to supply the element iron. The major iron-bearing materials are iron ore (Fe_2O_3 or Fe_3O_4), sinter and pellets. The achievement of high production rates and smooth movement of the burden in the furnace requires screening of iron ore to remove fines. Both sinter and pellets are agglomerates made from the portion of the ore that is too fine to be charged directly to the blast furnace.
2. **Coke,** which acts as the reducing agent, and
3. **Fluxes:** The major function of the fluxes, limestone and/or dolomite, is to combine with the ash in the coke and the gangue in the ore to make a fluid slag that can be drained readily from the furnace hearth.

The above inputs are continually added to the top of the furnace shaft. A blast of heated air and a gaseous, liquid, or powdered fuel are introduced through water-cooled openings called tuyeres located at the top of the hearth. The heated air burns the injected fuel and the coke charged in from the top to produce the heat required by the process and to provide reducing gas (CO) that removes oxygen from the ore. The reduced iron melts and runs down to the bottom of the hearth. The flux combines with the impurities in the ore to produce a slag which also melts and accumulates on top of the liquid iron in the hearth. The iron and slag are periodically drained out of the furnace through tapping holes or notches.

The hot metal from the furnace is transported in torpedo vessels to the steel plant or a casting machine. Blast furnace slag can be handled in a variety of ways. At many modern blast furnaces, the molten slag from the blast furnace is run into pits, where it is solidified with the help of water sprays. The slag treatment process causes air pollution through generation of hydrogen sulfide and sulfur dioxide. Emissions of particulate material, essentially iron oxide and primarily emitted during tapping operations are another source of air pollution from blast furnace ironmaking.

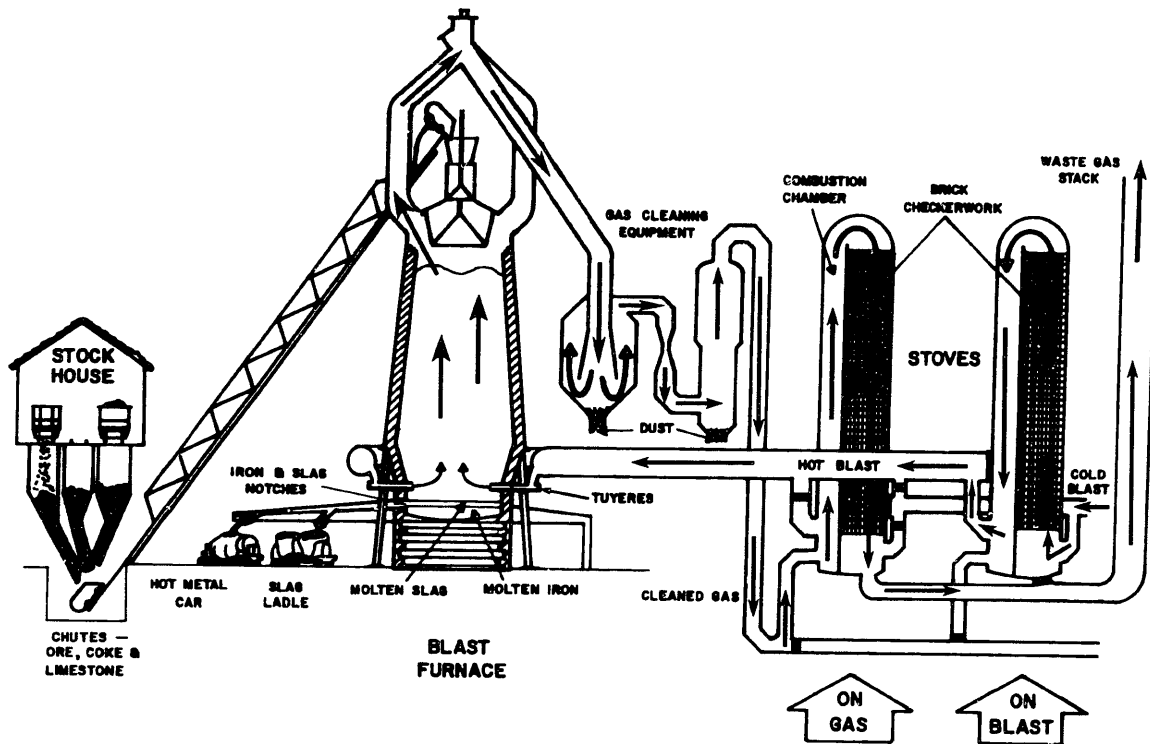


Figure 5-7 Schematic of a blast-furnace plant [22].

The gas from the top of the furnace is used to heat the blast air in hot-blast stoves. However, the gas contains significant amounts of dust. This dust is generally referred to as flue dust and is made up of fine particles of coke, burden material and chemical compounds that are formed from reactions within the blast furnace. Before the blast-furnace gas can be burned in the hot-blast stoves, it must be cleaned to remove the flue dust. The gas-cleaning equipment can lead to water pollution, justifying a minor digression here to explain its functioning. Figure 5-8 is a schematic of the cleaning equipment used. For the first step in the cleaning process, the gas is passed through a dry dustcatcher, where coarse particulates are removed. As the gas passes downward inside the dustcatcher its velocity decreases, and most of the dust coarser than 0.8 mm drops out of the gas stream and is deposited at the bottom of the dustcatcher. The dust that accumulates in the dustcatcher is generally removed through a pug mill. Water is added to the dust as it passes through the pug mill to prevent it from blowing into the atmosphere as it is discharged. After the gas has passed through the dry dustcatcher, it goes to a wet-cleaning system (venturi washer) where the very fine particles of dust are scrubbed out of the gas with water. The water used in the wet gas-cleaning systems contains between 30 and 50% of the total dust removed from the gas as it leaves the gas washer. Consequently, the suspended particles of dust are removed from the

water before it is reused or discharged. In addition to using water to remove flue dust, efficient operation of a blast furnace requires considerable amounts of water for cooling various parts of the furnace. As mentioned above, water is also used for slag processing operations.

An integral part of blast furnace operation are the hot-blast stoves. The stoves are tall, cylindrical steel structures lined with insulation and almost completely filled with checker brick. In the operation of the hot-blast system, the checkerwork of a stove is first heated by combustion of blast-furnace gas, and then the cold blast air is passed through the stove and is heated by the hot checkerwork. The combustion products generated in the hot-blast stoves are released to the waste gas stack.

The dust removed from the gas in the cleaning system is sintered for recycling back into the blast furnace. A better appreciation of the quantity of material and the amount of energy required for producing hot metal in the blast furnace can be obtained by referring to the material balance in Figure 5-9 and the energy balance in Table 5-2.

This technological description provides a framework for assessing the impact of environmental regulations that have been enumerated in the following chapter.

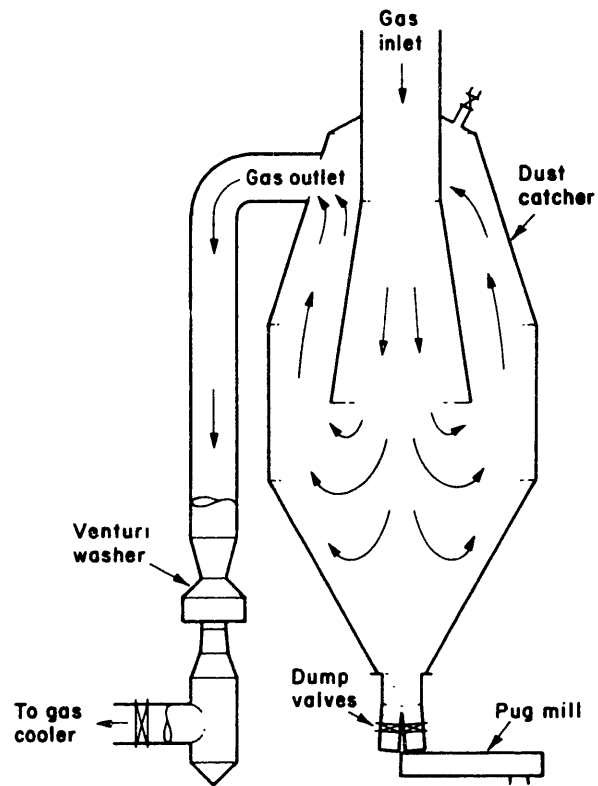


Figure 5-8 Blast-furnace gas cleaning equipment (dustcatcher and venturi washer).

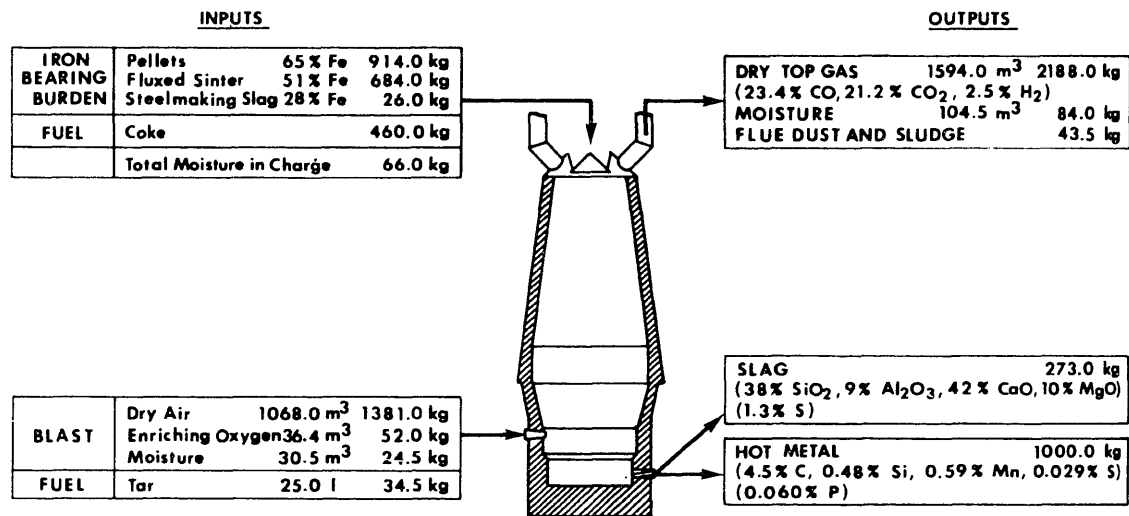


Figure 5-9 Blast furnace material balance (all quantities in amount/metric ton) [19].

Table 5-2 Blast-furnace energy balance [19].

	GJ per metric ton of hot metal
<i>Energy input</i>	
Blast sensible heat	1.64
Coke combustion	2.10
Injected fuel combustion	0.27
Decomposition of water	- 0.26
Total	3.75
<i>Energy output</i>	
Reduction of iron oxides	1.17
Reduction of metalloids	0.15
Slag sensible heat	0.48
Hot metal sensible heat	1.36
Top gas sensible heat	0.20
Vaporization of moisture from burden	0.13
Furnace heat loss	0.26
Total	3.75

6 Regulations

The present chapter discusses the major federal environmental statutes that affect the iron and steel industry. Emphasis is placed on the more significant changes over the last few years. Over the past 25 years, the U.S. iron and steel industry has invested approximately \$6 billion in pollution control systems. In a typical year, 15% of the industry's capital investments go toward environmental projects. Costs for operating and maintaining these facilities amount to \$10 to \$20 per ton of steel shipped [23]. In 1994 alone, the iron and steel industry had capital expenditures of \$231 million for pollution abatement, including \$45 million on water pollution control, \$20 million for solid/contained waste, and \$166 million for air pollution control. The figure for air pollution control (72% of total environmental expenditure) is primarily a result of operating coke ovens in compliance with the Clean Air Act (CAA) [1].

6.1 Clean Air Act

6.1.1 National Primary and Secondary Ambient Air Quality Standards 40CFR50

Title I of CAA addresses requirements for the attainment and maintenance of the National Ambient Air Quality Standards (NAAQS). The general idea behind the NAAQS program is that it is to be based on scientific determinations of threshold levels of air pollution. These standards establish numerical criteria to be applied uniformly throughout the country through State Implementation Plans (SIPs). National primary ambient air quality standards (NPAAQS) define levels of air quality which the EPA Administrator judges are necessary, with an adequate margin of safety, to protect the public health. National secondary ambient air quality standards (NSAAQS) define levels of air quality which the Administrator judges necessary to protect the public welfare from any known or anticipated adverse effects of a pollutant. EPA has set NAAQS for six *criteria pollutants*: SO_x, PM₁₀, CO, ozone, NO_x, and Pb. The methods for sampling and analyzing ambient air for these air pollutants are specified as reference methods in Part 50. Here, we provide brief information on the threshold levels set by EPA (see Table 6-1).

The levels of the annual and 24-hour NPAAQS for sulfur oxides are 0.03 ppm (annual arithmetic mean) and 0.14 ppm (24-hour average concentration), respectively. The level of the 3-hour NSAAQS for SO_x is 0.5 ppm (3-hour average concentration). The level of the national primary as

well as secondary annual and 24-hour ambient air quality standards for particulate matter is 50 $\mu\text{g}/\text{m}^3$ and 150 $\mu\text{g}/\text{m}^3$, respectively. The NPAAQS for CO are:

1. 9 ppm (10 mg/m^3) for an 8-hour average concentration.
2. 35 ppm (40 mg/m^3) for a 1-hour average concentration.

The annual NPAAQS and NSAAQS for nitrogen dioxide are 0.053 ppm (100 $\mu\text{g}/\text{m}^3$). For Pb, the standard is 1.5 $\mu\text{g}/\text{m}^3$, arithmetic mean averaged over a calendar quarter.

Table 6-1 National ambient air quality standards for criteria pollutants.

Pollutant	NAAQS	
	NPAAQS	NSAAQS
SO _x (ppm)	0.03 Annual	0.5 3-hr
	0.14 24-hr	
PM ₁₀ ($\mu\text{g}/\text{m}^3$)	50 Annual	
	150 24-hr	
CO (ppm)	9 8-hr	
	35 1-hr	
NO ₂ (ppm)	0.053 Annual	
Pb ($\mu\text{g}/\text{m}^3$)	1.5 Quarterly	

6.1.2 National Emission Standards for Hazardous Air Pollutants (NESHAPs)

In a manner similar to the pulp and paper industry, EPA has promulgated standards to control the emission of Hazardous Air Pollutants generated in the iron and steel sector. These standards are again based on the use of MACT. However, if a technology-based standard does not result in acceptable ambient concentration levels, the EPA is required to set stricter limitations based on risk estimations. These *risk-based standards* rely on the determination of an *ample margin of safety*. The EPA has interpreted ample margin of safety as that standard which protects the most exposed individual in the population to a risk of cancer below 1 in 10,000 and the majority of the population to less than 1 in 1 million.

National Emission Standards for Coke Oven Batteries 40CFR63 Subpart L

In 1992, the EPA released its new proposed rule on CAA standards for toxic emissions from coke ovens. Coke emissions are listed as a hazardous air pollutant under the Clean Air Act. Emission points associated with byproduct coke oven batteries that are subject to NESHAP limitations include charging operations, coke oven doors, topside port lids and offtake systems on the top side of the battery, and collecting mains. Operators may choose from two options. Under a standard time line, MACT must be achieved by 1995 and a risk-based standard by 2003.

The standard time line restrictions require that, by December 31, 1995, coke oven emissions from each existing byproduct coke oven battery not exceed: (1) 5.5% leaking doors for short batteries²⁸ and 6% for tall batteries²⁹; (2) 0.6% leaking topside port lids; (3) 3% leaking offtake systems; (4) 12 seconds of visible emissions per charge. Leaks from doors, lids, and offtake systems are measured as a percentage of doors, lids etc. in a coke oven battery that are leaking over some time interval. On and after January 1, 2003, leaking door limitations would be reduced to 5.5% for tall and 5% for short batteries. Visible emission limitations for a new byproduct coke oven battery are 0% leaking doors, topside port lids and offtake systems, and up to 34 seconds of visible emissions per charge. Table 6-2 summarizes these restrictions.

Table 6-2 National emission standards for coke oven batteries.

Emission point	Standard time line		Extended time line		
	<i>Compliance date</i>				
	Dec. 31, 1995	Jan. 1, 2003	Nov. 15, 1993	Jan. 1, 1998	2010
Oven door	5.5% (short) 6% (tall)	5% (short) 5.5% (tall)	7%	3.8% (short) 4.3% (tall)	3.3% (short) 4% (tall)
Topside port lids	0.6%	0% (new)	0.83%	0.4%	
Offtake system	3%	0% (new)	4.2%	2.5%	
Duration of visible emissions per charge	12 sec	34 sec (new)	12 sec	12 sec	

²⁸ Short coke oven battery means a battery with ovens less than 6m in height.

²⁹ Tall coke oven battery means a battery with ovens less than 6m or more in height.

The other choice allows for postponing the risk-based standards until 2020, but to qualify for the extension, progressively tighter standards must be met in 1998 and 2010. The batteries were expected to meet initial MACT emission limiting standards (7% leaking doors, 0.83% leaking top side port lids, 4.2% leaking offtake systems, and 12 seconds of visible charges) by November 15, 1993. In addition to meeting the initial MACT standards, coke batteries must meet even more stringent limits (known as Lowest Achievable Emission Rate or LAER limits) by January 1, 1998 (4.3% leaking doors for tall, 3.8% for short, 0.4% topside port lids, 2.5% off-takes, and 12 seconds of emissions per charge). The Act allows for promulgation of a new LAER standard (4% leaking doors for tall, 3.3% for short) in 2007 that batteries would have to meet by 2010.

National Emission Standard for Benzene Emissions from Coke Byproduct Recovery Plants 40CFR61 Subpart L

The provisions of this subpart apply to each of the following sources at coke byproduct recovery plants: tar decanters and storage tanks; tar-intercepting sumps³⁰; flushing liquor circulation tanks; light-oil condensers, decanters, sumps³¹, and storage tanks; wash-oil decanters³² and circulation tanks; naphthalene processing; BTX and excess ammonia-liquor storage tanks; final coolers and related equipment that is intended to operate in benzene service. Gases from each process vessel, tar storage tank and tar-intercepting sump need to be ducted to the gas collection system in the byproduct recovery process, where the benzene in the gas will be recovered or destroyed. The liquid surface in case of light-oil sumps should be enclosed and sealed to contain the emissions. These control systems will be designed and operated for no detectable emissions, as indicated by a concentration of less than 500 ppm above background levels. No emissions are allowed from naphthalene processing and final coolers.

National Emission Standards for Halogenated Solvent Cleaning 40CFR63 Subpart T

The provisions of this subpart apply to solvent cleaning machines that use any solvent containing methylene chloride, perchloroethylene, trichloroethylene, 1,1,1-trichloroethane, carbon tetrachloride, or chloroform, in a concentration greater than 5 wt. %. Of these, 1,1,1-

³⁰ A tar-intercepting sump means any tank, pit or enclosure that serves to receive or separate tars and aqueous condensate discharged from the primary cooler.

³¹ Light-oil condenser means any unit in the light-oil recovery operation that functions to condense benzene-containing vapors. A light-oil decanter functions to separate light oil from water downstream of the condenser. A light-oil sump serves to separate hydrocarbon liquids on the surface of the water in light-oil recovery.

³² Wash-oil decanter is a vessel that uses gravity to separate condensed water from wash-oil.

trichloroethane and trichloroethylene are among the top chemicals (by weight) that facilities within the iron and steel sector self reported as released to the environment based upon 1993 TRI data.

National Emission Standards for Hazardous Air Pollutants for Industrial Process Cooling Towers 40CFR63 Subpart Q

The provisions of this subpart apply to all new and existing industrial process cooling towers³³ (IPCTs) that are operated with chromium-based water treatment chemicals. IPCTs have been identified as potentially significant sources of chromium air emissions and chromium compounds are among the substances listed as HAPs in the CAA. The standard required the owner or operator of any affected IPCT to eliminate the use of chromium-based water treatment chemicals by 1994.

6.1.3 Pending and Proposed Regulations

Coke oven batteries face unknown but likely tighter technology-based standards in 2010 and risk-based ones in 2020. Although coke ovens are considered by many industry experts to be the biggest environmental problem of the iron and steel industry, proposed environmental regulations (such as those mentioned below) will affect other processes within the industry. MACT standards for emissions of compounds of Cr, Ni, Mn, Cd, and other heavy metals are expected to be established in 2000. Because many of these metals are routinely found in iron ore, scrap, and alloying materials that are processed in iron and steel plants, most steelmaking processes will be affected in some way. Hydrochloric acid and chlorine are among the pollutants listed as HAPs. Steel pickling processes that use hydrochloric acid have been identified as potentially significant sources of HCl and Cl₂ air emissions.

6.2 Clean Water Act

The primary objective of the Clean Water Act is to restore the chemical, physical, and biological integrity of the nation's surface waters. Pollutants regulated under the CWA include priority, conventional and non-conventional pollutants. The CWA regulates both direct and indirect discharges. Direct discharges or "point source" discharges are from sources such as pipes and sewers. The National Pollutant Discharge Elimination System (NPDES) program controls direct

³³ A cooling tower is a water recirculating device that uses fans or natural draft to draw or force ambient air through the device to cool warm water by direct contact.

discharges. A facility that intends to discharge into the nation's waters must obtain a NPDES permit prior to initiating its discharge. A permit applicant must provide quantitative analytical data identifying the types of pollutants present in the facility's effluent. The permit will then set forth the conditions and effluent limitations under which a facility may make a discharge [1]. NPDES permits, issued by either EPA or an authorized State contain industry specific technology-based and/or water-quality based limits. Water-quality based standards, unlike technological standards, generally do not take into account technological feasibility or costs and are designed to protect designated uses of surface waters, such as supporting aquatic life or recreation.

Another type of discharge that is regulated by the CWA is the indirect discharge of industrial pollutants to publicly-owned treatment works (POTWs) [1]. The national pretreatment program controls such indirect discharge. The goal of the pretreatment program is to protect municipal wastewater treatment plants from damage that may occur when wastes are discharged into a sewer system and to protect the quality of sludge generated by these plants. Many steel mills discharge industrial waste water through sewers to POTWs.

40CFR420 contains the technology-based effluent limitations guidelines and standards that EPA has developed for the iron and steel industry. These are implemented through the NPDES permit program and through pretreatment programs.

6.2.1 Effluent Limitations Guidelines and Standards 40CFR420

The pollutants regulated by 40CFR420 include the following:

1. Conventional pollutants: TSS, oil and grease, pH
2. Non-conventional pollutants: Ammonia, phenols
3. Priority or toxic pollutants: Cyanide, Chromium, lead, nickel, zinc, benzene, benzo-a-pyrene, naphthalene, tetrachloroethylene.

The regulation contains 12 subparts for 12 distinct manufacturing processes in the iron and steel industry, including cokemaking, sintering, ironmaking, steelmaking, continuous casting etc. The provisions of Part 420 for the by-product cokemaking and blast-furnace ironmaking processes have been summarized in Tables 6-3 and 6-4.

Table 6-3 Effluent limitations and standards for by-product cokemaking (maximum for one day, kg/kkg of product).

Pollutant	BPT	BAT	NSPS	PSES and PSNS ³⁴
TSS	0.253	-	0.172	-
Oil & Grease	0.0327	-	0.00638	-
Ammonia	0.274	0.0543	0.0543	0.0645
Cyanide	0.0657	0.00638	0.00638	0.0172
Phenols	0.00451	0.0000638	0.0000638	0.0430
pH	6.0-9.0	-	6.0-9.0	-
Benzene	-	0.0000319	0.0000319	-
Naphthalene	-	0.0000319	0.0000319	-
Benzo-a-pyrene	-	0.0000319	0.0000319	-

Table 6-4 Effluent limitations and standards for ironmaking in the blast furnace (maximum for one day, kg/kkg of product).

Pollutant	BPT	BAT	NSPS	PSES	PSNS
TSS	0.0782	-	0.0117	-	-
Oil & Grease	-	-	0.00292	-	-
Ammonia	0.161	0.00876	0.00876	0.00876	0.00876
Cyanide	0.0234	0.00175	0.000584	0.00175	0.000584
Phenols	0.00626	0.0000584	0.0000584	0.0000584	0.0000584
pH	6.0-9.0	-	6.0-9.0	-	-
Lead	-	0.000263	0.000263	0.000263	0.000263
Zinc	-	0.000394	0.000394	0.000394	0.000394

³⁴ PSES: Pretreatment Standards for Existing Sources, PSNS: Pretreatment Standards for New Sources

6.2.2 Regulations Governing Storm Water Discharges

The 1987 amendments to the CWA included a provision that required EPA to establish regulations for industrial storm water runoff. In response to this statutory command, EPA promulgated the NPDES storm water permit regulations to address storm water discharges associated with industrial activity. A “storm water discharge associated with industrial activity” is a discharge from any conveyance that is used for collecting and conveying storm water and that is directly related to manufacturing, processing, or raw materials storage areas at an industrial plant. Under this storm water permit program, discharges must comply with the applicable effluent limitations in Section 6.2.1 above. The regulations are of major concern to the iron and steel industry because of the nature of materials typically located on iron and steel manufacturing sites.

6.2.3 Pending and Proposed Regulations

In 1989, in recognition of the vulnerability of the Great Lakes to bioaccumulative chemicals, EPA and the states began the Great Lakes Water Quality Initiative (GLI), an effort to establish common regulatory practices for the Great Lakes waters. Under this initiative EPA has been involved in proposing uniform, water-quality based standards in the Great Lakes States. Approximately 80% of the U.S. integrated steelmaking capacity is located in the Great Lakes region and therefore, the initiative may have a significant impact on the industry [23]. The main concern the steel industry has with the GLI is the establishment of uniform water quality standards for all waters in the basin without regard to the multiple uses of water bodies in this region. Setting standards for the entire region on the basis of the most sensitive ecosystem, while at the same time disregarding the water-quality impacts of non-point sources such as urban or agricultural runoff, have the effect of imposing huge costs. To assess the impact of GLI rules, the American Iron and Steel Institute commissioned an engineering study to develop estimates of treatment facilities to meet the GLI standards. GLI compliance for the entire integrated steelmaking capacity in the region is estimated to amount to \$2.7 billion..

6.3 Resource Conservation and Recovery Act

The Resource Conservation and Recovery Act (RCRA) provides a cradle-to-grave regulatory scheme to track hazardous wastes from the point of generation to the point of disposal or treatment [24]. The basic components of the cradle-to-grave management system are: (1) identification and permitting system allowing the EPA and the states to regulate all facilities

involved in the treatment, storage, and disposal of hazardous waste; and (2) restrictions on the land disposal of hazardous waste.

The first step in the RCRA process is a determination of whether a material constitutes a solid waste. Essentially, a solid waste is any *discarded* material. After determining that the material in question is a solid waste, a party must determine whether the material is a hazardous waste. RCRA hazardous wastes include EPA specified types of solid wastes generated by particular industries (these are designated with the code K) or materials which exhibit a hazardous waste characteristic (ignitability, corrosivity, reactivity, or toxicity).

Several RCRA-listed wastes are produced during coke, iron and steelmaking operations. These wastes are identified in Table 6-5 by process.

Table 6-5 RCRA wastes generated during coke, iron and steelmaking operations [25].

Process and EPA hazardous waste number	Hazardous waste
<i>Iron and steel</i>	
K061	Emission control dust/sludge ³⁵ from the primary production of steel in electric arc furnaces
K062	Spent pickle liquor generated by steel finishing operations
<i>Cokemaking</i>	
K060	Ammonia still lime sludge
K087	Decanter tank tar sludge
K141	Process residues from the recovery of coal tar
K142, K147	Tar storage tank residues
K143	Process residues from the recovery of light oil
K145	Residues from naphthalene recovery

³⁵ Sludge means any solid, semi-solid or liquid waste generated from a municipal, commercial or industrial wastewater treatment plant, or air pollution control facility exclusive of the treated effluent from a wastewater treatment plant.

RCRA was amended in 1984 by the Hazardous and Solid Waste Amendments (HSWA). These amendments establish Land Disposal Restrictions (LDRs), that are regulations prohibiting the disposal of hazardous waste on land without prior treatment. Under the LDRs, materials must meet LDR treatment standards prior to placement in a land disposal unit (landfill, land treatment unit, or waste pile).

EAF dust has been the subject of particular regulatory attention by EPA. EAF dust is a listed hazardous waste and is subject to land disposal restrictions under RCRA. For EAF dust containing less than 15% zinc LDR treatment standards establish concentration limits for dust constituents including cadmium, chromium, lead, and nickel. For dust containing greater amounts of zinc, the standard is expressed as “no land disposal”.

Major concerns of the industry with respect to EAF dust rules are the limitations that are placed on the ultimate disposal or uses of non-hazardous residuals from the High Temperature Metals Recovery (HTMR) processes. These restrictions might serve to discourage metals recovery practices. Residues, such as slag, generated during high temperature metals recovery processing of K061, K062 waste are excluded from hazardous waste regulations *only* when they meet the generic exclusion levels identified in Table 6-6 for all constituents, and provided the residues do not exhibit hazardous waste characteristics.

The definition of a solid waste within RCRA includes materials that are recycled. The iron and steel industry has a special and unique interest in the recycling aspect of RCRA because of the huge amount of material handled between the time iron ore is removed from the ground until the steel product is made [23]. Commercial markets have been developed for secondary materials such as blast furnace slag and steelmaking slags. Other secondary materials such as iron-bearing dusts and sludge generated from a variety of sources within steel plants are returned to the steelmaking processes. Coke-oven waste materials are also commonly returned to the coke ovens, and used oils are reclaimed for reuse.

In accordance with 40CFR266 Subpart H, industrial furnaces that burn hazardous waste are subject to Boiler and Industrial Furnace³⁶ (BIF) regulations. For this subpart, *burn* means burning for energy recovery or processing for materials recovery. The BIF rules control emissions of toxic organic compounds, toxic metals, and particulate matter from industrial furnaces burning hazardous waste. To the degree iron and steel manufacturing facilities perform recycling in a

furnace, the process requires a BIF permit. Processes burning hazardous waste solely for metal recovery are not required to obtain a BIF permit. However, if the recycling process produces materials classified as hazardous waste, these residues should meet the generic exclusion levels described for high temperature metals recovery of K061.

Table 6-6 Generic exclusion levels for K061 HTMR residues [26].

Constituent	Maximum concentration (mg/l)
Antimony	0.100
Arsenic	0.500
Barium	7.600
Beryllium	0.010
Cadmium	0.050
Chromium	0.330
Lead	0.150
Mercury	0.009
Nickel	1.000
Selenium	0.160
Silver	0.300
Thallium	0.020
Zinc	70.00

HSWA also required EPA to implement *corrective action* at hazardous waste treatment, storage and disposal facilities regulated under RCRA. Permits issued to facilities must address corrective action for all releases from solid waste management units at the facility. EPA's requirements for such corrective action of waste management units are also of great concern to the steel industry [23]. Under RCRA, companies seeking permits are required to assess all historic releases of hazardous constituents from any solid waste management unit at the facility and to take corrective action to remediate those sites. Companies must also provide *financial assurance* for the costs of performing that corrective action. Because of the size and age of many steel plants and the

³⁶ Industrial furnace includes smelting, melting, and refining furnaces, coke ovens and blast furnaces.

diversity of operations and waste management practices over the life of those plants, there are commonly dozens or even hundreds of solid waste management units subject to corrective action requirements. An analysis of the cost exposure at integrated iron and steel plants has shown the potential cleanup costs to be approximately \$3 billion for the industry. Because of the magnitude of costs involved for corrective action, most steel companies will be unable to make the necessary demonstrations.

Having discussed the conventional technology in use in ironmaking, and the pertinent environmental regulations, the next chapter illustrates two technologies that have been used to combat pollution, while providing economic benefits.

7 No Regrets Pollution Prevention: Iron/Steel

7.1 Smelt Reduction

Smelt reduction processes combine coal gasification with the direct reduction of iron oxides. New smelting reduction processes are in various stages of development and include the following: the COREX process, the Japanese Direct Iron-Ore Smelting Reduction or DIOS process, and the HISmelt process. This report concentrates on the COREX process, as it is the only commercial process.

The COREX process (Figure 7-1) separates the iron-ore reduction and melting into two reactors that accomplish the following processing steps [27]:

1. Reduction of iron ore in a shaft furnace.
2. Generation of reducing gas and liberation of energy from coal for melting in a melter gasifier.

The lower portion of the melter gasifier is a fluidized bed, where reduction gas is generated by partial oxidation of coal. The gas temperature in the fluidized bed is in the range of 1600 to 1700°C. Coal is charged into the melter gasifier through a lock-hopper system. The coal then falls by gravity through the gasifier where it comes in contact with the reduction gas at a temperature of 1000 to 1200°C. Instantaneous drying and degasification of the coal particles occur in the upper portion of the melter gasifier.

The reduction gas generated in the melter gasifier mainly consists of CO and H₂, and is laden with coal, ash and iron dust. After leaving the gasifier, the reduction gas is cooled and the fine dust is separated in a hot-gas cyclone. By the addition of cooling gas, as shown in Figure 7-1, the reduction gas temperature is set to an optimum operating range between 800°C and 850°C. Downstream of the hot-gas cyclone, the reduction gas is fed into a reduction shaft furnace and ascends through the iron-ore burden. The iron ore, charged into the shaft through a lock-hopper system, descends by gravity. The top gas from the reduction shaft is cooled and cleaned in a scrubber and is available as export gas.

The Direct Reduced Iron (DRI) produced in the reduction shaft is charged continuously to the melter gasifier. The velocity of fall of the sponge iron particles is reduced in the fluidized bed of the gasifier so that complete reduction, heating and melting occurs. Liquid hot metal and slag

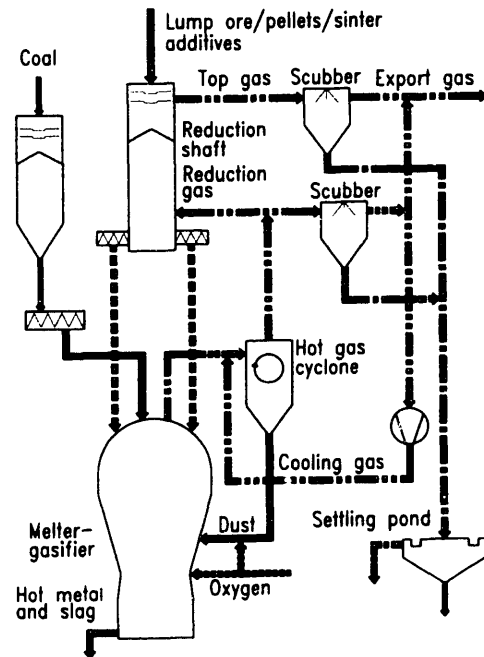


Figure 7-1 COREX process [28].

drop to the bottom of the melter gasifier and are discharged by conventional tapping procedures similar to those used in blast furnaces.

COREX is a new ironmaking technology for the production of hot metal that bypasses the coke-making step. Development of the COREX process started when gas prices increased dramatically towards the end of the 1970s. During that period, Deutsche Voest-Alpine Industrieanlagenbau (DVAI) was marketing mini-mills with iron produced by Midrex plants and based on reformed natural gas [29]. DVAI decided to develop a method to produce virgin iron units for the mini-mills by new and cost-saving coal-based processes. In 1981, a 60,000-tonnes of hot metal (thm)/year pilot plant was constructed at Kehl (former West Germany) to demonstrate the principles involved. In 1988, based on the results obtained at the pilot plant in Kehl, the first commercial COREX plant (a C-1000 module, nominal capacity 1000 thm/day or 330,000 thm/year) was started up in South Africa, producing pig iron for ISCOR's Pretoria steel works.

COREX is a coke-less technology that substitutes coal for coke in the blast furnace, eliminating the need for coke-making. When compared to the conventional integrated plant, the COREX process is designed to integrate the processes of coke production in coke ovens, ore preparation in sinter plants, and reduction of iron-ore in the blast furnace. Coke making and ore preparation are responsible for the largest part of emissions in the primary steel making route. The COREX

process, therefore, presents the potential to substantially reduce pollution. Dippenaar et al. [30] have compared the impact of COREX and the traditional blast furnace route on the environment and their analysis is presented below.

The sinter plant is the main source of sulfur dioxide emissions in the classical route of iron making. Sulfur dioxide is produced in the sinter plant under oxidizing conditions. Reducing conditions in the COREX plant reduce the possibility of sulfur dioxide formation. Hydrogen sulfide forms in the COREX plant, but most of it is absorbed in the reduction shaft by liquid iron, or by the lime and dolomite that are added specifically to remove sulfur. As a result, the sulfur content in the off-gas is very low. Table 7-1 compares the typical emissions for COREX and integrated iron making.

Table 7-1 Typical emissions from traditional and COREX processes [30].

Emission (kg/thm)	Traditional ³⁷	COREX ³⁸	COREX as % of traditional
Dust	2.1	0.018	0.9
SO ₂	3.3	0.025	0.8
NO ₂	1.2	0.023	1.9

The levels of the important contaminants in the scrubbing water are shown in Table 7-2, which compares typical values for European ironmaking facilities (comprising coke ovens, sinter plant, and blast furnace) with those for the COREX pilot plant at Kehl and the COREX commercial facility at ISCOR's Pretoria Works. The analysis for the scrubbing water of the integrated facilities refers to water that had been subjected to treatment to remove undesirable constituents, whereas the analysis for the COREX plants is for untreated scrubbing water issuing directly from the plant. Table 7-2 shows that the untreated water from the COREX plant is purer than the scrubbing water from conventional integrated facilities. The coke oven is the main source of organic substances that report in the scrubbing water for the integrated facilities. Organic substances are also formed in the COREX plant because coal is gasified in the melter gasifier.

³⁷ Coke oven, sinter plant, and blast furnace; typical values for integrated ironmaking facilities in Europe.

However, because organic substances are continuously withdrawn from the coke oven, significant amounts of hydrocarbons, which are distilled at temperatures between 100 and 1000°C, report in the water from the gas scrubber. Conversely, because all the gas from the gasifier in the COREX plant passes through a high-temperature zone (> 1000°C), the hydrocarbons released from coal during devolatilization are fully cracked, and carbon monoxide and hydrogen gas are the only products. For this reason, the concentration of organic constituents in the scrubbing water of the COREX process is much lower than in the scrubbing water of the conventional route.

Table 7-2 Analyses of process water from different ironmaking facilities [30].

Constituent (kg/thm)	Traditional route ³⁹	COREX process		
		Kehl pilot plant	Iscor production	Iscor as % of traditional
NH ₄	0.59	0.1500	0.0600	10.4
BOD	0.15	0.0360	n.d.	n.d.
COD	0.69	0.0960	0.1220	17.7
Phenol	0.08	0.0003	0.0006	0.7
H ₂ S	0.06	0.0003	n.d.	n.d.
Cyanide	0.02	n.d.	0.0005	2.3

The concentration of cyanide in the COREX water amounts to only 2% of the value for the water from the scrubbers of the integrated plant. The corresponding figure for the ammonia content is 10%. The comparatively low concentrations of cyanide and ammonia in the COREX water can be attributed to the use of pure oxygen to combust the coal in the COREX plant.

The chemical composition and temperature of the hot metal produced by the COREX process is well suited for BOF steel making. Table 7-3 compares the chemical composition of liquid iron produced by the blast furnace and COREX processes. The table shows that COREX liquid iron is

³⁸ Measured at the Kehl pilot plant.

³⁹ Coke oven, sinter plant, and blast furnace; typical values for integrated ironmaking facilities in Europe.

equivalent in quality to the blast furnace product. Therefore, COREX can either replace blast furnaces in capacities ranging from 300,000 to 700,000 thm/year in existing integrated steel plants or serve as a swing producer of hot metal to complement large blast furnace operations. Compared to the conventional coke-oven/blast furnace route, COREX has much lower specific investments costs (Figure 7-2). Capital costs of modern blast furnace-based plants are high due to the investments required in coke plants, ore preparation, and the blast furnace. Economies of scale typically result in large-scale primary steel plants. The lower capital costs for COREX are mainly the result of the absence of a coke-oven plant. The investments required for the COREX process are estimated to be \$210-250/thm annual capacity vs. \$330-350/thm annual capacity for blast furnace plants [31].

Table 7-3 Comparison of liquid iron made by the COREX and BF processes [32].

Constituent (%)	Recommended LD quality	IsCOR, Pretoria	
		BF No. 4	COREX
C	3.80-4.80	4.30	4.10
Si	0.20-1.00	1.20	0.40
Mn	0.20-1.50	0.20	0.20
P	0.08-0.20	0.08	0.11
S	0.01-0.05	0.05	0.06
Temp., °C		1440	1470

Compared to the blast furnace route, COREX produces hot metal at lower specific production costs. A comparison of hot metal production costs is shown in Figure 7-3. It is based on a coke-oven/blast furnace complex with an annual capacity of 1 million tons vs. two COREX modules each with an annual capacity of 500,000 tons. The COREX hot metal cost is 32% lower than from the blast furnace. The lower investment cost influences the cost of hot metal. In addition, coke plants need high grade coking or metallurgical coal types, which are more expensive than steam coal. COREX makes it possible to use steam coal, thereby reducing fuel costs. The U.S. is a net importer of metallurgical coke and coal. Because in the U.S. large fields of suitable coal types can be found, COREX will reduce the need for importing and using expensive metallurgical coal. The abandoned processes also lower the operating costs.

Commercial steel plants incorporating COREX in integrated steel production include the installation of a C-2000 module (nominal capacity 2200 tons/day) at POSCO's Pohang Works, Korea. This plant is designed for an annual production of 660,000 thm and was started up in 1995. Another greenfield COREX/BOF steelmaking complex, based on two C-2000 modules, has been under construction in India (see Figure 7-4). This unit will supply 1.4 million thm/year and was expected to be ready for operation in 1997 [28].

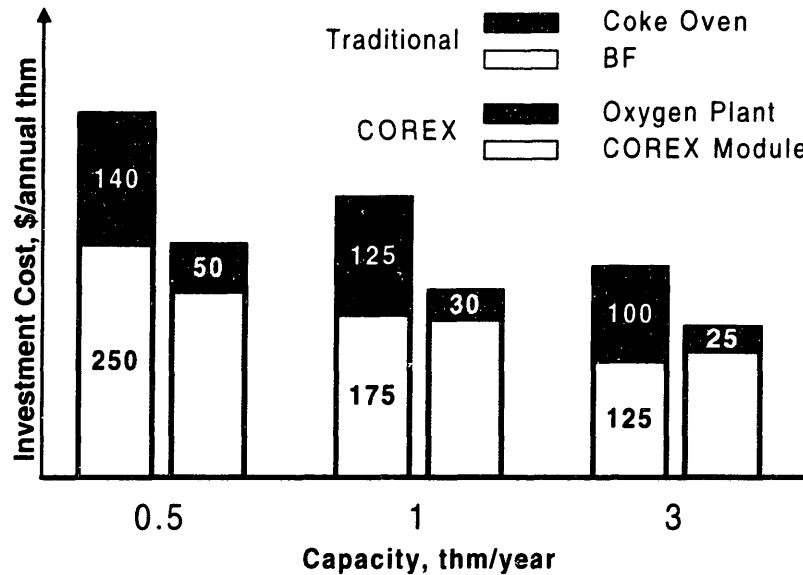


Figure 7-2 Investment costs for COREX and conventional coke-oven/BF facilities [27].

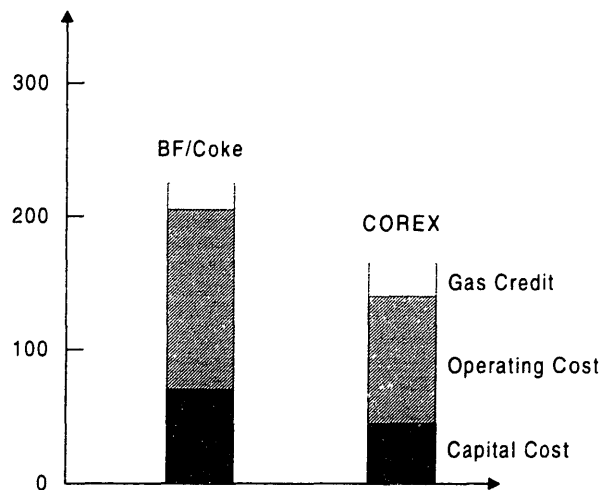


Figure 7-3 Cost of hot metal produced by COREX process and BF for 1 million tonne/year operation [27].

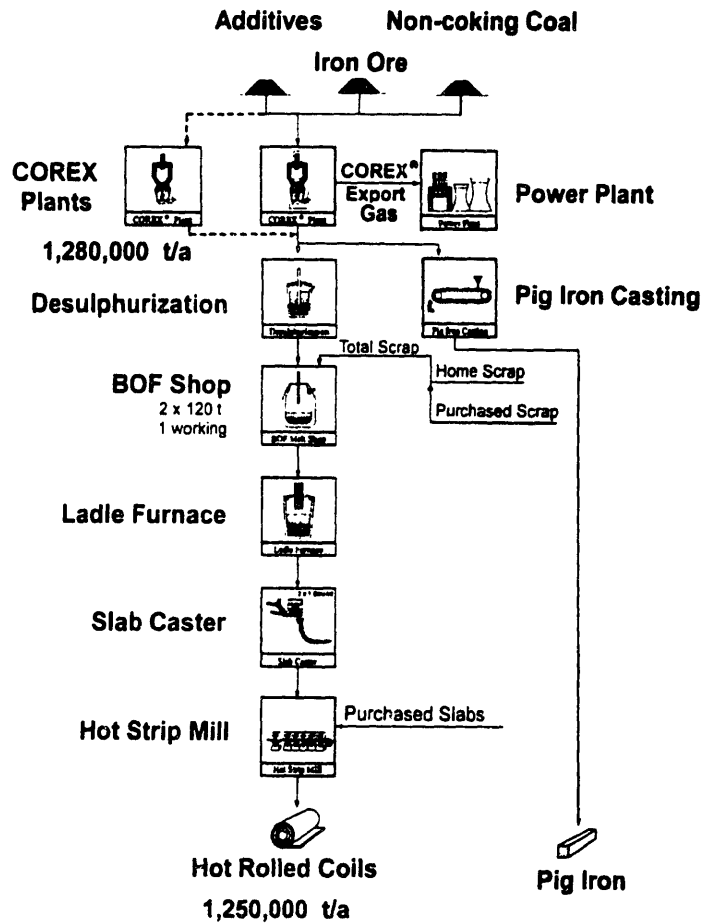


Figure 7-4 Process route at Jindal-Vijayanagar Steel, India.

For mini-mills, COREX provides the possibility of producing hot metal at low cost even in small capacities [27]. The success of mini-mills is based on the low cost production of long products, that do not need high quality steel. Electric arc furnace production is now extending into flat products as a result of the technological breakthrough in continuous casting. With this trend, steel makers are faced with steel quality requirements that will be difficult to meet with scrap-based electric arc furnace steelmaking. Residual elements, such as Mo, Cu, Ni, Sn, Cr, and As, which are increasing in scrap iron, cannot be removed during refining and remain in the steel. These residual elements affect the chemistry of steel making and the resultant properties of the finished product. For this reason, it is necessary to dilute the scrap by virgin iron and COREX hot metal can be used to meet the demands for high quality steel grades. Steel producers are also facing the long-term problems of variation in scrap price together with a short-fall in supply of scrap with low residuals. Another important factor in the production of high quality flat products is the elevated nitrogen content that occurs with scrap-based electric furnace steelmaking. While the nitrogen content of steel sheet is limited to 0.002 to 0.006% (nitrogen increases sensitivity to aging and brittle fracture), the nitrogen content from electric arc steelmaking exceeds 0.01% in most cases. The nitrogen content of COREX hot metal is only 0.002 to 0.003% and remains at this level during steelmaking.

In order to be independent from fluctuating scrap prices, for quality reasons, or due to a lack of scrap, mini-mills have used DRI in the charge. Figure 7-5 compares the economics of different steelmaking routes for mini-mills, including electric arc furnace operation using 100% scrap, with 50% scrap and 50% DRI, and 30-50% addition of COREX hot metal. Steelmaking costs for the first two options are almost the same because the increased cost for energy and capital when using DRI is compensated for by higher scrap costs. Savings are, however, achieved by substituting COREX hot metal for scrap. As compared to the scrap/DRI route, raw material costs are lower for the scrap/COREX option because coal is less expensive than natural gas. If DRI is charged in the electric arc furnace, the power consumption increases because of the gangue content and the remaining unreduced iron in the DRI. In contrast, the addition of hot metal in the charge lowers the power consumption because the hot metal added is already liquid and contains approximately 4% carbon, which generates additional heat during oxidation.

In addition to the production of high quality hot metal, the exported top gas of the COREX process has a lower heating value of approximately 7 MJ/Nm^3 and can be used for the generation of electrical energy and/or the production of DRI. The application of the process export gas in an adjacent direct reduction plant is illustrated in Figure 7-6, which is a schematic process route for a

proposed greenfield steelmaking complex at HANBO Asan Bay Works, Korea. The plant will incorporate two C-2000 modules with a total annual capacity of 1.5 million tons of hot metal. COREX export gas will be used to produce DRI from a Midrex plant with a capacity of approximately 900,000 thm/year. This combination plant will permit the production of deep drawing steel qualities required by the rapidly growing Korean automotive industry. Start-up of the plant was scheduled for 1997.

Due to the different reaction conditions and the full integration, the theoretical energy demand of smelt reduction is lower than that of a blast furnace route. Worrell and Moore [31] report that the COREX plant at Pretoria has shown an estimated net Specific Energy Consumption (SEC) of 17 GJ/thm. Since this figure is valid for a small first-of-a-kind plant, lower SEC's may be expected to be reached through increased capacities, optimization of the carbon monoxide/ore interaction, and optimization of export gas use. Second generation COREX plants are expected to have a net primary energy consumption of 15.1 GJ/thm. This would reduce energy use in ironmaking by 30% relative to the 1994 situation in the U.S. (blast furnace net consumption is 18.6 GJ/thm, including ore preparation, and coke production net consumption is 3.1 GJ/thm).

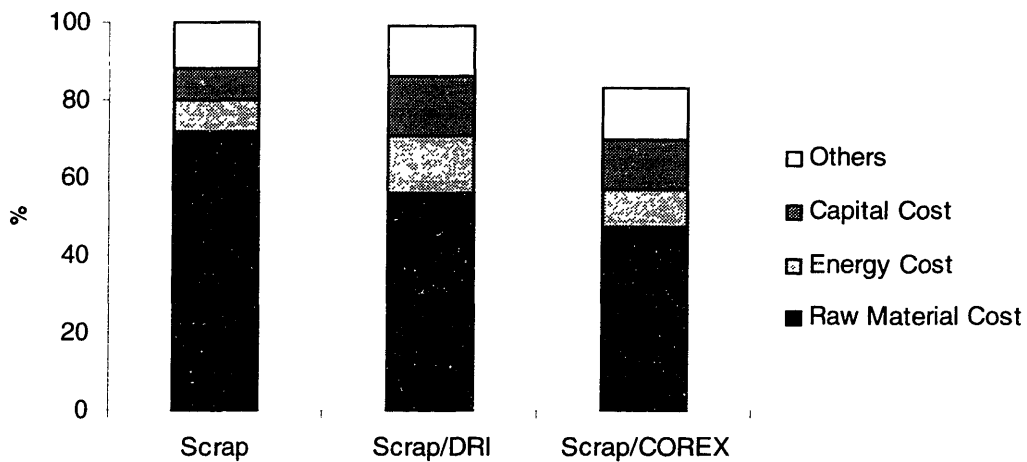


Figure 7-5 Relative costs of different steelmaking routes (annual capacity, 800,000 tons) [27].

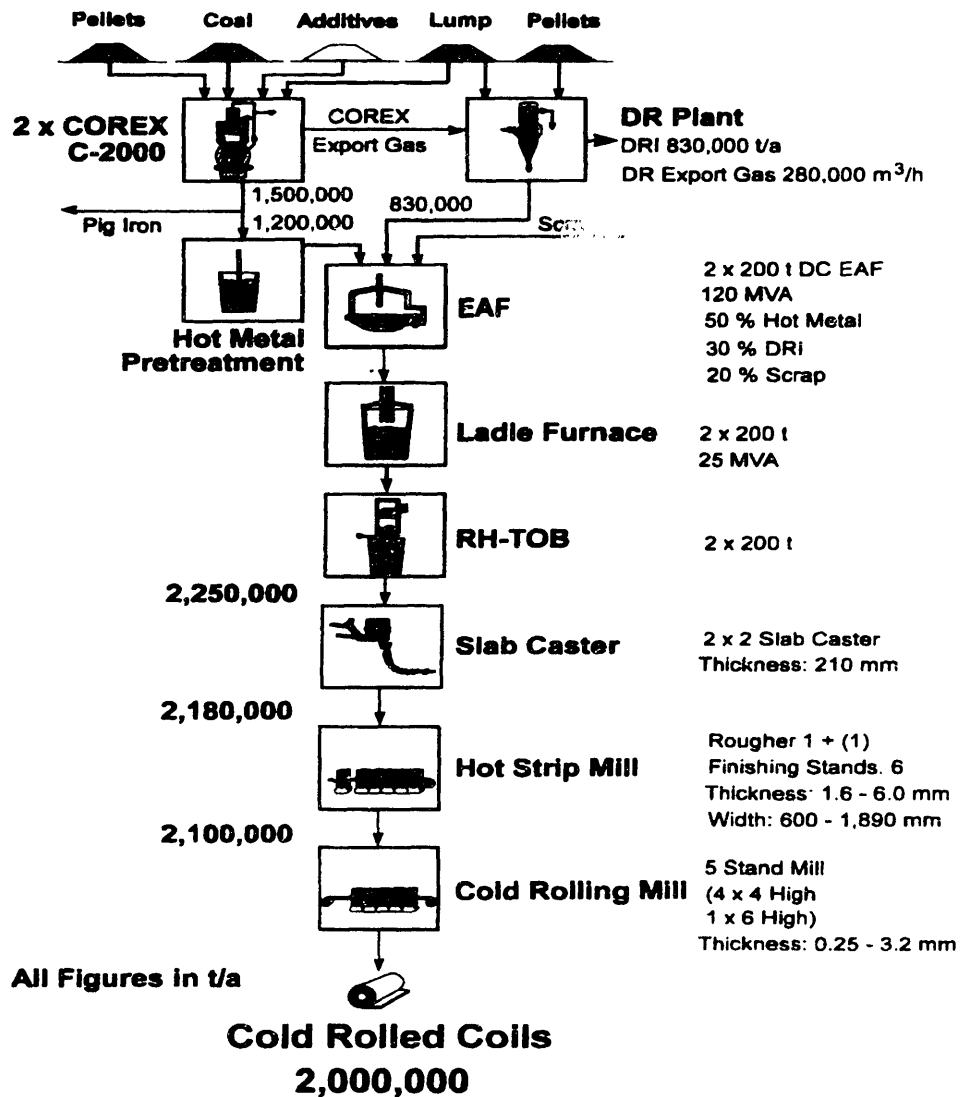


Figure 7-6 Process route at HANBO, South Korea [28].

7.2 Alternative Fuels

The blast furnace is the major producer of liquid hot metal that is refined into steel in the basic oxygen furnace process. Integrated steel producers can also inject other fuels, such as natural gas, oil, and coal instead of coke into the blast furnace, thus substituting a portion of the coke requirement. Motivation for injection of alternative fuels into the tuyere area of a blast furnace has historically been the cost or availability of metallurgical-grade coke [33]. The injection of fuel oil into blast furnaces was a regular practice until 1980, when the oil crisis resulted in a complete restructuring of the price level for fuels. The injection of fuel oil into blast furnaces became uneconomical due to rising prices and blast furnace operators adopted an all-coke operation.

In addition to reducing coke consumption, alternative fuel injection also leads to improved control over furnace reactions. It minimizes variation in hot metal composition by better control of raceway flame temperature. Many modern blast furnaces were designed and constructed assuming tuyere-level fuel injection, and conversion to all-coke operation often caused a reduction in iron quality and production rates. Such unstable conditions can be improved by lowering the blast temperature and increasing the blast humidity, but such adjustments result in an increase in coke consumption rate and a decrease in the blast furnace productivity. To effectively counteract these problems, integrated producers have developed coal injection systems. Of all the fuels injected into the blast furnace, coal has several advantages. Coal of suitable quality for injection is available in nearly all parts of the world. The supply is also not subject to unpredictable political pressures, as are petroleum products. This availability of coal promotes a more stable market with a favorable price compared to alternative fuels (Figure 7-7 shows the price differential between crude oil and coal).

Carbon from coal is consumed in the tuyere raceway zone of the blast furnace to form the hot reducing gases required to reduce iron oxides, preheat the burden materials, and produce molten metal and slag. A modern coal injection system consists of two sections:

1. Coal preparation system.
2. Transport and distribution system.

The coal preparation system (shown in Figure 7-8) consists of raw coal storage bins, a coal grinding, collection system and coal storage. Raw coal is fed to a grinding mill, where it is dried

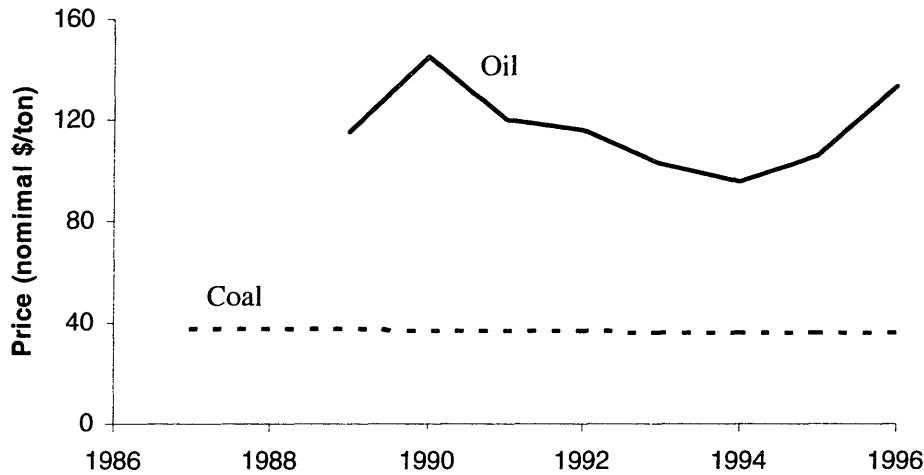


Figure 7-7 U.S. prices of crude oil and coal supply to industry [34][35].

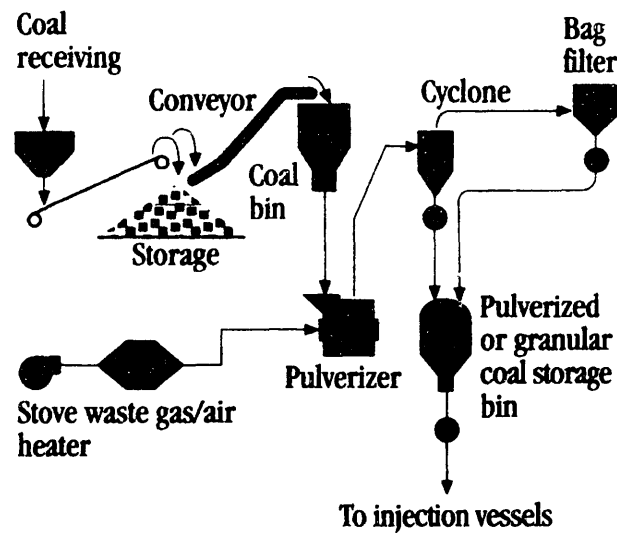


Figure 7-8 Diagram of a coal preparation and pulverization system [36].

and pulverized in one step. A primary fan and heater supply the pulverizer with hot air/blast furnace waste gas to dry the coal. The coal/gas stream from the mill then passes through a cyclone, where the primary separation of solids and gases is made. A bag filter is used to clean the gases before they are discharged to the atmosphere. The coal is next discharged for transport to the furnace injection facility storage bin. As shown in Figure 7-9, coal injection systems can be classified as follows:

1. Based on processed coal size specifications: Granular or Pulverized.

2. Based on the transport/distribution system utilized: Individual or distributed tuyere supply.

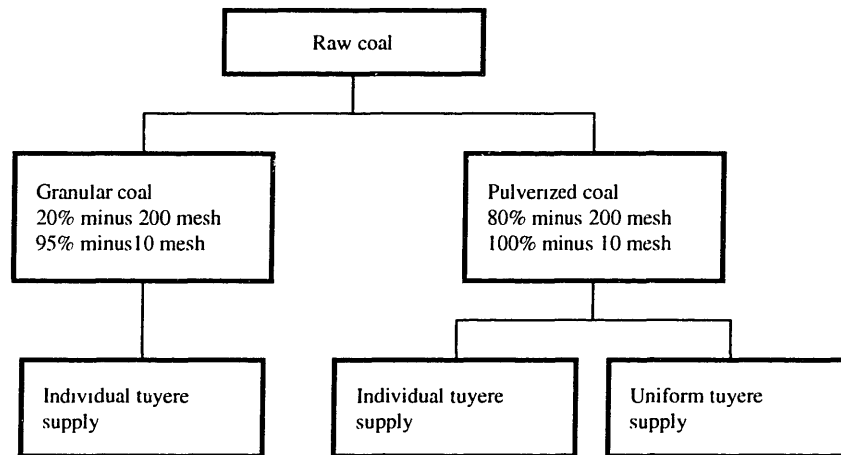


Figure 7-9 Processed-coal size ranges and the types of injection systems.

In the individual tuyere supply system (see Figure 7-10), coal is transported from the injector vessel to each tuyere in individual lines. In the uniform or distributed tuyere supply system, coal leaves the furnace injector vessel and passes through one or more distributors that split the main stream into streams for individual tuyeres.

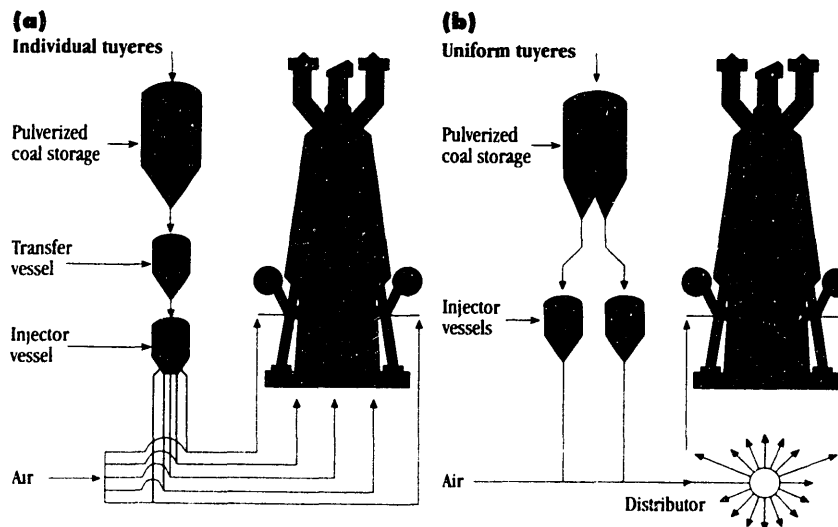


Figure 7-10 Comparison of the types of coal injection systems: (a) Individual tuyere supply and (b) Uniform tuyere supply [36].

Oshnock [36] has used a blast furnace thermochemical model to project the change in hot metal cost, due to coal injection, for a typical commercial blast furnace operation. The base case was developed for typical operations at U.S. Steel. Changes in coke requirements were first calculated for a coal injection rate of 134 kg coal/metric thm. A second case was evaluated in which oxygen enrichment was used to achieve a coal injection rate of 200 kg coal/metric thm. Coal is injected into the high temperature zone at a low temperature. Therefore, the raceway flame temperature decreases. Because the addition of oxygen to the hot blast air increases flame temperature, additional coal can potentially be injected if oxygen enrichment is utilized. The model was used to balance the energy required to make consistent hot metal quality (S, Si, and temperature), and to provide a stable operation. The results of the thermochemical projections, including the coal rates, coke rates, coke replacement ratios, and the change in hot metal cost are displayed in Table 7-4. It is projected that coal use could result in a 4.6% decrease in hot metal cost, if coke is delivered at a cost that is \$33/metric ton more expensive than coal delivered to the tuyere. Figure 7-11 more fully evaluates the effect of coke and coal cost on hot metal cost. As shown in the figure, hot metal cost savings are projected to increase as coal cost decreases and as coke cost increases.

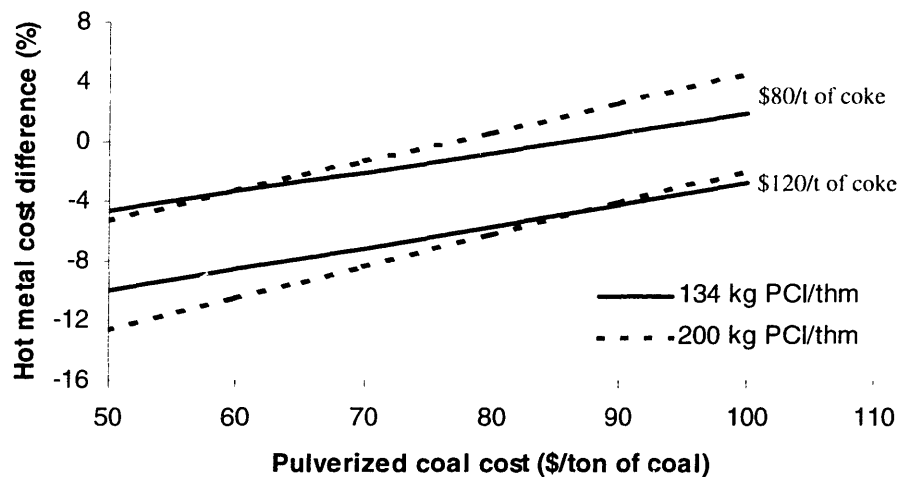


Figure 7-11 Effect of coke and coal cost on hot metal cost.

Table 7-4 Effect of coal injection on blast furnace performance.

	Base	Coal injection (kg/thm)	
		134 (without O ₂ enrichment)	200 (with O ₂ enrichment)
Production (ton/day)	2,800	2,800	2,800
Coal (kg/thm)	0	134	200
Coke	500	380	330
Coke/coal replacement ratio	Base	0.93	0.86
Hot metal cost difference (case-base, %)	Base	- 4.6	- 4.8

The cost of energy consumption comprises a major part of the cost of hot metal production and will be analyzed next. Uenaka et al. [37] have summarized the development of a commercial pulverized coal injection system at Kobe Steel. Table 7-5 lists the operational conditions and compares the energy balance in case of the all-coke and pulverized coal injection (PCI) operations for a blast furnace at Kobe Steel. Direct coal injection in the blast furnace saves energy by reducing the quantity of coke needed for hot metal production. Worrell et al. [38] have studied the specific energy consumption of a modern integrated steel plant, operated by Hoogovens in the Netherlands. In the year 1988, the blast furnaces in the plant (5 million tons/year crude steel) were operating at an injection rate of 115 kg coal/thm (coke/coal replacement ratio of 0.8). Energy consumption at Hoogovens for on-site coke production was 1.62 GJ fuel/ton crude steel (tcs) and 0.06 GJ/tcs. Assuming a practical maximum injection rate of 180 kg coal/thm in the year 2000, Worrell et al. estimate a savings of 13.5% of the energy demand of coke production.

Koen et al. [39] have reported on the costs of an all-coke operation and PCI operation at Hoogovens. Table 7-6 provides the relevant data to compare the energy and costs of the all-coke practice with the PCI practice. Figures 7-12 and 7-13 show that, in terms of energy consumption and total operating costs, the coal injection practice produces as much energy at a lower operating cost. It should be noted that Oshnock and Koen have not included the coal injection system capital costs in their evaluations. However, Koen et al. [39] mention that an extensive investigation at Hoogovens revealed that a coal injection system would require a smaller

Table 7-5 Comparison of energy balance between all-coke and PCI operation.

		All-coke	PCI
Operational conditions	Fuel rate (kg/thm)	491	482
	Coal rate (kg/thm)	0	48
	Blast temperature (°C)	1050	1119
Energy balance (10 ³ kcal/thm)	Coke	3514	3102
	Coal	0	348
	Hot stove	417	426
	Steam for blast	213	220
	Moisture	23	12
	BFG recovery	- 1146	- 1119
	Energy consumption (10 ³ kcal (in ratio with all-coke/thm)	3021 1	2989 0.989

investment than an expansion of the coking capacity to meet the requirements of the all-coke practice. The lower investment for coal injection provides further cost savings. The total investment for the pulverized coal injection plant at Hoogovens amounted to \$32 million (in 1982 U.S. dollars). It was estimated that additional coking capacity necessary to continue the all-coke practice would have required more than twice that investment.

Table 7-6 Data for comparing energy and cost of the all-coke and PCI practice at Hoogovens.

		All-coke	PCI
Blast furnace	Coke rate (kg/thm)	505	410
	Coal rate (kg/thm)	-	85
	Hot blast temp. (°C)	1075	1200
	O ₂ in hot blast, %	20.9	22.5
	Blast heating (MJ/thm)	2015	2080
Coke plant	Coal for coke production (kg/thm)	745	605
	Coke plant net gas and tar production (MJ/thm)	3920	3180

In the U.S., Armco has gained extensive experience with PCI. In 1981, the Amanda blast furnace at Armco's Ashland, KY works was operating at a coal injection rate of 65 kg coal/thm (see Table 7-7). Sexton and Wennerstrom [33] have estimated the capital costs for the PCI system (coal injection at 20 tons/hr) at Ashland to be \$15 million. With a coal cost of \$90/ton, coke cost of \$120/ton, an injection cost of \$8/ton (for the Amanda system), and a coke/coal replacement ratio of 0.8, coal has an advantage of \$18/ton over coke. If an injection rate of 20 tons/hr to a furnace with 95% availability is considered, the annual generated saving for the Ashland works is calculated to be \$3 million.

Compared with oil or natural gas, more coal can be injected into the blast furnace at a given condition. This is because the carbon/hydrogen ratio of coal is greater than that for oil or gas.

while still retaining sufficient flammability for combustion in the tuyere zone of the furnace. Flame temperature in the furnace raceway is diminished less by coal, permitting higher levels of injection. Oshnock has shown that coal injection has the potential to replace more tons of coke and lead to greater savings than other injectants. The relative economic effects of using different injectants with and without oxygen enrichment are shown in Figure 7-14.⁴⁰ Based on Oshnock's assumptions, coal has the potential to provide the largest cost savings when compared with oil and natural gas.

The injection of pulverized coal into the blast furnace tuyeres as a means to lower the coke rate and hot metal cost has been practiced for a long time. A commercial prototype coal injection system was installed at U.S. Steel's (now closed) South Works, near Chicago, IL, as early as 1969. Since 1973, the Amanda and Bellefonte furnaces at Armco's Ashland works have been operating with PCI rates averaging between 75 to 100 kg/metric t_{hm}. After the second oil crisis in 1979, application of PCI technology has progressed rapidly in both Europe and Japan. By the early 1990s, injection rates of nearly 200 kg coal/metric t_{hm} had been achieved by companies such as Thyssen, British Steel, and Hoogovens in Europe, and Kobe in Japan. By 1994, 26 of 32 operating blast furnaces in Japan had coal injection. However, in the U.S., the number of installations using pulverized coal was limited to three in 1995. Besides Armco's Ashland plant, coal injection systems in the U.S. include those at U.S. Steel's Gary, IN, mill, and the other at the Indiana Harbor Works of Inland Steel. Both facilities are designed to supply coal rates of 200 kg coal/metric t_{hm}, and were started up in 1993. In 1995, plans had been made to install this process in three other plants, namely Bethlehem Steel's Burns Harbor Division, the U.S. Steel/Kobe joint venture plant at Lorain, OH, and U.S. Steel's Fairfield, AL plant. The Lorain system is capable of injecting 250 kg coal/metric t_{hm}. Finally, the Canadian steelmaker Stelco has announced plans to build a \$60 million facility for the injection of pulverized coal at its blast furnace at the Hilton Works and thus reduce its coke requirement [33][36][40].

VSZ Steel Ltd. operates an integrated site in the Slovak Republic producing 4 million tons of steel per year. In 1991, work began on a project to decrease the consumption of coke in the two operational blast furnaces at the Kosice site by replacement with injected pulverized coal [21]. As indicated in Table 7-8, the coke consumption fell from 510-388 kg/t_{hm} and 514-415 kg/t_{hm} for BF2 and BF3, respectively. The advantages of coal injection were that a coke oven battery could

⁴⁰ Economics for Figure 7-14 are based on the following: coke-to-coal cost differential of \$33/ton, oil at \$0.40/gal., natural gas at \$2.61/GJ, oxygen at \$1.26/Mscf.

be closed down, without jeopardizing the coke supply to the blast furnaces, resulting in reduced emissions to air and water. The volume of phenol/ammonia laden waste water requiring treatment was reduced by 96,200 m³/yr, and air emissions were reduced as indicated in Table 7-9. The total investment cost for the project was \$35,000 and direct economic savings resulted from the reduced cost of waste water treatment and fees for air emissions, which amounted to \$13,500/yr and \$17,400/yr, respectively.

In general, Europeans have aimed for coal injection, as well as higher rates, sooner than the rest of the world because of aging coke-oven batteries and the stringent emission standards associated with them. Use of coal injection can replace 25-40% of coke in the blast furnace, and the subsequent reduction in coke production proportionally reduces the coking emissions. The value of coal injection will increase in the U.S., as the availability of metallurgical-grade coals decreases, as coke-oven productivity deteriorates, and as coke-oven environmental emission standards become more stringent.

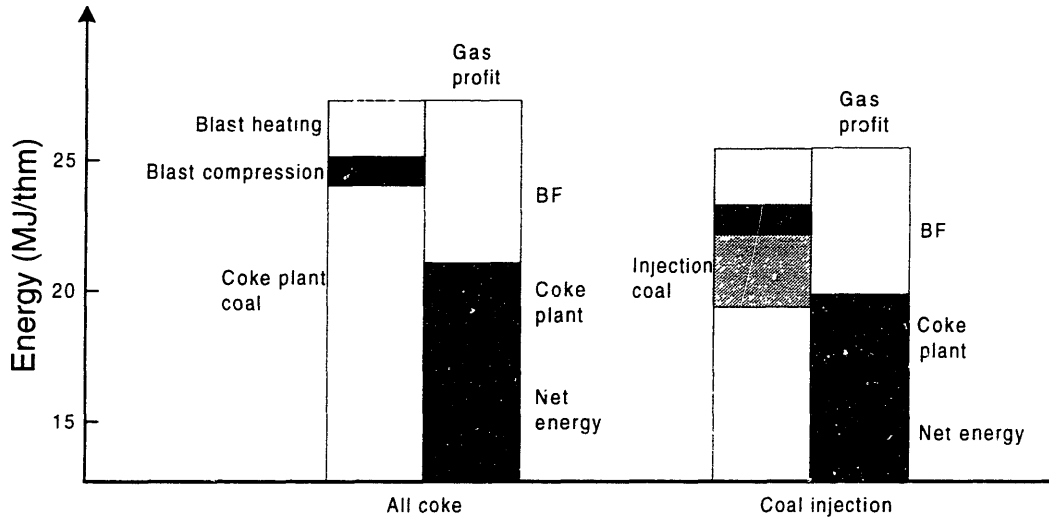


Figure 7-12 Influence of an all-coke operation and PCI operation on energy.

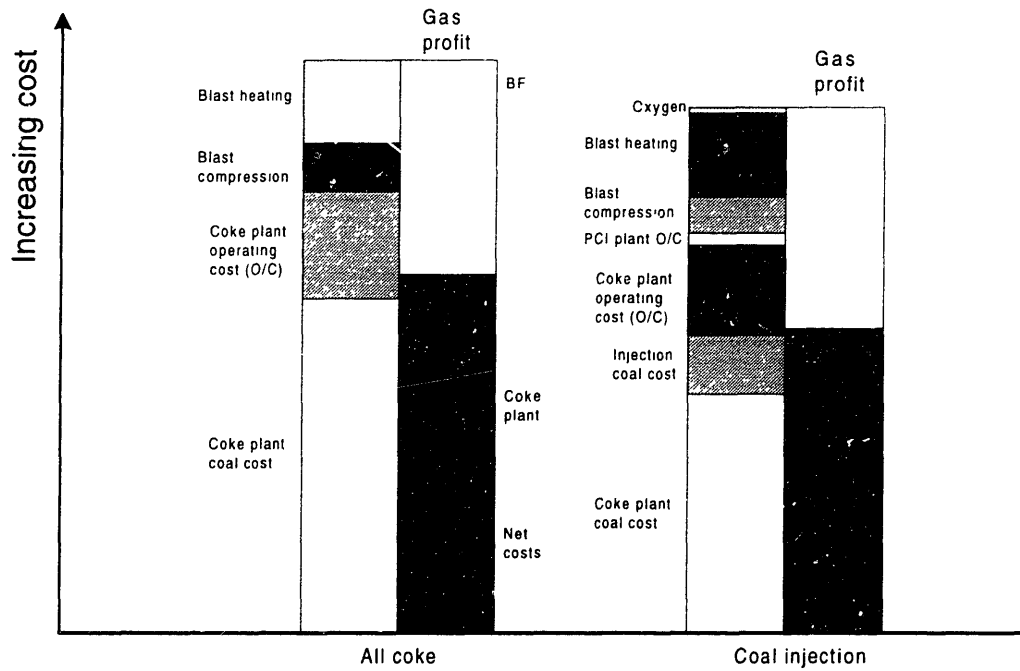


Figure 7-13 Influence of an all-coke operation and PCI operation on costs.

Table 7-7 Operating data for pulverized coal injection at Armco [33].

Coke rate (kg/ton)	506
Coal rate (kg/ton)	65
Replacement ratio	1.14
Blast temperature (°C)	843

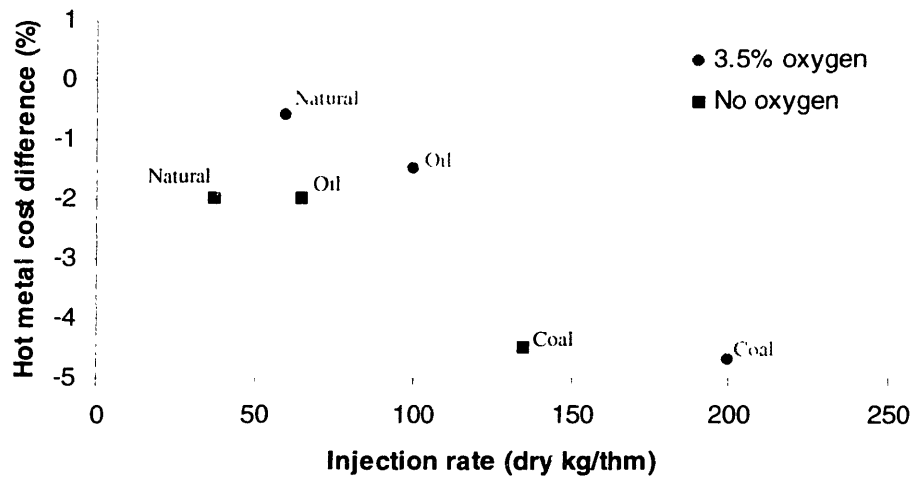


Figure 7-14 Comparison of hot metal costs for pulverized coal, oil and natural gas injection [36].

Table 7-8 Operational data for PCI operation at VSZ Steel Ltd. [21].

	1991	1996
Coke consumption (kg/thm)	510/513.9	388/414.6
Oil consumption (kg/thm)	16.6/17	-/-
Coal consumption (kg/thm)	-/-	136/106
Natural gas (Nm ³ /thm)	7.2/-	-/-
Equivalent coke consumption (kg/thm)	536.6/536.6	510.4/510

Table 7-9 Pollution reduction through installation of pulverized coal injection [21].

Pollutant (tons)	Coke operation	PCI installation
Particulate	213.4	108.8
SO ₂	188.9	96.3
NO _x	150.3	76.6
CO	415.9	212.1
Benzo-a-pyrene	2.0	1.0
Benzene	44.3	22.5
H ₂ S, HCN, phenol, pyridine	174.9	89.2
Naphthalene, toluene, xylene, biphenyl, NH ₃	85.5	43.6
Total	1275.2	650.1

8 Summary and Conclusion

The present investigation began by proposing the existence of no-regrets options in manufacturing processes. It was stipulated that, through recent technical advances, it should be possible to enable manufacturing processes to reduce pollutant emissions while retaining a net economic benefit. The case was demonstrated by focusing effort on two sectors within the manufacturing industry – pulp and paper and the iron and steel industries.

The conventional process route in each industry was elaborated to facilitate the placement of the pollution prevention technologies within the perspective of present day industry structure. The pollutants generated during conventional processing, as well as emission points, were identified so that the pollution reduction benefits offered by the novel technologies could be emphasized. The urgency of the need for industry to investigate pollution reduction opportunities was stressed by providing an update of environmental legislation in the U.S.

Finally, the technical and economic aspects of several pollution reduction technologies were studied for each industrial sector. Care was exercised in selecting those technologies that have already been implemented by industries to some extent. Discussion of the pollution reduction achieved for each technology, with the energy consumption, as well as operating/maintenance costs clearly demonstrates that these no-regrets options can allow the two sectors to reduce pollutant generation, while improving profitability and competitiveness.

The task ahead is not simple, however. While the industry has captured a few of the pollution reduction technologies, a host of market barriers to such efficiency investments persist. For example, although such technologies are cheaper on a life-cycle basis, they do involve up-front investments. Because of the need for up-front capital, public policies that promote financing and technical assistance are needed to facilitate investment. Although the focus of this investigation is on pollution reduction success stories, given such market hurdles to investments, public policy incentives are crucial to encourage adoption of these advances. The effects of tighter environmental regulations will increasingly make such investments a prudent pursuit for all manufacturing businesses.

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Appendix A

Controlled Hazardous Air Pollutants for the Pulp/Paper Sector

Table A-1 Hazardous air pollutants emitted from kraft pulp and paper mills.

Chemical name
1,4 – dichlorobenzene
2,4,5 – trichlorophenol
Methyl ethyl ketone
Acetaldehyde
Acetophenone
Carbon disulfide
Carbon tetrachloride
Chlorine
Chloroform
Formaldehyde
Hexane
Hydrochloric acid
Methanol
Methyl chloroform
Methylene chloride
Propionaldehyde
Toluene