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16. Abstract (Limit: 200 words)  <p>ABSTRACT: This information profile on ferrous smelting and steel manufacture (SIC-331) is part of a group of 46 such profiles that provide information about chemicals or industrial processes considered to be potential occupational hazards. Each profile contains summary data on known and suspected health effects, the extent of worker exposure and the industrial importance of either a single chemical, class of chemicals, or a particular industrial process. The report was developed for use by occupational safety and health professionals in industry, and labor and other areas, to provide them with a synopsis of information in their workplaces.</p>		
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## INTRODUCTION

An information profile is a working paper used by the National Institute for Occupational Safety and Health (NIOSH) to assist in establishing Institute priorities. It is an initial step in determining the need to develop comprehensive documents or to initiate research. Each profile summarizes data on known and suspected health effects, the extent of worker exposure, physical and chemical properties, and the industrial importance of individual chemicals and classes of chemicals. The profile may also be used by industry, labor, and the occupational health community as a synopsis of information on each subject and to identify possible health hazards associated with their workplaces.

Although detailed literature searches are conducted using computerized and manual searching techniques to identify pertinent and recent information, not all the literature obtained is incorporated in the report due to the summary nature of the profiles. Further, literature published after 1978 may not be included in these profiles because it was generally unavailable at the time the search was completed.



## FERROUS SMELTING AND STEEL MANUFACTURING

### I. SCOPE OF PROFILE

The processes used to (1) smelt iron ore to ferrous metal and (2) make and shape ferrous metal and scrap into finished steel products have been reviewed for the purpose of identifying the potential occupational health hazards associated with the iron and steel industry.

Ferrous smelting is engaged primarily in the recovery of iron from ores by a series of processes that consist of mining, beneficiating, and agglomerating the ore for thermal reduction by blast furnace operation to molten hot metal for steel making, or for casting into pig iron for gray iron and other cast iron foundry products. Production of the coke and limestone required by the blast furnace operation are also essential operations in the process.

Steel manufacturing involves, first, converting the molten hot metal from the smelting operation and from recovered scrap into specified quality steels by one of several oxidation methods, and second, casting the product into ingots or intermediate forms that are subsequently shaped by hot or cold rolling, forging, or other processes into final marketable plate, sheet, structural steel, wire, pipe, tubing, etc. Additions of nonferrous metals to form alloys and stainless grade steels are also included in these operations.

Mining, ferrous smelting, and steel manufacturing operations are categorized by the Standard Industrial Classification Manual (Anon., 1972a) as follows:

Mining	SIC 1011	Mining and beneficiating iron ores
Ferrous Smelting	SIC 3312	Blast furnaces (including coke ovens), steel works, and rolling mills
Steel Manufacturing	SIC 3313	Steel, steel alloys, stainless steel by electrometallurgical processes
	SIC 3315	Wire and related wire products from purchased ingots
	SIC 3316	Cold rolled steel, sheet, strip, and bars from purchased ingots
	SIC 3317	Steel pipe and tubes from purchased ingots





Complete descriptions of these categories are presented in Appendices A and B.

## II. SUMMARY

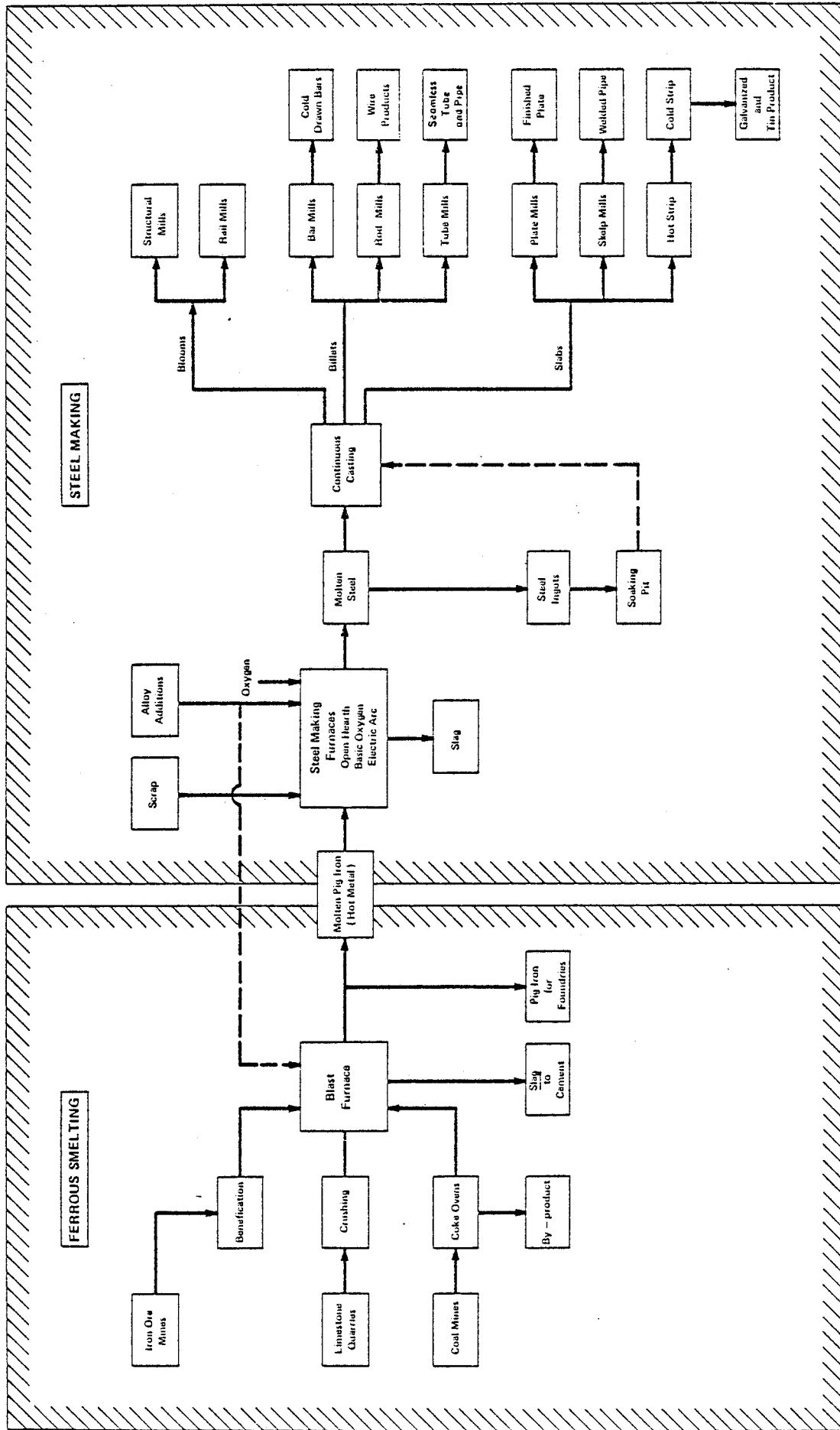
A flow chart summarizing the relationship between smelting and steel manufacturing processes is presented in Figure 1.

Ferrous smelting (SIC 3312) involves the recovery of metallic iron from ores either as melted hot iron for adjacent steel making operations, or as solid pig iron for custom foundries. Recovery includes a series of processes in which the ores are mined, concentrated, agglomerated into pellets or sinter, and finally reduced thermally with coke into molten hot metal by blast furnace operations. The nonferrous substances in the ore are largely removed in the furnaces as slag formed by fluxing with limestone or dolomite.

Steel manufacturing (SIC 3312, 3313, 3315, 3316, 3317) involves (1) conversion of the blast furnace product and scrap iron into specified quality steel by basic oxidation, open hearth, or electric furnace methods, and (2) shaping the product by hot or cold rolling, drawing, piercing, or forging into marketable forms.

The principal potential hazards associated with ferrous smelting and steel manufacturing processes are both physical and chemical in nature. Of the physical hazards, the high temperatures associated with the operation of furnaces, coke ovens, sintering and pelletizing equipment, and with material inprocessing and product finishing are notable. The most likely human health effects arising from exposure to chemical contaminants in the smelting and manufacturing environment appear to be respiratory disorders and lung cancer. The most significant pollutants contributing to these effects appear to be benzopyrene, carbon monoxide, coal and coke dust, coke oven emissions, manganese compounds, nitrogen oxides, particulates and sulfur oxides.

Figure 1  
IRON AND STEEL INDUSTRY



### III. STATISTICAL INFORMATION

In 1978, 593,891 workers were employed in 1151 iron and steel industrial establishments (Anon., 1978; AISI, 1979); 438,342 of these individuals were wage employees. The number of production workers employed in the processes, and the number and type of establishments are detailed in Table 1. Of approximately 42,000 ferrous smelter workers, 22,000 were involved in mining and ore preparation, and 20,000 with the operation of blast furnaces. About 70 smelting facilities (SIC 3312), employing over 200,000 production workers, are integrated with blast furnaces and shaping mills. Other mills start with semifinished steel, and over 600 use purchased ingots (SIC 3315, 3316, 3317). Thirty companies operate thirty-nine "mini plants," producing less than 500,000 tons per year (OSHA, 1976a).

The rates of occupational injuries and illnesses in blast furnaces and steel mills are presented in Table 2.

### IV. PRODUCTION AND TRENDS

The U.S. iron and steel industry produced 137 million tons of raw steel in 1978 with a total income of \$46.9 billion. Other production data for 1978 are summarized as follows (AISI, 1979):

Growth since 1969	minus 3%
Imported steel in 1979	18.1%
Location of production facilities	
Pennsylvania	20%
Indiana	20%
Ohio	18%
Illinois	7%
Others	35%
	<hr/>
	100%

Table 1. Employment in Iron and Steel Industry<sup>a</sup>  
1976

SIC Code	Process	Establish- ments No.	Production Workers (1000)	Production Workers per Estab.	Percent of establishments with employment less than										% over 500 workers	
					5	10	20	30	40	50	60	70	80	90	100	110
					24	34	39	47	35	75	82	18				
101	Iron ore mining and preparation	77	22 <sup>b</sup>	280												
3312	Blast furnaces and steel mills <sup>*</sup>	496	358	730	17	27	38	52	57	67	76	24				
3313	Electrometallurgical products	33	6.6	200	9	15	18	24	33	73	88	12				
3315	Steel wire and wire products	299	24.2	80	10	18	28	53	71	89	96	4				
3316	Cold finishing steel shapes	151	12.9	86	13	20	35	52	72	86	96	4				
3317	Steel pipe and tubes	164	16.7	102	8	12	18	36	53	83	91	9				
331	Total blast furnace and steel products	1151	418	365	14	22	33	52	62	72	87	13				

<sup>\*</sup>Distribution of SIC 3312 Employment<sup>c</sup>

SIC Code	Process	Operations	Establishments (Approx. No.)	Total (1000)	Production Workers Per Establishment	
3312-11	Fully integrated plants	Coke ovens, blast furnaces, <sup>d</sup> steel mills	50	200,000		4000
3312-12	Partially integrated plants	Steel mills, partially integrated with blast furnaces	20	35,000		2000
3312-13	Partially integrated plants	Steel mills with rolling mills	100	71,000		700
3312-14	Non-integrated plants	Rolling, shaping etc., mills	326	52,000		150
3312			496	358,000		730

<sup>a</sup>Anon., 1978

<sup>b</sup>Anon., 1978a

<sup>c</sup>Approximated from 1972 Census of Manufacturers (Anon., 1972)

<sup>d</sup>Approximate blast furnace operations (SIC 33121-11)=20,000

Table 2. Occupational Injuries and Illnesses<sup>a</sup>  
1977

SIC Code	Process	Production Workers (1000)	Incidence Rates per 100 Workers				
			Total cases	Injury	Illness	Lost work- day cases	Lost work days
3312	Blast furnace and steel mills	358	10.4	10.0	0.4	3.8	84.4
3313	Electrometallurgical products	6.6	14.7	14.1	0.6	5.5	106.6
3315	Steel wire and wire products	24.2	22.4	21.9	0.5	10.5	165.1
3316	Cold finishing	12.9	27.8	27.4	0.4	10.3	178.1
3317	Steel pipe and tubing	16.7	22.0	21.4	0.6	9.1	142.1
331			12.2	11.7	0.5	4.6	94.3
101	Iron ore mining		26	--	--	3.4	65
	All manufacturing		13.1	12.6	0.5	5.1	82.3

<sup>a</sup>Anon., 1979

Production information for the two sections of the industry, ferrous smelting and steel manufacturing, are summarized as follows (AISI, 1979):

#### Ferrous Smelting

Blast furnace production (1978)	=	87.8 x 10 <sup>6</sup>	tons
Concentrate consumption	=	104.5 x 10 <sup>6</sup>	tons
Raw ore equivalent*	=	83.4 x 10 <sup>6</sup>	tons
Coke consumption	=	51.3 x 10 <sup>6</sup>	tons
Limestone and dolomite flux	=	17.2 x 10 <sup>6</sup>	tons
Molten iron for steelmaking	=	83.6 x 10 <sup>6</sup>	tons
Pig iron for other steelmaking	=	4.2 x 10 <sup>6</sup>	tons
Number of blast furnaces (1/1/79)	=	168	

#### Steel Manufacture

Molten iron (not metal) consumed 1978	=	83.6 x 10 <sup>6</sup>	tons
Scrap iron consumed	=	76.2 x 10 <sup>6</sup>	tons
Products (1978)			
Bars and tool steel	=	18,113 x 10 <sup>6</sup>	tons
Cold rolled sheet	=	17,886 x 10 <sup>6</sup>	tons
Hot rolled sheet	=	16,693 x 10 <sup>6</sup>	tons
Galvanized and tin mill products	=	12,000 x 10 <sup>6</sup>	tons
Plate	=	8,623 x 10 <sup>6</sup>	tons
Pipe and tubing	=	8,650 x 10 <sup>6</sup>	tons
Structural, nails and accessories	=	6,734 x 10 <sup>6</sup>	tons
Ingots and semifinished products	=	5,753 x 10 <sup>6</sup>	tons
Wire, wire products, strip, etc.	=	7,131 x 10 <sup>6</sup>	tons
		101,583 x 10 <sup>6</sup>	tons

\*18% from Lake Superior area

### V. CHARACTERIZATION OF PROCESSES

The following discussion characterizing ferrous smelting and steel manufacturing processes is in large part compiled from the following sources:

The Making of Steel (AISI, 1967); Kirk-Othmer Encyclopedia of Chemical Technology (Knepper, 1967; McGannon, 1969; Perch, 1979); Making, Shaping and Treating Steel (USS, 1970); and Mineral Facts and Problems (Anon., 1975).

#### A. Ferrous Smelting

Ferrous smelting involves four separate operating processes:

1. Mining and preparing raw ore for blast furnace smelting.
2. Coking bituminous coal for the smelting operation.

3. Smelting the ore with coke and flux to molten ferrous metal and to slag that contains the waste materials.
4. Casting tapped metal into pig iron for foundries or tapping the hot metal into ladles for use by adjacent steel plants (Figure 1).

The four processes are outlined as follows:

1. Mining and Ore Preparation

Magnetite ( $\text{Fe}_3\text{O}_4$ ) containing 72.4% iron and hematite ( $\text{Fe}_2\text{O}_3$ ) containing 69.9% iron are the principal minerals used. Limonite ( $\text{HFeO}_3$ ), and siderite ( $\text{FeCO}_3$ ) are used to a lesser extent. Silica, phosphorous, alumina, and manganese are the principal impurities. About 80% of the ore is mined in the Lake Superior area, and 12% in the Western U.S. The ores run 40 to 60% iron as mined. Ore with over 20% iron is known as taconite.

Open pit mining, especially with large, heavy, 8-12 cubic yard shovels and 100 ton trucks, is principally used. Rotary drills are usually employed with prilled ammonium nitrate as the blasting powder (OSHA, 1976a).

Many types of beneficiating methods are used after crushing and screening the ore into coarse and fine fractions. Drying is sometimes required. Gravity, magnetic, and flotation are the principal methods used, depending on the ore. Grinding to 325 mesh is often required for good results.

The fraction of ground ore below 1/4 inch is agglomerated to obtain permeability and to minimize dust losses in the furnaces. Sintering and pelletizing are the usual methods.

Sintering consists of fusing the fines after mixing with coke breeze, following ignition with an oil or gas flame while traveling on a moving horizontal grate. The beds typically reach 2200-2600°F (1200-1430°C), and limestone or dolomite is usually included in the mix. The sinter is about 54% iron. Recycled flue dust, oxide, slags, and other recoverable materials may also be added.

Pellets are made by forming a mix of concentrates with bentonite into balls in a rotating drum machine. About 10% moisture is required. The pellets usually contain about 63% iron.

The concentrates are transported to the mills, in the case of Lake Superior products, principally in lake vessels of up to 300,000 tons capacity. The concentrates are unloaded with self unloaders of 10,000 tons per hour capacity (AISI, 1967).

## 2. Coke Oven Operation

The coke is produced by carbonizing a blend of high, medium, and low volatile bituminous coal that averages near 30% volatile. The amount of volatility affects coking pressure. Therefore, a mix is selected that will not exceed 1.5 psi during coking in order to avoid oven breakage. The blend is 75 to 85 percent crushed through 3 mm mesh, and 0.1 to 1 percent water or oil may be added to aid in the process (Perch, 1979).

The ovens are arranged into a battery of special silica brick retorts, 40 to 50 ft. long, 12 to 20 ft. high and 20 in. wide, that hold 15 to 30 tons of coal. The retorts are heated by combustion gases that flow through the intervening spaces or flues. Checkerwork regenerators are located under the ovens. These are heated in a reversing cycle by the exiting off-gases, which serve to preheat the air for the combustion. Off-gases from the ovens or blast furnace gas may also be used to preheat the combustion air.

Lorry cars are used to transport the coal from feed bins, and the coal is charged through openings in the top of the oven. The charges are spread over the ovens by leveling bars that are passed into the ovens through the ends. The charge holes are then sealed and the oven is opened to the gas collecting mains. Steamjet aspirators are used during charging to prevent emissions of dust and smoke from escaping into the air.



The coal is carbonized for a scheduled time, 16-24 hours, usually at temperatures between 1200°C and 1400°C. The hot finished coke is pushed out mechanically from the oven into the quenching cars, transported to a quenching station, sprayed with water to below ignition temperature, transferred to an air cooling dock and ultimately to blast furnace charge bins.

The gases generated during carbonization are collected by a suction main. They are then scrubbed in a series of washers that recovers the tars, light oils, and ammonia; these byproducts may be purified or sold in crude forms. Washed gases are composed of approximately 50-60% hydrogen and 30% methane, with smaller quantities of carbon monoxide, hydrogen sulfide, and hydrocarbons. Hydrogen sulfide scrubbers are used to clean the gas before cycling and burning. The tars contain cresol, naphthalene, phenol, xylols, and pitch. Crude light oil contains benzene, toluene, and xylene which may be processed for sale. The ammonia may be recovered by water scrubbing, lime treatment, distillation, and conversion to the sulfate.

### 3. Blast Furnace Operation

The blast furnace is a refractory lined steel shaft. It is charged continuously at the top through inverted bell seals with the mixture of prepared ore concentrates, coke, limestone, and dolomite. Preheated air is blown into the furnace through tuyeres near the bottom of the shaft. The exit gas from the top containing combustible carbon monoxide preheats the incoming air after burning in refractory checkerwork preheaters or "stoves," in which air heating and gas burning are reversed interchangeably for heat recovery.

The molten iron and fluxed materials or slag are tapped intermittently from the bottom of the furnace. The reduction reaction between iron oxide and carbon is principally  $\text{Fe}_2\text{O}_3 + 3\text{C} \longrightarrow 2\text{Fe} + 3\text{CO}$ . Slag is formed by the reaction of limestone or dolomite with silica and

alumina in the ore and coke. Some of the sulfur in the coke is absorbed by the slag (Knepper, 1967; AISI, 1967).

There is an increasing trend toward injecting oxygen into the furnace in order to speed up the reaction. This also reduces the inert nitrogen in the exit gas.

The molten iron is tapped from the lowest hole in the furnace into refractory lined ladles. Most of the metal is transferred by overhead cranes to the converters, where it is charged as the hot iron feed. The remainder, about 5%, is cast into pigs principally as gray casting iron for use in foundries.

The slag is usually granulated with water and may be used in concrete. To prevent slag from plugging the tuyeres, "punching" is performed through openings which are provided in the furnace for this purpose. Other operations involve flue dust collection and disposal, gray iron shipping, or transferring to a foundry operation.

Alternate processes based on prereduction and on direct reduction are being studied for possible economic advantages, but neither has, to date, reached significant commercial importance.

#### B. Steel Manufacturing

Steel making and shaping processes involve three steps:

1. Converting raw molten pig iron or "hot metal" and scrap into specified low carbon, low silicon steel.
2. Casting (1) into steel ingots or continuously into semifinished products, i.e., blooms, billets, or slabs.
3. Hot or cold rolling, drawing, piercing, or forging products from (2) into finished plate, sheet, structural shapes, wire, tube, etc. products.

## 1. Steel Conversion Processes

The principal reactions in the conversion processes lower the carbon and silicon contents, as well as phosphorus and sulfur, by oxidation and slagging. Excess oxygen is removed by the deoxidizing agents manganese and silicon.

The above reactions are conducted in three types of converters, e.g., the old basic open hearth, the newer basic oxygen process, and the electric arc process. Use of the basic oxygen process has been increased since 1955 to about 60% of total steel production, with a corresponding drop in use of the basic open hearth process. The electric arc process is used principally for special carbon, alloy, and stainless steels.

The basic open hearth process is conducted in a shallow, rectangular, refractory-lined, basin-shaped furnace. Magnesite and other basic refractories are used. The charge consists principally of melted hot iron and scrap, with fluxes and other additions that are heated by a gas or oil fired flame that passes over the charge in a reversing cycle. The exit gases flow into checkerwork regenerators, used alternately to heat the combustion air (McGannon, 1969). The basin is covered by an arched refractory roof. The feed is charged through doors along the side from buggies or boxes using a charging machine, and the steel is discharged through tapping spouts on the opposite side of the basin. The temperature reaches about 2900°F (1600°C) in a total cycle of 10 hours. Typical capacities are 200-225 tons of steel. Oxygen may be added by lances through the roof to speed the oxidation process. Carbon monoxide may be generated early in the cycle.

The contents, principally molten metal, are tapped into ladles. The slag in discharge overflows the ladle, and may be recovered and recycled because of its high iron content.

The basic oxygen process functions the same in removing the impurities from the iron, with the further advantage that the reaction is faster and that higher proportions of hot metal are used. The usual equipment consists of a cylindrical, basic lined furnace with a dished bottom and a conical shaped open top or charging mouth. The furnace is mounted so that it can be tilted for charging and discharging. The charge of molten hot iron is usually added on top of 30-40% scrap and is fed from an overhead crane system into the furnace in a tilted position. Oxygen is introduced by lance above the metal, which starts the reaction, and carbon monoxide is generated, which agitates the contents. Slag forming fluxes, burnt lime, fluorspar, and mill scale are added. Hoods collect the exit gases, which are then cleaned. If not contaminated, residual dust is recycled to the sintering plant; otherwise, it is washed to dumps or ponds. No heat is required for the reaction. The furnace is finally discharged by tilting the furnace into a ladle, and slag is dumped by tilting into reverse position into a slag pot. A 300 ton load can be produced in about 45 minutes (Anon., 1975).

Vacuum degassing is used to improve the quality of the product by removing entrained gas in all processes; in addition, manganese and silicon are added as required to remove excess oxygen.

The foregoing sequence describing the processing of the ore to the tapped steel is the basic structure of the ferrous smelting-steelmaking industry (Figure 1). About 95% of the production is steel and 5% is pig iron

for foundry and other uses. About 85% of the steel is processed directly on site into hot and cold rolled shapes and products. The remaining 15% is poured into ingots for sale to others, and for processing into shapes and other products.

Electric arc processing is another method for making steel, but is used principally for stainless, alloy, and tool steels. It has recently been used for carbon steel, principally in mini-mills. Scrap is the principal feed. Electrode melting is another method under development.

## 2. Steel Casting and Shaping

The steel in the ladles originating from the previously described convertors is poured through a bottom hole into ingot molds or into continuous casting machines. The ingots usually weigh between 10 and 40 tons, with the shape depending upon the intended use.

For continuous casting, the ladle is discharged through a "tundish" distributor that produces a strand of metal. The strand passes through a water-cooled chamber in the casting machine, forming a 2 inch by 8 inch ribbon that continues along, cooling and solidifying into cast form. The strand may be arranged to travel vertically or horizontally to the semi-finishing rolls (AISI, 1967).

The strand from the continuous casting machine is ultimately delivered to a series of vertically mounted stands of two to four roll sets, in which the still-hot metal is pressed by repeated passes into one of the following semifinished shapes:

- Blooms - 6 x 12 inch squares
- Billets - 2 x 5 inch squares
- Slabs - 2 x 9 inches thick by 24 to 60 inches wide

These are then surface conditioned by grinding, chipping, pit filling with oxygen torch, and finally stored for product shaping.

Ingots are stripped from the molds either for sale or for further processing. In either case, the ingot is reheated before processing to 2200°-2400°F (1177°C-1343°C) in a soaking pit. This is a large furnace below ground level heated by oil, gas, or electricity.

For final shaping into commercial products, the above semi-finished shapes are either reheated, in the case of hot rolling, to about 2200°F (1200°C), or cold rolled. In cold rolling, the shape and size is obtained by successive stage pressing by many passes through four roll stands. Tilting roller tables are used for feeding and handling the product between passes. About two-thirds of all sheet steel is cold rolled.

In hot rolling, the product is also shaped by successive stands of rolls. In this case, shaping is obtained more readily due to the softened heated metal. The product, however, has rougher surfaces compared with that obtained from cold rolling. Acid pickling, or shot blasting, is required to finish the surfaces. Oil may be added to prevent rusting. The shapes of the products are obtained by the contours of the rolls, and range from simple bars, plates, and sheets to irregular shapes such as I beams and rails.

Other products, such as wire, are formed by drawing rods through dies; seamless tubing and pipe are formed by drawing down pierced billets, and butt welded pipe is formed by rolling slabs into ribbon, or skelp, that is further rolled into a circular section, with butted joints that are finally resistance welded and drawn to the required pipe dimension. Annealing is a further treatment.

Hot galvanizing with zinc or tinning has been used to give steel corrosion-resistant coatings, but this method is being replaced by electrolytic methods. Zinc sulfate, alkaline stannates, and other electrolytes

containing the metals are used in electrolytic cells through which the sheet is passed.

#### VI. ENGINEERING CONTROLS

Information on specific design features of smelting and steel manufacturing equipment and processes is generally proprietary, and unavailable from published literature sources or industrial representatives. The lack of detailed control information precludes the identification of design features that may reduce employee exposure to hazards.

#### VII. POTENTIAL HEALTH HAZARDS

The occupational health hazards that potentially exist in ferrous smelting and in steel manufacturing can be deduced from the foregoing outlines of the process steps employed. The principal potential physical and chemical hazards that are associated with the various processes are subsequently summarized.

##### A. Physical Hazards

The high temperatures that are required for operating the furnaces, coke ovens, and sintering and pelletizing equipment, and for material in-processing and product finishing are considered to be hazardous. Burns and eye injury may result from accidental contacts, spills, or leakages. Additionally, without adequate protection or work scheduling, heat stresses in working areas may be significant and adversely affect workers.

Excessive exposure to loud noise, vibration, illumination (quantity and quality of lighting), and radiation (non-ionizing and ionizing) are also potentially hazardous. The major problem associated with exposure to infrared radiation is its heating effect; major sources of infrared radiation include furnace operations, soaking pits, hot slabs and ingots, molten metal, and kilns. Exposure to ultraviolet radiation is hazardous to the eyes and

skin; major sources of UV radiation in steel and related facilities are electrical and inert gas metal arc melting.

#### B. Chemical Hazards

In the production of iron and steel, many potentially hazardous compounds are used and generated. These contaminants vary widely in type and quantity, and the extent of human exposure may vary substantially depending on the utilization and efficiency of pollution control devices. Subsequently, a survey of the principal human health effects associated with the iron and steel industry is presented, first, by presenting epidemiological studies which have linked exposure to the industry with human effects, and, second, by summarizing the effects associated with specific potential toxicants generated during the production of iron and steel. This presentation is intended to provide merely an overview of major health problems and is neither critical nor comprehensive.

##### General Epidemiological Studies

Cancer mortality in the U.S. steel industry has been reviewed recently by Radford (1976). For steel workers dying during the period 1973-1974, significant increases were seen in mortality due to lung cancer ( $p < 0.05$ ) and residual cancer ( $p < 0.001$ ). Some increase in lung cancer may be expected in workers exposed to coke oven emissions (Table 4). Radford (1976) also noted a significant increase in lung cancer in workers in steel finishing operations. Of the residual cancers, the most profound increase was seen in the incidence of bladder cancer ( $p < 0.001$ ) which occurred in workers with no history of coke oven emission exposure. Increased lung cancer mortality in the general population has been noted in an iron industry city in the U.S.S.R. where levels of dust,  $SO_2$ , phenol, and benzopyrene exceeded the safety standards (Irodova, 1973).



In another U.S.S.R. study, changes in lung volume were noted in adults living near coke, chemical, and unspecified metallurgical plants. These changes were associated with air pollution by particulate matter, phenol, SO<sub>2</sub>, H<sub>2</sub>S, CO, CuO, NiO, Fe<sub>2</sub>O<sub>3</sub>, and MnO<sub>2</sub> (Khonakhbeev, 1972). As indicated in Tables 3 and 4, all of these pollutants are generated by the iron and steel industry.

#### Specific Toxicants

The metals commonly present in ferrous smelting and steel manufacturing environments are listed, with sources, in Table 3. Table 4 further characterizes the industrial origin of the materials, and summarizes their principal toxicological/physiological effects.

Based on the information presented in Table 4 and in the epidemiological studies section, respiratory disorders and lung cancer appear to be the most likely human health effects of iron and steel production. The most significant pollutants contributing to these effects appear to be benzopyrene, carbon monoxide, coal and coke dust, coke oven emissions, manganese compounds, nitrogen oxides, particulates, and sulfur oxides; however, it cannot be over-emphasized that this judgement is based on an extremely superficial review of the literature.

### VIII. PERTINENT NIOSH PUBLICATIONS

#### A. Criteria Documents

<u>Subject</u>	<u>NIOSH Publication No.</u>
Ammonia	74-136
Inorganic Arsenic	74-110
Inorganic Arsenic (revised)	75-149
Benzene (revised, 1976)	74-137
Boron Trifluoride	77-122
Cadmium	76-192
Carbon Monoxide	73-11000
Chromium (VI)	76-129
Coke Oven Emissions	73-11016
Inorganic Fluoride	76-103
Hydrogen Cyanide and Cyanide Salts	77-108

Table 3. Substances Present in Ferrous Smelting and Steel Manufacturing

	Mining	Preparation	Coke Ovens	Blast Furnaces	Steel Furnaces	Finishing
<u>Process Materials</u>						
Ammonium nitrate	x					
Bentonite		x				
Coal	x					
Coke		x	x	x		
Dolomite				x		
Fluorspar		x		x	x	
Iron ore (magnetite, hematite, etc.)		x		x		
Iron scrap				x	x	
Limestone		x		x	x	
Oxygen				x	x	
<u>Inprocess Materials</u>						
Carbon monoxide				x	x	
Carbon dioxide			x	x	x	
Hydrogen			x			
Methane			x			
Nitrogen oxides			x	x		
Flotation reagents		x				
Sulfuric acid						x
Hydrochloric acid						x
Slags				x	x	
Magnesite				x	x	
Silica			x			
Lime				x	x	
<u>Byproducts</u>						
Ammonium sulfate			x			
Aromatics			x			
Benzene			x			
Hydrocarbons			x			
Phenol			x			
Tar			x			
Toluene			x			
Xylene			x			
Sulfur dioxide		x				

Table 3. Substances Present in Ferrous Smelting and Steel Manufacturing (Cont'd)

Emissions	Mining	Preparation	Coke Ovens	Blast Furnaces	Steel Furnaces	Finishing
Dusts (coal, coke, limestone)	x	x	x	x	x	
Coke oven			x			
Blast furnaces			x	x		
Steel furnaces					x	
<u>Metal Additives</u>						
Aluminum					x	
Bismuth					x	
Boron					x	
Cadmium					x	
Chromium					x	
Cobalt					x	
Copper					x	
Lead					x	
Magnesium					x	
Manganese				x	3	
Molybdenum					x	
Nickel					x	
Niobium					x	
Rare earths					x	
Silicon				x	x	
Tellurium					x	
Tin						x
Titanium					x	
Tungsten					x	
Vanadium					x	
Zinc						x

Table 3. Substances Present in Ferrous Smelting and Steel Manufacturing (Cont'd)

	Mining	Preparation	Coke Ovens	Blast Furnaces	Steel Furnaces	Finishing
<u>Miscellaneous Impurities, etc.</u>						
Hydrogen sulfide			x	x		
Chlorine						
Fluorine				x		
Ozone				x	x	
Graphite					x	x
Hydrogen cyanide			x	x		
Calcium cyanide			x	x	x	
Silica						
Phosphorus compounds				x		
Arsenic				x		
<u>Miscellaneous Conditions</u>						
Noise	x			x	x	x
Vibration	x	x	x	x	x	x
Heat			x	x	x	x
Infrared Radiation			x	x	x	x

TABLE 4

TOXICOLOGICAL/PHYSIOLOGICAL PROPERTIES OF CHEMICAL SUBSTANCES  
ENCOUNTERED DURING FERROUS SMELTING AND STEEL MANUFACTURING

Substance	Source	Toxicological/Physiological Effects	
		Acute	Chronic
Aluminum Compounds	Constitute up to 11% of particulate emissions; up to 9% slag from ferromanganese blast furnaces; and up to 5% of particulate emissions from open-hearth, blast, electric arc, and basic oxygen furnaces and cupola gases (23,28,58,64).	No important effects.	$Al_2O_3$ is regarded as an inert particle, although when inhaled with silica fumes, it may contribute to the development of pulmonary disease. Elevated aluminum levels have been found in the teeth of workers in iron-ore enriching plants (1,32).
Ammonia Compounds	Have been detected in coking plant emissions (60kg/hr); in primary water from coke oven gases (50-2000 mg/l); and in blast furnace gas scrubbers (27.4 kg/2500 metric tons of iron/day) (28,58,60).	Ammonia may cause temporary blindness and intolerable irritation of mucous membranes at concentrations above 200 ppm (4).	Ammonia may cause eye and mucous membrane irritation and affect ciliary clearance; odor threshold is 20 ppm or less (1,4).
Aromatic Hydrocarbons	Ambient coke plant emissions; 8 plants emitted 1600 tons of benzene per year. 80 kg of unspecified aromatic hydrocarbons emitted per hour from plant producing 9500 tons of dry coke per day (39).	Benzene is a potent narcotic at 200 ppm (4).	Benzene is myelotoxic (resulting in blood changes, aplastic anemia, and death), leukemogenic, and may be absorbed through the skin (1,4,46).

TABLE 4 (Continued)

TOXICOLOGICAL/PHYSIOLOGICAL PROPERTIES OF CHEMICAL SUBSTANCES  
ENCOUNTERED DURING FERROUS SMELTING AND STEEL MANUFACTURING

Substance	Source	Toxicological/Physiological Effects	
		Acute	Chronic
Arsenic Compounds	Crude coal and coal tar pitch contain 2-11 ppm arsenic. Arsenites occur in coke oven plant emissions (33,34).	Trivalent arsenic compounds are corrosive to mucous membranes and skin. Ingestion of inorganic arsenic compounds leads to constriction of the throat followed by dysphagia, epigastric pain, vomiting, watery diarrhea, shock, and death. Inhalation produces cough, chest pain, dyspnea, giddiness, headache, extreme weakness, and gastrointestinal symptoms (65).	Trivalent arsenic has been implicated in lung and skin cancer, and depresses bone marrow function (erythropoiesis and myelopoiesis). Chronic inhalation produces sequentially: 1) weakness, loss of appetite, nausea, vomiting, diarrhea, sense of heaviness in stomach; 2) conjunctivitis, catarrhal state of respiratory mucous membranes, coryza, hoarseness, mild tracheobronchitis, perforation of nasal septum, and skin lesions; 3) peripheral neuritis sometimes leading to motor paralysis (65).
Benzopyrene	Found in coke oven gas and in emissions from iron and steel industries. A 4 million ton per year steel plant emitted 1.3-4 kg benzopyrene/year; concentrations of 1.75-5.0 µg/100 cu m were found near a metallurgical center; 0.065-2.9 µg/100 cu m benzopyrene were detected 3 km from a ferrous-metallurgy plant (25, 36,45,58,59,61,63,68,69).	No important effects.	Carcinogenic in mice; increased human cancer rates associated with background and occupational exposure to benzopyrene from ferrous metallurgy plants. Benzopyrene (with dust, SO <sub>2</sub> , and phenols) pollution from iron production implicated in increased rates of community lung cancer (24,63).

TABLE 4 (Continued)

TOXICOLOGICAL/PHYSIOLOGICAL PROPERTIES OF CHEMICAL SUBSTANCES  
ENCOUNTERED DURING FERROUS SMLTING AND STEEL MANUFACTURING

Substance	Source	Toxicological/Physiological Effects	
		Acute	Chronic
Bismuth	Used in tempering baths for steel alloys (65).	Intravenous or intramuscular injection of soluble salts may cause near death or death; target organs are kidneys and liver (65).	Chronic intoxication causes "bismuth line," a gum condition with black spots of buccal and colonic mucosa, superficial stomatitis, bad breath, salivation (65).
Boron	Alloyed to iron and steel to increase hardness(65).	No acute effects of boron have been encountered. Boric acid and borax locally irritate the central nervous system and the gastrointestinal tract (65).	Affects nervous system, enzyme activity, carbohydrate metabolism, hormone function, oxidation processes, and may produce allergic effects (65).
Cadmium Compounds	Steel mill dust, particulate emissions from electric arc furnaces; elevated levels in air near steel plant (58).	Cadmium oxide exposure produces nausea, vomiting, salivation, choking attacks, diarrhea, loss of consciousness, abdominal pain, catarhal and ulcerative gastroenteritis, pulmonary infarcts and subdural hemorrhages. Death due to pulmonary injury has occurred after short exposure to approximately 50 mg/cu m (4).	Pulmonary, renal, and gastrointestinal disorders, and anemia. Heavy smoking considerably increases tissue Cd levels. Rats exposed to 0.1-10 ppm Cd for one year stored Cd in lungs, kidneys, liver, bone, teeth, and blood, resulting in anemia, liver cirrhosis, and splenic hyperplasia (1,4).

TABLE 4 (Continued)

TOXICOLOGICAL/PHYSIOLOGICAL PROPERTIES OF CHEMICAL SUBSTANCES  
ENCOUNTERED DURING FERROUS SMELTING AND STEEL MANUFACTURING

Substance	Source	Toxicological/Physiological Effects	
		Acute	Chronic
Calcium Compounds	Calcium oxide (CaO) is present in 5% or less of particulate emissions from blast furnaces, open-hearth furnaces, basic oxygen furnaces, and cupola gases. 8-15% of dust from ferromanganese blast furnaces, and up to 22% of dust from electric furnaces is CaO. Slag is 39.8% CaO. Dust from basic oxygen furnaces is $\approx 0.4\%$ calcium peroxide ( $\text{CaO}_2$ ) (23,28,58).	No important effects.	Iron and steel industries report no adverse effects from CaO and $\text{CaO}_2$ . CaO is an irritant to the skin and respiratory tract; however, atmospheric moisture converts it to innocuous CaOH (1).
Carbon Monoxide	Generated or emitted by blast furnaces, bessemer converters, basic oxygen furnaces, and coking from iron and steel industries. 8 coke plants have emitted 3030 tons CO per year; coke plant producing 9500 tons dry coke per day has emitted 2700 kg CO/hour; electric furnaces generate about 18 pounds CO per ton of metal produced (28,37,58).	Combines reversibly with oxygen-carrying sites on hemoglobin with an affinity 210-240 times greater than that of oxygen. Symptoms include: rapid heart beat, headache, dizziness, nausea, unconsciousness, and death at concentrations above 1200 ppm (4).	Similar to acute effects but less severe; may have cardiovascular and developmental effects (1,41,42,43).



TABLE 4 (Continued)

TOXICOLOGICAL/PHYSIOLOGICAL PROPERTIES OF CHEMICAL SUBSTANCES  
ENCOUNTERED DURING FERROUS SMELTING AND STEEL MANUFACTURING

Substance	Source	Toxicological/Physiological Effects	
		Acute	Chronic
Chromium Compounds	Cr <sub>2</sub> O <sub>3</sub> occurs (up to 14%) in the particulate emissions from electric arc furnaces. Elevated chromium levels have been monitored in the air near a steel plant (20,28,58).	Trivalent salts have a low order of toxicity. They are readily absorbed through the skin. Hexavalent compounds are irritants and corrosive when ingested, inhaled or absorbed through the skin (4,58).	History of lung cancer among hexavalent chromium (chromate) workers. Chromates cause lesions of mucosa and submucosa of the respiratory tract, and spleen and kidney changes (4).
Coal and Coke Dust	Coal dust from handling and storage of coal. 8 coke plants have emitted 9900 tons coal dust/year. Coke particles emitted in steam plume during coke quenching. 190 kg coal and coke dust/hour emitted from a plant producing 9500 tons dry coke/day (16,28,37).	No important effects.	Workers exposed to coal dust have developed pneumoconiosis. Reduction in exposure to coal dust (also carbon monoxide, cyanide, and ammonia) decreased inflammations of nose and throat, bronchitis, and total sick rate for coke oven workers (1,27).
Cobalt	Used as a steel alloying element (4).	Pulmonary irritant in animal studies; ingestion may cause vomiting, diarrhea, sensation of hotness (4,12).	Minute quantities may cause allergic sensitivity and dermatitis. Inhalation of dust, perhaps in combination with other dusts, may cause asthma-like disease with coughing and dyspnea which may progress to interstitial pneumonia with marked fibrosis and reversible pneumoconiosis (4).

TABLE 4 (Continued)

TOXICOLOGICAL/PHYSIOLOGICAL PROPERTIES OF CHEMICAL SUBSTANCES  
ENCOUNTERED DURING FERROUS SMELTING AND STEEL MANUFACTURING

Substance	Source	Toxicological/Physiological Effects	
		Acute	Chronic
Coke Oven Emissions	Coke ovens.	No important effects.	Associated with cancer of kidney and lung in coke oven workers; non-oven workers in coke by-product operations have elevated levels of colon and pancreas cancer. Benzo-pyrene, present in coke oven gases, has been associated with higher levels of community and occupational lung cancer (see Benzopyrene) (11, 17, 24, 40, 49, 51, 55, 63).
Copper Compounds	Cupric oxide (CuO) is a minor contaminant (<2%) in emissions from electric arc steel furnaces, open-hearth furnaces, and basic oxygen furnaces (20, 28, 58).	Exposure may induce metal fume fever (43).	No relevant effects.
Cyanides	Water pollution from coking, blast furnace gas scrubbing, and case hardening of steel; in ammonia liquor of coking (principally hydrogen cyanide at levels up to 150 mg/l). 34.9 kg cyanide/day produced from the gas cleaning of a blast furnace producing 2740	Low levels of hydrogen cyanide may cause weakness, headache, confusion, nausea and vomiting. Inhalation, ingestion, or skin absorption of larger doses may result in loss of consciousness, cessation of respiration, and death by asphyxiation (58).	Exposure to hydrogen cyanide during metal hardening operations is reported to cause signs of neurological damage (1).

TABLE 4 (Continued)

TOXICOLOGICAL/PHYSIOLOGICAL PROPERTIES OF CHEMICAL SUBSTANCES  
ENCOUNTERED DURING FERROUS SMELTING AND STEEL MANUFACTURING

Substance	Source	Toxicological/Physiological Effects	
		Acute	Chronic
Cyanides (continued)	tons of iron/day; quenching of waters from case hardening of steel contain 50-120 mg/l free cyanide. Air pollution from the volatilization of cyanides from washwater; 100g cyanides/cu m washwater flowing at a rate of 2 cu m/100 cu m of cooled gas. 8 coking plants have emitted 99 tons cyanide/yr. Coke oven plants have emitted 3 g cyanide/ton coal used (1,13,15,16,28,35,37,48,60).		
Fluorides	Sintering of high fluoride ores releases hydrofluoric acid and silicon tetrafluoride. Fluoride is found in emissions from blast, open-hearth, and electric arc furnaces, and in blast furnace gas washwater. 57 kg fluoride compounds were found in water from a furnace producing 2740 tons of iron/day. Fluorspar fluxes reduce the viscosity of slag (28,38,53,58,60,64).	Fluorides irritate the eyes, mucous membranes, and lungs. Inhalation of hydrogen fluoride may produce bronchospasm, laryngospasm, pulmonary edema and sometimes gastrointestinal symptoms. Ingestion of fluorides may result in nausea, vomiting, abdominal cramps, diarrhea, twitching of the muscles, tonic and clonic convulsions, and coma (58).	Inhalation may result in nosebleed and sinus trouble. Fluorides are stored in bone, and may cause osteosclerosis and some ossification of ligaments (73).

TABLE 4 (Continued)

TOXICOLOGICAL/PHYSIOLOGICAL PROPERTIES OF CHEMICAL SUBSTANCES  
ENCOUNTERED DURING FERROUS SMELTING AND STEEL MANUFACTURING

Substance	Source	Toxicological/Physiological Effects	
		Acute	Chronic
Iron Compounds	Iron compounds (up to 90% $\text{Fe}_2\text{O}_3$ , <5% $\text{FeO}$ ) can be major components in dust from blast, open-hearth, electric arc, and basic oxygen furnaces, and cupolas. 0.37-1.8 mg $\text{Fe}_2\text{O}_3/\text{cu m}$ in the air was recorded 1 km from metallurgical, coke, and chemical plants (20,23,28,58,64).	No important effects.	Siderosis in workers exposed to iron oxide fumes. Increased iron levels in teeth of workers at iron-ore enriching plant (1,32,59).
Lead Compounds	$\text{PbO}$ is a minor (<1%) contaminant in emissions from electric arc and open-hearth furnaces and may be a minor contaminant in steel mill emissions (14,20,28).	Gastrointestinal disorders, colic, constipation in extreme overexposures; "chronic" effects can result after brief exposures (4).	Continuation of acute symptoms; presence of stippled cells, anemia; weakness (and sometimes paralysis) of extensor muscles, primarily of wrists; encephalopathy in severe poisonings (4).
Magnesium Compounds	Slag contains 12.9% magnesium oxide ( $\text{MgO}$ ). $\text{MgO}$ is a minor component in the particulate emissions from ferromanganese blast furnaces, electric arc steel furnaces, and open-hearth and basic oxygen furnaces (28,58).	No important effects.	No important effects.

TABLE 4 (Continued)

TOXICOLOGICAL/PHYSIOLOGICAL PROPERTIES OF CHEMICAL SUBSTANCES  
ENCOUNTERED DURING FERROUS SMELTING AND STEEL MANUFACTURING

Substance	Source	Toxicological/Physiological Effects	
		Acute	Chronic
Manganese Compounds	Major component (22.5-37.5 tons Mn/1000 net tons of metal produced) in dust from ferromanganese blast furnaces; up to 40% of cupola gases. Minor (<5%) component in dusts from electric arc steel furnaces and basic oxygen and open-hearth furnaces. 1.2% of slag is manganese (20,23,28,50,58).	No important effects.	"Manganism," a disease characterized by unaccountable laughter, euphoria, impulsiveness, and insomnia; followed by overpowering somnolence; occasionally cramps, headache, and sexual excitement followed by impotence. As poisoning develops, victim approaches absolute detachment. Poisoning permanently disabling unless treated (4).
Molybdenum	Used as a steel alloying agent (4).	Inhalation of molybdenum trioxide may produce irritation of the eyes and mucous membranes; animals exposed to high concentrations experience weight loss, diarrhea, loss of muscular coordination and death (4).	Excessive intake may induce copper deficiency (4).
Nickel Compounds	Nickel Oxide (NiO) is a minor (0-3%) constituent of particulate matter from electric furnaces. Levels of 0.012-0.09 mg NiO/cu m have been reported one km from metallurgical, coke, and chemical plants (28,29).	Severe, transient pneumonitis; animal studies have shown pneumonia, pathological changes in lung, and hyperplasia of lymphoid tissue (4).	Evidence of significant increase in lung cancer among exposed workers; dermatitis; nickel is both a skin and respiratory tract sensitizer (4).

TABLE 4 (Continued)

TOXICOLOGICAL/PHYSIOLOGICAL PROPERTIES OF CHEMICAL SUBSTANCES  
ENCOUNTERED DURING FERROUS SMELTING AND STEEL MANUFACTURING

Substance	Source	Toxicological/Physiological Effects	
		Acute	Chronic
Nitrogen Oxides	From open-hearth furnaces (2.6 tons/day from a 50 ton furnace) and electric arc steel furnaces (0.7-4.1 lbs/hr/furnace). Air near plasma smelting facilities has contained 0.5 mg/cu m. May make up 10-20% of pollution from steel mills. By 1980, it is projected that boilers in iron and steel industries will emit 161,500 tons/yr (18,26,50,56,58).	Pulmonary irritation and methemoglobinemia. High concentrations of nitrogen dioxide may cause malaise, cyanosis, cough, dyspnea, chills, fever, headache, nausea, vomiting, collapse, and death. If acute episodes with nitrogen oxides are not fatal, bronchiolitis fibrosa oblitterans may develop a few days to six weeks later (65).	Dyspnea upon exertion and pulmonary dysfunction (decreased vital capacity, maximum breathing capacity, and lung compliance, and increased residual volume of lungs). Symptoms suggestive of emphysema (65).
Ozone	Probably emitted from electric arc steel furnaces; measured at <0.99 mg/cu m in plasma arc smelting environments (50,58).	Low levels may cause pulmonary congestion, edema, and hemorrhage, and, in the tissues, defective dissociation of oxygen from oxyhemoglobin (1).	Bronchiolitis and bronchitis developed in animals exposed to slightly more than 1 ppm O <sub>3</sub> six hours daily for one year (1).
Particulate Matter	Virtually every phase of iron and steel production. Yearly particulate matter emissions from sintering in U.S.A., 45,500 kg; from pelletizing, 36,320 kg; 408,600 tons particulate matter/yr projected from boilers, by 1980. Significant air pollution in U.S.A. and Europe (16,20,22, 28,58,64).	Generalizations difficult due to complex chemical composition of particulate matter. For more information see detailed reviews (44,64).	Range from altered lung function to increased mortality. Particulates are associated with polycyclic organic matter (POM), including benzo-pyrene. Some POM are carcinogenic to rodents; other produce mutations in cell cultures (44,57,64).

TABLE 4 (Continued)

TOXICOLOGICAL/PHYSIOLOGICAL PROPERTIES OF CHEMICAL SUBSTANCES  
ENCOUNTERED DURING FERROUS SMELTING AND STEEL MANUFACTURING

Substance	Source	Toxicological/Physiological Effects	
		Acute	Chronic
Phenols	Monohydric and dihydric phenols in wastewater from coking plants and blast furnace gas scrubbers. Wastewater phenol concentrations of 10-2000 mg/l reported from a plant producing 9500 tons of dry coke/day, and 27 kg phenol reported in washings from a blast furnace producing 2740 tons of iron/day. Air pollution from coking and ferrous metallurgy plants (15,16,19,28,31,60).	Phenol exposure (inhalation, skin, ingestion) produces intense burning at contact point, cyanosis, muscular weakness, tremors, convulsions, and collapse (4).	Toxic amounts may be absorbed through the skin (4).
Phosphorus Pentoxide	Makes up <1% of particulate emissions from open-hearth, electric arc steel, blast, and basic oxygen furnaces (28,58,64).	No important effects.	No important effects.
Silica	Makes up 5-40% of cupola gases, 35.8% of slag, 10% of blast furnace dust, 9-19% of ferromanganese blast furnace dust, and <5% of emissions from open-hearth, electric arc, and basic oxygen furnaces (23,28,58,64).	No important effects.	Exposure to crystalline silica produces cumulative and progressive development of pneumoconiosis (silicosis); diffuse nodules which may increase in size until they interfere with pulmonary function; dyspnea; emphysema; chronic bronchitis (4).

TABLE 4 (Continued)

TOXICOLOGICAL/PHYSIOLOGICAL PROPERTIES OF CHEMICAL SUBSTANCES  
ENCOUNTERED DURING FERROUS SMELTING AND STEEL MANUFACTURING

Substance	Source	Toxicological/Physiological Effects	
		Acute	Chronic
Sulfur Compounds	In sintering, 30-40% of the sulfur in the charge is liberated. Sulfur oxides (mostly SO <sub>2</sub> ) are in emissions from open-hearth, blast, electric, and basic oxygen furnaces. SO <sub>2</sub> is also released during pelletizing and coking. Hydrogen sulfide is generated by coking. Pickling can contaminate water with sulfuric acid. By 1980, 472,000 tons of SO <sub>2</sub> /yr will be released from boilers in the iron and steel industries (16,22,28,58).	Damage to respiratory system. Sulfuric acid can also severely irritate the eyes (1,4).	Damage to respiratory system; sulfuric acid exposure leads to tracheobronchitis, stomatitis, conjunctivitis, gastritis, and erosion of teeth. Atmospheric levels of <0.05-0.15 mg SO <sub>2</sub> /cu m reportedly retarded growth in children. Animal studies suggest SO <sub>2</sub> is a co-carcinogenic agent. SO <sub>2</sub> levels have been correlated with increased mortality from breast, lung, stomach and total cancers, and from heart disease (1,4,21,65,67).
Vanadium	Vanadium and vanadium pentoxide are used mostly in high speed and other alloy steels; small amounts in tool and structural steels (4).	Compounds, especially the pentoxide, are irritating to eyes and skin, and inhalation of dusts or fumes may irritate the respiratory tract. Higher exposures may result in pulmonary edema and pneumonia which may be fatal (4).	Respiratory tract irritation (4).
Zinc Compounds	Zinc oxide is a minor (<5%) contaminant of emissions from blast, electric, open-hearth, and basic oxygen furnaces. 5% of workers are exposed to excessive zinc levels during iron and steel melting (28,62).	Inhalation of freshly formed zinc oxide results in "metal fume fever," with symptoms resembling those of influenza: chills, fever, elevated body temperatures, and recovery within 48 hours (1,4).	No important effects.



<u>Subject</u>	<u>NIOSH Publication No.</u>
Inorganic Lead	73-11010
Inorganic Lead (revised)	78-158
Inorganic Nickel	77-164
Phenol	76-196
Crystalline Silica	75-120
Sulfuric Acid	74-128
Sulfur Dioxide	74-111
Vanadium	77-222
Zinc Oxide	76-104

B. Health Hazard Evaluations (HHE's)

<u>Subject</u>	<u>HHE Report No.</u>	<u>Date</u>
Empire Detroit Steel Co. New Boston, Ohio	72-49-45	1973
Southwestern Ohio Steel, Inc. Hamilton, Ohio	73-155-112	1974
Youngstown Sheet and Tube Co. East Chicago, Indiana	74-40-167	1975
Bishop Tube Division, Christiana Metals, Inc. Frazer, Pennsylvania	77-128-470	1978
Midwest Steel Division National Steel Corp. Portage, Indiana	77-34-471	1978

C. Other NIOSH Publications

<u>Title</u>	<u>NIOSH Publication No.</u>
Working with Ammonia (folder)	73-11003
Effects of Carbon Monoxide on Vigilance Performance	77-124
Chronic Animal Inhalation Toxicity to Cobalt	74-115
Industrial Exposure to Ozone	74-118
Working with Lead in Industry (folder)	74-125
Behavioral Effects of Occupational Exposure to Lead	75-164
Health Effects of Occupational Lead and and Arsenic Exposure: A Symposium	76-134

<u>Title</u>	<u>NIOSH Publication No.</u>
Report on Analytical Methods used in a Coke Oven Effluent Study	74-105
Environmental Conditions in U.S. Copper Smelters	75-158
Environmental Surveys of Aluminum Reduction Plants	74-101
Comparative Cause - Specific Mortality Patterns by Work Area within the Steel Industry	75-157
Mortality of Steel Workers Employed in Hot Jobs	77-219
Health and Safety Guide for Foundries	76-124
Pattern Shop, Core Room, Molding Shop, and Sandhandling Department -- Health Hazards in a Foundry	77-102
Melting and Pouring Departments -- Health Hazards in a Foundry	77-103
Shakeout, Cleaning, Grinding, and Inspection Departments -- Health Hazards in a Foundry	77-104

#### IX. EXISTING STANDARDS

Table 5 presents a list of current ACGIH threshold limit values (TLV's), OSHA promulgated standards, and NIOSH recommended limits for typical process materials, byproducts, emissions, additives, and impurities associated with ferrous smelting and steel manufacturing.

#### X. EXPOSURE ESTIMATES

As detailed in Section III (Statistical Information), 593,891 workers were employed in 1151 iron and steel industrial establishments during 1978.

TABLE 5

## THRESHOLD LIMIT VALUES, OSHA STANDARDS, NIOSH RECOMMENDED STANDARDS

Substance	TLV (ACGIH, 1977)		OSHA (NIOSH, 1977b)		NIOSH (NIOSH, 1977b)	
	ppm	mg/m <sup>3</sup>	ppm	mg/m <sup>3</sup>	ppm	mg/m <sup>3</sup>
Aluminum metal and oxide (Al <sub>2</sub> O <sub>3</sub> )	-	10 <sup>a</sup>	-	-	-	-
Ammonia	25	18	50	-	50 (ceiling, 5 minutes)	34.8 (ceiling, 5 minutes)
Aromatic hydrocarbons (benzene, skin)	10	30	10 25 (acceptable ceiling) 50 (ceiling, 10 minutes)	-	1 (ceiling, 60 minutes)	3.2 (ceiling, 60 minutes)
Arsenic and compounds	-	0.5	-	0.5	-	.002 (ceiling, 15 minutes)
Benzopyrene	-	-	-	-	-	-
Bismuth telluride	-	10	-	-	-	-
Boron oxide	-	10	-	-	-	-
Cadmium compounds	-	0.05 (dusts and salts)	-	fume: 0.1 (0.3 ceiling) dust: 0.2 (0.6 ceiling)	-	0.04 0.2 (ceiling, 15 minutes)
Calcium oxide	-	2 <sup>b</sup>	-	5	-	-
Calcium peroxide	-	-	-	-	-	-
Carbon monoxide	50	55	50	-	35	40
Chromium (VI)	-	0.05	-	0.01	-	0.001 (carcinogenic) 0.025 (other) 0.050 (ceiling, 15 minutes)
Coal and coke dust	-	2	-	-	-	-
Cobalt	-	0.1 <sup>b</sup>	-	-	-	-
Coke oven emissions	-	-	-	.150	-	-
Copper fumes	-	0.2	-	-	-	-
Fluorides (inorganic)	-	2.5	-	2.5	-	2.5
Hydrogen cyanide (skin)	10	11	10	-	-	5 (ceiling, 10 minutes)

<sup>a</sup>1977 addition<sup>b</sup>intended change

TABLE 5 (Continued)

## THRESHHOLD LIMIT VALUES, OSHA STANDARDS, NIOSH RECOMMENDED STANDARDS

Substance	TLV (ACGIH, 1977)		OSHA (NIOSH, 1977b)		NIOSH (NIOSH, 1977b)	
	ppm	mg/m <sup>3</sup>	ppm	mg/m <sup>3</sup>	ppm	mg/m <sup>3</sup>
Iron oxide (fumes; Fe <sub>2</sub> O <sub>3</sub> )	-	5	-	-	-	-
Lead (as Pb)	-	0.15	-	0.2	-	<.1
Magnesium oxide fumes	-	10	-	-	-	-
Manganese and compounds (as Mn)	-	5	-	-	-	-
Molybdenum and compounds						
soluble	-	5	-	-	-	-
insoluble	-	10	-	-	-	-
Nickel compounds (as Ni)	-	0.1	-	1	-	.015
Nitrogen oxides (as NO <sub>2</sub> )	5	-	5	-	1 (ceiling, 15 minutes)	1.8 (ceiling, 15 minutes)
Ozone	0.1	0.2	-	-	-	-
Particulate Matter	-	-	-	-	-	-
Phenols (skin)	5	19	5	-	5.2 15.6 (ceiling, 15 minutes)	20 60 (ceiling, 15 minutes)
Phosphorus Pentoxide	-	-	-	-	-	-
Silica	-	10 mg/m <sup>3</sup> % respirable quartz +2	-	10 mg/m <sup>3</sup> % respirable quartz +2	-	.05 (respirable free silica)
Sulfur Compounds						
Sulfur Dioxide	5	13	5	-	0.5	1.3
Sulfuric Acid	-	1	-	1	-	1
Vanadium Pentoxide (as V)						0.5 (vanadium compounds, ceiling, 15 min.)
Dust	-	0.5	-	0.5 (ceiling)	-	-
Fume	-	0.05	-	0.1 (ceiling)	-	-
Zinc Oxide						
Dust	-	10	-	-	-	-
Fume	-	5	-	5	-	5
						15 (ceiling, 15 minutes)

## XI. ONGOING STUDIES

A manual search of Tox-Tips for the last twelve months (through December, 1978) has identified the following relevant ongoing studies:

1. Project Title: Mortality Study of Steelworkers  
Performing Organization: NIOSH; Cincinnati, Ohio and University  
of Pittsburgh, Pittsburgh, PA  
End Date: September 1979  
Source: Tox-Tips, No. 38, July 1979, p. 29
2. Project Title: Mortality and Industrial Hygiene Study of  
Foundry Industry  
Performing Organization: NIOSH; Cincinnati, Ohio  
End Date: June, 1980  
Source: Tox-Tips, No. 37, June 1979, p. 35
3. Project Title: Carcinogenesis of Foundry Pyrolysis Effluent  
Performing Organization: NIOSH; Cincinnati, Ohio  
End Date: Not Specified  
Source: Tox-Tips, No. 27, August 1978, p. 3

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#### Industry Contacts

American Iron and Steel Institute  
1000 16th St. N.W.  
Washington, D.C. 20036  
W. J. Nuselt - (202) 452-7100

United States Steel Corporation  
600 Grand St.  
Pittsburgh, Pa. 15230  
Dr. Forrest Fisher - (216) 433-1121

Bethlehem Steel Corporation  
Bethlehem, Pa. 18016  
Thomas Kobrick - (215) 694-2424

Republic Steel Corporation  
1523 Republic Building  
Cleveland, Ohio 44101  
Patrick O'Neal

## APPENDIX A

(Anon., 1972)

### Major Group 10.—METAL MINING

#### *The Major Group as a Whole*

This major group includes establishments primarily engaged in mining, developing mines, or exploring for metallic minerals (ores). These ores are valued chiefly for the metals contained, to be recovered for use as such or as constituents of alloys, chemicals, pigments, etc. This major group also includes all ore dressing and beneficiating operations, whether performed at mills operated in conjunction with the mines served or at mills, such as custom mills, operated separately. These include mills which crush, grind, wash, dry, sinter, or leach ore, or perform gravity separation or flotation operations. Magnesite and brucite operations are classified in Industry 1459, and crushed dolomite operations in Industry 1422. Smelters and refineries are classified in Major Group 33, Primary Metal Industries, and establishments engaged in producing primary magnesium metal in Industry 3339. The operation of brine wells or sea water plants for the production of magnesium is classified in Major Group 28.

Exploration under preliminary phases of operation should be classified according to the type of ore expected to be found, when performed by operators of the properties. Exploration performed on a contract, fee, or similar basis is classified in Industry 1081.

Group Industry  
No. No.

#### 101 IRON ORES

##### 1011 Iron Ores

Establishments primarily engaged in mining, beneficiating, or otherwise preparing iron ores and manganiferous ores valued chiefly for their iron content. This industry includes production of sinter and other agglomerates except those associated with blast furnace operations. Blast furnaces primarily engaged in producing pig iron from iron ore are classified in Industry 3312.

Brown ore mining  
Hematite mining  
Iron agglomerate and pellet production  
Iron ore, block  
Iron ore dressing (beneficiation) plants  
Iron ore mining  
Limonite mining

Magnetite mining  
Manganiferous ore mining, valued chiefly  
for iron content  
Siderite mining  
Sintering of iron ore at the mine  
Taconite mining

APPENDIX B  
(Anon., 1972)

## Major Group 33.—PRIMARY METAL INDUSTRIES

### *The Major Group as a Whole*

This major group includes establishments engaged in the smelting and refining of ferrous and nonferrous metals from ore, pig, or scrap; in the rolling, drawing, and alloying of ferrous and nonferrous metals; in the manufacture of castings and other basic products of ferrous and nonferrous metals; and in the manufacture of nails, spikes, and insulated wire and cable. This major group also includes the production of coke. Establishments primarily engaged in manufacturing metal forgings or stampings are classified in Group 346.

Group Industry  
No. No.

#### 331 BLAST FURNACES, STEEL WORKS, AND ROLLING AND FINISHING MILLS

##### 3312 Blast Furnaces (Including Coke Ovens), Steel Works, and Rolling Mills

Establishments primarily engaged in manufacturing hot metal, pig iron, silvery pig iron, and ferroalloys from iron ore and iron and steel scrap; converting pig iron, scrap iron and scrap steel into steel; and in hot rolling iron and steel into basic shapes such as plates, sheets, strips, rods, bars, and tubing. Merchant blast furnaces and byproduct or beehive coke ovens are also included in this industry. Establishments primarily engaged in manufacturing ferro and nonferrous additive alloys by electrometallurgical processes are classified in Industry 3313.

Armor plate, made in steel works or rolling mills  
Axles, rolled or forged: made in steel works or rolling mills  
Bars, iron: made in steel works or rolling mills  
Bars, steel: made in steel works or hot rolling mills  
Beehive coke oven products  
Billets, steel  
Blackplate  
Blast furnace products  
Blooms  
Car wheels, rolled  
Chemical recovery coke oven products  
Coal gas, derived from chemical recovery coke ovens  
Coal tar crudes, derived from chemical recovery coke ovens  
Coke, produced in beehive ovens  
Coke, produced in chemical recovery coke ovens  
Cold rolled strip steel, flat bright: made in hot rolling mills  
Distillates, derived from chemical recovery coke ovens  
Fence posts, iron and steel: made in steel works or rolling mills  
Ferroalloys, produced in blast furnaces  
Flats, iron and steel: made in steel works and hot rolling mills  
Forgings, iron and steel: made in steel works or rolling mills  
Frogs, iron and steel: made in steel works or rolling mills  
Galvanized hoops, pipes, plates, sheets, and strips: iron and steel  
Gun forgings, iron and steel: made in steel works or rolling mills  
Hoops, galvanized iron and steel: made in steel works or rolling mills  
Hoops, iron and steel: made in steel works or hot rolling mills  
Hot rolled iron and steel products  
Ingots, steel  
Iron, pig  
Iron sinter, made in steel mills  
Nut rods, iron and steel: made in steel works or rolling mills  
Pipe, iron and steel: made in steel works or rolling mills

Plates, made in steel works or rolling mills  
Rail joints and fastenings, made in steel works or rolling mills  
Railroad crossings, iron and steel: made in steel works or rolling mills  
Rails, iron and steel  
Rails, rerolled or renewed  
Rods, iron and steel: made in steel works or rolling mills  
Rounds, tube  
Sheet pilings, plain: iron and steel—made in steel works or rolling mills  
Sheets, iron and steel: made in steel works or rolling mills  
Shell slugs, steel: made in steel works or rolling mills  
Skelp, iron and steel  
Slabs, steel  
Spiegeleisen, made in blast furnaces  
Spikes and spike rods, made in steel works or rolling mills  
Sponge iron  
Stainless steel  
Steel works producing bars, rods, plates, sheets, structural shapes, etc.  
Strips, galvanized iron and steel: made in steel works or rolling mills  
Strips, iron and steel: made in steel works or hot rolling mills  
Structural shapes, iron and steel  
Tar, derived from chemical recovery coke ovens  
Terneplate  
Ternes, iron and steel: long or short  
Tie plates, iron and steel  
Tin free steel  
Tin plate  
Tool steel  
Tube rounds  
Tubes, iron and steel: made in steel works or rolling mills  
Tubing, seamless: steel  
Well casings, iron and steel: made in steel works or rolling mills  
Wheels, car and locomotive: iron and steel—*mitse*  
Wire products, iron and steel: made in steel works or rolling mills  
Wrought pipe and tubing, made in steel works or rolling mills

Group Industry  
No. No.

331 BLAST FURNACES, STEEL WORKS, AND ROLLING AND FINISHING MILLS—  
Continued

3313 Electrometallurgical Products

Establishments primarily engaged in manufacturing ferro and nonferrous additive alloys by electrometallurgical or metallothermic processes, including high percentage ferroalloys and high percentage nonferrous additive alloys.

Additive alloys, except copper: not produced in blast furnaces	Ferrotitanium
Electrometallurgical products, except aluminum, magnesium, and copper	Ferrotungsten
Ferroalloys, not made in blast furnaces	Ferrovandium
Ferrochromium	High percentage ferroalloys, not produced in blast furnaces
Ferromanganese, not produced in blast furnaces	Manganese metal, not produced in blast furnaces
Ferromolybdenum	Molybdenum silicon, not produced in blast furnaces
Ferrophosphorus	Nonferrous additive alloys, high percentage: except copper
Ferrosilicon, not produced in blast furnaces	Steel, electrometallurgical

3315 Steel Wire Drawing and Steel Nails and Spikes

Establishments primarily engaged in drawing wire from purchased iron or steel rods, bars, or wire and which may be engaged in the further manufacture of products made from wire; establishments primarily engaged in manufacturing steel nails and spikes from purchased materials are also included in this industry. Rolling mills engaged in the production of ferrous wire from wire rods or hot rolled bars produced in the same establishment are classified in Industry 3312. Establishments primarily engaged in drawing nonferrous wire are classified in Group 335.

Brads, steel: wire or cut	Tacks, steel: wire or cut
Cable, steel: insulated or armored	Wire, ferrous
Horseshoe nails	Wire products, ferrous: made in wire drawing plants
Nails, steel: wire or cut	Wire, steel: insulated or armored
Spikes, steel: wire or cut	
Staples, steel: wire or cut	

3316 Cold Rolled Steel Sheet, Strip, and Bars

Establishments primarily engaged in (1) cold rolling steel sheets and strip from purchased hot rolled sheets; (2) cold drawing steel bars and steel shapes from purchased hot rolled steel bars; and (3) producing other cold finished steel. Establishments primarily engaged in the production of steel, including hot rolled steel sheets, and further cold rolling such sheets are classified in Industry 3312.

Cold finished steel bars: not made in hot rolling mills	Razor blade strip steel, cold rolled: not made in hot rolling mills
Cold rolled steel strip, sheet, and bars: not made in hot rolling mills	Sheet steel, cold rolled: not made in hot rolling mills
Corrugating iron and steel, cold rolled: not made in hot rolling mills	Wire, flat: cold rolled strip: not made in hot rolling mills
Flat bright steel strip, cold rolled: not made in hot rolling mills	

3317 Steel Pipe and Tubes

Establishments primarily engaged in the production of welded or seamless steel pipe and tubes and heavy riveted steel pipe from purchased materials. Establishments primarily engaged in the production of steel, including steel skelp or steel blanks, tube rounds, or pierced billets, are classified in Industry 3312.

Boiler tubes, wrought: <i>mfp</i>	Tubing, mechanical and hypodermic sizes: cold drawn stainless steel— <i>mfp</i>
Conduit: welded, lock joint, and heavy riveted— <i>mfp</i>	Well casing, wrought: welded, lock joint, and heavy riveted— <i>mfp</i>
Pipe, seamless steel: <i>mfp</i>	Wrought pipe and tubes: welded, lock joint, and heavy riveted— <i>mfp</i>
Pipe, wrought: welded, lock joint, and heavy riveted— <i>mfp</i>	
Tubes, seamless steel: <i>mfp</i>	

## THE FERTILIZER INDUSTRY

### I. SCOPE OF PROFILE

The processes used for manufacturing fertilizer products have been reviewed for the purpose of identifying the potential occupational hazards associated with the industry.

The fertilizer manufacturing establishments are included in Standard Industrial Classification (SIC) Group No. 287 (Agricultural Chemicals), and are specifically categorized as follows:

- Nitrogenous Fertilizers - SIC No. 2873
- Phosphatic Fertilizers - SIC No. 2874
- Mixing Plants - SIC No. 2975

SIC 2873 & 2874 include the manufacturing establishments.  
SIC 2875 applies only to establishments where products from purchased fertilizer materials are mixed.

The mining and recovery of potassium minerals and phosphate rock are included in SIC Industry Nos. 1474 and 1475 (Chemical and Fertilizer Mineral Mining). Full descriptions of the SIC industrial classifications are presented in Appendix A.

### II. SUMMARY

The fertilizer industry is engaged primarily in the manufacture of the three following basic plant nutrient materials:

- Ammonia, by the fixation of atmospheric nitrogen
- Phosphatic materials, by acidulating phosphate rock
- Potash salts, by refining mined potash minerals

The origin and interrelationships of these nutrients in the industry are summarized in Figure 1. The base products--ammonia, superphosphate and muriate of potash (potassium chloride)--are either applied directly to the soils or converted into other fertilizer compounds. Mixtures or solutions of two or more of the nutrients are also prepared because they are more easily applied.