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ŞEPA ALTERNATIVE CONTROL TECHNIQUES DOCUMENT- NO_x EMISSIONS FROM IRON AND STEEL MILLS

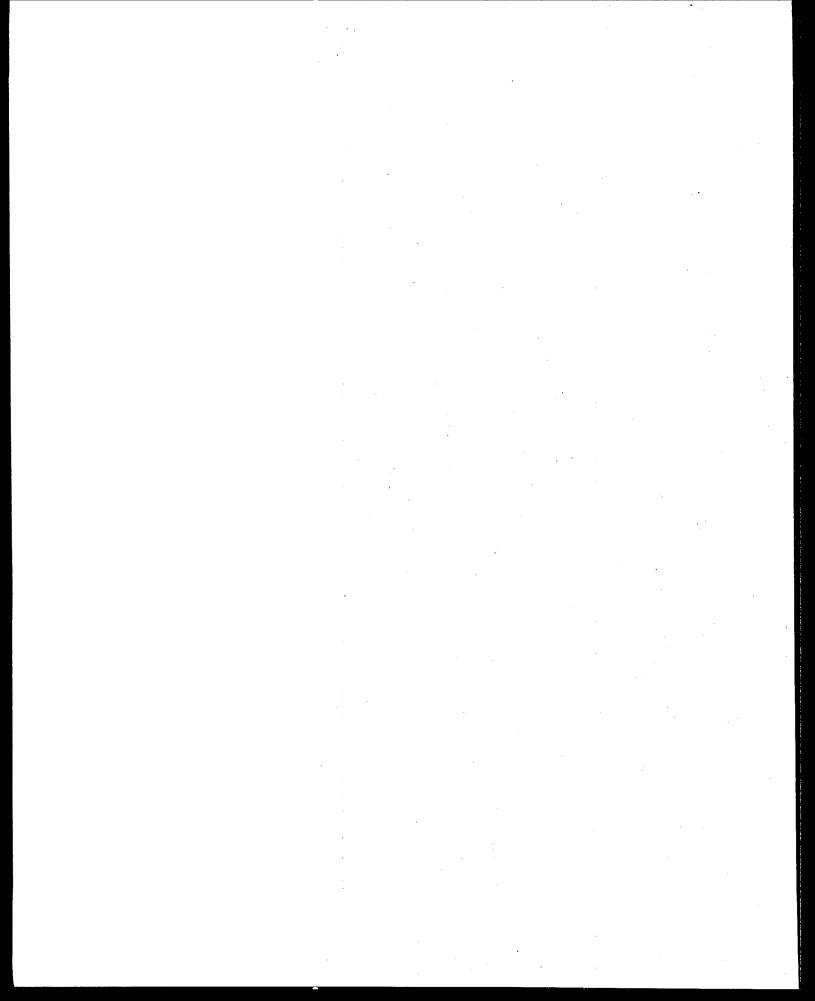


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ALTERNATIVE CONTROL TECHNIQUES DOCUMENT -NO_x EMISSIONS FROM IRON AND STEEL MILLS

Emission Standards Division

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Radiation
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711
September 1994



ALTERNATIVE CONTROL TECHNIQUES DOCUMENTS

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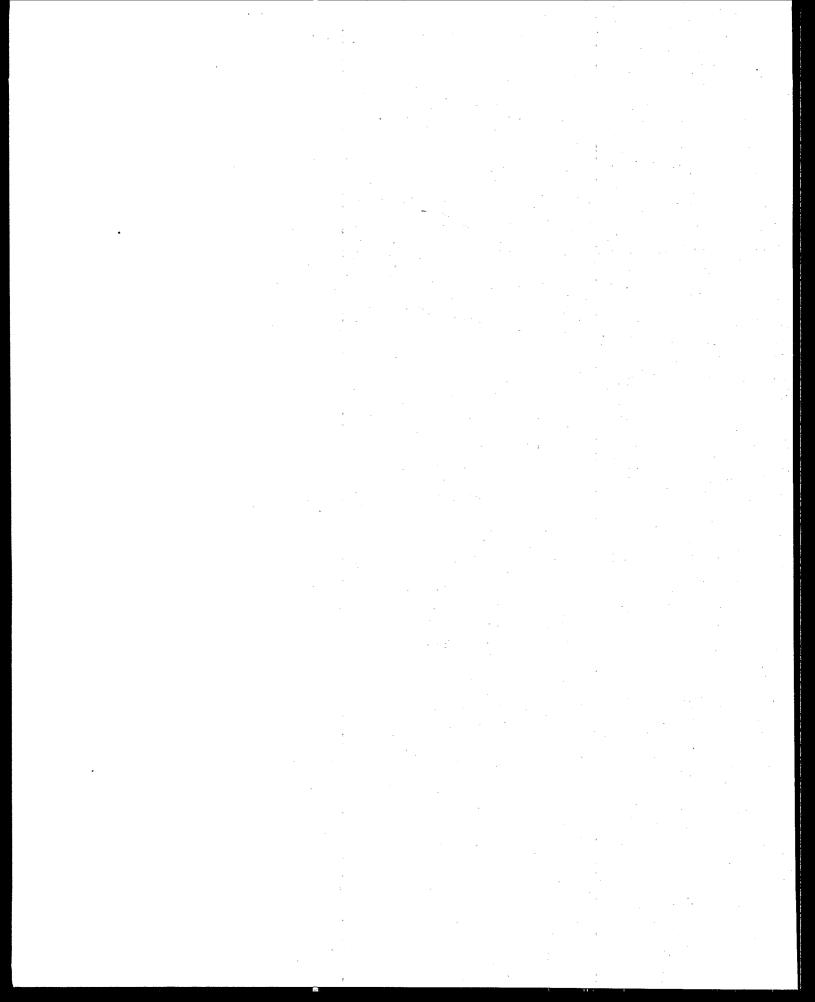


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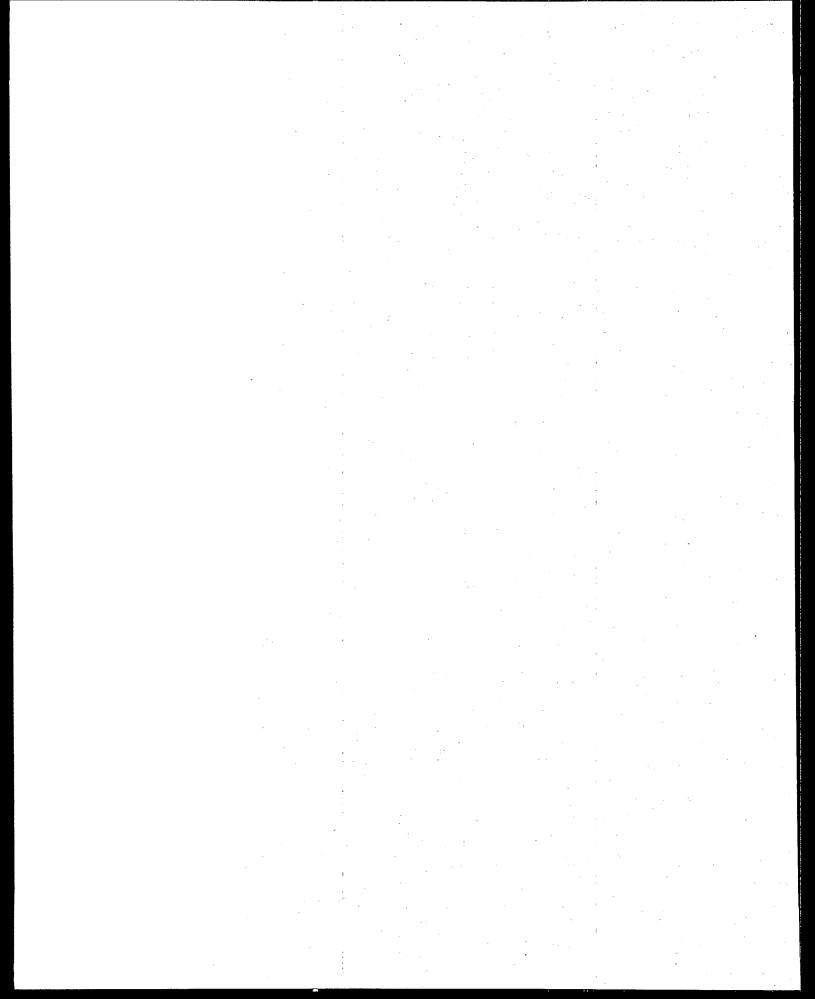
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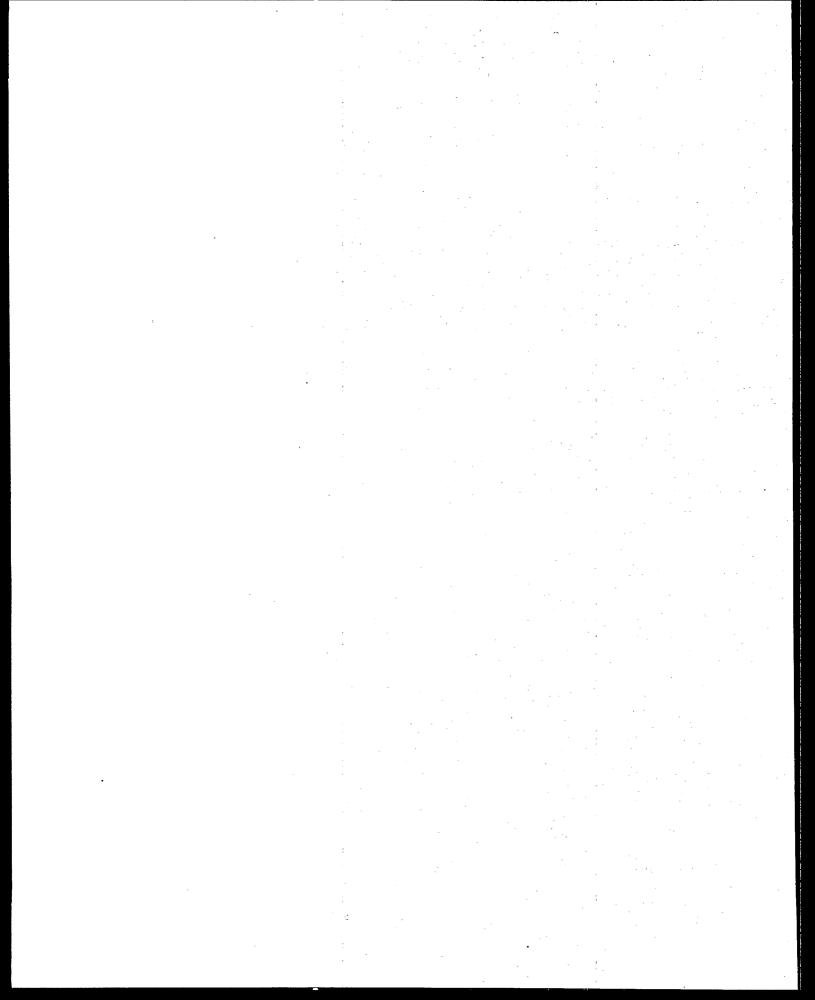
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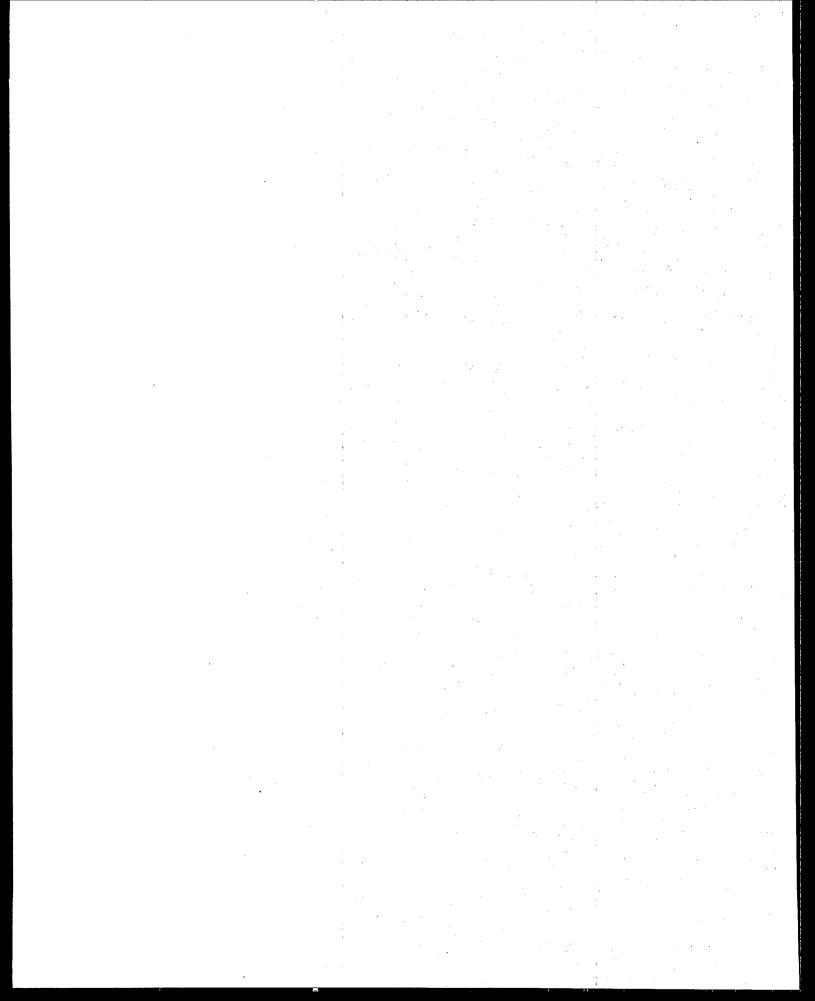
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CHAPTER 1

INTRODUCTION

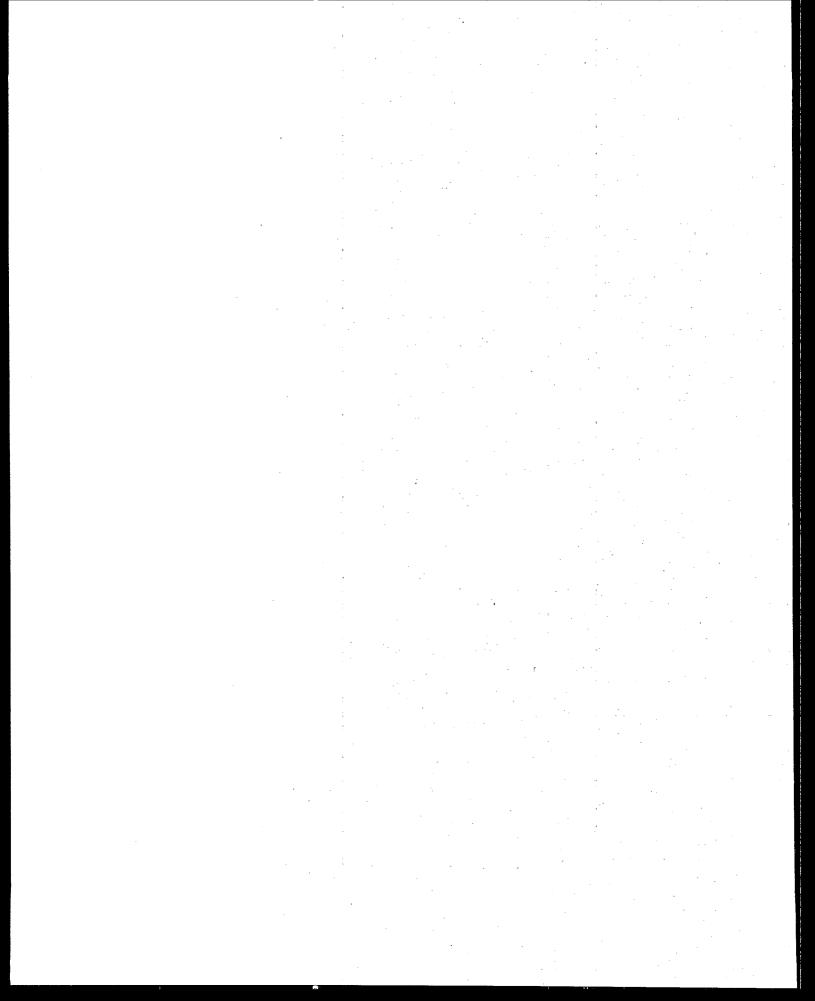
Congress, in the Clean Air Act Amendments of 1990 (CAAA), amended Title I of the Clean Air Act (CAA) to address ozone nonattainment areas. A new Subpart 2 was added to Part D of Section 103. Section 183(c) of the new Subpart 2 provides that:

[w]ithin 3 years after the date of the enactment of the [CAAA], the Administrator shall issue technical documents which identify alternative controls for all categories of stationary sources of ... oxides of nitrogen which emit, or have the potential to emit 25 tons per year or more of such air pollutant.

These documents are to be subsequently revised and updated as determined by the Administrator.

Iron and steel mills have been identified as a stationary source category with emission sources that emit more than 25 tons of nitrogen oxides (NO_x) per year. This alternative control techniques (ACT) document provides technical information on various NO_x controls for various iron and steel mill processes that State and local agencies may use to develop and implement regulatory programs to control NO_x emissions from iron and steel mills. Additional ACT documents have been developed for eight other stationary source categories.

The information in this ACT document was generated from previous EPA documents and literature searches and contacts with iron and steel manufacturers, engineering firms, control equipment vendors, and Federal, State, and local regulatory agencies. Chapter 2 presents a summary of the findings of this study. Chapter 3 provides a process description and industry characterization of iron and steel mills. A discussion of uncontrolled NO_x emission levels is presented in Chapter 4. Alternative control techniques and achievable controlled emission levels are discussed in Chapter 5. Chapter 6 presents control costs and cost effectiveness for each control technique. Environmental and energy impacts associated with the use of NO_x control techniques are discussed in Chapter 7.



CHAPTER 2

SUMMARY

2.1 SOURCES OF NO_x EMISSIONS

Integrated iron and steel mills produce steel by reducing iron ore to iron in a blast furnace and, subsequently, removing excess carbon and other impurities from the iron in a basic oxygen furnace. Other processes involve beneficiating iron ore (e.g., pelletizing), recycling of iron-bearing materials (e.g., sintering), coke-making, and steel finishing processes such as shaping, annealing, and galvanizing. All of these are high temperature processes, usually involving the combustion of fossil fuels, and all are potential sources of NO_X emissions.

Mini mills and specialty producers process steel through some subset of the full range of processes found in integrated iron and steel mills. Typically, they enter the process by melting scrap steel in an electric arc furnace, bypassing the iron-making process and attendant support activities such as sintering and coke making.

The processing order is illustrated in the simplified flow diagram in Figure 2-1. In coke making, coal is destructively distilled in coke ovens that are fired with, typically, a mixture of coke oven gas (COG) and natural gas (NG) and/or blst furnace gas(BFG). Coke oven underfiring is a high-temperature process and NO_{X} emissions from coke making are appreciable.

In the sinter plant, iron ore fines, coke fines, other iron-bearing materials, and (often) flux are well-mixed and spread uniformly on a traveling grate and ignited, typically with NG. As the grate travels, a forced draft causes the coke fines and other combustibles in the bed to burn. The mixture is thus heated to a fusion temperature, creating a sinter suitable for use in the blast furnace.

In the blast furnace, iron ore is reduced to molten iron (also called pig iron or hot metal). The blast furnace is a closed system with no atmospheric emissions. The effluent from the furnace, blast furnace gas (BFG) that is rich in carbon monoxide (CO), is cleaned of particulates and used as a fuel in the blast furnace stoves. Each blast furnace has three or four associated stoves that preheat the air blast supplied to the blast furnace. Because these stoves are heated primarily with BFG, NO, emissions from the stoves have low concentrations.

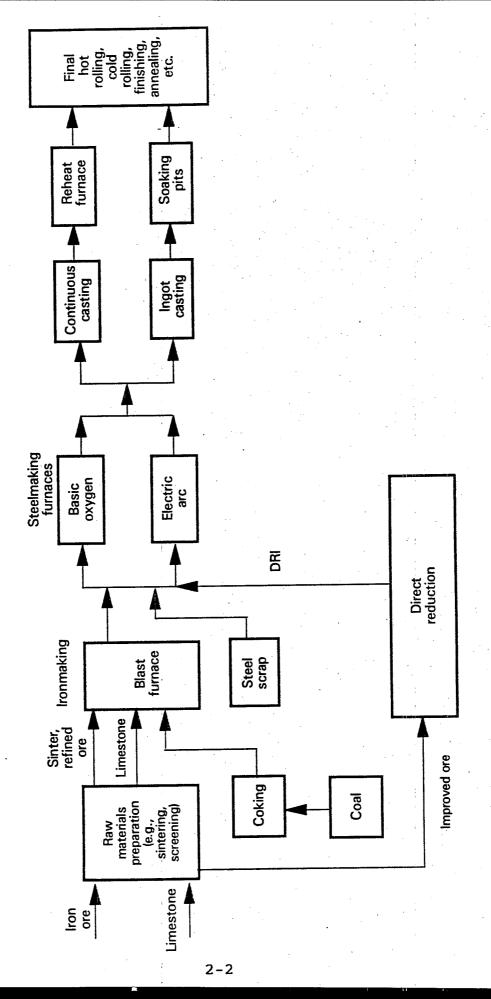


Figure 2-1. Simplified steelmaking flow chart.

Molten iron from the blast furnace, along with scrap steel, is charged to the basic oxygen furnace (BOF) where high-purity oxygen is blown on the molten bath (or upward through the bath in the case of a Q-BOP [basic oxygen process] type furnace). The oxidation of undesired elements in the bath (carbon, silicon, manganese, etc.) converts the hot metal into steel and brings the bath to a suitable pouring temperature. Combustible off-gases from the process are typically collected in an open hood above the furnace that admits air and are burned. Some furnaces are equipped with suppression-type hoods that prevent air from mixing with the off-gases above the furnace, and the off-gas is subsequently flared. During the combustion of the off-gas, thermal $NO_{\rm X}$ is generated.

Scrap steel is melted in electric arc furnaces (EAF's) where radiant heat from an electric arc established between the electrodes (usually powered from a three-phase utility-based supply) and the scrap or molten steel bath is used to bring the charge to pouring temperature. Heating due to the electric current passing through the scrap or molten bath is a minor part of the total heat input. The use of electricity for steel melting transfers the generation of NO_x from the iron and steel mill to a utility generating plant. However, oxygen and NG are sometimes used to preheat the charge. Thus EAF's are NO_x emission sources.

Molten steel from steel-making furnaces is typically processed through a continuous caster where it is shaped into slabs, billets, or blooms. Alternatively, it may be cast into ingots and stored for subsequent processing. Slabs, billets, and blooms from the continuous caster are typically reheated to suitable working temperatures in reheat furnaces prior to being passed through mills for further shaping. Ingots are typically reheated in soaking pits prior to subsequent processing. Reheat furnaces and soaking pits are high-temperature, fossil fuel (typically natural gas) burning furnaces and are sources of NO_x emissions.

Finishing processes such as annealing and galvanizing also involve reheating steel products to suitable temperatures for processing. Consequently, these finishing processes are also sources of NO, emissions.

2.2 UNCONTROLLED NO_x EMISSIONS

There are three fundamentally different mechanisms of NO_x formation. These mechanisms yield (1) thermal NO_x , (2) fuel NO_x , and (3) prompt NO_x . The thermal NO_x mechanism arises from the thermal dissociation and subsequent reaction of nitrogen (N_2) and oxygen (O_2) molecules in combustion air. The fuel NO_x mechanism arises from the evolution and reaction of fuel-bound nitrogen

compounds with oxygen. The prompt NO_x mechanism involves the intermediate formation of hydrogen cyanide (HCN), followed by the oxidation of HCN to NO. Natural gas and most distillate oils have no chemically bound fuel nitrogen and essentially all NO_x formed from the combustion of these fuels is thermal NO_x . Residual oils and coals all have fuel-bound nitrogen and, when these are combusted, NO_x is formed by all three mechanisms.

Iron and steel mill processes tend to use gaseous fuels, i.e., NG, COG, BFG, and oxygen, and the NO $_{\rm x}$ generation tends to be thermal NO $_{\rm x}$. Exceptions include sintering where coke fines are burned as a fuel and coke ovens where coal is destructively distilled in the absence of air. Emissions from sintering and fugitive emissions from coke ovens may be sources of fuel NO $_{\rm x}$ emissions. Prompt NO $_{\rm x}$ formation is not a major factor. It forms only in fuel-rich flames, which are inherently low NO $_{\rm x}$ emitters. Thermal NO $_{\rm x}$ formation is the predominant mechanism of NO $_{\rm x}$ generation at iron and steel mills.

Very little NO_x emissions data are available in the literature relevant to iron and steel processes. Table 2-1 summaries uncontrolled NO_x emissions from the major process facilities found in iron and steel mills. This summary is based on the available emissions data obtained during the preparation of this document. The data are presented in Appendix A of this document.

The uncontrolled NO_x emissions tabulated in Table 2-1 indicate that coke-oven underfiring, sintering, reheat furnaces, annealing furnaces, and galvanizing furnaces are facilities with emission factors that range from 120 to 940 ppm at 3 percent O_2 . Data available for both preheated combustion air and cold combustion air furnaces show that NO_x emission factors are much higher when the combustion air is preheated. For some facilities, e.g., reheat furnaces, there is much scatter in the data, and the averages presented in Table 2-1 may not be representative of individual furnaces.

2.3 NO_X EMISSIONS REDUCTION TECHNIQUES

Control techniques for NO_x emissions can be placed into one of two basic categories: techniques designed to minimize NO_x generation and techniques to remove previously generated NO_x from the waste effluent stream. Combustion modification techniques such as low- NO_x burners (LNB's) and flue gas recirculation fit into the first category. Add-on flue gas treatment techniques such as selective catalytic reduction (SCR) and selective noncatalytic reduction (SNCR) are examples of the second.

Few facilities found at iron and steel mills have ${\rm NO}_{\rm x}$ controls. For many facilities, a suitable control technique has

TABLE 2-1. SUMMARY OF AVERAGE UNCONTROLLED NO $_{\rm X}$ EMISSIONS

| တ္က | | | | | | | | | | | | | | | | | | | |
|--|-----------------------|-----------|----------------------|----------------------|----------------------------|-----------------|-----|--------------|-------------|----------------|--------------|----------|-------------------|--------------|----------|---------------------|--------------|----------|---|
| UNCONTROLLED EMISSIONS (LB/MMBtu) | 99.0 | 0.47 | 0.021 | | 1 1 | i i i | | 0.14 | 990.0 | 0.79 | 0.20 | 0.14 | 1.15 | 0.40 | 0.15 | 1.2 | 0.40 | 0.14 | |
| UNCONTROLLED EMISSIONS (PPM @3% O ₂) | 800 | 340 | 30 | | 09 | 280 | 10 | 1 1 | t 3 1 | 650 | 220 | 120 | 780 | 330 | 120 | 940 | 330 | 120 | |
| FIRING TYPE | Ī | 1 | ; ; | | ; ; | i | ï | Preheat | Cold-Air | Regenerative | Recuperative | Cold-Air | Regenerative | Recuperative | Cold-Air | Regenerative | Recuperative | Cold-Air | |
| PROCESS FACILITY | Coke-oven underfiring | Sintering | Blast furnace stoves | Basic Oxygen Furnace | during O ₂ blow | during non blow | EAF | Soaking Pits | | Reheat Furnace | | | Annealing Furnace | | | Galvanizing Furnace | | | - |

not been demonstrated. These facilities include sinter plants, coke ovens, blast furnace stoves, and steelmaking furnaces. The Japanese have investigated using SCR for sinter plants and coke ovens. These efforts appear to be experimental, and SCR is not used routinely on these facilities in Japan. Iron and steel process facilities known to have NO_{x} controls applied are reheat furnaces, annealing furnaces, and galvanizing furnaces. Control techniques known to have been applied to these facilities are as follows:

Reheat furnaces Low excess air (LEA)

LNB's

LNB plus flue gas recirculation (FGR)

Annealing furnaces LNB

LNB plus FGR

SCR

LNB plus SCR

Galvanizing furnaces LNB

LNB plus FGR.

Other control techniques are discussed in this document.

Table 2-2 summarizes controlled NO_x emissions data and estimates and percent reductions. Percent reductions range from 13 to 90%. For reheat furnces controlled emissions range from 25 ppm @ 3% O_2 for cold air furnace controlled by LNB+ FGR to 560 ppm for a regenerative furnace controlled by LEA. Emissions reductions for the reheat furnaces with preheated combustion air range from 0.03 lb $NO_x/MMBtu$ for an LEA-controlled recuperative-fired furnace to 0.61 lb $NO_x/MMBtu$ for regenerative-fired furnace. Due to low uncontrolled NO_x emissions, the emissions reductions for cold air reheat furnace are much lower.

For annealing furnaces, controlled emissions range from 10 ppm for a cold-air fired furnace controlled by LNB+SCR to 390 ppm for a regenerative-fired furnace controlled by LNB. Annealing furnace emissions reductions range from 0.07 lb $NO_x/MMBtu$ for a cold-fired furnace with LNB to 0.85 lb $NO_x/MMBtu$ for a regenerative-fired furnace with LNB plus SCR controls.

For galvanizing furnaces, controlled emissions range from 50 ppm for a cold- air fired furnace controlled by LNB+FGR to 470 ppm for a regenerative-fired furnace controlled by LNB. Emissions reductions for galvanizing furnaces range from 0.07 lb/MMBtu for a cold-air fired furnace with LNB to 0.69 lb/MMBtu to a regenerative-fired furnace controlled by LNB+FGR.

TABLE 2-2. NO_X CONTROLLED EMISSIONS AND PERCENT REDUCTIONS

| PERCENT REDUCTION | 13 | 99 | 7.7 | 20 | 09 | 09 | 85 | 80 | 06 | 50 | 09 |
|---|--------|-------|---------|-----------|---------|------|------|----------|---------|-------------|---------|
| EMISSIONS (LB/MMBtu) COLD-AIR | 0.12 | 0.046 | 0.031 | 0.07 | 0.07 | 0.07 | 0.02 | 0.03 | 0.015 | 0.07 | 0.06 |
| EMISSIONS (LB/MMBtu) RECUPERATIVE | 0.17 | 0.068 | 0.046 | 0.20 | 0.16 | 0.16 | 90.0 | 0.08 | 0.04 | 0.20 | 0.16 |
| EMISSIONS (LB/MMBtu) REGENERATIVE | 69.0 | 0.27 | 0.18 | 0.48 | 0.38 | 0.38 | 0.14 | 0.19 | 0.095 | 0.57 | 0.46 |
| CONTROL | LEA | LINB | LNB+FGR | LINB | LNB+FGR | SNCR | SCR | LNB+SNCR | LNB+SCR | LINB | LNB+FGR |
| FURNACE TYPE | REHEAT | | | ANNEALING | | | | | | GALVANIZING | |

2.4 COSTS AND COST EFFECTIVENESS OF NO_X CONTROL TECHNIQUES

Tables 2-3 thru 2-5 present costs and cost- effectiveness estimates for NO_x controls for reheat, annealing and galvanizing furnaces, respectively. These estimates are based on a limited data base. Controlled NO_x missions (and, consequently, emissions reductions) are often based on test data from a single furnace. Costs are also based on limited data, often a single example furnace, that do not account for site-specific factors. All costs are in April 1994\$.

Costs and cost effectiveness vary with furnace firing capacity. In discussing cost effectiveness in Tables 2-3 thru 2-5, values used refer to the mid-size capacity furnace unless stated otherwise and are for existing furnaces. For combustion modification controls such as LNB and LNB/FGR, costs and cost effectiveness for new furnaces are approximately 1/3 - 1/4 the corresponding number for new sources. For add-on controls only(SNCR and SCR), costs and cost effectiveness are the same for both new and existing sources.

As shown in Table 2-3, the cost effectiveness of existing mid-size reheat furnaces of all control techniques range from \$90/ton NO_x removed (LNB on a regenerative-fired furnace) to \$2,400/ton NO_x removed (LEA on a cold-air fired furnace). Only LEA has cost effectiveness greater than \$700/ton. Capital costs and annual costs for the various controls range from \$190,000 to 340,000 and \$51,000 to 83,000 respectively.

For existing mid-size annealing furnaces (Table 2-4) cost effectiveness of all control techniques range from \$200/ton NO_x removed (for LNB at a regenerative fired annealing furnace) to \$7,900/ton NO_x removed (for LNB+SCR at a cold-air fired furnace). Capital costs range from \$540,000 to 4,500,000 and annual costs from \$77,000 to 870,000.

For existing mid-size galvanizing furnaces (Table 2-5), cost effectiveness of all control techniques range from \$110/ton for LNB on a regenerative-fired furnace to \$1,200/ton for LNB+FGR on a cold-air fired furnace. Capital costs for the two controls are \$250,000 and \$380,000. Annual costs are \$58,000 and \$70,000.

2.5 IMPACTS OF NO_x CONTROLS

All of the $\rm NO_x$ control techniques listed in Section 2.3 have the potential to impact other air emissions in addition to $\rm NO_x$, and all may have energy impacts. SCR units may have a solid waste impact in the disposal of spent SCR catalyst. None of the listed techniques have a wastewater impact.

TABLE 2-3. COSTS AND COST EFFECTIVENESS - EXISTING REHEAT FURNACES (300 MMBtu/hr)

| Control | Firing Type | Capital | Annual | NO _v Reduction | Cost |
|---------|--------------|----------------|---------------|---------------------------|---------------|
| · | | Cost (\$1,000) | Costs | (tons/yr) | Effectiveness |
| | | (41,000) | (161,000/191) | | (\$/ton) |
| LEA | Regenerative | 190 | 51 | 120 | 410 |
| | Recuperative | 190 | 51 | 30 | 1,600 |
| | Cold-air | 190 | 51 | 20 | 2,400 |
| LNB | Regenerative | 230 | 09 | 620 | 06 |
| | Recuperative | 230 | 09 | 160 | 350 |
| | Cold-air | 230 | 09 | 110 | 400 |
| LNB/FGR | Regenerative | 340 | 83 | 730 | 110 |
| | Recuperative | 340 | 83 | 180 | 460 |
| | Cold-air | 340 | 83 | 120 | 069 |
| | | | | | |

TABLE 2-4. COSTS AND COST EFFECTIVENESS - EXISTING ANNEALING FURNACES (200 MMBtu/hr)

| Control | Firing Type | Capital Cost | Annual Costs | NO _x Reduction (tons/yr) | Cost Effectiveness |
|-----------|--------------|-----------------|-----------------|--|-----------------------|
| T ND | Dogogowating | (41,000) | (16 1000, 14) | 380 | (4) (01) |
| avia | Negenerative | 0+0 | | 200 | 700 |
| · | Recuperative | 540 | 77 | 160 | 480 |
| | Cold-air | 540 | 77 | 09 | 1,300 |
| LNB + FGR | Regenerative | 810 | . 120 | 450 | 260 |
| | Recuperative | 810 | 120 | 200 | 280 |
| | Cold-air | 810 | 120 | 70 | 1,600 |
| SNCR | Regenerative | 069 | 260 | 450 | 580 |
| , | Recuperative | 069 | 260 | 200 | 1,300 |
| | Cold-air | 690 | 260 | 70 | 3,700 |
| SCR | Regenerative | 4,000 | 062 | 640 | 1,200 |
| | Recuperative | 4,000 | 790 | 270 | 2,900 |
| | Cold-air | 4,000 | 790 | 110 | 7,200 |

TABLE 2-3 (Continued)

| Control | Firing Type | Capital Cost (\$1,000) | Annual Costs (\$1,000/yr) | NO _x Reduction (tons/yr) | Cost Effectiveness (\$/ton) |
|----------|--------------|------------------------------|---------------------------------|--|-----------------------------------|
| LNB+SCR | Regenerative | 4,500 | 870 | 089 | 1,300 |
| | Recuperative | 4,500 | 870 | 280 | 3,100 |
| , | Cold-air | 4,500 | 870 | 110 | 7,900 |
| LNB+SNCR | Regenerative | 1,200 | 340. | 009 | 570 |
| | Recuperative | 1,200 | 340 | 250 | 1,100 |
| | Cold-air | 1,200 | 340 | 100 | 3,400 |

TABLE 2-5. COSTS AND COST EFFECTIVENESS - EXISTING GALVANIZING FURNACES (100 MMBtu/hr)

| Control | Firing Type | Capital Cost (\$1,000) | Annual Costs (\$1,000/yr) | NO _x Reduction (tons/yr) | Cost Effectiveness (\$/ton) |
|---------|--------------|------------------------------|---------------------------------|--|-----------------------------|
| | Regenerative | 250 | 40 | 340 | 110 |
| | Recuperative | 250 | 40 | 120 | 320 |
| | Cold-air | 250 | 40 | 40 | 006 |
| LNB/FGR | Regenerative | 380 | 09 | 420 | 140 |
| | Recuperative | 380 | 09 | 140 | 410 |
| | Cold-air | 380 | 09 | 50 | 1,200 |

2.5.1 Air Impacts of Combustion Modification Techniques

All of the listed combustion modification NO_x control techniques, LEA, LNB, and LNB plus FGR, may increase CO and unburned hydrocarbon (HC) emissions. The NO_x reduction mechanisms inherent in these modification techniques are the reduction of peak flame temperatures, which is exponentially related to the formation of thermal NO_x and the reduced availability of excess oxygen needed to form NO_x . Reducing the availability of oxygen to the combustion process increases the likelihood that some HC will not be burned and that some CO will not be oxidized to CO_2 . However, if the control is properly designed and applied, NO_x control can be achieved without increasing CO or HC emissions.

Data contained in the process heaters and glass ACT documents indicate that decreases in excess oxygen levels begin to impact CO emissions below 3 percent excess oxygen. Data in the utility boilers ACT document show that CO emissions increase for some boilers and decreace for others when implementing combustion modifications. In a steel reheat furnace with LEA for NO_x control, CO emissions of 39 ppm at 3 percent O₂ and 26 ppm at 3 percent O₂ are reported for the uncontrolled and controlled tests, respectively. These results indicate that CO emissions do not necessarily increase when LEA is implemented for NO_x control.

Other available information reports CO emissions from an LNB-controlled reheat furnace to be 20 to 30 ppm at 3 percent $\rm O_2$. Further, laboratory and field tests on a galvanizing furnace yielded NO_x emissions of 550 to 1,200 ppm at 3 percent $\rm O_2$ and, concurrently, negligible CO emissions. Modifications to the burners reduced NO_x emissions to 350 to 430 ppm at 3 percent $\rm O_2$ and, concurrently, increased CO emissions to 30 to 60 ppm at 3 percent $\rm O_2$. The purpose of the modifications was to reduce NO_x.

No explicit data are available relevant to the impact of NO_x control techniques on HC emissions from iron and steel process facilities. In general, controls that reduce NO_x by reducing the availability of excess oxygen in the high-temperature regions of a furnace would not increase either CO or HC emissions unless oxygen availability was reduced excessively. Limite d data in the Industrial-Commercial-Institutional Boilers ACT document indicate that HC emissions do not change due to the implementation of combustion modifications.

Reheat, annealing, and galvanizing furnaces predominantly use natural gas as a fuel. Natural gas does not contain sulfur and, consequently, SO_2 is not emitted. Gaseous fuels, including natural gas, can produce soot and carbon black when burned if insufficient oxygen is present. However, no evidence indicates that NO_x controls increase particulate emissions in these iron

and steel facilities.

2.5.2 Air Impacts of SCR and SNCR

SCR units are add-on, flue gas treatment facilities that reduce NO_x by injecting ammonia (NH_3) upstream of a catalyst reactor. Within the catalyst, NO_x reacts with the NH_3 and is reduced to N_2 and water (H_2O) . There is a potential for unreacted NH_3 to escape with the flue gas from the SCR unit. Any such emissions are referred to as ammonia slip.

Two examples of SCR controls on annealing furnaces at iron and steel mills are reported. One of these units is operational with more than 3 years' operating history, and one is still under construction. In the case of the former, the NH₃ slip was guaranteed to be less than 10 ppm initially and less than 12 ppm after 1 year. The observed NH₃ was initially less than 10 ppm. Subsequent observations are not reported. The typical NH₃/NO_x molar ratio for this unit is 0.9.

Other reports indicate that NO_x removal rates of 70 to 90 percent can be achieved with SCR using NH_3/NO_x molar ratios between 0.9 and 1.0, and that the NH_3 slip will be between 5 and 10 ppm. These levels are considered to be well below health and odor thresholds.

SNCR has not been applied to iron and steel mill process facilities. In other SNCR applications, ammonia slip is controlled to acceptable levels by controlling the ammonia to NO_x molar ratio. These levels are similar to ammonia emissions from SCR applications, e.g., 10 ppm.

Pilot-scale testing and chemical kinetic modeling of SNCR processes have shown that nitrous oxide (N_2O) emissions are a byproduct of both ammonia (NH_3) and urea injection. The N_2O formation resulting from these processes has been shown to be dependent on the reagent used, the amount of reagent injected, and the injection temperature.

Full-scale tests on fossil-fuel-fired boilers have shown that direct emissions of N_2O are less than 15 ppm and do not generally correlate with NO_x emissions. N_2O production is higher for urea injection than it is for NH_3 injection.

2.5.3 Solid Waste Impacts

The only NO_x control with solid waste impacts is SCR due to

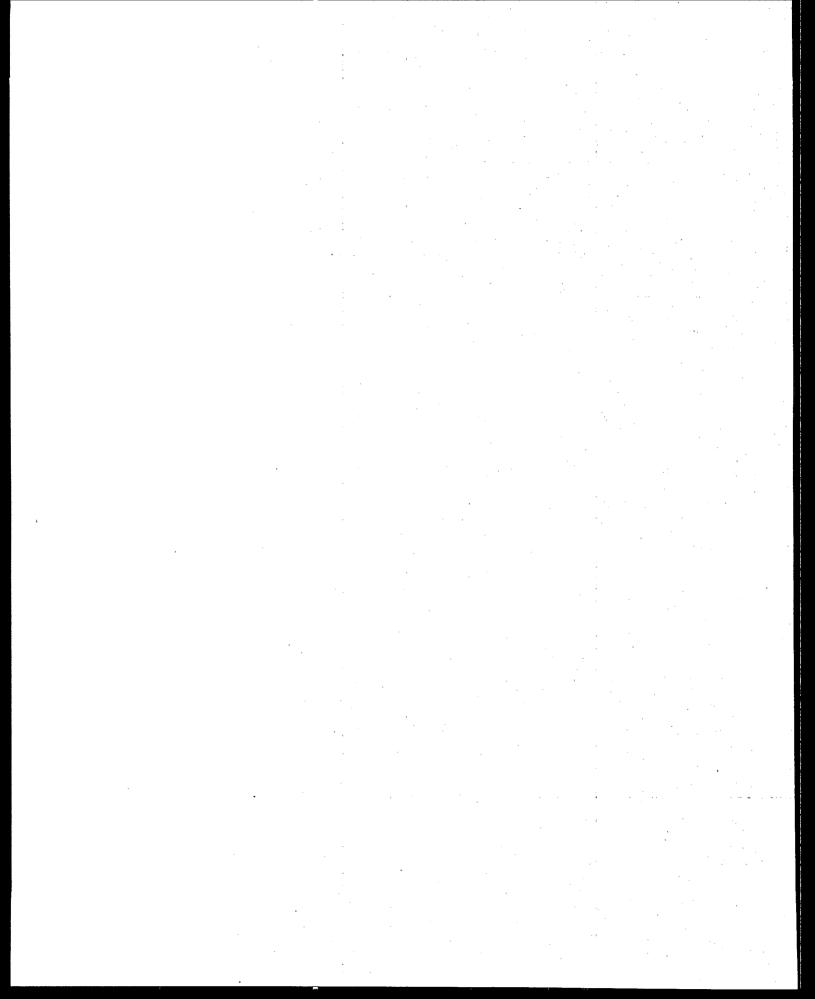
the disposal of spent catalyst materials. Titanium dioxide and vanadium/titanium have been identified as the catalysts in the two SCR annealing furnace applications cited. Other commonly used materials are vanadium pentoxide, tungsten trioxide, platinum, zeolites, and ceramics. Of these, vanadium pentoxide is a toxic compound and a cause for concern. However, worker safety precautions adequately prevent any increased risk to workers handling the catalyst, and stack emissions of vanadium pentoxide are 1 million times less than industrial worker exposure.

Most catalyst manufacturers arrange to recycle and reactivate the catalyst. When that is not practical, the spent catalyst can be disposed of in an approved landfill in accordance with the Land Disposal Restrictions in 40 CFR Part 268, Subpart D.

2.5.4 Energy Impacts

All of the combustion modification control techniques have the potential to impact energy requirements by affecting the thermal efficiency of the process. No data are available to quantify the impact of these controls on iron and steel mill process facilities.

SCR results in a pressure drop across the catalyst that requires additional electrical energy for the flue gas fan. One estimates a cost of \$537/yr assuming 8,000 hours operation per year and electricity at 8 cents/kWh.



CHAPTER 3

INDUSTRY DESCRIPTION

Iron and steel are essential commodities in a modern, industrialized society. Steel is a widely used industrial material affecting every facet of society. Steel is a major component of every transportation system, present in every motorized vehicle and in the network of highways, bridges, and traffic controls. It is a widely used construction material, present in every home, skyscraper, and dam. Steel is essential for most industrial facilities, prevalent in defense hardware, and found in most durable goods. The uses of steel are too prevalent and too diverse to be listed completely or to serve as a basis for classification.

Section 3.1 of this chapter presents a brief background/ historical discussion of the evolution of iron and steel processing. Section 3.2 is a brief industry characterization including an overview description of the major production processes and an overview of the industry. Section 3.3 presents a description of those processes with a potential for large NO_x -emissions.

3.1 BACKGROUND

Iron (Fe) is one of the more abundant and widely distributed elements in the earth's crust, constituting not less than 4 percent of the total crust. It is the fourth most abundant element in the earth's crust, outranked only by aluminum, silicon, and oxygen. Pure iron is a silvery white, relatively soft metal that readily combines with other elements, e.g., oxygen and sulfur. Consequently, native metallic iron is rarely found in nature. 1,2 Iron oxides are the most prevalent natural form of iron. That portion of the iron oxides that is of commercial significance, i.e., economically and spatially available for industry use, is referred to as iron ore, and iron ore deposits are widely distributed. These deposits vary widely in mineralogy, chemical composition, and physical characteristics. The United States has abundant reserves of iron ore. These reserves are grouped into five areas: Lake Superior, Northeastern, Missouri, Southeastern, and Western. Of these, the Lake Superior reserves are the most important.3

Steel is the generic name for a group of ferrous metals composed principally of iron which, because of their abundance, durability, versatility, and low cost, are among the most useful metallic materials known. Most steels contain more than 98 percent iron. Steel also contains carbon, up to about 2 percent, and may contain other elements. By controlling the carbon

content and alloying elements, and by proper selection of heat treatment in the finishing processes, steel can be produced with a wide range of mechanical and physical properties.

3.1.1 A Historical Perspective

Facilities for reducing iron ore (iron oxide) to metallic iron have evolved to the modern blast furnace that produces iron from ore and other iron-bearing materials (e.g., sinter, pellets, steelmaking slag, and scrap), coke, and flux (limestone and dolomite). In the blast furnace, a blast of heated air and, in most instances, a gaseous or liquid fuel, are injected near the bottom of the furnace. The heated air burns the fuel and the coke to produce the heat required by the process and the reducing gas that removes oxygen from the ore. The reduced iron melts and pools in the bottom of the furnace where it is periodically drained through tapping holes as molten pig iron or hot metal.⁴

Modern steel making dates from the introduction of the pneumatic or Bessemer process in 1856. The Bessemer process involved forcing air through molten pig iron to oxidize the major impurities (silicon, manganese, and carbon). The Bessemer process was quickly followed by development of the open-hearth furnace that evolved into the principal means of producing steel throughout the world. Open-hearth furnaces were used in the United States to produce steel into this decade, but all have now been replaced by modern basic oxygen furnaces (BOF).

In the modern basic oxygen furnace, high-purity oxygen is blown onto the surface of the hot metal (top-blown or basic oxygen process) or up through the hot metal (bottom-blown or Q-BOP process), oxidizing or removing excess carbon, silicon, manganese, and other impurities from the hot metal to produce steel of a desired composition.

3.1.2 An Overview of the U.S. Iron and Steel Industry

Steel production is an international industry serving a highly competitive, international market. The United States is one of about 85 steel-producing nations and accounts for about 12 percent of the 1991 world production. In 1990, the United States produced about 99 million tons of raw steel. Of this total, 37 percent was produced in EAF's and the balance predominantly by BOF's. In 1991, the United States produced about 87 million tons of raw steel. In 1991, 76 percent of the steel produced was processed through continuous casting machines rather than through ingot casting. Continuous casting is projected to account for about 84 percent in 1995. It should be noted that 1991 was not a good year for steel production. World steel production was down about 5 percent from 1990, and U.S. production was down 12 percent. Shipments to both the automobile and construction

industries were down significantly in 1991. The automobile industry is the largest single consumer of steel in the United States, and the construction industry is also a large consumer.

Emphasizing the international character of the steel industry, the import share of the United States steel market, during the first half of 1991, was 8.24 million tons or 18.9 percent. Exports for the same period were 3.2 million tons.

Annual steel production capacity in the United States in 1991 was about 120 million tons. High and low capacities in recent times were 160 million tons in 1977 and 112 million tons in 1988. In 1990, the steel industry in the United States was composed of approximately 300 companies, of which 83 produced raw steel at 127 locations.

Table 3-1 summarizes data pertinent to the iron and steel industry to characterize the current status of the industry. Basic oxygen converters (BOP's and Q-BOP's) remain the major source of steel production, but electric arc furnaces now account for about 37 percent. Open hearth furnaces are no longer in use in the United States.

A 1991 directory of iron and steel plants in North America defines three categories of steel producers as follows:9

- Integrated Steel Producers are defined as those companies having blast furnace or direct reduction facilities and whose principal commercial activity is the production and sale of carbon steel.
- Specialty Producers are defined as those companies whose principal commercial activity is the production and sale of stainless steels, alloy steels, tool steels, bars, wires, pipe, etc.
- Mini-Plants or mini-mills are defined as those companies whose production is based on electric furnace-continuous caster-rod/bar mill operations, generally rolling carbon steel products--rebar, rounds, flats and small shapes.

The differences between these categories are not always clear. Some companies in all three categories use EAF's to melt steel and have continuous casters. The integrated producers are the

TABLE 3-1. SUMMARY OF CURRENT STEEL INDUSTRY FACTS7,8

| | | 1991 | 1992 | 1993 |
|---|--|------|------|------|
| U.S. percentage of world production (%) | | 11.6 | | |
| Total U.S. production (106 tons) | | 87 | 92.9 | 96.1 |
| Total U.S. shipments (10 ⁶ tons) | | 79 | 82.2 | 88.5 |
| Total production by (%): Basic oxygen converter EAFs Open hearths | | 37 | | |
| U.S. raw steel capacity (10 ⁶ tons) | | 120 | 113 | 110 |
| Number of companies | | | , | |
| Raw steel producers | | 83 | . : | |
| Imports (105 tons) | | | | |
| Percent by continuous casting (%) | | 75.8 | | |

most distinct group because they alone produce iron from iron ore in blast furnaces or direct reduction iron (DRI) facilities. Integrated producers also use coke in blast furnaces and either produce coke on site or purchase it from coke producers. As of May 1991, there was only one DRI facility in the United States. Mini-mills use only electric arc furnaces and use scrap steel as feed stock.

- 3.1.2.1 <u>Integrated Producers</u>. The integrated producers, although much fewer in number than specialty producers and minimils, produce the greater volume of steel. In 1990, integrated producers accounted for about 70 percent of raw steel production in the United States.^{7,11} The referenced 1991 directory lists 20 integrated steel producers in the United States. However, it is not clear that all of those listed conform to the preceding definition of an integrated producer, i.e., use blast furnaces or DRI facilities and produce carbon steel. Those known to be integrated producers are listed in Table 3-2 along with other available information.⁹
- 3.1.2.2 Mini-Mills. The mini-mills are a growing segment of the steel-producing companies that, in 1991, accounted for more than 20 percent of production in the United States. It has been suggested that the term mini-mill is a misnomer. The steelmelting facility used by mini-mills (i.e., EAF's) can produce up to 130 tons of steel per hour, not far from the 200- to-300-tons/hr typical of a BOF. 12 Once viewed as suppliers of unsophisticated, low-quality products requiring minimal technology, mini-mills are now recognized as playing a growing technological role and for having made permanent inroads into the traditional domain of integrated producers. 13 In 1990, Nucor Corporation and North Star Steel Company, two mini-mill producers, ranked seventh and eighth, respectively, among United States steel producers. Nucor, for example, has an annual production capacity of 3 million tons, and North Star an annual capacity of about 2.5 million tons. By contrast, USX Corporation (formerly U.S. Steel Corporation), the nation's leading steel producer, shipped about 12 million tons in 1990. 9,12 The 1991 directory of iron and steel plants lists 42 mini-mill companies.
- 3.1.2.3 Specialty Producers. It is more difficult to characterize the specialty producers than integrated or mini-mill producers. There are more companies, a total of about 120; they produce a wide variety of specialty products; and it is difficult to ascertain the starting point in their production process from the literature. Company sizes vary widely (e.g., the number of employees number from as few as 8 to as many as 5,000) and annual capacities range from 62,000 to 1,500,000 tons of product. As a group, they operate EAF's and a host of other furnaces including annealing and reheat furnaces. By contrast, some weld or do

SUMMARY INFORMATION RELEVANT TO INTEGRATED STEEL PRODUCERS? TABLE 3-2.

| Company name/ company address | Products | Capacity (ton/yr) | Number of employees | Plant location |
|---|--|--|------------------------|-------------------|
| ACME STEEL CO. Riverdale, IL 60627-1182 (708) 849-2500 | Coke, pig iron, sheet, bars | 1,000,000 | 2,900 | 11 |
| ARMCO Steel Company, L.P. Middletown, Ohio 45043 (513) 425-5000 | Slabs, coke, chemicals, sheet, strip galvanized | 4,000,000 | 7,600 | он, ку |
| ВЕТНІЕНЕМ STEEL CORP. Bethlehem, РА 18016-7699 (215) 694-2424 | Coke, wire, rods, ingots, slabs, plates, rails, bars, billets, blooms, pig iron, chemicals, tin plate, sheet, strip galvanized | | | PA, MD, IN |
| GENEVA STEEL Provo, UT 84603 (801) 227-9090 | Coke, iron ore, sheet, plate, pipe, bands, coils | 1,400,000 | 2,700 | Ē |
| GULF STATES STEEL, INC. Gadsden, AL 35901-1935 (205) 543-6100 | Coal, chemicals, plate, sheet, strip galvanized | 1,800,000 actual prod: 1,200,000 | 2,219 | Ąŗ. |
| INLAND STEEL INDUSTRIES, INC. Chicago, IL 60603 (219) 399-1200 | Sheets, plate, coal, chemicals, bar, beam, billet | | | NI |
| LTV STEEL CO., INC. Cleveland, OH 44115 (216) 622-5000 | Ingot, billet, slab, coke, tubing, pipe | | | OH, IN |
| McLOUTH STEEL Trenton, MI 48183 (313) 285-1200 | Plate, sheet, stip alloy galvanized | | | IW . |

| Company name/ company address | Products | Capacity (tons/yr) | Number of employees | Plant location ^a |
|---|---|--------------------|------------------------|--------------------------------|
| NATIONAL STEEL CORP. Mishawaka, IN 46545 (219) 273-7000 | <pre>Coal, chemicals, plate, sheet, ingot, galvanized, siding</pre> | | | MI, IN, IL |
| ROUGE STEEL CO. Dearborn, MI 48121 800-241-1580 | Ingot, slab, sheet | | | M |
| SHARON STEEL CORP. Farrell, PA 16121 (412) 981-1375 | Strapping, coke pipe, tubing gavlvanized, alloy | 1,400,000 | 170 | ВА |
| USX CORP. Pittsburgh, PA 15219-4776 (412) 433-1121 | Coke, pig iron, ingot, pipe, rods, plate, galvanized, alloy | | | AL, PA, IN, IL |
| WARREN CONSOLIDATED INDUST. Warren, OH 44483 (216) 841-8218 | Sheet, flat rolled electrical steels | 1,500,000 | | Ю |
| WEIRTON STEEL CORP. Weirton, WV 26062 (304) 797-2000 | Rolled sheets galvanized zinc coated | | | WM |
| WHEELING-PITTSBURGH STEEL CORP. Wheeling, WV 26003 (304) 234-2400 | Coke, sheet, ingot tinplate, galvanized roofing products | | | НО |

* Integrated plant locations by States.

other single-function operations that do not include the onsite combustion of fuels. Products may range from a single item such as cold-drawn wire to highly specialized steels. In terms of their contribution to domestic capacity and production, they are grouped with mini-mills.

3.2 INDUSTRY CHARACTERIZATION

3.2.1 An Overview of Iron and Steel Manufacturing

Figure 3-1 is a simplified flow diagram illustrating the principal steps involved in the production of steel. All of these processes, and more, are found in modern integrated steel mills. An overview of these processes is presented here. Individual processes that produce NO_{x} are discussed in more detail in Section 3.3 of this chapter.

3.2.1.1 Raw Materials and Preparatory Processes. With reference to Figure 3-1, the basic raw material input for the production of iron and steel is iron ore, which is reduced to metallic iron in the blast furnace. The principal iron ore beneficiating processes are pelletizing and sintering. Pelletizing is usually accomplished in specially designed furnaces located at or near iron ore mines rather than at iron and steel mills. Its purpose is to pelletize fine, low-grade ores prior to shipping to an iron and steel mill. Pelletizing is rarely practiced in an iron and steel mill.

In contrast to pelletizing, sintering is often practiced at integrated iron and steel mills. Its primary purpose is to agglomerate dusts and fines from other process, e.g., ore fines, coke fines, and flue dust, into particles with suitable mass, size, porosity, and strength to charge into the blast furnace. Fines charged to a sintering furnace differ in size from those charged to a pelletizing furnace, and they originate at the iron and steel mill rather than at the mine. Alternatively, fine particles charged into the blast furnace will be blown out by the rapid countercurrent flow of the furnace gases.

Another basic material used in the conversion of iron ore into metallic iron is coke. Coke is the primary residue that remains when a blend of pulverized coking coals is heated gradually to high temperatures, about 900 to 1,100 °C (1,650 to 2,010 °F) in the absence of air for approximately 18 hours. About 90 percent of the coke produced in the United Stated is charged to blast furnaces for the production of pig iron. 14

The conversion of coal to coke is performed in long, narrow, slot ovens, i.e., by-product coke ovens, which are usually designed and operated to permit the separation and recovery of the volatile materials evolved from the coal during the coking

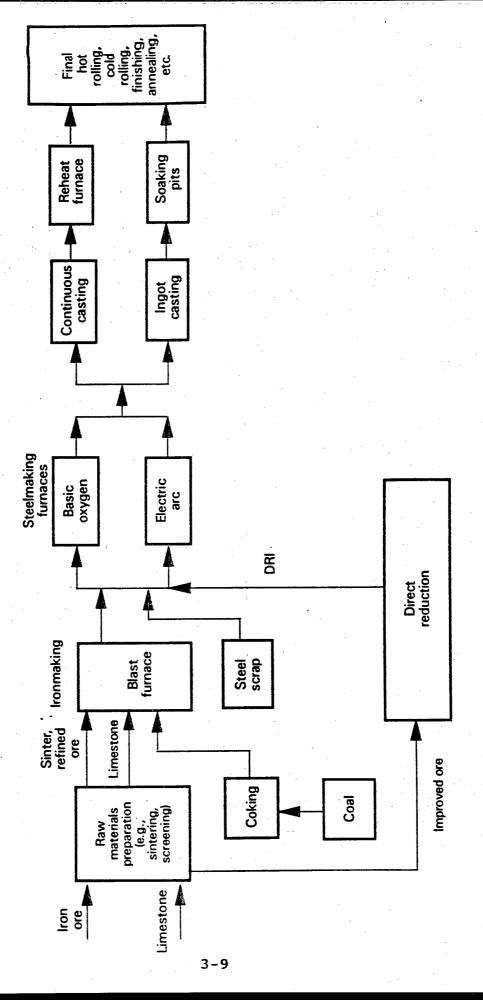


Figure 3-1. Simplified steelmaking flow chart.

process. In addition to coke, the primary product, a number of by-products may also be recovered including breeze, crude tar, crude light oil, ammonia, and coke oven gas. These may be used on site or marketed. Coke is likely to be used on site but may be marketed, coke oven gas is likely to be used on site, and breeze is likely to be recycled to the sintering process. 15

A third raw material input to the iron and steel making process is flux. In the iron smelting process, i.e., when iron is separated from the ore by fusion in a blast furnace, a flux is used to enhance the process by combining with ash in the coke and gangue in the ore to make a fluid slag that can be readily separated from the molten iron. Selection of the proper flux for a given process is a well-established process requiring knowledge of the composition and properties of the materials involved. Limestone and/or dolomite are the fluxes used in blast furnaces. The proportions of each depend principally on the constituents of the slag and the amount of sulfur that the slag must remove. 16

In the basic oxygen steelmaking process, lime normally is added as calcined or burnt lime or burnt dolomite. The calcium oxide in either the burnt lime or burnt dolomite fluxes the silica formed upon the oxidation of silicon in the hot metal. 17

Often, limestone is also charged into the sinter plant to produce a precalcined or self-fluxing sinter. The use of self-fluxing sinter has both economic and performance advantages. 18

3.2.1.2 <u>Ironmaking</u>. Iron ore, coke, selected fluxes (e.g., prepared limestone), and sinter are charged to the blast furnace where iron is reduced from its ore. The product of the blast furnace contains more than 90 percent iron and is referred to as pig iron or, if in a molten form, hot metal. Most of the blast furnace product is transported directly to onsite steelmaking furnaces as hot metal.

The blast furnace charge of iron-bearing materials (including iron ore, sinter, mill scale, steelmaking slag, and scrap), coke, and flux (limestone and/or dolomite) is placed in the furnace, and a blast of heated air and, in most instances, a gaseous, liquid, or powdered fuel is introduced through openings near the bottom of the furnace just above the furnace's hearth crucible. The blast of heated air burns the injected fuel and most of the coke to produce the heat required by the process and the reducing gas that removes oxygen from the ore. The reduced iron melts and pools in 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. Periodically, the iron and the slag are drained from the furnace through tapping holes.⁴

The blast air delivered to the process through the furnace tuyeres is preheated by passing it through regenerative blast-furnace stoves that are heated primarily by combustion of the blast furnace off-gas. Blast furnace gas is often enriched with fuel of a higher calorific value such as natural gas to achieve higher temperatures. Thus, some off-gas energy is returned to the blast furnace in the form of sensible heat. This procedure enhances the efficiency of the process by lowering fuel requirements.

A modern blast furnace will typically have three or four blast furnace stoves as auxiliaries. These are alternately fired with blast furnace gas to raise the temperature of the stoves' brick lining and then, by reversing the gas flow, preheat the supply of blast air to the blast furnace to temperatures of 760 to 1,150 °C (1,400 to 2,100 °F). 19

To produce a metric ton of pig iron requires about 1.7 metric tons of ore or other iron-bearing material, 450 to 650 kg of coke and other fuel, about 250 kg of limestone or dolomite, and 1.6 to 2.0 metric tons of air.4

Although the blast furnace remains the dominant source of iron for steelmaking, there are processes that produce iron by the reduction of iron ore below the melting point of iron. These are classified as direct reduction processes, and the products are referred to as direct-reduced iron(DRI). DRI produces several percent of the total iron produced worldwide. The major part of DRI production is used as a substitute for scrap in electric-arc steelmaking furnaces. There are many DRI processes. The objective of these processes is to improve iron ore until it is sufficiently iron-rich to be charged to an electric arc furnace. A typical process uses heat to drive oxygen from the ore, leaving an iron-rich residue called sponge iron.

3.2.1.3 Steelmaking. Steel is made from molten iron (hot metal), delivered directly from a blast furnace, and scrap in steelmaking furnaces. Two basic types of steelmaking furnaces dominate this process: (1) the BOF and (2) the EAF. The openhearth steelmaking furnace, developed in the 19th century and a major source of steel well into the latter half of the 20th century, is no longer used in the United States. There are three basic types of the BOF. All use oxygen of high purity (>99.5 percent) to oxidize excess carbon, silicon, and other impurities in the hot metal, thereby producing steel. One type of BOF blows the oxygen on the top of the hot metal pool. United States, this process is called the basic oxygen process or BOP. The second type blows the oxygen through tuyeres in the bottom of the furnace and is referred to as the bottom-blown or Q-BOP process. The BOP process is the most widely used form in

the United States. The third type of BOF is a combination of the other two.

To make steel in a BOF, molten pig iron (hot metal) and usually scrap steel are charged to the furnace. The scrap consists of the by-products of steel fabrication and wornout, broken, or discarded articles containing iron and steel. furnace is mounted in a trunnion ring to facilitate tilting during processing. At the beginning of a heat, i.e., the processing of a batch of materials to make steel, the furnace is tilted to receive a charge of materials through the open top. Scrap steel, if any, is charged first. Scrap can form up to 30 percent of the total charge (up to 45 percent if preheated).1 The furnace is then tilted in the opposite direction to receive a charge of hot metal (molten iron) from a transfer ladle. The furnace is then returned to the vertical position and a watercooled retractable lance is inserted through the open top of the furnace and positioned above the bath level. A water-cooled hood is positioned over the open top. A jet of gaseous oxygen is blown at high velocity onto the surface of the hot metal bath. No external heat source is required during this process.

Slag-forming fluxes, e.g., burnt lime, dolomitic lime, and fluorspar, are added in controlled amounts through a chute built into the side of the hood. The flux is added shortly before or after the oxygen jet is started.

The oxygen striking the surface of the molten bath immediately forms iron oxide, part of which disperses rapidly through the bath. The iron oxide reacts with carbon in the molten bath to form carbon monoxide, which gives rise to a violent circulation that accelerates the refining process. Impurities such as carbon, manganese, silicon, sulfur, and phosphorus are oxidized and transferred to the slag. These oxidizing reactions take place very rapidly. A 300-metric-ton heat (or charge), for example, can be processed in about 30 minutes.

During the oxygen blowing, gases emitted by the process are collected by the water-cooled hood and conducted to a cleaning system where solids are removed from the effluent gas before it is discharged to the atmosphere. The solids may be returned to the sintering process or discarded, depending on whether or not they contain contaminants. When the oxygen blowing is completed, the lance is withdrawn and the molten steel is checked for temperature and composition. If the steel is too hot, it is cooled by the addition of scrap or limestone. If the steel is too cold, the oxygen lance is reinserted and additional oxygen is blown. When the temperature and composition are satisfactory, the steel is tapped into a waiting ladle where alloying materials are added. Subsequently, the remaining slag is dumped from the

furnace, and the furnace is returned to a charging position to begin the next heat. 1,6,22

The bottom-blown or Q-BOP process is also used in the United States. The Q-BOP furnace has tuyeres or double pipes in the bottom of the furnace. Oxygen is blown into the furnace through the center pipe and natural gas or some other hydrocarbon is blown into the furnace through the annular space between the two pipes. Considerable heat is generated when the oxygen oxidizes the carbon, silicon, and iron in the molten bath. The hydrocarbon stream provides essential cooling by thermal decomposition. Without this cooling, the refractories surrounding the oxygen jet would be destroyed. 1,6

Although the BOP and Q-BOP processes have many similarities, there are also significant differences. The Q-BOP process operates much closer to equilibrium conditions between the metal and the slag and is therefore much lower in oxidation potential than the BOP. The manifestations of this characteristic of the Q-BOP are lower iron losses as ferric oxide (FeO) to the slag, higher manganese recoveries, faster blow times, improved phosphorus and sulfur control, and lower dissolved oxygen and nitrogen contents. Because of these improvements, yield of the Q-BOP is 1.5 to 2.0 percent higher than the BOP, i.e., there is less iron loss as FeO to the slag. The lower FeO generation, however, results in lower scrap melting in the Q-BOP as compared to the BOP. Process control of the Q-BOP is much easier than the BOP because of the highly consistent metallurgical behavior of the O-BOP reactions and the absence of the variability caused by oxygen lance practices as encountered in the BOP.21

The second major classification of steelmaking furnaces is the EAF. In 1991, EAF production accounted for about 37 percent of the total steel produced in the United States and Canada. Almost all of the balance was produced in basic oxygen furnaces.

Electric arc furnaces produce liquid steel primarily by melting steel scrap. However, metallic iron, including pig iron and direct-reduced iron, are sometimes added to the charge. Generally, steel is produced in an EAF from a metallic charge of about the same composition as the steel to be made. Reactions taking place in the EAF are similar to those in the basic oxygen furnace. The charge is melted, impurities are oxidized, fluxes are added to aid in the formation of slag, and alloying elements are added to achieve the desired composition.

There are several different variations of the EAF. However, the direct-arc, three-phase electric furnace is the most common. In operation, the three-phase electric current flows from one electrode, through an arc between the electrode and charge, through the charge, then through an arc between the charge and a

second electrode. The charge is heated primarily by radiation from the arc although heat developed by current through the electrical resistance of the charge makes a slight contribution. Three electrodes are used in the EAF, and the current flow to and from the electrodes is consistent with the features of the utility-based, three-phase power supply.

Electric arc furnaces offer several advantages including low construction cost, flexibility in the use of raw materials (steel can be made directly from scrap without having a source of molten iron), the ability to produce steels over a wide range of compositions, improved process control, and the ability to operate below full capacity. The improved process control makes the EAF well suited for stainless steel and other high-alloy steels. Economic constraints tend to favor the use of EAF's for low to medium tonnage steelmaking facilities. 1,24

Molten steel, whether from a BOF or an EAF, is tapped from the furnace to a ladle and transported to a finishing process. Specialty steels, i.e., "clean" steels which meet extraordinarily stringent requirements of certain critical applications, may be subjected to additional processing in the ladle. These processes are generally referred to as ladle metallurgy and as secondary steelmaking. There are numerous ladle metallurgy processes including ladle temperature control, composition control, deoxidation, degassing, cleanliness control, and others. 25

3.2.1.4 Finishing. Although there are many variations, most steel follows one of two major routes to final processing. routes produce solid, semifinished products: ingots or cast The more traditional route is the ingot route. Molten slabs. steel is poured from the ladle into an ingot mold where it cools and begins to solidify from the outside toward the center. When the ingot is solid enough, the mold is stripped away and the ingots are transported to a soaking pit or reheat furnace where they are soaked in heat until they reach a suitable, uniform temperature throughout. The reheated ingots are then transported to a roughing mill where they are shaped into semifinished steel products, usually blooms, billets, or slabs. Blooms are large and mostly square in cross section, and they are frequently used in the manufacture of building beams and columns. Billets, which are made from blooms, are also mostly square, but are smaller in cross section and longer than blooms. Billets are processed further to produce bars, pipes, and wire. Slabs are the wide, semifinished product from which sheets, strip, and other flat rolled products are made. The roughing mills may be the first in a series of continuous mills that continue to shape the steel into more useful, more finished products.

More recently, molten steel is increasingly routed to a continuous casting process that bypasses the soaking pit or

reheat furnace process associated with the ingot route. In this process, the molten steel is lifted in the ladle to the top of the continuous caster where it is allowed to flow into a reservoir called the tundish and from the tundish into the molds of the continuous casting machine. These molds are cooled with water so that a thin skin forms on the outside of the liquid metal. Emerging from the mold, the continuous column of steel is further cooled by a water spray, causing the skin to thicken. The steel is further shaped by various designs of casters as it continues to flow. As in the ingot process, the steel may be shaped into blooms, billets, or slabs and, subsequently, into more useful products. The continuous casting process has a significant advantage in that the soaking-reheating step is eliminated. Thus, it offers a fuel savings and the potential to reduce undesirable emissions including NO_x.

Downstream of the series of mills (roughing stands and finishing stands) that shape the steel blooms, billets, slabs, and other semifinished products are a multitude of processing steps that may be used to produce finished steel products. The actual processes followed may include a combination of many, few, or perhaps none of this multitude of options. The processes that may be encountered include pickling, annealing, galvanizing, coating, painting, and additional mechanical finishing steps. Some of these steps require additional heating or perhaps reheating and, thus, pose a potential for further combustion of fuels with the attendant potential for generating additional NO_x emissions. These include annealing and all reheating furnaces.

3.3 PRODUCTION PROCESSES WITH NO_x EMISSIONS

In this section, iron and steel processes with a potential to produce NO_x emissions are discussed in detail. Sintering, coke ovens, soaking pits, and reheat furnaces are identified as some of the more important iron and steel combustion processes and, thus, some of the largest sources of NO_x emissions.

3.3.1 Sintering

The sintering and pelletizing processes are the two most important processes used to improve iron ore prior to making iron. Of these, pelletizing is usually accomplished near iron-ore mines where ore is ground to fine particles, separated from the gangue minerals either magnetically or by flotation, and then made into pellets. This process is usually carried out at or near the mines to reduce the cost of shipping the beneficiated ore to iron and steel mills. At iron and steel mills, a parallel process, sintering, takes fine iron-bearing materials recovered from ore handling and other iron and steel operations and fuses these fine particles into materials suitable for charging to blast furnaces or direct reduction facilities to make iron. 26

In sintering, the mixture of iron ore fines and other ironbearing materials (iron-bearing dusts and slags) and fluxes (lime or dolomite) are thoroughly mixed with about 5 percent of a finely divided fuel such as coke breeze or anthracite and deposited on a traveling grate. The traveling grate is shaped like an endless loop of conveyor belt forming a shallow trough with small holes in the bottom. The bed of materials on the grate is ignited by passing under an ignition burner that is fired with natural gas and air. Subsequently, as the grate moves slowly toward the discharge end, air is pulled down through the As the coke fines in the bed burn, the generated heat sinters, or fuses, the fine particles. The temperature of the bed reaches about 1,300 to 1,480 °C (2,370 to 2,700 °F). At the discharge end of the sintering machine, the combustion will have progressed through the thickness of the bed. The sinter is then crushed to eliminate lumps, is then cooled, and finally screened. 1,18

Good sintering requires thorough mixing of the feed materials and careful deposition on the traveling grate so as to achieve a uniform bed. Proper ignition is also important, and some processes replace part of the solid fuel with gaseous fuel to improve ignition and improve the sinter. Plants using this process have approximately 25 percent of the length of the sinter bed covered with a gas-fired ignition-type hood. Temperature in the hood ranges from about 1,150 °C (2,100 °F) where ignition begins to about 800 °C (1,500 °F) at the exit of the hood. Depending upon characteristics of the ore materials and sintering conditions, average production rates of 22 to 43 metric tons/m²/day (2.3 to 4.4 tons/ft²/day) of grate area are expected, and rates in excess of 49 metric tons/m²/day (5 net tons/ft²/day) have been attained. 27

The major source of energy used in the production of sinter is the carbon content of coke breeze and flue dust. The amount of ignition fuel required is about 140 J/g (0.12 MMBtu/ton) of sinter produced. The total fuel requirement, including coke breeze, is about 1.74 kJ/g (1.5 MMBtu/ton) of sinter produced. The total fuel requirement.

Beyond the sintering grate, the sinter is cooled so that it can be transported by conveyor belts. The exhaust air from these coolers is normally at too low a temperature to permit economical recovery of heat. Recent developments in sinter cooling have been directed toward on-strand cooling, which could improve heat recuperation, sinter quality, and dust collection. The use of sinter in the blast furnace charge, and especially fluxed sinter, also improves blast furnace performance. One improvement is that less coke is required in the blast furnace. Available data indicate that for each net ton of limestone removed from the blast-furnace burden and charged to the sinter plant to make fluxed sinter, approximately 182 kg (400 lb) of metallurgical

coke is saved. 18 This also has a potential for reducing NO_x emissions through fuel conservation.

3.3.2 Cokemaking

Coke is an essential component in the production of pig iron (hot metal) in a blast furnace. Consequently, coke ovens are found in most integrated steel plants. Coke ovens are constructed in batteries that contain as few as 10 to more than 100 ovens. Coking chambers in a battery alternate with heating chambers so that there is a heating chamber on each side of a coking chamber. Underneath the coking and heating chambers are regenerative chambers, a brick checkerwork that preheats combustion air to conserve fuel, increase thermal efficiency, and give a higher flame temperature. The ovens are constructed of refractory brick.

In operation, selected blends of coal are charged to the ovens through openings in the tops. Subsequently, the coal undergoes destructive distillation during a heating period of about 16 to 18 hours. At the end of this portion of the coking cycle, doors at both ends of the oven are opened and the incandescent coke is pushed from the oven into a railroad-type car called a quench car. The coke is then transported to the end of the battery to a quench tower where it is deluged with water to end the burning process. The operation of each oven in the battery is cyclic, but the batteries usually contain a large number of ovens so that the yield of by-products is essentially continuous. The individual ovens are charged and discharged at approximately equal time intervals. Practically all of the coke produced in the United States is made by this process.¹³

The product of a coke battery is either furnace coke (requiring 15 to 18 hours of distillation) or foundry coke (requiring 25 to 30 hours of distillation). The by-products of the process are driven off during distillation and are recovered in the by-product coke-making process through condensation. These by-products include tar, light oils, and heavy hydrocarbons. The noncondensable gaseous product remaining is known as coke oven gas, which, on a dry basis, has a heating value of about 22 MJ/Nm³ (570 Btu/ft³). Approximately 35 percent of the coke oven gas produced is used in heating the ovens. 24,27

Excess coke produced in a cokemaking operation that is sold to others is referred to as merchant coke, and merchant coke can be either furnace coke or foundry coke.

In 1983, about one-sixth of the total bituminous coal produced in the United States was charged to coke ovens. On the average, 1.4 kg of coal is required for each kilogram of coke produced. Each kilogram of coal carbonized requires 480 to 550

kJ (450 to 520 Btu) of energy. Flue temperatures are as high as 1,480 °C (2,700 °F). 27

Current annual coke production in the United States is about 29 million tons. Of this amount, about 72 percent or 21 million tons comes from steel plant coke ovens (furnace coke) with the balance from independent coke producers (merchant coke). All of this coke is produced in 12 States, and approximately 70 percent is produced in five States: Pennsylvania, West Virginia, Ohio, Indiana, and Illinois. The only nonrecovery coke-oven facility producing metallurgical coke in the United States is located in Virginia.²⁸

The underfire combustion of fuel in coke ovens produces NO_x, among other emissions. Because of the many different emissions from coke ovens, coke ovens will be subjected to more stringent environmental regulations in the 1990's and beyond. Apart from these environmental concerns, most coke ovens in the United States have reached obsolescence. The International Iron and Steel Institute projects that approximately 40 percent of the coke ovens in North America must be replaced within the next 10 years unless technology to extend their life is developed. The costs of replacing these facilities, already considerable, are significantly increased by the costs of meeting increasingly stringent environmental regulations. These issues are of much concern to the steel industry because coke is an essential material for the integrated steel producers. \$28

3.3.3 Blast Furnaces and Blast Furnace Stoves

Iron ore is converted to molten iron in a blast furnace. A charge consisting of iron ore, sinter, limestone, and coke is charged to the top of the vertical-shaft blast furnace. The coke provides thermal energy for the process and a reductant gas for the iron-ore conversion, and it serves as the pathway passage for gases that pass through the furnace burden. The limestone becomes calcined, melts, reacts with, and partially removes sulfur from the molten iron.

Heated air is injected through tuyeres near the bottom of the furnace and moves upward through the burden, consuming the coke carbon and thereby providing energy for the process. Blast furnace gas leaves the furnace through offtakes at the top of the furnace, is cleaned of particulates, and subsequently used as a fuel. The BFG contains about 1 percent hydrogen and about 27 percent carbon monoxide, and it has a heating value that ranges from about 2,540 kJ/Nm³ (65 Btu/ft³) to 3,600 kJ/Nm³ (92 Btu/ft³). Between 2.2 and 3.5 kg of BFG is generated for each kilogram of pig iron produced in the blast furnace. The strength of the strengt

Molten iron and slag are tapped periodically from the bottom

of the furnace. In operation, the blast furnace is kept under pressure by an arrangement of pressure locks that function to seal the top of the furnace. These locks are in the form of two inverted cones, called bells, which operate sequentially to maintain a seal in the furnace. Thus, the blast furnace is a closed unit with no atmospheric emissions.²⁷

A blast furnace typically has about three blast furnace stoves associated with it. These stoves primarily burn BFG in a process designed to preheat the air used to combust the fuel in the blast furnace they serve. In an installation with three associated blast furnace stoves, for example, two are generally being preheated while the third is supplying preheated air to the furnace. While being heated, hot gases from the blast furnace are cleaned, cooled, and some portion is then routed to the stoves that are being heated where it is burned, often with other gases, to heat a thermal storage, regenerative checkerwork (refractory material) in the stove. The heat thus stored is then used to preheat combustion air to the blast furnace. The BFG may also be burned elsewhere in a steel plant. The blast furnace stoves require very large quantities of fuel for heating. However, because the stoves are heated primarily with BFG, the flame temperature is reduced, which reduces NO, generation.27

The BFG burned in the blast furnace is often enriched by the addition of fuels with a higher calorific value such as coke-oven gas or natural gas to obtain higher hot-blast temperatures, often in excess of 1,100 °C (2,010 °F). This enhances the efficiency and productivity of the process. 19

3.3.4 Basic Oxygen Furnaces

Most of the steel produced in the United States is made using an oxygen steelmaking process. There are three oxygen steelmaking processes: a top blown process called the BOP process, a bottom blown process called the Q-BOP process, and a third process, which is a combination of the other two. In all three processes, scrap and molten iron (hot metal) are charged to the furnace and high-purity (>99.5 percent) oxygen is used to oxidize excess carbon and silicon in the hot metal to produce steel. The major differences between the three processes are in the design of the furnace and the equipment for introducing oxygen and fluxes. These differences do not have any significant impact on the potential for NO_x generation and are not discussed at length here. The BOP process is the most commonly used process in the United States.

In the BOP process, oxygen is blown downward through a water-cooled lance onto a bath of scrap and hot metal. Heat produced by the oxidation of carbon, silicon, manganese, and phosphorus is sufficient to bring the metal to pouring

temperature, and auxiliary fuel is not required.1

Oxygen striking the surface of the molten bath immediately forms iron oxide. Carbon monoxide generated by the reaction of iron oxide with carbon is evolved, giving rise to a violent circulation that accelerates refining. The oxidizing reactions take place so rapidly that a 300-metric-ton heat, for example, can be processed in about 30 minutes. The intimate mixing of oxygen with the hot metal permits this rapid refining. Figure 3-2 is a schematic representation of the refining in a top-blown BOF. It illustrates the decreasing content of several undesirable elements in the molten metal bath during the period of an oxygen blow. 21

Scrap use in a BOP furnace is limited to about 30 percent of the charge. If the scrap is preheated, the scrap content can be increased to about 45 percent. In addition to scrap preheating, other fuels may be burned to dry out refractories and to keep the BOF furnace from cooling between heats. The use of fuel for the latter two purposes amounts to about 230 kJ/kg (200,000 Btu/ton) of steel produced.

About 470 kJ of carbon monoxide are produced in the BOF per kilogram of steel produced (400,000 Btu/ton). Typical practice is to burn combustible gases in water-cooled hoods mounted above the BOF vessel. In most cases, the BOF vessels are equipped with open hoods that admit air for combustion of carbon monoxide on a relatively uncontrolled basis. Some new plants use suppressed combustion hoods, which do not inspire air and burn off-gases. New BOF capacity is expected to continue this trend, which may cause a decrease in total NO_x emissions. During the combustion of the waste gas, the potential for NO_x production exists.

3.3.5 Soaking-Pit and Reheat Furnaces

Soaking-pit and reheat furnaces are large furnaces used to raise the temperature of steel in the course of processing to a temperature suitable for hot working or shaping. They are designed to accommodate the steel being processed at a suitable rate, heat it uniformly, and hold it at a desired temperature for a specified length of time. There are numerous design variations. Two major variations are batch-type and continuoustype furnaces. Within the latter category are variations on how the charge is moved through the furnace. These variations include roller hearth furnaces in which the material moves as the series of rollers that constitute the hearth rotate, walking-beam furnaces in which material is moved in a controlled step-wise manner, pusher-type furnaces in which a continuous line of material is pushed over skids, and rotary-hearth furnaces with circular hearths that rotate in a horizontal plane. Other variations involve the introduction and removal of the charge and

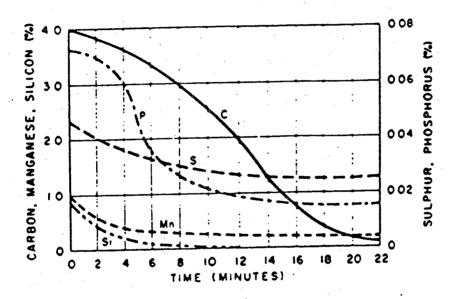


Figure 3-2. Schematic representation of progress of refining in a top-blown basic-lined BOF.²¹

the circulation of heat. The circulation of heat in fuel-fired soaking pit and reheat furnaces is accomplished by natural convection and stack draft.²⁹

The sizes of soaking-pit and reheat furnaces are usually described by their hearth area. Soaking-pit furnaces range from about 100 ft2 to over 300 ft2, and reheat furnaces range up to 4.000 ft² of hearth area.²⁹ The capacity of these furnaces is determined primarily by the area of the surface of the material to be heated; the shape, thickness, and composition of the material; and the temperature of the material and the furnace. The thermal efficiency (defined in this case as the amount of heat required to raise the temperature of the charge from its initial to its desired temperature as a percentage of the gross heat input to the furnace) also varies widely due to differences in the temperatures of the heated stock and of the charged material, provisions for heat recovery, furnace insulation, operating schedules, and heating requirements. Large productionline furnaces, such as continuous furnaces with recuperators and good insulation, generally give over 30 to 40 percent thermal efficiency over an average month's operation.2

Soaking-pit furnaces provide uniform heating of ingots to the desired temperature with a minimum of surface overheating. The normal range for heating ingots is between 1,180 °C and 1,340 °C (2,150 °F and 2,450 °F). Soaking pits also function as a reservoir to correct irregularities in the flow of ingots between the steelmelting facilities and the primary rolling mills.

The use of continuous casters is affecting the operations of both soaking pits and reheat furnaces. There is less need for soaking pits as more steel is routed to reheat furnaces and, in general, the steel is entering reheat furnaces at higher temperatures. The net effect is that, in the aggregate, less fuel is being consumed in soaking pits and reheat furnaces. In 1991, about 76 percent of the steel produced was processed by continuous casting rather than forming ingots that subsequently needed to be processed in a soaking-pit furnace. Although the trend to continuous casting will continue, some soaking-pit capacity will likely be retained to cope with upset or irregular conditions.

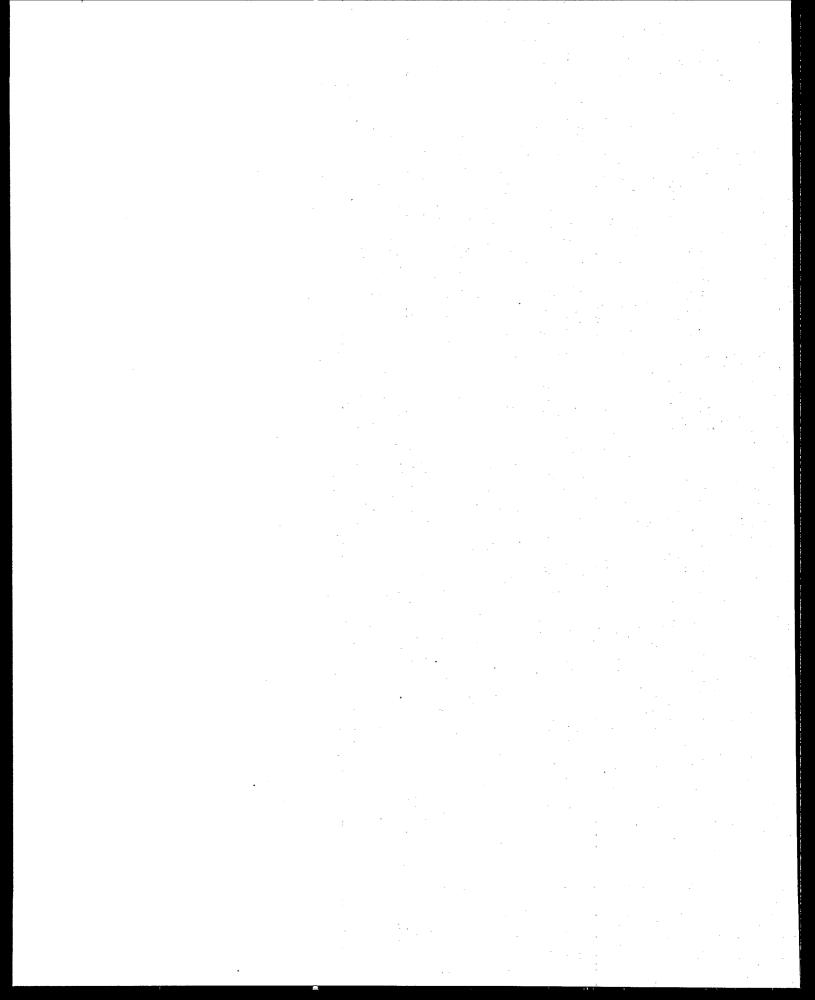
Reheat furnaces function to adjust or to maintain steel at a suitable temperature as the steel is processed. They are similar in many respects to soaking-pit furnaces. Reheat furnaces are being integrated into continuous casting facilities for slabs, blooms, and billets. When these are charged hot into a reheat furnace, a moderate fuel savings results. Fuel inputs to large soaking-pit and reheat furnaces range from 1.2 to 5.4 MJ/kg (1.0 to 4.7 MMBtu/ton) heated.²⁷

3.3.6 Annealing Furnaces

Flat-rolled steel products such as coils of sheet steel are sometimes annealed to enhance some physical properties of the product. Annealing involves subjecting the product to a supplemental heat treatment under controlled conditions. Only a portion of the steel produced is annealed. It is usually cold-reduced coils that are annealed because hot-rolled coils are "self-annealed." The great bulk of annealing is done at temperatures of about 675 °C (1,250°F). Some products are annealed at much higher temperatures[760 °C to 1,210 °C, (1,400 °F to 2,200 °F)]. Annealing is done in a protective, deoxidized atmosphere that is predominately nitrogen.

Annealing can be a batch or a continuous process although the trend is strongly toward continuous annealing. Batch annealing is done in a box-type furnace that consists of a stationary base, several stools on which coils of steel are stacked, individual cylindrical covers for each coil stack (to provide for the protective atmosphere), and the furnace, which is lowered by crane over the base with its load, stools, and cylindrical covers. Subsequently, the charge is heated slowly but uniformly to a specified temperature, soaked for a period of time, and then allowed to cool. After a period of cooling, the furnace is removed to begin a cycle on another base. the inner covers are left in place to preserve the protective atmosphere. After the charge has cooled to about 150 °C (300 °F), the charge can be exposed to air without oxidizing. this cycle, the cooling period takes at least as long as heating and soaking combined.

Continuous annealing is done in large furnaces in which the steel coil is threaded vertically around rollers located at the top and bottom of the furnace. Thus, the residence time of the steel in the furnace is dramatically increased as it passes continuously through the furnace. A typical, continuous annealing furnace will have several zones including a gas-fired heating zone, an electrically heated holding zone, an electrically heated slow cooling zone, and a fast cooling zone. Steel coil will thread through these zones at a rate of about 1,500 ft/min (7.6 m/s). Threading back and forth, the steel will make 10 passes through the heating zone in about 20 seconds. Subsequently, it will be cooled to about 540 °C (1,000 °F) in the slow cooling zone and then to 115 °C (240 °F) in the fast cooling zone. The entire process takes about 2 minutes and is carried out in an atmosphere of nitrogen (95 percent) and hydrogen (5 percent).31



3.4 References

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CHAPTER 4

UNCONTROLLED NO. EMISSIONS

This chapter presents available information on uncontrolled NO_x emissions from process facilities at iron and steel mills. Section 4.1 discusses the mechanisms of NO_x formation. Section 4.2 discusses emission factors and emissions from specific sources, and Table 4-4 presents a summary of emissions from these sources. Appendix A is a tabulation of the available emissions data.

4.1 MECHANISMS OF NO. FORMATION

Nitrogen oxides refer to the combination of nitric oxide and nitrogen dioxide. However, flue gas resulting from the combustion of fossil fuel consists primarily of NO with NO representing 90 to 95 percent of the total NO, due to kinetic limitations in the oxidation of NO to NO2. There are three fundamentally different mechanisms of NO, formation. These mechanisms are (1) thermal NO_x , (2) fuel NO_x , and (3) prompt NO_x . The thermal NO, mechanism arises from the thermal dissociation and subsequent reaction of nitrogen and oxygen molecules in combustion air. The fuel NO_{x} mechanism is the evolution and reaction of fuel-bound nitrogen compounds with oxygen. The prompt NO, mechanism involves the intermediate formation of hydrogen cyanide, followed by the oxidation of HCN to NO. Natural gas and most distillate oils have no chemically bound fuel nitrogen and essentially all NO, formed from the combustion of these fuels is thermal NO. Residual oils and coals all have fuel-bound nitrogen and, when these are combusted, NO, is formed by all three mechanisms. The formation of prompt NO, is only significant in very fuel-rich flames. These three mechanisms are discussed in more detail in the following subsections.

4.1.1 Thermal NO_x Formation

At the temperatures encountered in combustion air, both N_2 and O_2 molecules are dissociated into their respective atomic states, N and O. The subsequent reaction of these atoms to create thermal NO_x is thought to proceed through mechanisms first formulated by Zeldovich: 1,2

$$N_2 + 0 \rightleftharpoons NO + N$$
 $k_f = 2 \times 10^{14} \exp(-76500/RT)$ (4-1)

$$N + O_2 \rightleftharpoons NO + O$$
 $k_f = 6.3 \times 10^9 \exp(-6300/RT)$ (4-2)

In each reaction, k_f is the forward rate constant for that reaction. The high activation energy of reaction (4-1), 76.5 kcal/mol, shows that this reaction is the most temperature sensitive. These relationships assume that the combustion has

reached equilibrium. Because it has a large activation energy, reaction (4-1) is generally believed to be rate limiting. Oxygen atom concentrations are assumed to have reached equilibrium according to

$$O_2 + M \rightarrow O + O + M \tag{4-3}$$

where M denotes any third substance (usually N_2).³

Experiments at atmospheric pressure have indicated that, under certain conditions, the amount of NO formed in heated N_2 , O_2 , and argon (Ar) mixtures can be expressed as³

[NO] =
$$k_1 \exp(-k_2/T) [N_2] [O_2]^{1/2} t$$
 (4-4)

where

[NO] = mole fraction

 $k_1, k_2 = constants$

T = temperature, and

t = time.

Although equation (4-4) cannot adequately describe NO formation in a turbulent flame, it does point out several features of thermal NO_x formation. Like reactions (4-1) and (4-2), it reflects a strong, exponential relationship with NO emissions and temperature. It also suggests that NO formation is directly proportional to N₂ concentration, residence time, and the square root of O₂ concentration. Moreover, equation (4-4) also suggests several control measures for reducing thermal NO_x formation:

- Reduce local nitrogen concentrations at peak temperatures,
- Reduce local oxygen concentrations at peak temperatures,
- Reduce the residence times at peak temperatures, and
- Reduce peak temperatures.

These control measures are discussed further in Chapter 5.

For the purposes of the computations presented in Table 4-1, the N_2 and O_2 concentrations in flue gas are defined to be 76 percent and 3.3 percent, respectively. The strong, exponential dependency on temperature is evident in these tabulations, and a dependency on O_2 concentration can be inferred. Note, for example, that the equilibrium NO_x is much higher in air where the O_2 concentration is higher than it is in flue gas.

TABLE 4-1.CALCULATED EQUILIBRIUM CONCENTRATIONS OF NO AND $\mathrm{NO_2}$ IN AIR AND FLUE GAS 4 (ppm)

| Tem | perature | Air | | Flue gas | 3 |
|-------|----------|--------------|-----------------|------------|-----------------|
| K | °F | NO | NO ₂ | NO | NO ₂ |
| 300 | 80 | 3.4 (10) -10 | 2.1(10)4 | 1.1(10)-10 | 3.3(10)-3 |
| 800 | 980 | 2.3 | 0.7 | 0.8 | 0.1 |
| 1,400 | 2,060 | 800. | 5.6 | 250. | 0.9 |
| 1,873 | 2,912 | 6,100. | 12. | 2,000. | 1.8 |

In practice, flue gas NO_x concentrations tend to be much higher than suggested by the computations in Table 4-1. After NO_x is formed in the high temperatures of a flame, the rate of its decomposition (the reverse of reactions (4-1) and (4-2)) is kinetically limited at the lower temperatures and lower N and O atomic concentrations characteristic of the postcombustion zone of the flame. Thus, although NO_x is thermodynamically unstable even at high temperatures, its decomposition is kinetically limited. The result is that the NO_x concentration in flue gas is higher than predicted by equilibrium and depends, to a large extent, on the mixing of fuel and combustion air in the flame.

The factors discussed above affect thermal NO_x formation on a macroscopic scale. However, local microscopic conditions ultimately determine the amount of thermal NO_x formed. These conditions are intimately related to a host of variables such as local combustion intensity, heat removal rates, and internal mixing effects.

Studies on the formation of thermal NO_x in gaseous flames, for example, have confirmed that internal mixing can have large effects on the total amount of NO_x formed.³ Burner swirl, combustion air velocity, fuel injection angle and velocity, quarl angle, and confinement ratio all affect the mixing between fuel, combustion air, and recirculated products. Mixing, in turn, alters the local temperatures and specie concentrations, which control the rate of NO_x formation.

Generalizing these effects is difficult because the interactions are complex. Increasing swirl, for example, may both increase entrainment of cooled combustion products (lowering peak temperatures) and increase fuel/air mixing (raising local combustion intensity). Thus, the net effect of increasing swirl can be to either raise or lower NO_x formation. In summary, a hierarchy of effects, depicted in Table 4-2, produces local combustion conditions that promote thermal NO_x formation.³

4.1.2 <u>Fuel NO_x Formation</u>

Nitrogen oxides can also be produced by oxidation of nitrogen compounds contained in fossil fuels. The mechanisms are more complex than the Zeldovich model for thermal NO_x formation. Several studies indicate that the fuel-bound nitrogen compounds react to form NO_x in two separate mechanisms, one a solid-phase char reaction (with solid fuels) and the other a homogeneous gasphase reaction resulting from evolution and cracking of volatile compounds (solid and liquid fuels).

TABLE 4-2. FACTORS CONTROLLING THE FORMATION OF THERMAL NO,

| Secondary Fundamental combustion parameters | | COMDUSTION INCENSICY | Heat removal rate Oxygen level | Mixing of combustion Peak temperature products into flame | Exposure time at Local fuel/air ratio peak temperature | cortion | of flame zone |
|---|-----------------------------|----------------------|--------------------------------|---|--|----------------------------------|---------------|
| Primary equipment and fuel parameters | Inlet temperature, velocity | Firebox design | Fuel composition | Injection pattern | of fuel and air | Size of droplets or particles | |

External mass addition

The char nitrogen reaction is not well understood although data show that the char nitrogen conversion to NO_x is weakly dependent on the flame temperature and strongly dependent on stoichiometric ratio, fuel/air mixing, and on the char characteristics. The precise relationships, however, are not known. Conversion rates to NO_x of 15 to 35 percent have been documented.

The gas-phase reaction is postulated to include a number of intermediate species (e.g., HCN, HOCN, $\rm NH_2$) which are produced at rapid reaction rates. The decay rate of the intermediate species into $\rm N_2$ (fuel-rich) and $\rm NO_x$ (fuel-lean) is slower by at least an order of magnitude. These reaction rates are strongly dependent upon the stoichiometric ratio and the gas phase fuel nitrogen concentration and weakly dependent upon the flame temperature and the nature of the organic nitrogen compound. It is the weak influence of temperature on gas-phase $\rm NO_x$ conversion that reduces the effectiveness of $\rm NO_x$ controls that rely on temperature effects in the combustion of nitrogen-bearing fuels.

The relative contribution of fuel NO $_{x}$ and thermal NO $_{x}$ to total NO $_{x}$ emissions from sources firing nitrogen-containing fuels has not been definitively established. Estimates indicate that fuel NO $_{x}$ is significant and may even predominate. In one laboratory study, residual oil and pulverized coal were burned in an argon/oxygen mixture to eliminate thermal NO $_{x}$ effects. Results show that fuel NO $_{x}$ can account for over 50 percent of total NO $_{x}$ production from residual oil firing and approximately 80 percent of total NO $_{x}$ from coal firing.

The nitrogen content of most residual oils varies from 0.1 to 0.5 percent. Nitrogen content of most U.S. coals lies in the 0.5 to 2 percent range. Fortunately, only a fraction of the fuel nitrogen is converted to NO_x for both oil and coal firing. Furthermore, the percent of fuel nitrogen converted to NO_x decreases as nitrogen content increases. Thus, although fuel NO_x emissions undoubtedly increase with increasing fuel nitrogen content, the emissions increase is not proportional. In fact, data indicate only a small increase in NO_x emissions as fuel nitrogen increases.

4.1.3 Prompt NO. Formation

Prompt NO_x is produced by the formation first of intermediate HCN via the reaction of nitrogen radicals and hydrocarbons,

$$NO + HC + H2 \rightarrow HCN + H2O$$
 (4-5)

followed by the oxidation of the HCN to NO. The formation of prompt NO_x has a weak temperature dependence and a short lifetime of several microseconds. It is only significant in very fuel-rich flames, which are inherently low-NO, emitters. 1

4.2 NO, EMISSIONS FROM IRON AND STEEL MILLS

Integrated iron and steel mills import three basic raw materials and process these to produce steel in a variety of compositions and forms. The conversion processes, described in Chapter 3 of this document, tend to be high-temperature processes in which large quantities of fuels are consumed. As a consequence, most of these processes are sources of NO_x emissions.

Mini-mills and specialty producers do not have the full range of processing facilities characteristically found in integrated plants. They do not, for example, produce coke or sinter for use in blast furnaces or operate blast furnaces to produce pig iron or hot metal. Instead, they may produce steel by melting scrap in an electric-arc furnace, and they may use some subset of the processes found in integrated mills to produce a variety of steel products. They, too, may use a number of high-temperature, fuel-consuming processes and produce NO_x emissions. In this section, the major sources of NO_x emissions inherent in steelmaking plants are identified along with the fuels and process temperatures characteristically used in these processes. Further, estimates of uncontrolled NO_x emissions are also given.

The following subsections discuss uncontrolled NO_x emission factors and NO_x emissions from specific iron and steel process facilities. These data appear in the literature or were provided by Section 114 responses for a variety of units, many of which cannot be easily interpreted for other conditions. These data are summarized in tabular form in Section 4.2.11 and are tabulated in Appendix A.

4.2.1 Emission Factors

 ${
m NO_x}$ emissions data in the literature relevant to iron and steel mill processes are limited. This lack of a good emissions database is reflected in the major compilations of emission factors. Table 4-3 is a compilation of emissions factors from AP-42 and from the National Acid Precipitation Assessment Program (NAPAP). Note that the units used for these factors are unusual and not easily interpreted or used. Also, note that their quality ratings are poor (D for AP-42 and E for NAPAP), i.e., they are based on a single observation of questionable quality or an extrapolation from another factor for a similar process. If these emission factors are to be used, it has been recommended that AP-42 factors be used whenever possible and that the NAPAP emission factors be used when AP-42 factors are unavailable. These emission factors are not used in this document.

4.2.2 Coke-oven Underfiring

As described in Chapter 3, coke is made by the destructive distillation of coal in the absence of air. During distillation,

NITROGEN OXIDE EMISSION FACTORS FROM AP-42 AND NAPAP68 TABLE 4-3.

| Units | 10° ft³ burned | Tons coal charged Tons coal charged Tons coal charged Tons coal charged Tons coal charged | Tons sinter produced | Tons produced Tons produced Tons produced Tons produced Tons produced Tons produced |
|--|---------------------------|---|----------------------|--|
| NO _x (1b/unit) ^{b,e} (NAPAP) | 23.0 80.0 | 0.03 0.6 0.04 | | 0.1 Neg 0.08 0.02 0.1 |
| NO _x (1b/unit)**° (AP-42) | | 0.03 | | 19 |
| Operation/procевв | Process gas BFG COG | By-product coke mfg. Charging Pushing Quenching Underfiring Door leaks Top-side leaks | Sintering Windbox | Steel production Electric arc furnace: stack Soaking pits BOF: Open hood-stack Tapping: BOF Continuous casting Heat-treating furnaces, annealing Coating (tin, zinc, etc.) |

These factors have a D quality rating. Thus, they are based on a single observation of questionable quality or extrapolated from another factor for a similar process. These factors have an E quality rating. Thus, they are based on a single observation of questionable quality or extrapolated from another factor for a similar process. Units are listed in the right-most column.

a noncondensable gaseous product known as coke-oven gas (COG), with a heating value of about 22 MJ/Nm³ (570 Btu/ft³), is evolved. The major combustible component of COG is methane; thus, it is very similar to natural gas. Some 30 to 40 percent of the COG is used to heat the coke oven, and the remainder is used in other heating processes in the plant. Coking is accomplished at temperatures that range from about 900 to 1,100 °C (1,650 to 2,010 °F), and flue-gas temperatures can reach about 1,480°C (2,700 °F). A regenerative, reversible checkerwork is used to preheat the combustion air used to burn the COG, yielding fuel conservation and a higher flame temperature. Nitrogen oxides emissions from coke underfiring result from the high temperatures and the large quantity of fuel consumed. Uncontrolled NO_x emissions reported for coke ovens are tabulated in Appendix A.

The wide range of NO_x emissions from heating of coke ovens is due to wide variations in the geometry of the combustion chambers and the combustion variables of fuel and air mixtures, temperature, humidity, and other factors. While the principle of all coke ovens is the same, each coke oven and coke-oven operation is unique.

Much of the coke oven data included in Appendix A is incomplete such that it cannot be compared on a common basis with other data. The data that can be compared on a common basis (ppm @ 3% 0, lb/MMBtu, and lb/ton of product) are summarized below.

| | ppm @ 3% 0_2 | lb/MMBtu | lb/ton |
|----------------|----------------|----------|--------|
| n(No. Samples) | 8 | 11 | 12 |
| Min. Value | 254 | 0.10 | 0.15 |
| Max. Value | 1452 | 2.06 | 2.15 |
| Avg. Value | 802 | 0.66 | 0.88 |
| Std. Dev. | 448 | 0.72 | 0.64 |

4.2.3 Sintering

Sintering is a continuous operation in which feed materials, including coke breeze or fines and flue dust, are deposited in a uniform bed on a traveling grate and ignited by passing under burners fired with natural gas. Beyond the ignition region, air is pulled down through the bed. The coke fines in the bed continue to burn, generating the heat required for the sintering to proceed. Ignition temperatures range from about 1,150 °C (2,100 °F), where ignition begins, to about 800 °C (1,500 °F) at the ignition hood exit. As the coke fines in the bed burn, bed temperatures reach 1,300 to 1,480 °C (2,370 to 2,700 °F). Available uncontrolled NO_x emissions data for sinter plants are tabulated in Appendix A. These data vary widely, and much of these data are incomplete, i.e., test conditions are seldom specified. A summary of these data is tabulated below. The data in terms of lb/ton show a wide range from 0.007 to 0.70.

| | ppm @ 3% 0 ₂ | 1b/MMBtu | lb/ton |
|----------------|-------------------------|----------|--------|
| n(No. Samples) | 2 | 4 | 16 |
| Min. Value | 284 | 0.22 | 0.007 |
| Max. Value | 395 | 0.59 | 0.70 |
| Avg. Value | 339 | 0.47 | 0.34 |
| Std. Dev. | | 0.17 | 0.28 |

4.2.4 Blast Furnaces and Blast Furnace Stoves

The blast furnace is fueled by the combustion of coke that, along with iron ore and flux, is a component of its charge, and the off-gas is recovered and burned for its fuel value. It is a closed unit that does not have atmospheric emissions. However, the associated blast furnace stoves do generate NO_x emissions. These stoves, typically three or four for each blast furnace, burn the blast furnace gas (BFG) to preheat the combustion air supplied to the blast furnace. The BFG has a low heating value ranging from 3.0 to 3.5 MJ/Nm³ (80 to 95 Btu/ft³). More recently, values ranging from a low of 2.5 MJ/Nm³ (65 Btu/ft³) have been reported with changes in blast furnace burdens cited as the cause of the deterioration. Blast furnace gas burns with a low flame temperature. Its combustible component is carbon monoxide, which burns clean. However, the BFG is often enriched with other fuels (e.g., natural gas or COG) to obtain blast-air temperatures as high as 1,100 °C (2,010 °F).

The available uncontrolled NO_{x} emissions data for blast furnace stoves are tabulated in Appendix A. These data vary widely in terms oflb/MMBtu and lb/ton, and much of these data are incomplete, i.e., test conditions are seldom specified. A summary of these data is shown below.

| | ppm @ 3% 0 ₂ | 1b/MMBtu | lb/ton |
|----------------|-------------------------|----------|--------|
| n(No. Samples) | 1 | 11 | 10 |
| Min. Value | | 0.002 | 0.003 |
| Max. Value | | 0.057 | 0.072 |
| Avg. Value | 28. | 0.021 | 0.037 |
| Std. Dev. | | 0.019 | 0.022 |

4.2.5 Basic Oxygen Furnace

The basic oxygen process of steelmaking is an exothermic process that does not require the burning of fossil fuels. The process does produce off-gases, principally carbon monoxide, which are usually burned prior to discharge into the atmosphere. Some newer BOF facilities use suppressed combustion hoods, which suppress the influx of air, and the off-gases are subsequently flared. A potential for NO_x generation does exist during the combustion of waste gases. Nitrogen oxides production from this process has been estimated to range from 30 to 80 ppm, or 180 to 500 ng NO_x/kg (0.36 to 1 lb NO_x/ton) of steel produced. 10

Appendix A presents NO_x emissions data for BOFs, including Q-BOPs, and these data are summarized below. Data for which the status of the furnace is unknown (i.e., whether or not the furnace is in an 0_2 blow period) are not included in the summary. A wide range in terms of ppm@ $3\$O_2$ is reported (18-180) but in terms of lb/ton the range is much narrower (0.042-0.22).

During 0, Blow Period

| | ppm (avg) | ppm @ 3% 0 ₂ | lb/ton |
|----------------|-----------|-------------------------|--------|
| n(No. Samples) | 12 | 7 | 7 |
| Min. Value | 12.3 | 18 | 0.042 |
| Max. Value | 84.0 | 180 | 0.222 |
| Avg. Value | 24.0 | 58 | 0.119 |
| Std. Dev. | 19.6 | 56 | 0.059 |

During Non 0, Blow Period

| • | ppm (avg) | $ppm @ 3% 0_2$ | <u>lb/ton</u> |
|----------------|-----------|----------------|------------------|
| n(No. Samples) | 2 | 2 | - |
| Min. Value | 14.3 | 200. | . , - |
| Max. Value | 14.5 | 366. | - |
| Avg. Value | 14.4 | 283. | - |

4.2.6 Electric-Arc Furnace

The electric arc furnace largely transfers the generation of NO_x emissions from the steelmelting facility to a utility plant where it is easier to control. The only use of fossil fuels in the electric arc facility is for scrap preheating, which may or may not be practiced. However, some EAFs also fire oxy-fuel burners in addition to electric arcs during meltdown. The available NO_x emissions data, presented in Appendix A and summarized below, suggest that concurrent oxy-fuel firing during meltdown does increase NO_x emissions above the emissions from electric-arc melting alone as NO_x increased from 12 to 98 ppm. The range of NO_x emissions is narrow from 0.5 - 0.6 lb/ton and 83 - 100 lb/heat.

EAF With Concurrent Oxy-fuel Firing

| | ppm (avg.) | <u>lb/ton</u> | <u>lb/heat</u> |
|----------------|------------|---------------|----------------|
| n(No. Samples) | 6 | 6 | 6 |
| Min. Value | 80. | 0.50 | 83 |
| Max. Value | 110. | 0.60 | 100 |
| Avg. Value | 98. | 0.54 | 89 |
| Std. Dev. | 10. | 0.05 | 8.2 |

EAF Without Concurrent Oxy-fuel Firing

| | ppm (avq.) |
|----------------|-------------|
| n(No. Samples) | 2 |
| Min. Value | 7 |
| Max. Value | 17 ' |
| Avg. Value | 12 |

4.2.7 Soaking Pits

Soaking pits reheat or hold slabs, ingots, and other forms of steel to temperatures suitable for further shaping and processing. They predominantly use natural gas for fuel although some COG and fuel oil are used. In recent years, the use of soaking pits has declined as the use of continuous casters increased.

The available NO_x emissions data for soaking pits are included in Appendix A. These data correspond to a range of conditions that are not always specified. A summary of these data are tabulated below:

Summary of all Appendix A Soaking Pit Data

| | lb/MMBtu | lb/ton | ppm @ 3% 02 |
|----------------|----------|--------|-------------|
| n(No. Samples) | 5 | 9 | 3 |
| Min. Value | 0.064 | 0.091 | 49 |
| Max. Value | 0.148 | 0.361 | 689 |
| Avg. Value | 0.108 | 0.175 | 307 |
| Std. Dev. | 0.039 | 0.078 | 337 |

A sub-set of the Appendix A data for soaking pits includes more test-condition information than is available for the remainder of the data. It is clear that these data correspond to a complete cycle of the soaking pits. Hot and cold charges are specified and the temperature of the combustion air is given. A summary tabulation corresponding to this sub-set is presented below, and a distinction is made between soaking pits with preheated combustion air and those with cold or ambient combustion air. NO_x for the preheat air is approximately doubled that for the cold air soaking pit.

Summary of a Sub-set of Appendix A Soaking Pit Data

| | <u>lb/M</u> | MBtu | <u>lb/ton</u> | • |
|---------------|-------------|-------------|---------------|-------------|
| | Cold Air | Preheat Air | Cold Air | Preheat Air |
| n(No. Samples | 3 2 | 3 | 2 | 3 |
| Min. Value | 0.064 | 0.121 | 0.091 | 0.164 |
| Max. Value | 0.069 | 0.148 | 0.104 | 0.194 |
| Avg. Value | 0.066 | 0.135 | 0.098 | 0.164 |
| Std. Dev. | | 0.016 | | 0.016 |

4.2.8 Reheat Furnaces

Most reheat furnaces are either recuperative- or regenerative-fired, i.e., they preheat the combustion air in order to increase fuel efficiency. Some use cold combustion air. The temperature of the combustion air has a large impact on uncontrolled NO $_{\rm x}$ emissions. Increasing the combustion air temperature from 38 °C (100 °F) to 540° C (1,000 °F), for example, will increase uncontrolled NO $_{\rm x}$ emissions by a factor of about 6. 12

Combustion air preheated in regenerators has a much higher temperature than air preheated in recuperators. While the higher combustion air temperature increases furnace fuel efficiency, it also increases NO_x generation and NO_x emissions. Consequently, regenerative-firing is not usually practiced without combustion modifications for NO_x control, but there may be exceptions.

Appendix A contains a tabulation of available uncontrolled emissions data for reheat furnaces. These data correspond to a variety of condition, some known and some unknown. Summaries of the Appendix A data follow. The first summary represents all of the Appendix A data except three values that are more than an order of magnitude lower than any other value and two values from an ejector stack that may not be representative. Included are data for both regenerative- and recuperative-fired furnaces and others for which the firing configurations are not specified. This tabulation shows a wide range (0.023 - 0.91 lb/MMBtu).

Summary of Appendix A Reheat Furnace Data

| 1b/MMBtu | $ppm @ 3% 0_2$ | <u>lb/ton</u> |
|----------|-------------------------------|--|
| 28 | 14 | 11 |
| 0.023 | 65. | 0.054 |
| 0.909 | 740. | 0.327 |
| 0.226 | 292. | 0.198 |
| 0.198 | 166. | 0.084 |
| | 28 0.023 0.909 0.226 | 28 14 0.023 65. 0.909 740. 0.226 292. |

The following is a summary of the Appendix A data for recuperative-fired reheat furnaces.

Summary of Recuperative-fired Reheat Furnace Data From Appendix A

| | lb/MMBtu | ppm @ 3% 0 ₂ | lb/ton |
|----------------|----------|-------------------------|--------|
| n(No. Samples) | 16 | · 8 | 8 |
| Min. Value | 0.080 | 65. | 0.157 |
| Max. Value | 0.40 | 326. | 0.327 |
| Avg. Value | 0.200 | 220. | 0.237 |
| Std. Dev. | 0.101 | 81.5 | 0.058 |

The following is a summary of the Appendix A data for regenerative-fired reheat furnaces. Data from the recuperative-fired furnace is much lower than regenerative reheat furnaces (0.2 vs. 0.91 lb/MMBtu and 220 vs. 740 ppm at 3% O₂.

Summary of Regenerative-fired Reheat Furnace Data From Appendix A

| | 1b/MMBtu | ppm @ 3% 0 ₂ |
|----------------|----------|-------------------------|
| n(No. Samples) | 2 | 2 |
| Min. Value | 0.675 | 550. |
| Max. Value | 0.909 | 740. |
| Ave. Value | 0.792 | 645. |

None of the reheat furnace emissions data in Appendix A are known to correspond to cold combustion air firing. For the purposes of this Chapter, the uncontrolled emissions data for cold-air-fired reheat furnaces are estimated using controlled emissions data from an LNB-controlled reheat furnace (80 ppm at 3% 0_2) assuming a control efficiency of 27 percent. Thus, uncontrolled emissions from cold-air-fired reheat furnaces are estimated to be 110 ppm at 3% 0_2 (0.135 lb/MMBtu).

4.2.9 Annealing Furnaces

Annealing processes vary greatly depending on specific objectives and starting materials. In general, annealing furnaces subject steel products to a planned time-temperature profile in a reducing atmosphere with heating supplied from gas-fired, radiant-tube burners. There are two basic approaches. Batch annealing typically includes slow heating of the steel to a desired temperature, soaking at temperature, and controlled slow cooling, a process that may take several days. In continuous annealing, steel sheet is passed continuously through an annealing furnace where it is subjected to a desired time-temperature profile. Temperatures typically peak at about 675 °C (1,250 °F). However, some processes may require temperatures as high as 760 to 1,200 °C (1,400 to 2,200 °F).

Uncontrolled NO $_{\rm x}$ emissions data from operating annealing furnaces are not available. The emissions data included in Appendix A are based on estimates and on laboratory measurements of emissions from furnaces without NO $_{\rm x}$ controls. These data were provided for new furnaces or, in one case, for a furnace still under construction. In each case, the furnace is regenerative fired. For the purposes of this Chapter, the average of the two values is used as the uncontrolled emissions from a regenerative-fired annealing furnace, i.e., 775 ppm at 3% 0_2 (0.952 lb/MMBtu). The actual value would be affected by the temperature of the preheated air. The 1,000 ppm value is possible for regenerative-fired furnaces without No $_{\rm x}$ controls (because the air preheat is very high with regenerator technology), but this configuration is not used in practice (there may be exceptions). 16

In lieu of uncontrolled emissions data for recuperative- and cold-air-fired annealing furnaces, estimated values are used for the purposes of this Chapter. Values of 204 and 450 ppm at 3% 0_2 (0.25 and 0.55 lb/MMBtu) have been suggested as reasonable for recuperative-fired furnaces. ^{16,19} The average of these is 327 ppm at 3% 0_2 (0.402 lb/MMBtu). A value of 120 ppm at 3% 0_2 (0.147 lb/MMBtu) has been suggested as reasonable for cold-air-fired furnaces. ¹⁹

4.2.10 Galvanizing Furnaces

Appendix A lists uncontrolled NO_x emissions from two regenerative-fired galvanizing furnaces. (These furnaces are described as galvanizing/galvannealing and aluminizing furnaces.) One estimate is based on measurements at laboratory facilities with NO_x control features disabled, and the second is based on field measurements. These values are 1,000 and 880 ppm at 3% O_2 , respectively, and the average is 940 ppm at 3% O_2 (1.15 lb/MMBtu).

No uncontrolled NO_x emissions data are available for recuperative- or cold-air-fired galvanizing furnaces. In lieu of any data, values for annealing furnaces are used as estimates for the purposes of this Chapter, i.e., 327 ppm at 3% O_2 (0.402 lb/MMBtu) and 120 ppm at 3% O_2 (0.147 lb/MMBtu) for recuperative-fired and cold-air-fired galvanizing furnaces, respectively. In practice, the actual value would depend on many variables including furnace and combustion air temperatures.

4.2.11 Summary

Table 4-4 is a summary tabulation of uncontrolled NO_x emissions from the major NO_x -emitting sources at iron and steel mills. These values are based on the available emissions data presented in Appendix A and, in instances where no data are available, on estimates. There is not an abundance of data, and test conditions are often not specified. For example, NO_x emissions will vary with furnace operating temperature and combustion air temperature, and these conditions are usually not specified. In each case, the text of this Chapter and Table 4-4 includes information indicative of the quantity and quality of the data. The uncontrolled NO_x emissions data tabulated in Table 4-4 are used to calculate NO_x emissions reductions and cost effectiveness of NO_x controls in Chapters 5 and 6, respectively.

TABLE 4-4. SUMMARY OF UNCONTROLLED NOX EMISSIONS

| Process/facility | | Ave | Average NO, Emissions | issions | | | | Range NO _x Emi | Emissions |
|---|-------------------------|-----------------------|-------------------------|----------------------------|-----------|-------|-------------------------|------------------------------------|-------------|
| | ppm @ 3 \$ 0₂ | ជ | 1b/MMBt u | ជ | 1b/ton | u | ppm © 3\$ 0₂ | 1b/MMBtu | lb/ton |
| Coke-oven underfiring | 800 | æ | 0.658 | 11 | 0.882 | 12 | 254- 1452 | 0.10-2.06 | 0.15-2.15 |
| Sintering | 340 | 7 | 0.465 | 4 | 0.341 | 16 | 248-395 | 0.213- 0.589 | 0.007-0.341 |
| Blast-furnace Stoves | 28 | ₽ | 0.021 | 11 | 0.037 | 10 | - | 0.002- 0.057 | 0.003-0.072 |
| Basic oxygen furnaces (including QBOP) during O ₂ blow during non blow | 58 283 | 7 2 | 1 1 | 1 | 0.119 | ۲. | 18-180 200-366 | 1 1 | 0.042-0.222 |
| Electric-arc furnace (concurrent oxy-fuel firing) (without oxy-fuel firing) | 12 | 7 | , I | 1 1 | 0.54 | 9 ' | - 7-17 ppm | | 0.50-0.60 |
| Soaking Pits Preheat comb. air Cold comb. air | 1 1 | ı | 0.135 | E 2 | 0.164 | 2 3 | ı ı | 0.121- 0.148 0.064- 0.069 | 0.164-0.194 |
| Reheat Furnaces Regenerative- fired Recuperative- fired Cold-air-fired | 645 220 110 | 2 8 Note 1 | 0.792 0.200 0.135 | 2 16 Note 1 | 0.237 | 1 & 1 | 550-740 65-326 | 0.675- 0.909 0.080-0.40 | 0.157-0.327 |
| Annealing furnaces Regenerative- fired Recuperative- fired Cold-air-fired | 775 330 120 | 2 Note 3 Note 3 | 0.952 0.402 0.147 | Note 2 Note 2 Note 2 | į I I 40° | | 550- 1000 204-450 | 0.25-0.55 | 1 1, 1 |

SUMMARY OF UNCONTROLLED NO_X EMISSIONS TABLE 4-4.

| Process/facility | | Ave | Average NO, Emissions | issions | | | | Range NO, Emissions | ssions |
|---|---------------------------|-----------------------|------------------------|----------------------------|----------|----|----------------------------|---------------------|-----------|
| | ppm @3\$0 ₂ | n | 1b/MMBt u | n | lb/ton n | п | ppm @ 3% 0 ₂ | 1b/MMBtu | lb/ton |
| Coke-oven underfiring | 800 | 8 | 0.658 | 11 | 0.882 | 12 | 254 - 1452 | 0.10-2.06 | 0.15-2.15 |
| Galvanizing furnace Regenerative- fired Recuperative- fired Cold-air-fired | 940 330 120 | 2 Note 4 Note 4 | 1.15 0.402 0.142 | Note 2 Note 4 Note 4 | 1 1 1 | | 875- 1000 - | 1 1 1 | 1 1 1 |

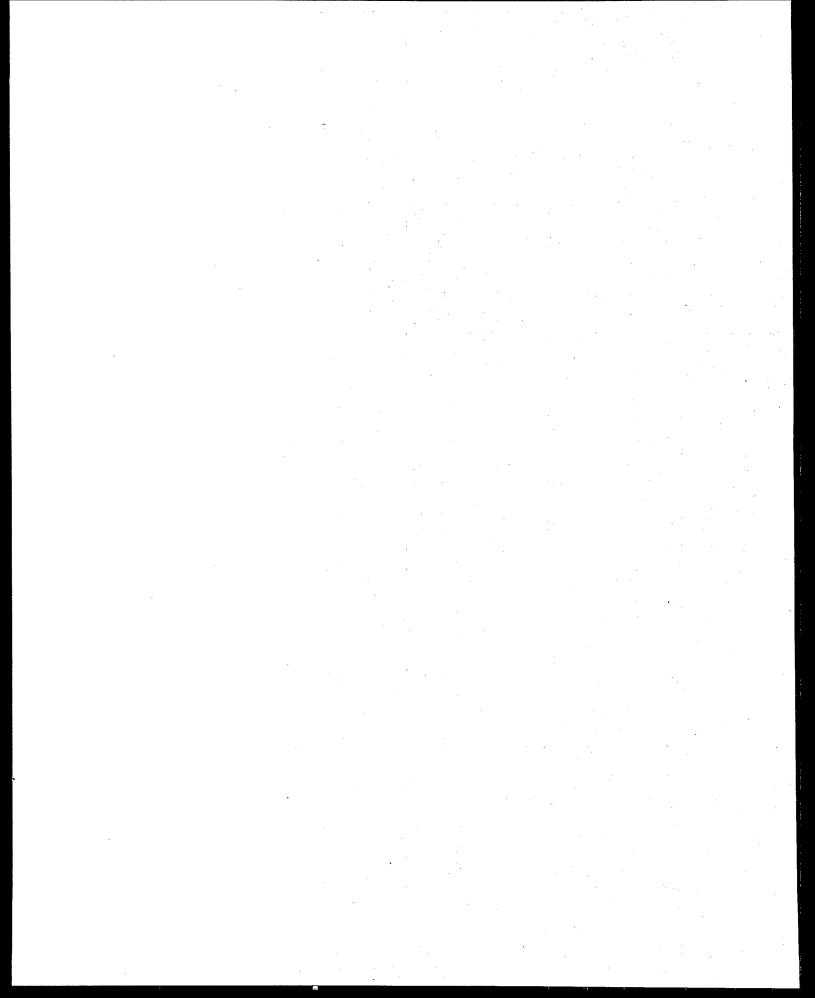
Number values in average. Estimated from an assumed control efficiency of 27 percent. Computed from ppm @ 3% θ_2 assumming NG as fuel.

n: Note 1: Note 2:

Note 3: Note 4:

4-17

From estimates provided by vendors. In lieu of any data, values from annealing furnaces are used.



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CHAPTER 5

NITROGEN OXIDES CONTROL TECHNIQUES

5.1 BACKGROUND

Because the types of process facilities involved in the making of iron and steel are numerous and different, they are discussed separately in this chapter. Control techniques applicable to each process facility are identified in the appropriate subsection.

Control techniques for NO_x emissions can be placed into one of two basic categories: techniques designed to minimize NO_x generation and techniques designed to remove previously generated NO_x from the waste effluent stream. Combustion modification techniques, including low NO_x burners(LNB's) and flue gas recirculation(FGR), fit into the first category. Add-on flue gas treatment techniques such as selective catalytic reduction(SCR) and selective noncatalytic reduction(SNCR) are examples of the second. Table 5-1 summarizes these techniques and indicates that combustion modifications tend to be less effective than flue gas treatment as a NO_x control. Of these techniques, low excess air(LEA), LNB's, FGR, SCR, and combinations of these controls are known to be used to control NO_x emissions from iron and steel process facilities. It should be noted that LNB's and often FGR incorporate staged combustion in their burner design.

5.2 CONTROL TECHNIQUES APPLICABLE TO IRON AND STEEL FACILITIES

Historically, few facilities found at iron and steel mills have NO_x controls. Requests for information from the industry and control equipment vendors on NO_x controls yielded information on only a few facilities with NO_x controls. Those facilities are either new or are still under construction, and little performance data are available. The control techniques known to be used (LEA, LNB's, FGR, and SCR) are discussed in Section 5.2.1. These techniques are applied to reheat furnaces, annealing furnaces, and galvanizing furnaces. The applications are discussed in Section 5.3. Other control techniques that may be applicable to iron and steel processes are discussed in Section 5.2.2.

5.2.1 Control Techniques Applied

Control techniques known to have been used on iron and steel process facilities are LEA (reheat furnaces), LNB (reheat furnaces and galvanizing furnaces), LNB plus FGR (reheat furnaces, annealing furnaces, and galvanizing furnaces), SCR (annealing furnaces), and LNB plus SCR (annealing furnaces).

TABLE 5-1 OVERVIEW OF $\mathrm{NO}_{\mathbf{x}}$ CONTROL TECHNIQUES¹

| - | | |
|----------------------------------|-----------------------|---|
| Technique | Emission reduction | Comments |
| Combustion modification | 10 to 50+ percent | One or more of these has the potential for |
| Low excess air | | application to any combustion unit. |
| Staged combustion | | Performance and costs are highly site specific. |
| Flue gas recirculation | • | andria (1915), <mark>T</mark> arakan da Salaha. Marajaran |
| Low-NO _x burners | | |
| Flue gas treatment | | |
| Selective noncatalytic reduction | 30 to 80 percent | Ammonia and urea injection are used on fossil-fuel-and refuse-fired units in the U.S., Japan, and Europe. |
| | | |
| Selective catalytic reduction | 50 to 90+ percent | Used in U.S. on gas turbines, interal combustion engines, process heaters and some |
| | | boilers. Used on gas-, oil-, coal-, and refuse-fired units in Japan and Europe. |

These control techniques are discussed in the following subsections.

5.2.1.1 <u>Low Excess Air</u>. Low excess air (LEA) is a combustion modification technique in which NO_x formation is inhibited by reducing the excess air to less than normal ratios.² It reduces the local flame concentration of oxygen, thus reducing both thermal and fuel NO_x formation. It is easily implemented and is used extensively in both new and retrofit applications, either singly or in combination with other control measures. It can be used with all fuels and all firing methods.^{2,3}

The potential of LEA as a NO_x control technique is limited by the onset of smoke or CO emissions. Tests on utility boilers have indicated that LEA firing can reduce NO_x emissions between 16 and 21 percent as compared to baseline levels.² Other sources have suggested reductions of up to 15 percent.⁴ In the case of utility boiler applications, LEA also increases thermal efficiency. It decreases the volume of combustion air to be heated, allowing more heat of combustion to be transferred, thus lowering fuel requirements for a given output.³ To maintain proper control of the furnace pressure, positive pressure must be maintained in the furnace to prevent the influx of tramp air.⁵

A number of other factors affect the excess air levels that can be implemented. These include the type of fuel fired, uniformity of the air/fuel ratio, air and fuel control lags during load swings, and other combustion control features such as staging of fuel or air.²

For utility boilers, LEA firing is considered a routine operating procedure and is incorporated in all new units. Because it is efficient and easy to implement, expectations are that LEA will be used increasingly in other applications as well. Although it is a feasible technique for furnaces, specifically commercial furnaces, the trend in NO_x control for these sources has been in improved burner design.²

In a reheat furnace application at a steel mini-mill, LEA as a NO_x control technique yielded a NO_x emission reduction of about 13 percent.⁶ This application is described in Section 5.3.6.

5.2.1.2 <u>Low NO_x Burners</u>. Low NO_x burners (LNB) have been used since the early 1970's for thermal NO_x control. These specially designed burners employ a variety of principles including LEA, off-stoichiometric or staged combustion (OSC), and FGR. The objective in the application of LNB's is to minimize NO_x formation while maintaining acceptable combustion of carbon and hydrogen in the fuel.²

Literature references to LNB applications discuss industrial and utility boiler and process heater applications primarily. However, they are applicable to other combustion processes including reheat furnaces and continuous annealing and galvanizing line furnaces. Annealing and galvanizing line furnaces are more like boilers and process heaters in that their operating temperatures are in the same range. Reheat furnaces and soaking pits, in general, operate at much higher temperatures.

The differences between a low NO, burner and a burner featuring LEA or FGR, for example, are not always clear. general, LNB's implement LEA, OSC, FGR, or a combination of these techniques. In a stricter sense, LNB's have been defined as burners that control NO_x formation by carrying out the combustion in stages (OSC) and, further, by controlling the staging at and within the burner rather than in the firebox. Consistent with this definition, there are two distinct types of designs for LNB's: staged air burners and staged fuel burners. Staged air burners are designed to reduce flame turbulence, delay fuel/air mixing, and establish fuel-rich zones for initial combustion. The reduced availability of oxygen in the initial combustion zone inhibits fuel NO, conversion. Radiation of heat from the primary. combustion zone results in reduced temperature as the final unburned fuel gases mix with excess air to complete the combustion process. The longer, less intense flames resulting from the staged stoichiometry lower peak flame temperatures and reduce thermal NO, formation.

Figure 5-1 is an illustration of a staged-air LNB. All of the fuel and less-than-stoichiometric air (primary air) are initially supplied to the primary combustion zone. Staged or secondary air is supplied beyond the primary zone where combustion of the fuel is completed, again under offstoichiometric conditions. Staged air burners generally lengthen the flame configuration so their applicability is limited to installations large enough to avoid flame impingement on internal surfaces. The installation of replacement burners may require substantial changes in burner hardware, including air registers, air baffles and vanes, fuel injectors, and throat design. Existing burners can incorporate staged air burner features by modifying fuel injection patterns, installing air flow baffles or vanes, or reshaping the burner throat. Staged air burners are effective with all fuel types.

Figure 5-2 is an illustration of a staged-fuel LNB. 3 Staged fuel burners mix a portion of the fuel and all of the air in the primary combustion zone. The high level of excess air greatly lowers the peak flame temperature achieved in the primary combustion zone, thereby reducing formation of thermal NO_x . The secondary fuel is injected at high pressure into the combustion

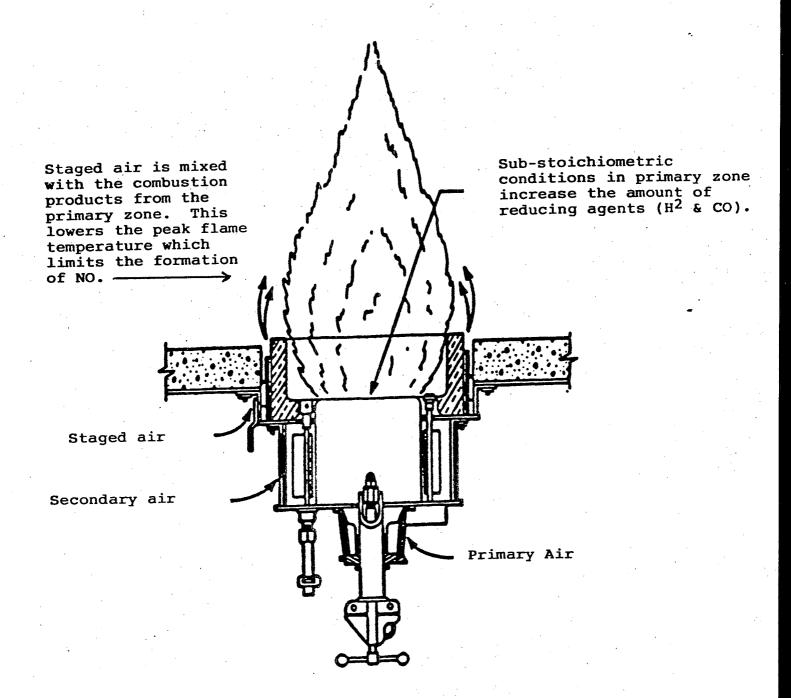


Figure 5-1. Staged-air Low No_X burner.³

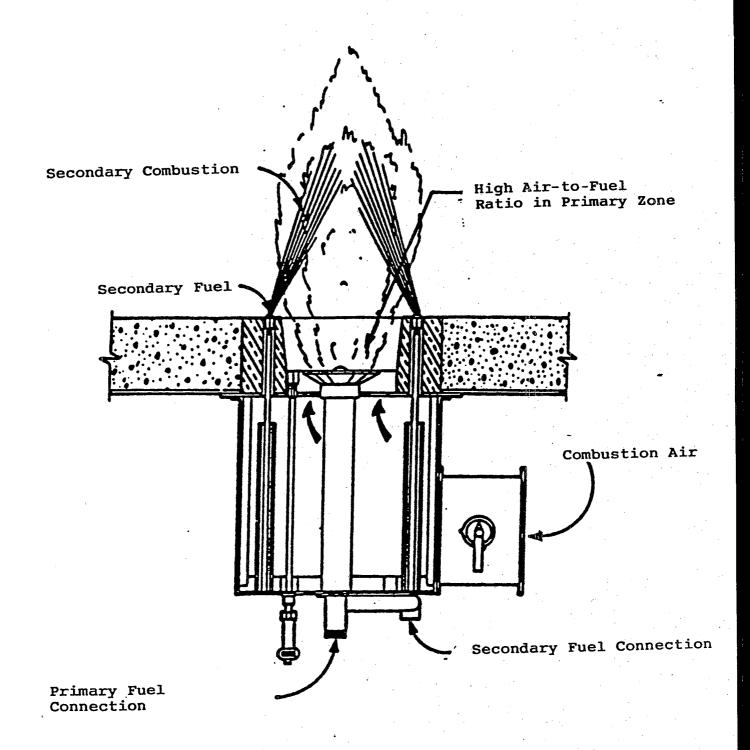


Figure 5-2. Staged-fuel Low NO_{χ} burners.³

zone through a series of nozzles that are positioned around the perimeter of the burner. Because of its high velocity, the fuel gas entrains furnace gases and promotes rapid mixing with first-stage combustion products. The entrained furnace gases simulate flue gas recirculation. Heat is transferred from the first-stage combustion products prior to the second-stage combustion. As a result, second-stage combustion is achieved with lower partial pressures of oxygen and temperatures than would normally be encountered.³

Unlike the staged air burner, staged fuel burners are designed only for gas firing. The staged fuel burner is able to operate with lower excess air levels than the staged air burner due to the increased mixing capability resulting from the high-pressure second-stage fuel injection. An additional advantage of the staged fuel burner is a compact flame. Cooling of the combustion products from the first-stage zone in the staged air burner is accomplished primarily by radiation to the process. However, in a staged fuel burner the entrained furnace products give additional cooling to the flame. This particular characteristic permits more intense combustion with reduced NO_x levels.³

In addition to the common viewpoint of LNB as a burner that stages combustion within the burner rather than in the firebox other designs also include FGR within the burner. The FGR feature may be a more effective control than OSC. For example, a radiant tube burner that uses a vitiated air stream (i.e., a burner featuring FGR) is being developed. The combustion takes place within the burner, and reduced NO_x generation has been demonstrated.

Full-scale tests on boilers in Japan have shown NO_x emissions reductions from 40 to 60 percent with gas-fired LNB's. Other subscale test results with LNB's include 55 percent NO_x reduction with specially designed nozzles and burner blocks, and 55 percent NO_x reduction with designs that create fuel-rich and fuel-lean combustion zones (staged combustion).²

Other estimates on NO_x reductions for LNB's include 20 to 50 percent NO_x reductions in oil- and gas-fired package boilers using shaped fuel injection ports and controlled air-fuel mixing, and 55 percent (typical) NO_x reductions in process furnaces using self-recirculating (an FGR feature) and staged combustion type burners. In summary, LNB's appear to offer potential NO_x reductions around 50 percent in boiler and process heater applications.²

There are three known applications of LNB's used by the iron and steel industry in the United States. LNB's are being used at a reheat furnace, an annealing furnace, and a galvanizing

furnace. The use of LNB's may change the heat transfer characteristics and the oxidizing/reducing atmosphere of a furnace. This is not a problem for new furnaces as the design and construction of new furnaces can accommodate these changes. For existing furnaces, in particular annealing furnaces, which operate at a very specific flame and furnace geometries to achieve a specific "set point" at which steel processing is most efficient, major problems may occur for a specific furnace without a large amount of equipment reconstruction.

5.2.1.3 Low NO_x Burner Plus Flue Gas Recirculation. As discussed earlier, LNB's are often designed to incorporate OSC and FGR within the burners. However, additional, external FGR is added to enhance NO_x control in some furnace installations. Flue gas recirculation is implemented by recycling a portion of the flue gas to the primary combustion zone. This principle is illustrated for a boiler in Figure 5-3. It reduces NO_x formation by two mechanisms. The recycled flue gas contains combustion products that act as inerts during combustion and lower the peak flame temperature, reducing thermal NO_x formation. To a lesser extent, FGR also reduces thermal NO_x formation by lowering the oxygen concentration in the primary flame zone. These factors lower flame temperature, altering heat distribution and reducing fuel efficiency.

Flue gas recirculation has been applied principally to boilers and to a few process heaters. Emissions tests on utility boilers with flue gas recirculation control have achieved NO_x reductions of 13 to 60 percent.²

Controlled NO_x emissions data are available for two reheat furnaces, an annealing furnace, and a galvanizing furnace with LNB plus flue gas recirculation control. 9,10 These data are discussed in Section 5.3.

5.2.1.4 Selective Catalytic Reduction. SCR is the most advanced of the flue-gas treatment methods for reducing NO_x emissions and the one on which the great majority of flue gas treatment units is based.² The principle of SCR is illustrated in Figure 5-4. SCR units use NH_3 to selectively reduce NO_x . The ammonia, usually diluted with air or steam, is injected through a grid system into the flue/exhaust gas stream upstream of a catalyst bed. On the catalyst surface, the ammonia reacts with NO_x to form molecular nitrogen and water. Depending on system design, NO_x removal rates of 80 to 90 percent and higher are achievable.³

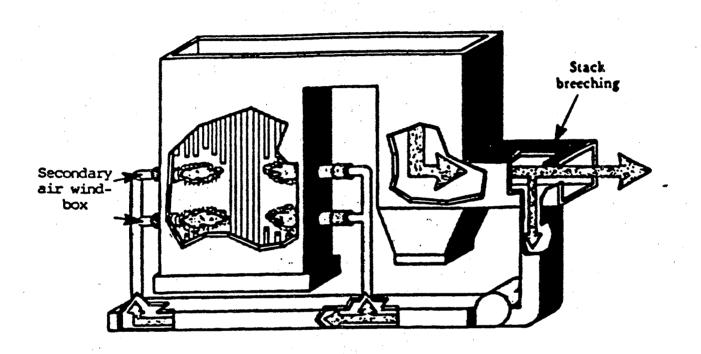


Figure 5-3. Illustration of flue gas recirculation. 11

The major reactions that occur in SCR are the following:

$$4NO + 4NH_3 + 0_2 \rightleftharpoons 4N_2 + 6H_20$$
, and (5-1)
 $2NO_2 + 4NH_3 + 0_2 \leftrightharpoons 3N_2 + 6H_20$. (5-2)

Of these, reaction (5-1) predominates since flue gas NO_x consists primarily of NO. The optimum temperature range for these reactions is generally 260 to 540 °C (500 to 1,000 °F). At higher temperatures, the NH_3 oxidizes to NO_x or ammonium nitrate and ammonium nitrite. Lower temperatures do not provide sufficient energy to initiate the reaction. The catalysts used in SCR units are predominately oxides of titanium and vanadium. However, platinum, zeolites, and ceramics are also used. In gas-fired applications, catalyst pellets in a fixed bed are commonly used. For oil- or coal-fired applications where the flue gas contains particulate matter, catalyst designs usually include honeycomb, pipe, or parallel shapes, which allow the flue gas to pass along the catalyst surface.

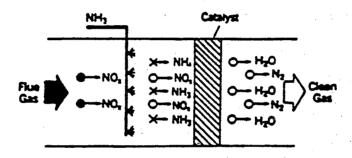


Figure 5-4 Illustration of the SCR principle. 12

The effectiveness of the SCR in removing NO_x is also dependent on the $NH_3:NO_x$ mole ratio. As the $NH_3:NO_x$ mole ratio increases, the NO_x reduction increases and ammonia slip (i.e., unreacted ammonia slipping through the catalyst bed) increases. In practice, removal efficiencies of up to 90 percent are commonly achieved with ammonia slip values below 5 ppm. On-line NO_x analyzers and feed-back control of NH_3 injection are required to maintain control of the SCR process.

Site-specific factors other than temperatures and $NH_3:NO_x$ ratios that affect NO_x emission rates achievable with SCR include the ratio of flue gas flow rate to catalyst volume (the inverse of residence time), catalyst poisoning (by metals, acid gases, or particulate entrainment), and pressure drop across the catalyst which reduces fuel efficiency. Most of these potential problems have been addressed successfully in commercial operations.³

There has been limited experience with SCR at iron and steel mill. This is primarily due to the lack of stringent NO_x regulations. In the U.S., SCR has been applied to oil and gas fired combustion units such as gas turbines, internal combustion engines, and process heaters and several coal-fired boilers. At iron and steel mills, there are 2 SCR units in the U.S. An SCR unit is being used to control NO_x emissions from a gas-fired, radiant tube, continuous annealing furnace at a steel mini-mill in the United States. This furnace also has LNB's. Controlled emissions from this unit are about 33 ppm at 3 percent O₂. A second SCR unit, currently under construction, will be used to control NO_x emissions from an annealing furnace at an integrated steel plant in the United States. This furnace does not have LNB's. The unit has a guaranteed NO_x reduction of 90 percent.

Techniques for NO_x control adopted by the Japanese iron and steel industry are, for the most part, based on combustion modifications. However, the Japanese have investigated "flue gas denitrification" using the SCR process for sintering plants, coke ovens, and reheating furnaces. They concluded that the SCR process was impractical for use on sintering plants due to the many technical problems that remain to be solved. These problems include the limited service life of the catalysts, energy requirements to raise the exhaust gas temperature, and the large installation space required. However, in some environmentally critical areas, flue gas denitrification units (presumably SCR) are used on sinter plants. SCR applications to coke ovens and reheat furnaces appear to be experimental. They are not routinely used on these facilities in Japan.

5.2.2 Other Control Techniques

LEA, LNB's, LNB plus FGR, SCR, and SCR plus LNB are NO_x control techniques that have been used to reduce NO_x emissions from iron and steel process facilities in the United States. Other techniques that may be applicable, some of which have been used in Japan, are discussed in this section.

5.2.2.1 Off-Stoichiometric or Staged Combustion (OSC). OSC reduces NO_x generation by carrying out initial combustion in a primary, fuel-rich combustion zone and subsequently completing combustion at lower temperatures in a second, fuel-lean zone. This technique is essentially the control technique implemented through the use of LNB's; however, it can be implemented using conventional burners by staging the combustion in the furnace or firebox rather than within the burner itself as is done with LNB's.

In practice, OSC is implemented through biased burner firing (BBF), burners out of service (BOOS), or overfire air (OFA). BBF and BOOS are very similar and are generally applicable to

furnaces with multiple burners arranged in rows. In BBF, fuel distribution among the burners is redistributed so that the lower rows of burners are fired more fuel-rich than the upper rows, as illustrated in Figure 5-5. The additional air needed to complete combustion is provided through the upper rows of burners, which are fired fuel-lean. In BOOS firing, selected burners or rows of burners are made inactive (taken out of service) by turning off their fuel supply and using them to admit air only to the furnace. The total fuel demand is supplied by the remaining or active burners. Thus, the active burners are fired fuel-rich, and the additional air required to complete combustion is supplied through the BOOS or air-only burners. This principle is illustrated in Figure 5-6. Both BBF and BOOS implement staged combustion by creating two combustion zones within the firebox: one fired fuel-rich or with low excess air and the second fired with excess air at a reduced temperature. These methods are applicable to all fuels, and both fuel- and thermal-NO, formation are reduced.2

These techniques, BBF and BOOS, are attractive options for existing facilities with suitably configured burners since few equipment modifications are required. In some cases, process facilities may need to be derated if the active burners (BOOS) or fuel-rich burners (BBF) have limited firing capacities.

Implementing BBF or BOOS requires careful, accurate monitoring of the combustion process and the flue gas in order to control the process. Alternatively, furnace efficiency and safety may be compromised.²

Emissions tests of BOOS firing on utility boilers have indicated average NO_x reductions of 31 to 37 percent for coal, oil, and natural gas firing compared to baseline values.² It seems reasonable that BBF would yield similar results due to the similarity of the two techniques.

A third type of staged combustion, illustrated in Figure 5-7, is OFA. With OFA, the burners are fired more fuel-rich than normal, and the additional air needed to complete combustion is admitted through overfire air ports or an idle top row of burners. This technique is applicable with all fuels. In emissions tests on utility boilers, OFA has achieved average NO, reductions of 24 to 59 percent with oil, coal, and natural gas firing compared with baseline levels.²

These staged combustion techniques, especially OFA, are more easily implemented on large, utility-scale boilers than on smaller units and furnaces.² As furnace size decreases, furnace volume decreases more quickly than furnace wall area. Thus, residence times for fuel combustion may become a problem in smaller units. Moreover, space for additional ductwork, furnace

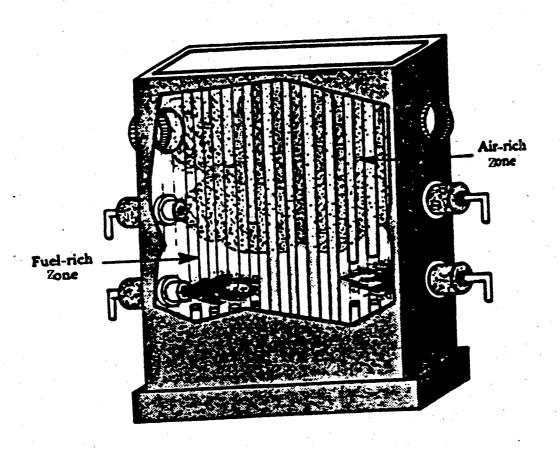


Figure 5-5. Biased Burner Firing11

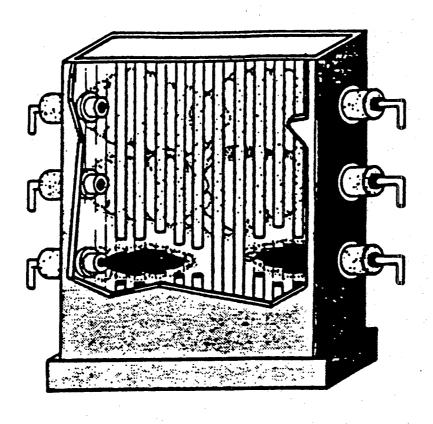


Figure 5-6. Burners out of service. 11

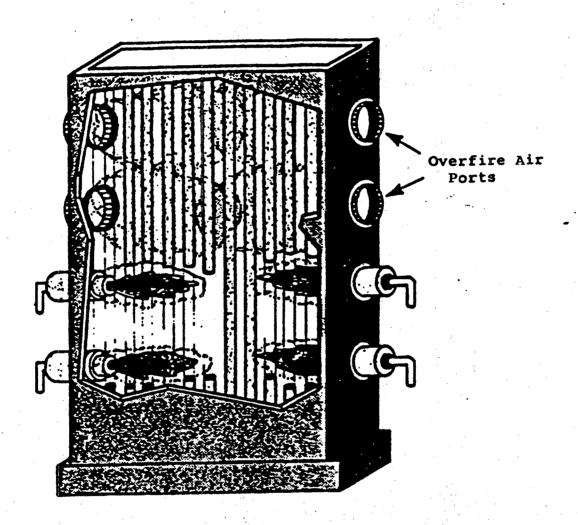


Figure 5-7. Overfire air. 11

penetrations, and fans may be a problem if these additions are needed. These factors are potential impediments to implementing these OSC techniques in iron and steel process facility furnaces, especially on a retrofit basis.

There is no evidence that FGR has been used to control NO_x emissions from iron and steel process facilities. However, a radiant tube LNB featuring a vitiated air stream concept (i.e., FGR) is being developed. As discussed in Section 5.2.1.3, FGR has been used with LNB's to reduce NO_x emissions from a reheat furnace.

5.2.2.2 <u>Fuel Switching</u>. Fuel switching and fuel denitrification are possible NO_x control techniques. In Japan, these techniques are currently used or have been used to reduce NO_x emissions from reheat furnaces, sintering furnaces, and coke ovens (denitrification of fuel only).

Natural gas is an attractive fuel from a NO_x control perspective because of the absence of fuel-bound nitrogen (fuel NO_x) and the flexibility it provides for implementing other combustion modification control techniques. Because natural gasis already the principal fuel used in reheat furnaces in the United States, fuel switching is not a reasonable NO_x control option for reheat furnaces (or soaking pits, for the same reason) in the United States. Moreover, for large fuel-burning processes, fuel choice decisions tend to be based on fuel costs and on other regulatory constraints.

Coke ovens reduce coal to coke in a reasonably closed reducing environment. There are fugitive emissions of NO_x from leaks and during charging and pushing operations. Coke oven underfiring is done predominantly with coke oven gas, blast furnace gas, natural gas ,or some combination of these three. It is not clear that fuel switching is a reasonable option for NO_x reduction in the case of coke ovens in the United States, and it is not clear from the literature to what extent the Japanese use fuel switching as a coke oven NO_x control strategy. Two strategies are cited. These are (1) switching to lighter fuel oil (not an option if COG, BFG, and NG are baseline fuels), and (2) taking credit for the nitrogen removal that is incidental to the desulfurization of COG (an oxides of sulfur control measure).

5.2.2.3 <u>Selective Noncatalytic Reduction</u>. SNCR is generally an applicable NO_x control technique for applications that are suitable for SCR. SNCR is very similar to SCR: i.e., NH_3 or urea is injected into the flue gas stream where the temperature is suitable for the reaction with NO_x to proceed. However, SCR and SNCR differ in that their ideal reaction

temperatures differ. Depending on catalyst type, the optimum temperature for SCR reactions is 260 to 450 °C [500 to 840 °F], and the optimum temperature for SNCR is 870 to 1,250 °C (1,600 to 2,300 °F). Generally, 40 to 70 percent NO $_{\rm x}$ reduction is achieved with NH $_3$:NO $_{\rm x}$ molar ratios of 1:1 to 2:1. This control efficiency generally results from the difficulty of achieving uniform mixing of NH $_3$ with the flue gas and from the variations of flue gas temperature and composition usually present.

There are two commercially available SNCR processes that use either ammonia or urea. The SNCR process that uses ammonia is the Thermal DeNO $_{\rm x}$ (TDN) system developed by EXXON. In this process, gaseous ammonia is injected into the air-rich flue gas stream where it reacts with NO $_{\rm x}$ in accordance with two competing reactions:

$$2NO + 4NH_3 + 2O_2 \rightarrow 3N_2 + 6H_2O$$
, and (5-3)

$$4NH_1 + 5O_2 \rightarrow 4NO + 6H_2O$$
 (5-4)

Thus, the TDN process has the potential to either reduce NO_x in accordance with reaction (5-3) or increase NO_x in accordance with reaction (5-4). Temperature is the primary variable for controlling the rates of these reactions. In the temperature range of 870 to 1,200 °C (1,600 to 2,200 °F), reaction (5-3) dominates, resulting in a reduction of NO_x . Above 1,200 °C (2,200 °F), reaction (5-4) dominates, resulting in an increase of NO_x . Below 870 °C (1,600 °F), neither reaction is of sufficient activity to either increase or decrease NO_x . The reduction of NO_x is maximized in the relatively narrow range of 870 to 1,040 °C (1,600 to 1,900 °F) with an optimum temperature of about 950 °C (1,750 °F). The favorable, 170 °C (300 °F) reaction window for reaction (5-3) can be lowered to about 700 to 820 °C (1,300 to 1,500 °F) by introducing hydrogen, a readily oxidizable gas.^{3,17}

Without the use of a catalyst to increase the reaction rates, adequate time at optimum temperatures must be available for the NO_x reduction reaction to occur. Design considerations should allow ample residence time and good mixing in the required temperature range. Long residence times (>1 second) at optimum temperatures tend to promote relatively high performance even with less than optimum initial mixing or temperature/velocity gradients. However, when the NH₃ injection zone is characterized by low temperature and/or steep temperature declines, a loss of process efficiency results.

The initial ratio of ammonia injected to NO_x concentrations is another parameter to control in the process. Maximum NO_x reductions (50 to 70 percent) require 1.5 to 2.0 $NH_3:NO_x$ injection ratios. At these ratios, significant concentrations of NH_3 can

exit the convective zone, creating corrosive ammonium sulfates and/or a visible NH₃ stack plume. Unreacted ammonia emissions from a TDN system are usually higher than from SCR systems.³

The second of the two commercially available SNCR processes is the Nalco/Fuel Tech NO $_x$ OUT process. In this process, a ureatype compound is injected at a favorable location to reduce NO $_x$ according to the following reaction:

$$NH_2 + NO \rightarrow N_2 + H_2O \tag{5-5}$$

The exact chemical mechanism is not fully understood, but it involves the decomposition of urea $[C(NH_2)_2O]$. The likely decomposition products include the NH_2 groups. The reaction takes place at temperatures of 870 to 1,200 °C (1,600 to 2,300°F).

Originally developed by the Electric Power Research Institute (EPRI) in the early 1980's, the process is currently licensed by Nalco/Fuel Tech where patented process modifications and control techniques, combustion unit computer modelling and proprietary additives that allow NOx reduction capability over a temperature range of 760 to 1,200 °C (1,400 - 2,300 °F) have been developed. As with the other post-combustion NO, control systems, temperature is the primary control variable for the selective reactions. NO_x reductions up to 80 percent are achievable with this technology. The performance of the urea injection process is limited by the time/temperature/flow characteristics of the flue gas. Residence time in the temperature window and the urea-to-NO, ratio impact the performance in a manner similar to that for Thermal DeNOx. NO, reduction capability is limited by mixing because the reaction times are relatively quick.3

The SNCR technique is discussed here because of its successful application to facilities that are similar to iron and steel facilities, e.g., hot-side, coal-fired utility boilers, heavy oil fired industrial boilers, and wood-waste fired co-gen plants. In general, SNCR is applicable in applications where a temperature suitable for a favorable reaction is acheivable. SNCR has not been used for any iron and steel mill processes.

5.3 NITROGEN OXIDES CONTROLS FOR SPECIFIC FACILITIES

In this section, the NO_x emission sources at iron and steel mills are discussed with a view toward identifying and evaluating applicable control techniques.

5.3.1 Coke Ovens

Coke ovens produce metallurgical coke from coal by the

distillation of volatile matter. A by-product of the process is coke oven gas, a fuel commonly used (along with blast furnace gas) to fire the ovens. Although NO_x emissions tend to be minimized by slow mixing in the combustion chamber, they are nonetheless substantial because of the large quantity of fuel consumed. Coke ovens are among the major NO_x emission sources at iron and steel mills.² Coke ovens with NO_x controls in the United States have not been found.

The Japan Iron and Steel Federation has reported the installation of flue gas denitrification (SCR) units on coke ovens. They also cite low-air-ratio combustion and denitrification of fuel as NO_x control techniques applicable to coke ovens. Denitrification of fuel may refer to the practice of desulfurizing coke gas, which also has the effect of removing nitrogen and, thus, reduces NO_x emissions. Flue gas recirculation is also cited. The Japanese acknowledge that there are many limitations and difficulties associated with applying these controls and some may be applicable only to new ovens. No details are provided about the effectiveness or levels of performance of these controls.

5.3.2 Sinter Plants

Sintering is also a major source of NO_x emissions from iron and steel mills. In general, only integrated steel plants operate sinter plants where the sinter is charged to a blast furnace.

Sinter is produced from iron ore fines, limestone fines, coke fines or breeze, flue dust, and possibly other additives. These materials are mixed, uniformly distributed onto a traveling grate, ignited, and heated to a fusion temperature that causes the materials to agglomerate into sinter. Subsequently, the sinter is cooled, crushed, and screened for size prior to charging to a blast furnace.

The major source of energy used in the production of sinter is the carbon content of the coke breeze and flue dust. An auxiliary fuel such as natural gas or coke oven gas is used to ignite the bed. This ignition fuel typically represents about 8 to 10 percent of the thermal energy required by the process. Following ignition, combustion is continued by forcing air through the bed as it travels with the grate. The combustion of the coke breeze and flue dust (about 5 percent of the bed material) creates sufficient heat and temperature [about 1,300 to 1,480 °C (2,370 to 2,700 °F)] to sinter the fine ore particles into porous clinkers that, following cooling and screening, are a suitable burden for a blast furnace. No information was obtained on NO, emission control techniques for sinter plants in the United States.

Japanese sources cite sinter plants as a major source of $\text{NO}_{\boldsymbol{x}}$

emissions at steel plants and report on research on SCR applications, an electron beam radiation process, and technology for reducing nitrogen in the coke breeze as they apply to sinter plants. The results of the research on reducing N_2 in the coke breeze are not readily available; however, it is noted that many problems remained to be solved. 16

More recently, the Japanese have reported that some steel mills have controlled NO_x generation at sinter plants by pretreating the sinter materials, i.e., lowering the oxidation level of the sintering atmosphere through adjustment of the coke blending ratio, basicity, etc.⁷ Most of the NO_x in sinter plant flue gas appears to come from coke in the sinter bed, which usually contains about 1 percent nitrogen. Japanese research in this area progressed from batch tests to a continuous test plant with a capacity for treating 20 tons of coke per day. The process was to preheat pulverized coke in a two-stage, fluidized-bed heater and then use an electric furnace to heat the coke to 1,700 °C (3,090 °F) using an electric current through the coke itself. The retention time is about 2 hours. The coke is subsequently cooled.¹⁹

About 70 percent of the N is removed from the coke by heating to 1,700 °C (3,090 °F). It is claimed that by removing 70 percent of the N from coke, the NO_x in the flue gas was also reduced by about 70 percent. This indicates that, in the sinter plant, most of the NO_x is generated from N in the coke.¹⁹

It was estimated that the coke denitrification process requires about 30 kWh of electricity per ton of sintered iron ore. Concern was also expressed about the flue gas from the treatment process, i.e., its composition and treatment. The Japanese were also uncertain as to whether the process could be commercialized.

The Japanese also report that some sintering plants, located in areas where national emission standards are not met sufficiently to ensure environmental quality, are equipped with flue gas denitrification units. These are SCR units, and there are still technical problems with this application, e.g., the catalyst life is limited and large amounts of additional heating energy are required.

In one sinter plant application, the commercial SCR plant was constructed as a permitting compromise when a large, new blast furnace was constructed. The capacity of the SCR unit was 750,000 Nm³/hr. The sinter flue gas contained considerable amounts of particulates and SO_3 and, thus, was difficult to treat. The flue gas treatment consisted of a flue gas desulfurization (FGD) process followed by a wet electrostatic precipitator (ESP). The cleaned gas was then heated to 400 °C (750 °F) for SCR treatment. Sinter flue gas typically has a temperature of about 150 °C (300 °F), 150 to 300 ppm of NO $_x$ (mostly NO), 150 to 400 ppm of SO_x , and 200 to 300 mg/Nm³ of

particulates containing ferric oxide and potassium chloride vapor. It is not an easy gas to treat with SCR because the effluent gas has to be heated and because particulates and potassium chloride vapor in the effluent tend to contaminate the catalyst. 19

The following information was obtained about this major SCR

Completed Treated facility Capacity Load factor Pretreatment of gas Iron ore sintering plant 762,000 Nm³/hr 70 to 100 percent Electrostatic precipitator Flue gas desulfurization

Wet ESP Heating

SCR inlet

200 to 300 ppm NOx 5 to 20 ppm SOx

3 to 10 mg/Nm³ particulates 11.2 percent O2

Reaction temperature

380-390 °C (716-734 °F) 1:1 1 year 95 percent

NO.:NH; ratio Catalyst life No. removal

In 1979, the Japanese assessment of this control application was that the investment and operating costs were so high that the process could not be widely used. 19

5.3.3 Blast Furnaces and Blast Furnace Stoves

The blast furnace is a tall, shaft-type furnace where iron-bearing materials (iron ore, sinter, slag, scrap, etc.) are reduced to iron (pig iron or hot metal). The burden or charge to the blast furnace also includes flux (limestone or dolomite) and coke. A preheated air blast is charged to the blast furnace through tuyeres, nozzle-like openings near the bottom of the furnace. The coke in the burden produces the heat required for smelting the charge, and it provides carbon and carbon monoxide required for reducing the iron ore. Moreover, because the coke retains its strength at temperatures above the melting temperature of pig iron and slag, it provides the structural support that keeps the unmelted burden materials from falling into the hot, molten metal that collects in the hearth. A description of the blast furnace and its operation can be found in Chapter 3 of this document, and a very detailed discussion can be found in Reference 18.

The blast furnace itself is a closed unit with no atmospheric emissions. The hot air blast reacts with the coke in the $\bar{\text{furnace}}$ to produce more carbon monoxide than is needed to reduce the iron ore. The excess CO leaves the top of the blast

furnace with other gaseous products and particulates. This blast furnace effluent, called BFG, is captured, cleaned, cooled, and subsequently used as a fuel in other processes. BFG contains about 1 percent hydrogen and 27 percent CO and has a heating value of about 2,540 - 3,600 kJ/Nm³ (65 - 92 Btu/ft³).

A blast furnace typically has three or four blast furnace stoves as auxiliaries. These stoves are used to heat the blast air required by the blast furnace. They function somewhat like a regenerator in that one or more of the stoves are on blast (i.e., they are being used to heat the blast air being used by the blast furnace) while the others are being heated. They differ from a regenerator in that the source of heat is the combustion of a fuel rather than the extraction of heat from an effluent stream.

Between 2.2 and 3.5 kg of BFG are generated for each kilogram of pig iron produced in a blast furnace. About 18 to 24 percent of this gas is used to heat the checker brick in the associated stoves.² The remainder is used elsewhere in the plant. Because of its low heating value, the BFG used in the stoves is often enriched by the addition of fuels with a much higher calorific value such as natural gas or coke-oven gas to obtain higher blast air temperature, often in excess of 1,100 °C - (2,010 °F).¹⁸

Blast furnace stoves are a NO_x emissions concern because they consume large quantities of fuel. However, the primary fuel is BFG, which is largely CO, has a low heating value, and contains inerts, factors that reduce flame temperature. Thus, the NO_x concentration in blast furnace stove flue gas tends to be low and the potential for NO_x reduction is considered to be small.²

Apparently there are no blast furnace stoves with NO_x emissions controls in the United States. The Japanese also indicate that NO_x emissions from blast furnace stoves are not a concern for the reasons noted above. They also suggest that LEA combustion can be implemented, but they do not explicitly claim to have implemented LEA.

5.3.4 Basic Oxygen Furnace

The BOF is the principal steelmaking process used in the United States. In operation, the BOF is tilted to receive a charge of scrap metal and, subsequently, molten pig iron from a blast furnace. After charging, it is returned to a vertical position and blown with high-purity oxygen, which converts the charge to steel. It is finally tapped and the molten steel is poured into a transfer ladle. Following tapping, the BOF is again tilted to discharge the remaining slag. A more detailed description of the BOF facility and the oxygen steel-making

process can be found in Chapter 3 of this document and in Reference 18.

In the BOF, oxygen is blown onto the bath at supersonic velocity (to penetrate slag and metal emulsions) where it oxidizes impurities in the bath to create steel. The oxidation of carbon produces about 467 kJ of CO per kilogram of steel (400,000 Btu/ton). Typically, the off-gas, which is mainly CO, is burned in an open, water-cooled hood mounted above the BOF. These hoods admit air for combustion of the CO on an uncontrolled basis. Some newer BOF's use suppressed combustion hoods that do not admit air or burn the off-gas. In these instances, the effluent gas is flared.

The combustion of the waste gas results in the generation of NO_x . There is no information available to indicate that existing BOF's have any kind of NO_x emission controls or that any control techniques are suitable.²

A variation on the BOF is the Q-BOP furnace. It differs from the BOF principally in that oxygen is blown through the molten metal bath through tuyeres in the bottom of the vessel rather than onto the top surface of the bath. From a NO_x emissions and controls perspective, the two processes appear to be essentially the same, i.e., there is no indication that Q-BOP furnaces have NO_x emissions controls or that any control techniques are suitable. In each case, NO_x is generated during the oxygen blow when CO in the off-gas is combusted either at the mouth of an open, combustion-type hood or at the flare of a suppressed hood system. 20

5.3.5 Electric Arc Furnaces

The use of electricity to melt steel scrap in the EAF transfers NO_x generation from the steel mill to a utility power plant. There is no information that NO_x emissions controls have been installed on EAF's or that suitable controls are available.

5.3.6 Reheat Furnaces

Reheat furnaces bring steel to a uniform temperature of about 1,180 to 1,340 °C (2,150 to 2,450 °F), a temperature suitable for hot working. They are major fuel-consuming facilities and major sources of NO_x emissions.

LEA, LNB's, and LNB plus FGR are being used to control NO_x emissions from reheat furnaces in the United States. 5,10,11,21 Major modifications to furnace structure and refractories to install alternate burners may be required in some existing reheat furnaces. In an LEA application, the control was retrofitted to

a 98-ton/hr (112-MMBtu/hr) capacity reheat furnace. LEA was selected as the most cost-effective option because the burner system did not need replacement. Alternatively, another control option would likely have been chosen. A test report shows the LEA control efficiency to be 14 percent. Assuming uncontrolled emissions of 220 ppm at 3 percent O2 (0.200 lb NO2/MMBtu) (from Table 4-4) for a recuperative furnace and a control efficiency of 13 percent, controlled NO2 emissions are estimated to be 190 ppm at 3 percent O2 (0.174 lb NO2/MMBtu). The corresponding NO2 reduction is 0.026 lb NO2/MMBtu. For regenerative furnaces, controlled emissions are 560 ppm at 3% O2 and 0.689 lb/MMBtu. For cold-air fired reheat furnaces, LEA lowers emissions to 96 ppm at 3%O2 and 0.117 lb/MMBtu.

LNB or FGR may require major modifications to furnace structures and refractories to install alternate burners. These combustion modifications do not necessarily reduce efficiency and capacity. The addition of LNB to a recuperative-fired furnace is not likely to affect either capacity or fuel requirements. The addition of FGR to a recuperative-fired furnace with or without LNBs will likely involve derating the furnace. The addition of LNB plus FGR to a regenerative fired furnace will not likely reduce capacity.²²

Average controlled NO_x emissions from two reheat furnaces (regenerative-firing) with LNB plus FGR controls are 150 ppm at 3 percent O_2 (0.18 lb $NO_x/MMBtu$). Thus, the control efficiency is 77 percent and the NO_x removed is 0.61 lb $NO_x/MMBtu$. This efficiency is also used for recuperative and cold air firing.

Two reheat furnaces with LNB NO $_{x}$ control, one using regenerative preheated combustion air and one using cold combustion air, have controlled NO $_{x}$ emissions of 220 ppm at 3 percent O $_{2}$ (0.27 lb NO $_{x}$ /MMBtu) and 80 ppm at 3 percent O $_{2}$ (0.10 lb NO $_{x}$ /MMBtu), respectively. 11,24 There are no uncontrolled NO $_{x}$ emissions data available for either of these furnaces. Uncontrolled NO $_{x}$ emissions from reheat furnaces using preheated regenerative combustion air are estimated to be 645 ppm at 3 percent O $_{2}$ (0.792 lb NO $_{x}$ /MMBtu) as shown in Table 4-4. Thus, for the reheat furnace using regenerative preheated combustion air, the control efficiency is estimated to be 66 percent, and the NO $_{x}$ removed is 0.52 lb NO $_{x}$ /MMBtu.

From Table 4-4, the uncontrolled NO_x emissions for cold-air fired reheat furnaces are 110 ppm @ 3% O_2 (0.135 lb/MMBtu). The control efficiency is therefore 27% or 0.035 lb/MMBtu. For recuperative-fired reheat furnaces, the controlled efficiency for LNB is estimated to be 45% or controlled emissions are 120 ppm@ 3% O_2 (0.11 lb NO_x /MMBtu). The NO_x removal is 0.09 lb/MMBtu.

In Japan, fuel switching, denitrification of fuel, LEA, and LNB's have been used to reduce NO_{x} emissions from reheat

furnaces. 8,19 No details about the performances of these controls are available.

5.3.7 Soaking Pits

Soaking pits have many similarities to reheat furnaces. Both are used to raise or maintain the temperature of steel in preparation for hot working or shaping. They burn the same fuels (natural gas predominantly, but also COB, BFG, and oil) and operate at approximately the same temperatures. Soaking pits tend to be smaller than reheat furnaces and, in the aggregate, use much less fuel. In 1979, for example, soaking pits used only about one-fifth the fuel used in reheat furnaces. Subsequently, the use of soaking pits has continued to decline as the practice of continuous casting has increased.

No examples of soaking pits with NO_x emissions controls were found. However, the similarity of reheat furnaces and soaking pits indicate that controls suitable for reheat furnaces would also be suitable for soaking pits.

5.3.8 Annealing and Galvanizing

Annealing and galvanizing are two finishing processes often practiced in iron and steel mills. They are separate, independent processes; however, both can be accomplished in a single continuous-type facility that includes, for example, a continuous annealing furnace followed immediately by a galvanizing facility in which the continuously moving steel sheet is immersed in a molten zinc bath. As compared with most iron and steel process, which take place at temperatures of 1,090 to 1,650 °C (2,000 to 3,000 °F), annealing and galvanizing are accomplished at moderate temperatures usually below 540 °C (1,000°F); however, some annealing processes may require higher temperatures. Because of these much lower temperatures, NO_x emissions from these processes should be lower. These two finishing processes are discussed independently in the following subsections.

5.3.8.1 Annealing Furnaces. Annealing may be accomplished in a large, batch-type furnace processing tons of coiled steel in a single, multiday cycle or in a large continuous-type furnace processing a continuous sheet of steel passing through the furnace. Annealing is a highly specialized technology that can alter the properties of steel in useful ways. In general, annealing relieves cooling stresses induced by hot-or-cold-working and softens the steel to improve its machinability or formability. This is accomplished by subjecting the steel to a controlled thermal profile or cycle with moderate peak temperatures.

SCR plus LNB, LNB plus FGR, and SCR are being used in the United States to control $NO_{\rm x}$ emissions from annealing furnaces.

Information is available on four annealing furnaces, one that is operational and three that are under construction. 11,14,15 All are radiant tube, continuous annealing furnaces firing natural gas. Due to the many exhaust collection points at annealing furnaces there may be problems in installing SCR at existing furnaces.

The control efficiency of the SCR unit alone on the LNB-plus-SCR controlled furnace is consistently 90 percent or more, and controlled emissions at or near capacity firing rates average 33 ppm at 3 percent O_2 (0.04 lb $NO_x/MMBtu$). There are no uncontrolled emissions data available for this furnace, only NO_x concentration data referenced to the inlet of the SCR. Uncontrolled NO_x emissions from two annealing furnaces are reported to be 1,000 ppm at 3 percent O_2 (1.23 lb $NO_x/MMBtu$) (from Table 4-4). Thus, the control efficiency of the LNB plus SCR control is estimated to be 97 percent. Individual control efficiencies of 53 percent for the LNB's and 93 percent for the SCR, for example, would yield this result. The NO_x removed by this control combination is 1.19 lb $NO_x/MMBtu$.

Laboratory data are available for one of the two LNB-plus-FGR-controlled annealing furnaces under construction. Controlled NO_x emissions from this furnace are reported to average 180 ppm $^{\circ}$ at 3 percent O₂ (0.22 lb NO_x/MMBtu). Uncontrolled emissions, from Chapter 4, are 1,000 ppm at 3 percent O₂ (1.23 lb NO_x/MMBtu). Thus the control efficiency is estimated to be 82 percent, and the NO_x removed is estimated to be 1.01 lb NO_x/MMBtu.

Controlled NO_x emissions for the SCR-controlled annealing furnace under construction are estimated using 1,000 ppm at 3 percent O_2 as uncontrolled emissions (from Chapter 4) and assuming a control efficiency of 85 percent. This yields estimates of controlled emissions and NO_x removed of 150 ppm at 3 percent O_2 (0.18 lb $NO_x/MMBtu$) and 1.1 lb $NO_x/MMBtu$, respectively.

Although no data or examples are available, controlled NO_x emissions and NO_x removed for annealing furnaces with only LNB's for control are estimated by assuming a control efficiency of 50 percent. The resulting values are controlled NO_x emissions of 500 ppm at 3 percent O_2 (0.61 lb $NO_x/MMBtu$) and 0.61 lb $NO_x/MMBtu$ removed.

No evidence of the use of SNCR for NO_x control on annealing furnaces (or other iron and steel facilities) has been found. However, because of SNCR's similarity to SCR, NO_x emissions from annealing furnaces with SNCR controls are estimated. As discussed in Section 5.2.2.3, favorable temperature windows for the desired reactions differ between SCR and SNCR, and the point of injection for the ammonia or urea reactant will differ. These are design issues that will have to be considered if SNCR is adapted to annealing furnaces. Assuming a control efficiency of 60 percent for the SNCR control unit yields controlled emissions and NO_x removed estimates of 400 ppm at 3 percent O_x (0.49 lb

NO_x/MMBtu) and 0.74 lb NO_x/MMBtu, respectively.²

Similarly, controlled emissions and NO $_{\rm x}$ removed estimates are made for LNB-plus-SNCR-controlled annealing furnaces by assuming a control efficiency of 80 percent (50 percent for LNB control and 60 percent for SNCR control). The resulting estimates are controlled NO $_{\rm x}$ emissions of 200 ppm at 3 percent O $_{\rm 2}$ (0.25 lb NO $_{\rm x}$ /MMBtu) and 0.98 lb NO $_{\rm x}$ /MMBtu removed.

5.3.8.2 <u>Galvanizing Furnaces</u>. Steel products are often coated with a protective layer of zinc, aluminum, terne (a leadtin alloy) or a zinc-aluminum alloy to provide protection against corrosion. This process is called galvanizing. At iron and steel mills, steel sheets, strips, and other products with a light cross section are typically galvanized. A typical moltenzinc bath temperature, for example, is 450 °C (840 °F). 18

Controlled emissions data are available for two, preheated combustion air galvanizing furnaces with LNB plus FGR NO_x controls and one cold combustion air galvanizing furnace with LNB NO_x controls. Controlled NO_x emissions from the preheated combustion air furnaces average 220 ppm at 3 percent O₂ (0.27 lb NO_x/MMBtu). Given uncontrolled emissions (from Chapter 4) of 940-ppm at 3 percent O₂ (1.15 lb NO_x/MMBtu), the LNB plus FGR control efficiency is 77 percent and the NO_x removed is 0.88 lb NO_x/MMBtu.

Controlled NO_x emissions data for the cold combustion air, relatively low-temperature, LNB-controlled galvanizing furnace are given as 21 ppm at 3 percent O_2 (0.026 lb NO_x/MMBtu). In Chapter 4, uncontrolled NO_x emissions for this furnace were estimated from the controlled emissions assuming a 34 percent control efficiency. The NO_x removed is estimated to be 0.014 lb NO_x/MMBtu.

5.4 SUMMARY OF CONTROLLED NO_X EMISSIONS

Table 5-2 summarizes controlled $NO_{\rm x}$ emissions data and estimates for controlled facilities taken from preceding sections of this chapter. The values tabulated in Table 5-2 are used in Chapter 6 to estimate cost effectiveness of the control No controls are reported for coke ovens, sinter techniques. plants, blast furnaces or blast furnace stoves, basic oxygen furnaces, electric arc furnaces, or soaking pits in the United States. The Japan Iron and Steel Federation reports experimental work with coke oven controls (LEA, fuel denitrification, and flue gas denitrification), but no definitive data are provided. They also report experimental work with sinter plant controls (pretreating sinter materials and SCR). 19 Again very little information is provided. This work appears to be experimental, very selectively applied, and not appropriate for application in the United States.

TABLE 5-2. NO_X CONTROLLED EMISSIONS AND PERCENT REDUCTIONS

| L X | | | | | | | | | | | |
|---|--------|-------|---------|-----------|---------|------|------|----------|---------|-------------|---------|
| PERCENT REDUCTION | 13 | 99 | 77 | 50 | 09 | 09 | 82 | 80 | 06 | 20 | 09 |
| EMISSIONS (LB/MMBtu) COLD-AIR | 0.12 | 0.046 | 0.031 | 0.07 | 0.07 | 0.07 | 0.02 | 0.03 | 0.015 | 0.07 | 90.0 |
| EMISSIONS (LB/MMBtu) RECUPERATIVE | 0.17 | 0.068 | 0.046 | 0.20 | 0.16 | 0.16 | 90.0 | 0.08 | 0.04 | 0.20 | 0.16 |
| EMISSIONS (LB/MMBtu) REGENERATIVE | 69.0 | 0.27 | 0.18 | 0.48 | 0.38 | 0.38 | 0.14 | 0.19 | 0.095 | 0.57 | 0.46 |
| CONTROL | LEA | LINB | LNB+FGR | LNB | LNB+FGR | SNCR | SCR | LNB+SNCR | LNB+SCR | LINB | LNB+FGR |
| FURNACE TYPE | REHEAT | | | ANNEALING | | | | | | GALVANIZING | |

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CHAPTER 6

COSTS OF NO_x CONTROLS

In Chapter 5, reheat furnaces, annealing furnaces, and galvanizing furnaces were identified as iron and steel mill processes to which NO_x emissions control techniques have been applied. In this chapter, costs and cost-effectiveness estimates are developed for controls applied to these process facilities. The applicable control techniques for these furnaces are as follows:

| <u>Facility</u> | Control technique |
|---------------------|--|
| Reheat furnace | LEA LNB LNB plus FGR |
| Annealing furnace | LNB SCR SNCR LNB plus FGR LNB plus SCR LNB plus SNCR |
| Galvanizing furnace | LNB LNB plus FGR |

Controls applicable to reheat furnaces are also considered to be applicable to soaking pits because of the similarity of soaking pits and reheat furnaces. They have similar purposes (i.e., they keep or reheat steel to temperatures suitable for further processing), burn the same fuels (usually natural gas), and operate at about the same temperature (e.g., 1,320 °C [2,400 °F]).

Costs and cost-effectiveness estimates are developed for controls for models of each of the three process facilities described above. For each facility, the models correspond, approximately, to small, middle, and large sizes selected from information obtained from iron and steel industry personnel and control apparatus vendors.

All costs are in April 1994 dollars. Costs are based on the Chemical Engineering Plant Cost Index.

No differentiation is made in this chapter between new and retrofit installations of SCR and SNCR NO $_{\rm x}$ control techniques. These control technologies are add-on units, and cost differences would be site-specific. In the case of LNB and LNB plus FGR controls, new burners and associated peripherals (ducts, plumbing, and controls) may not be required in existing burners. For new units the costs associated with combustion modifications are based on the incremental increase in costs for these burners over the cost of an ordinary burner. In the case of LEA, the total capital investment (TCI) costs are for monitors and combustion controls that would be required for either new or retrofit installations.

In lieu of definitive cost data, the following generally accepted relationship for scaling costs between facilities of different size or capacity is used as needed in this chapter:²

Capital costs are annualized as needed in this chapter using the following capital recovery factor:³

$$CRF = \frac{i(1+i)^{n}}{(1+i)^{n}-1} , \qquad (6-2)$$

where

CRF = capital recovery factor,
i = annual interest rate, and

n = system economic life in years.

An interest rate of 7 percent is used in this chapter. The system economic life used, n, was taken from equipment life predictions provided by Section 114 respondents. Cost effectiveness is determined by dividing the total annual cost of the NO_x controls by the tons of NO_x removed per year by the control.

6.1 STEEL REHEAT FURNACES

6.1.1 Model Furnaces

Steel reheat furnace capacities of 75, 150, and 250 tons of steel processed per hour are reasonably representative of small, mid-size, and large furnaces, respectively. Therefore, these capacities are selected as model facilities. Further, a linear regression of available data from 10 examples that define both production capacities (in tons per hour) and fuel firing capacities (in million Btu's/hr) indicates that the corresponding fuel-firing capacities for these three sizes are 140, 300, and

The 10 reheat furnaces used to generate Equation (6-3) use preheated combustion air, i.e., they are either recuperative or regenerative furnaces. However to cover the entire population, reheat furnaces are separated into regenerative, recuperative and cold-air furnaces. The uncontrolled emission factors are shown in Table 4-2 and are listed below. These emission rates are assumed to be relatively constant over a wide range of firing rates and furnace capacities.

| | Uncontrolled Emissions | |
|--------------|-------------------------|-----------------|
| Firing Type | ppm @ 3% O ₂ | <u>lb/MMBtu</u> |
| Regenerative | 645 | 0.792 |
| Recuperative | 220 | 0.200 |
| Cold-air | 110 | 0.135 |
| | | |

6.1.2 <u>Costs and Cost Effectiveness of LEA Control for Reheat Furnaces</u>

Costs and cost-effectiveness estimates for LEA controls for reheat furnaces are based on a single example for which costs and NO, emissions estimates are available. NO, emissions for this furnace are estimated to be reduced by 13% by low excess air. The TCI costs and annual operating costs for this 112-MMBtu/hr furnace are \$101,000 and \$12,500/yr, respectively.4 In Table 6-1, these costs are scaled to the model reheat furnaces using Equation (6-1). Capital costs range from \$120,000 to 260,000. The TCI costs are annualized using Equation (6-2), assuming an economic life of 10 years and 7 percent interest. For each furnace, the annual costs are the sum of the annualized TCI and operating costs. Annual costs range from \$32,000 to 70,000. NO_{x} reductions are computed as the difference between uncontrolled and controlled emissions assuming 8,000 operating hours annually at capacity rate. The cost effectiveness ranges from \$330/ton for the 520-MMBtu/hr regenerative reheat furnace to \$3,200/ton for the 140-MMBtu/hr cold-air reheat furnace. For the same size furnace, cost effectiveness for recuperative and coldair fired furnaces are approximately four and six times that of regenerative furnaces.

6.1.3 <u>Costs and Cost Effectiveness of LNB Control for Reheat</u> Furnaces

The costs and cost effectiveness of LNB controls for regenerative and recuperative-fired reheat furnaces presented here are based on NO_x emission reduction of 66%. LNB costs were

TABLE 6-1. COSTS AND COST EFFECTIVENESS OF LEA FOR REHEAT FURNACES

| | | - | | · · · · · · · | | | | | |
|--|--------------|--------------|----------|---------------|--------------|----------|--------------|--------------|----------|
| Cost Effectiveness (\$/ton) | 550 | 2,100 | 3,200 | 410 | 1,600 | 2,400 | 330 | 1,300 | 1,900 |
| NO _x Reduction (tons/yr) | 09 | 15 | 01 | 120 | 30 | 20 | 220 | 09 | 40 |
| Annual Costs (\$1,000/yr) | 32 | 32 | 32 | 51 | 51 | 51 | 07 | 70 | 70 |
| Operating Costs (\$1,000/yr) | 14 | 14 | 14 | 23 | . 23 | 23 | 32 | 32 | 32 |
| Capital Cost (\$1,000) | 120 | 120 | 120 | 190 | 190 | 190 | 260 | 260 | 260 |
| Firing Type | Regenerative | Recuperative | Cold-air | Regenerative | Recuperative | Cold-air | Regenerative | Recuperative | Cold-air |
| Furnace Capacity (MMBtu/hr) | 140 | | | 300 | | | 520 | | |

determined by using the costs for LNB/FGR for reheat furnaces shown in Section 6.1.4 and multiplying these costs by 0.67. The ratio in TCI's for LNB versus LNB+FGR capital costs is 0.67 for 265 MMBtu/hr natural gas fired boiler in the Industrial/Commercial/Institutional Boiler ACT Document. 10 This. data is used as data was limited for the iron and steel industry. The only data for reheat furnace with LNB were for a 440 MMBtu/hr furnace where the PEC costs were \$300,000 and the total burner system PEC plus direct and indirect installation costs for a 233 TPH(555 MMBtu/hr) furnace under construction are \$ 3,110,000.7 As shown in Table 6-2, TCI for LNB controls for existing model furnaces range from \$ 150,000 to 310,000 and for new furnaces from \$40,000 to 90,000. These costs are annualized using Equation (6-2), assuming a 5-year economic life and 7 percent interest (CRF = 0.244). As shown on Table 6-2, annual costs range from \$ 38,000 to 74,000 for existing furnaces and from \$10,000 to \$21,000 for new furnaces. A control efficiency of 66% was used. Cost effectiveness for new reheat furnaces range from \$20/ton for the 520-MMBtu/hr regenerative-fired reheat furnace to \$ 200/ton for the 140-MMBtu/hr cold-air-fired reheat furnace. Cost effectiveness for existing furnaces range from \$70/ton for the 520-MMBtu/hr regenerative-fired furnace to \$760/ton for the 140-MMBtu/hr cold-air-fired reheat furnace.

6.1.4 Costs and Cost Effectiveness of LNB Plus FGR Control

Purchased equipment costs (PEC) were provided for three examples of LNB plus FGR controls for reheat furnaces. 6,7 Estimates of direct and indirect installation costs were also provided for one of these examples, and the sum of these costs is 106 percent of the PEC. Therefore, to convert PEC into total capital investment (TCI) a factor of 2.8 is used which is consistent with the factors used in other NO, ACT documents. The example furnace capacity is 78 tons/hr (assuming a hot charge) and 154 MMBtu/hr. Thus, it is reasonably consistent with Equation (6-3). Its burner system PEC is \$735,000 and thus, the TCI for this example furnace is \$ 2,060,000 for retrofit installlations (78 TPH). For a new 78 tons/hr reheat furnace the capital cost is 0.275(\$2.0 million) or \$ 550,000. The portion of the TCI attributable to the LNB plus FGR NO_x control system over the TCI of a conventional burner system is 15% of the total. 11 Therefore, the TCI is \$ 230,000.

In Table 6-3, the TCI for the NO_x control system for this example furnace is scaled to the model furnaces using the relationship defined in Equation (6-1). It is recognized that costs for a given facility, new or retrofit, are site-specific and may differ greatly from the values used in this chapter. Capital costs vary from \$ 62,000 to \$130,000 for new sources and from \$230,000 to 460,000 for existing sources.

TABLE 6-2. COSTS AND COST EFFECTIVENESS OF LNB FOR REHEAT FURNACES

| Furnace Capacity (MMBtu/hr) | Firing Type | Capital Cost (\$1,000) | (tal sst 200) | Annua Cost (\$1,000/ | Annual Cost (\$1,000/yr) | NO _x Reduction (tons/yr) | C Effect (\$/ | Cost Effectiveness (\$/ton) |
|-----------------------------------|--------------|------------------------------|---------------------|----------------------------|--------------------------------|---|---------------------|-----------------------------------|
| | | Existing | New | Existing | New | i | Existing | New |
| 140 | Regenerative | 150 | 40 | 40 | 10 | 09 | 130 | 30 |
| | Recuperative | 150 | 9 | 40 | 01 | 15 | 510 | 140 |
| | Cold-air | 150 | 40 | 40 | 10 | 10 | 760 | 200 |
| 300 | Regenerative | 230 | 09 | 09 | 15 | 120 | 8 | 25 |
| | Recuperative | 230 | 09 | 09 | <u>\$1</u> | 30 | 350 | 8 |
| | Cold-air | 230 | 60 | 60 | 15 | 20 | 400 | 140 |
| 520 | Regenerative | 310 | · 8 | 74 | 20 | 220 | 02 | 20 |
| | Recuperative | 310 | 8 | 74 | 82 | 09 | 260 | 75 |
| | Cold-air | 310 | 86 | 74 | 20 | 40 | 390 | 110 |

TABLE 6-3. COSTS AND COST EFFECTIVENESS OF LNB/FGR FOR REHEAT FURNACES

| g New Existing New 60 56 15 60 56 15 60 56 15 90 83 23 90 83 23 90 83 23 130 110 30 130 110 30 | Furnace Capacity (MMBtu/hr) | Firing Type | Capital Cost (\$1,000) | tal st 1000) | Annual Cost (\$1,000/yr) | ual st o/yr) | NO _x Reduction (tons/yr) | C. Effecti (\$/ | Cost Effectiveness (\$/ton) |
|---|-----------------------------------|--------------|------------------------------|--------------------|--------------------------------|-----------------|---|-----------------------|-----------------------------------|
| Regenerative 230 60 56 15 Recuperative 230 60 56 15 Cold-air 340 90 83 23 Regenerative 340 90 83 23 Cold-air 340 90 83 23 Regenerative 460 130 110 30 Recuperative 460 130 110 30 | | | Existing | New | Existing | New | , | Existing | New |
| Recuperative 230 60 56 15 Cold-air 340 90 83 23 Recuperative 340 90 83 23 Cold-air 340 90 83 23 Regenerative 460 130 110 30 Recuperative 460 130 110 30 | 140 | Regenerative | 230 | 09 | 26 | 15 | 340 | 160 | 40 |
| Cold-air 230 60 56 15 Regenerative 340 90 83 23 Recuperative 340 90 83 23 Cold-air 340 90 83 23 Regenerative 460 130 110 30 Recuperative 460 130 110 30 | | Recuperative | 230 | 09 | 56 | 15 | 8 | 620 | 170 |
| Regenerative 340 90 83 23 Recuperative 340 90 83 23 Cold-air 340 90 83 23 Regenerative 460 130 110 30 Recuperative 460 130 110 30 | | Cold-air | 230 | 09 | 26 | 15 | 09 | 930 | 250 |
| Recuperative 340 90 83 23 Cold-air 340 90 83 23 Regenerative 460 130 110 30 Recuperative 460 130 110 30 | 300 | Regenerative | 340 | 8 | 83 | 23 | 730 | 110 | 30 |
| Cold-air 340 90 83 23 Regenerative 460 130 110 30 Recuperative 460 130 110 30 | | Recuperative | 340 | 8 | 83 | 23 | 180 | 460 | 130 |
| Regenerative 460 130 110 30 Recuperative 460 130 110 30 | | Cold-air | 340 | 26 | | 23 | 120 | 069 | 190 |
| 460 130 110 30 | 520 | Regenerative | 460 | 130 | 110 | 30 | 1,300 | 8 | 30 |
| | | Recuperative | 460 | 130 | 110 | 30 | 320 | 340 | 100 |
| 110 30 | | Cold-air | 460 | 130 | 110 | 30 | 220 | 200 | 150 |

The annual costs in Table 6-3 are the annualized costs of the TCI. In lieu of definitive cost data, it is assumed that other cost components, e.g., annual operating costs, are approximately the same as comparable costs for conventional burners and should not be charged to NO_x control. In annualizing these costs, a 5-year life is assumed for the LNB system (estimates from 3 to 7 years are provided), and a 7 percent interest rate is used. These costs are annualized using the capital recovery factor (CRF) defined in Equation (6-2). The CRF is 0.244. Annual costs range from \$15,000 to 32,000 for new reheat furnaces and \$56,000 to 110,000 for existing furnaces.

The ${\rm NO_x}$ reductions in Table 6-3 are computed from the controlled and uncontrolled emissions assuming 8,000 hours of operation per year. A control efficiency of 77% is used to determine emission reductions. For new reheat furnaces, the cost effectiveness ranges from \$ 30/ton for the 520-MMBtu/hr regenerative-fired reheat furnace to \$ 930/ton for the 140-MMBtu/hr cold-air fired reheat furnace. The cost effectiveness for retrofit reheat furnaces are 3-4 times the cost effectiveness of new reheat furnaces.

6.2 ANNEALING FURNACES

6.2.1 Model Furnaces

Information was obtained on four annealing furnaces, one that is operational with an operating history and three that are under construction. All are strip-anneal rather than batch-type furnaces. The operating furnace has LNB plus SCR for $\rm NO_x$ emissions control. 12 Of the furnaces under construction, two will have LNB plus FGR and the third will have SCR for $\rm NO_x$ control. 5,7,13 One of the LNB-plus-FGR-controlled furnaces is nearing completion and some emissions data are available. The furnace capacities are given or estimated from data as 127 ton/hr and 95 MMBtu/hr, 126 ton/hr and 180 MMBtu/hr, and 140 ton/hr and 95 MMBtu/hr. No explanation for the sharp difference in product capacity to firing capacity ratios is provided. For the purposes of this section, furnaces with firing capacities of 100, 200, and 300 MMBtu/hr are selected as model annealing furnaces.

The uncontrolled emission factors used in this section to calculate emission reductions are listed below:

| <u>Firing Type</u> | <u>PPM@ 3% O2</u> | <u>LB/MMBTU</u> |
|--------------------|-------------------|-----------------|
| Regenerative | 645 | 0.792 |
| Recuperative | 220 | 0.200 |
| Cold-air | 110 | 0.135 |

6.2.2 <u>Costs and Cost Effectiveness of LNB Control of Annealing Furnaces</u>

The control efficiency used for LNB control is 50%. Costs and cost effectiveness are shown in Table 6-4. Cost estimates for LNB controls are calculated by multiplying the cost of LNB/FGR as given in Section 6.2.4 by 0.67 as was done for reheat furnaces. Only cost data for LNB/FGR were available for annealing furnaces. The results of these estimates are presented As was done earlier for reheat furnaces, the in Table 6-4. capital costs for new furnaces was determined by multiplying the costs for existing furnaces by 0.275. Capital costs for retrofit applications vary from \$ 360,000 to 690,000 and for new sources from \$100,000 to 190,000. To determine annual costs a life of 10 years and an interest rate of 7% were used. Annual costs for existing furnaces vary from \$50,000 to 98,000 and for new annealing furnaces from \$14,000 to 27,000. For existing annealing furnaces, cost effectiveness ranges from \$170/ton for a 300 MMBtu/hr regenerative furnace to \$1,680/ton for a 100 MMBtu/hr regenerative furnace. For new annealing furnaces, the cost effectiveness range from \$50/ton for the 300-MMBtu/hr regenerative annealing furnace to \$470/ton for the 100-MMBtu/hr annealing furnace fired with cold-air.

6.2.3 Costs and Cost Effectiveness of LNB plus FGR

The control efficency for this control was estimated to be 60%. This reflects the efficiency achieved by this control for boilers. Costs for an LNB+FGR controlled, 180-MMBtu/hr annealing furnace are estimated as \$2,400,000 for the burner system PEC. 5,7 Using the 106 % (for installation costs costs) and 15 % (LNB plus FGR cost premium over a conventional burner system). TCI estimate of \$760,000 for LNB+FGR control for 180 MMBtu/hr is obtained. Equation 6-1 is used to calculate costs for the model furnace sizes.

In Table 6-5, the costs and cost effectiveness of the LNB plus FGR control for model annealing furnaces are given. For new annealing furnaces, capital costs range from \$150,000 to \$280,000; annual costs from \$21,000 to 40,000 and cost effectiveness from \$60/ton to 530/ton. Only the cold-air furnaces had cost effectiveness greater than \$220/ton. For existing annealing furnaces, capital costs range from \$530,000 to 1.03 million; annual costs from \$75,000 to 146,000 and cost effectiveness from \$210/ton to 1,900/ton.

6.2.4 <u>Costs and Cost Effectiveness of SNCR for Annealing Furnaces</u>

SNCR has not been applied to any iron and steel mill facilities. However, the similarity of SNCR to SCR suggests that

TABLE 6-4. COSTS AND COST EFFECTIVENESS OF LNB FOR ANNEALING FURNACES

| Furnace Capacity | Firing Type | Capital Cost | ital Sst | Annual | nual ost | NO _x Reduction | C Effect | Cost Effectiveness |
|---------------------|--------------|-----------------|-------------|----------|-------------|------------------------------|-------------------------|-----------------------|
| (IVIIVEDIU/III) | | (m,1¢) | (m) | D,(1¢) | (1,000,11) | (tons/yr) | \earticle (\frac{1}{2}) | (\$/ton) |
| | | Existing | New | Existing | New | · | Existing | New |
| 100 | Regenerative | 360 | 100 | 50 | 14 | 190 | 260 | 70 |
| | Recuperative | 360 | 100 | 20 | 14 | 80 | 640 | 180 |
| | Cold-air | 360 | 100 | 20 | 41 | 30 | 1680 | 470 |
| 200 | Regenerative | 540 | 150 | 77 | .21 | 380 | 200 | 55 |
| | Recuperative | 540 | 150 | 11 | 21 | 160 | 480 | 130 |
| | Cold-air | 540 | 150 | 77 | 21 | 09 | 1280 | 350 |
| 300 | Regenerative | 069 | 190 | 86 | 27 | 280 | 170 | 50 |
| | Recuperative | 069 | 190 | 86 | 27 | 240 | 400 | 110 |
| | Cold-air | 069 | 190 | 86 | 27 | % | 1100 | 300 |

TABLE 6-5. COSTS AND COST EFFECTIVENESS OF LNB/FGR FOR ANNEALING FURNACES

| Cost Effectiveness (\$/ton) | New | 8 | 210 | 530 | 70 | 160 | 440 | 09 | 130 | 400 |
|-------------------------------------|----------|--------------|--------------|----------|--------------|--------------|----------|--------------|--------------|----------|
| C Effect (\$/ | Existing | 320 | 750 | 1900 | 260 | 280 | 1600 | 210 | 490 | 1500 |
| NO _x Reduction (tons/yr) | | 230 | 100 | 40 | 450 | 200 | 70 | 089 | 300 | 100 |
| Annual Cost (\$1,000/yr) | New | 70 | 70 | 20 | 30 | 30 | 30 | 8 | 6 | 40 |
| Annual Cost (\$1,000/y | Existing | 75 | 75 | 75 | 120 | 120 | 120 | 150 | 150 | 150 |
| tal st 000) | New | 150 | 150 | 150 | 220 | 220 | 220 | 280 | 280 | 280 |
| Capital Cost (\$1,000) | Existing | 230 | 530 | 530 | 810 | 810 | 810 | 1030 | 1030 | 1030 |
| Firing Type | | Regenerative | Recuperative | Cold-air | Regenerative | Recuperative | Cold-air | Regenerative | Recuperative | Cold-air |
| Furnace Capacity (MMBtu/hr) | | 100 | | - | 200 | | | 300 | | |

SNCR is potentially applicable to facilities that are controlled with SCR provided the flue gas stream to be controlled has a suitable temperature for the SNCR reaction to proceed. As discussed in Chapter 5, a temperature suitable for the SNCR control reaction to proceed is much higher than the temperature required for the SCR control reaction. SNCR is considered feasible for annealing furnaces and the potential control costs and cost effectiveness of SNCR were developed.

Cost estimates have been developed for SNCR applications to process heaters. In the process heater ACT, TCI for an SNCR unit for an 80-MMBtu/hr heater is \$392,000. In lieu of better data, it is assumed that this TCI is the same as for an SNCR unit for an annealing furnace of the same firing capacity. In Table 6-6, TCI for the model annealing furnaces are scaled from the process heater example using Equation (6-1). Capital costs range from \$460,000 to 880,000.

Operating costs are modeled in Reference 14 as follows:

- 1. NH_3 Costs = (Q)*(lb $NO_x/MMBtu$)* [0.370 (lb per mole NH_3/lb per mole NO_x)]*(mole $NH_3/mole$ NO_x)*(\$/lb NH_3)*(8,760 hr/yr)*(CF), (6-5)
- 2. Electricity Costs = $(0.3 \text{ kWh/ton NH}_3) * (\text{tons NH}_3/\text{yr}) * (\$/\text{kWh})$, and (6-6)
- 3. Fuel Penalty Costs = $(0.015)*(Q)*(8,760 \text{ hr/yr})*($ \text{ fuel } \cos ts/MMBtu)*(CF),$ (6-7)

where Q is the furnace-firing capacity in MMBtu/hr and CF is the capacity factor, i.e., operating hours per year/8,760. The tons of NH $_3$ /yr value in Equation (6-6) is computed as (Q)*(controlled emissions-uncontrolled emissions)*[0.370(lb per mole NH $_3$ /lb per mole NO $_x$)]* (moles NH $_3$ /moles NO $_x$)*(CF)*(8760/2000). The 0.3 kWh/ton NH $_3$ value is taken from Reference 14. The fuel penalty cost estimate (1.5 percent or the 0.015 factor in Equation 6-7) represents a loss in thermal efficiency in a process heater and is used here to account for possible thermal losses from using SNCR on an annealing furnace. I

For the purposes of this section, the parameter values used in the operating cost models are as follows:

Natural gas costs = $$3/10^3$ ft³, NH₃ cost = \$164/ton, Moles NH₃/moles NO_x = 1.5, \$/kWh = 0.07, and CF = 8000/8760.

TABLE 6-6. COSTS AND COST EFFECTIVENESS OF SNCR FOR ANNEALING FURNACES

| Furnace Capacity (MMBtu/hr) | Firing Type | Capital Cost (\$1,000) | Annual Operating Costs (\$1,000/yr} | Total Annual Costs (\$1,000/yr) | NO _x Reduction (tons/yr) | Cost Effectiveness (\$/ton) |
|-----------------------------------|--------------|------------------------------|-------------------------------------|---------------------------------|---|-----------------------------------|
| | | | | | | |
| 100 | Regenerative | 460 | 08 | 150 | 230 | , 0 59 |
| | Recuperative | 460 | 08 | 150 | 100 | 1500 |
| | Cold-air | 460 | 80 | 150 | 40 | 3800 |
| 200 | Regenerative | 069 | 160 | 260 | 450 | 280 |
| | Recuperative | 069 | 160 | 260 | 200 | 1300 |
| | Cold-air | 069 | 160 | 260 | 70 | 3700 |
| 300 | Regenerative | 088 | 240 | 370 | 089 | 540 |
| | Recuperative | 880 | 240 | 370 | 300 | 1200 |
| | Cold-air | 880 | 240 | 370 | 100 | 3700 |

The annual operating costs are estimated using the preceding models and parameters. The total annual costs are the sum of the annualized TCI plus the annual operating costs. Costs are the same for both existing and new furnaces although there may be a wide variation in costs from one furnace to another. As shown on Table 6-6, the total annual costs range from \$150,00 to 370,000.

The NO_x reductions in Table 6-6 are estimated with a NO_x reduction efficiency of 60%. Eight thousand hours of operation per year at furnace capacities is assumed. The cost effectiveness ranges from \$540/ton for the regenerative-fired 300-MMBtu/hr annealing furnace to \$3,800/ton for the 100-MMBtu/hr cold-air furnace.

6.2.5 Costs and Cost Effectiveness of SCR Control

The control efficiency assumed for SCR is 85%. The PEC for an SCR unit in a construction permit for an 95 MMBtu/hr annealing furnace is \$1.25 million. Converting this to April 1994 \$(multiplying by 1.018), converting PEC to TCI by multiplying by 2.06 and using Equation 6-1, the capital costs as shown in Table 6-7 range from \$2.7 million to \$5.1 million. annual operating and maintenance costs were determined by using the costs in the Process Heaters ACT Document for the 69 MMBtu/hr distillate oil-fired heater and using Equation 6-1.14 The total annual costs are the sum of the annual o&m costs and the annualization of the total capital costs. An interest rate of 7% and a life of 10 years were used to calculate the annualization of capital costs. As shown on Table 6-7, annual costs range from \$550,000 to \$1,040,000. Also on this Table, cost effectiveness varies from \$1,100/ton to \$11,000/ton. Only the regenerative fired annealing furnaces have cost effectiveness less than \$2,000/ton.

6.2.6 <u>Costs and Cost Effectiveness of LNB plus SNCR for Annealing Furnaces</u>

The control efficiency for LNB plus SNCR was estimated to be 80%. Capital and annual cost estimates for these controls are taken by adding the respective numbers in Tables 6-4 (for LNB) and 6-6 (for SNCR). The resulting estimates of costs, NO_x reduction, and cost effectiveness are tabulated in Table 6-8. For existing annealing furnaces, capital costs range from \$820,000 to \$1.6 million; annual costs from \$200,000 to 470,000 and cost effectiveness from \$520/ton to 5,000/ton. For new annealing furnaces, capital costs range from \$560,000 to \$1.1 million; annual costs from \$160,000 to 400,000 and cost

TABLE 6-7. COSTS AND COST EFFECTIVENESS OF SCR FOR ANNEALING FURNACES

| Furnace Capacity (MMBtu/hr) | Firing Type | Capital Cost (\$10°) | Total Annual Cost (\$1,000/yr) | NO _x Reduction (tons/yr) | Cost Effectiveness (\$/ton) |
|-----------------------------------|--------------|----------------------------|---|---|-----------------------------------|
| | · | | | | |
| 100 | Regenerative | 2.7 | 550 | 320 | 1,700 |
| | Recuperative | 2.7 | 250 | 130 | 4,200 |
| | Cold-air | 2.7 | 550 | 20 | 11,000 |
| 200 | Regenerative | 4.0 | 790 | 640 | 1,200 |
| | Recuperative | 4.0 | 790 | 270 | 2,900 |
| | Cold-air | 4.0 | 790 | 110 | 7,200 |
| 300 | Regenerative | 5,1 | 1,040 | 096 | 1,100 |
| | Recuperative | 5.1 | 1,040 | 410 | 2,500 |
| | Cold-air | 5.1 | 1,040 | 150 | 6,900 |

TABLE 6-8. COSTS AND COST EFFECTIVENESS OF LNB+SNCR FOR ANNEALING FURNACES

| Furnace Capacity (MMBtu/hr) | Firing Type | Capital Cost (\$10 ⁶) | tal st) ⁶) | Annual Cost (\$1,000/yr) | iual sst 00/yr) | NO _x Reduction (tons/yr) | C Effect (\$/ | Cost Effectiveness (\$/ton) |
|-----------------------------------|--------------|---|-------------------------------|--------------------------------|-----------------------|---|---------------------|-----------------------------------|
| | | Existing | New | Existing | New | | Existing | New |
| 100 | Regenerative | 0.82 | 0.56 | 200 | 160 | 300 | 0/9 | 530 |
| | Recuperative | 0.82 | 0.56 | 200 | 160 | 120 | 1700 | 1300 |
| | Cold-air | 0.82 | 0.56 | 700 | 160 | 40 | 5000 | 4000 |
| 200 | Regenerative | 1.2 | 0.84 | 340 | 280 | 009 | 570 | 470 |
| | Recuperative | 1.2 | 0.84 | 340 | 280 | 250 | 1100 | 1100 |
| | Cold-air | 1.2 | 0.84 | 340 | 280 | 100 | 3400 | 2800 |
| 300 | Regenerative | 1.6 | 1.1 | 470 | 400 | 006 | 520 | 440 |
| | Recuperative | 1.6 | 1:1 | 470 | 400 | 380 | 1200 | 1050 |
| | Cold-air | 1.6 | 1.1 | 470 | 400 | 140 | 3400 | 2900 |

effectiveness from \$440/ton to \$4,000/ton. Only the cold-air annealing furnace has cost effectiveness greater than \$2,000/ton.

6.2.7 <u>Costs and Cost Effectiveness of LNB plus SCR for Annealing</u>. Furnaces

The control efficiency for LNB plus SCR is 90%. Capital and annual costs for the LNB-plus-SCR are estimated by adding the respective numbers in Tables 6-4 (for LNB) and 6-7 (for SCR). NO, reductions used in these computations are based on an assumed 8,000 hours of operation per year at furnace-firing capacities. As shown in Table 6-9, for existing annealing furnaces, capital costs range from \$ 3.1 million to 5.8 million; annual costs from \$600,000 to \$1.14 million and cost effectiveness from \$1,100/ton to \$12,000/ton. For new annealing furnaces, capital costs range from \$2.8 million to 5.3 million; annual costs from \$560,000 to 1.07 million and cost effectiveness from \$1,000 to 11,000/ton. Only the regenerative furnace had cost effectiveness less than \$2,000/ton.

6.3 GALVANIZING FURNACES

6.3.1 Model Furnaces

Information was obtained on three galvanizing furnaces. One is a 79-ton/hr furnace, and the firing capacity of this furnace is estimated from a test report to be 150-MMBtu/hr. Firing capacities of the other two are given as 38 MMBtu/hr and 179 MMBtu/hr. Using these furnaces as representative of galvanizing furnaces, firing capacities of 50, 150, and 200 MMBtu/hr are selected as model furnaces. The 150-MMBtu/hr furnace has LNB's for NO_x control, is a cold combustion air furnace, and its operating temperature is several hundred Fahrenheit degrees below many other galvanizing furnaces. The other two furnaces have LNB plus FGR for NO_x control and are preheated combustion air furnaces.

The uncontrolled emission factors used to calculate emission reductions are shown below:

| Firing Type | | mqq | @ 3%O ₂ | lb/MM | Btu |
|--------------|-----|-----|--------------------|----------|-----|
| Regenerative | | 940 | | 1.15 | + 4 |
| Recuperative | • * | 330 | | 0.40 | |
| Cold-Air | | 120 | | 0.14 | *** |

6.3.2 <u>Costs and Cost Effectiveness of LNB Plus FGR Controls for Galvanizing Furnaces</u>

Burner system purchased equipment costs for the 38-MMBtu/hr and 179-MMBtu/hr furnaces are given as \$511,000 and \$1,430,000, respectively. Assuming the 106 percent (for installation costs)

TABLE 6-9. COSTS AND COST EFFECTIVENESS OF LNB+SCR FOR ANNEALING FURNACES

| Furnace Capacity (MMBtu/hr) | Firing Type | Capital Cost (\$10°) | ital sst 0 ⁶) | Annual Cost (\$1,000/yr) | nual 13st 10/yr) | NO _x Reduction (tons/yr) | C Effect (\$/ | Cost Effectiveness (\$/ton) |
|-----------------------------------|--------------|----------------------------|---------------------------------|--------------------------------|------------------------|---|---------------------|-----------------------------|
| | | Existing | New | Existing | New | | Existing | New |
| 100 | Regenerative | 3.1 | 2.8 | 009 | 260 | 340 | 1,800 | 1,600 |
| | Recuperative | 3.1 | 2.8 | 009 | 260 | 140 | 4300 | 4,000 |
| | Cold-air | 3.1 | 2.8 | 009 | 260 | 920 | 12,000 | 11,000 |
| 200 | Regenerative | 4.5 | 4.1 | 870 | 810 | 089 | 1,300 | 1,200 |
| | Recuperative | 4.5 | 4.1 | 870 | 810 | 280 | 3,100 | 2,900 |
| | Cold-air | 4.5 | 4.1 | 870 | 810 | 110 | 7,900 | 7,400 |
| 300 | Regenerative | 5.8 | 5.3 | 1,140 | 1,070 | 1020 | 1,100 | 1,000 |
| - | Recuperative | 5.8 | 5.3 | 1,140 | 1,070 | 430 | 2,600 | 2,500 |
| | Cold-air | 5.8 | 5.3 | 1,140 | 1,070 | 160 | 7,100 | 6,700 |

and 15 percent (cost premium for LNB plus FGR as compared with conventional burner systems) factors, the TCI costs for NO_x control for the two burner systems are \$158,000 and \$442,000, respectively. These costs were converted to April 1994 \$ by multiplying by 1.018. A cost was obtained per MMBTU (\$4,240 for 38 MMBtu/hr and \$2,510/MMBtu) for the 179 MMBtu/hr. For the 50 MMBtu/hr model furnace, the capital cost for existing galvanizing furnaces was determined by multiplying 50 by \$4,240. For the 150 and 200 MMBtu/hr furnaces, \$2,510/MMBtu was used. The capital costs for new galvanizing furnaces were determined by multiplying the capital costs for existing furnaces by 0.275. As shown on Table 6-10, capital costs for existing furnaces range from \$210,000 to 500,000 and for new furnaces from \$60,000 to 140,000.

Operating costs are assumed to be approximately the same as operating costs for a conventional burner system and, thus, not chargeable to NO_x control. Capital costs were annualized using an useful life of 9 years and an interest rate of 7% giving a CRF of 0.153. Annual costs for existing furnaces range from \$32,000 to 77,000 and for new furnaces \$9,000 to 21,000.

The control efficiency estimated for LNB + FGR is 60%.

The emission reductions shown on Table 6-10 are also based on anassumed 8,000 operating hours per year at furnace-firing
capacity. Cost effectiveness for existing furnaces range from
\$140/ton to 2,000/ton. For new furnaces, cost effectivenes range
from \$40/ton to 560/ton.

6.3.3 <u>Costs and Cost Effectiveness of LNB for Galvanizing</u> <u>Furnaces</u>

In lieu of any cost data for the LNB-controlled galvanizing furnace, the cost estimates used in Table 6-10 for the LNB-plus-FGR-controlled model furnaces are multiplied by 0.67 to obtain the costs for LNB only controls. This is the same factor used earlier to calculate costs for these combustion controls for reheat and annealing furnaces.

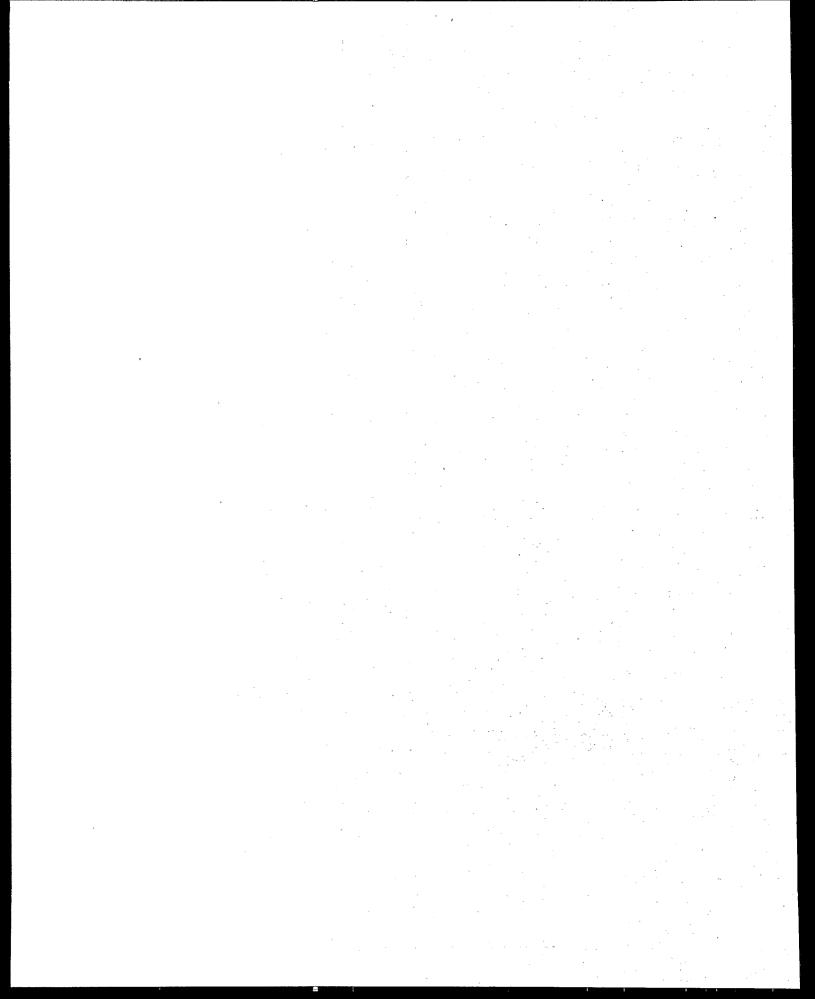
LNB is assumed to reduce NO_x by 50%. This estimate is used to compute the NO_x reductions included in Table 6-11. These reductions are based on an assumed 8,000 operating hours per year at furnace- firing capacity. The capital costs range from \$140,000 to 340,000 for existing furnaces and 40,000 to 90,000 for new furnaces. Annual costs range from \$21,000 to 52,000 for existing furnaces and from 6,000 to 14,000 for new furnaces. Cost effectiveness range from \$110/ton to \$1,500/ton for existing furnaces and from \$30/ton to 430/ton.

TABLE 6-10. COSTS AND COST EFFECTIVENESS OF LNB+FGR FOR GALVANIZING FURNACES

| Furnace Capacity (MMBtu/hr) | Firing Type | Capital Cost (\$1,000) | (tal sst 2000) | Annual Cost (\$1,000/5 | Annual Cost (\$1,000/yr) | NO _x Reduction (tons/yr) | C Effect (\$/ | Cost Effectiveness (\$/ton) |
|-----------------------------------|--------------|------------------------------|----------------------|------------------------------|--------------------------------|---|---------------------|-----------------------------|
| | | Existing | New | Existing | New | | Existing | New |
| 20 | Regenerative | 210 | 09 | 32 | 6 | 140 | 230 | 70 |
| | Recuperative | 210 | 09 | 32 | 6 | 50 | 640 | 180 |
| | Cold-air | 210 | 09 | 32 | 6 | 20 | 2000 | 260 |
| 100 | Regenerative | 380 | 100 | .58 | 15 | 420 | 140 | 40 |
| | Recuperative | 380 | 100 | 28 | 15 | 140 | 410 | 110 |
| | Cold-air | 380 | 100 | 58 | 15 | 50 | 1200 | 300 |
| 150 | Regenerative | 200 | 140 | 77 | 21 | 250 | 140 | . 64 |
| | Recuperative | 200 | 140 | 71 | 21 | 190 | 400 | 110 |
| | Cold-air | 200 | 140 | 77 | 21 | 70 | 1100 | 300 |

TABLE 6-11. COSTS AND COST EFFECTIVENESS OF LNB - GALVANIZING FURNACES

| Furnace Capacity (MMBtu/hr) | Firing Type | Capital Cost (\$1,000) | tal st x00) | Annual Cost (\$1,000/yr) | ual sst (O/yr) | NO _x Reductio n (tons/yr) | Cost Effectiveness (\$/ton) | Cost ectiveness (\$/ton) |
|-----------------------------------|--------------|------------------------------|-------------------|--------------------------------|----------------------|--------------------------------------|-----------------------------------|--------------------------------|
| | | Existing | New | Existing | New | | Existing | New |
| 20 | Regenerative | 140 | 40 | 21 | 9 | 110 | 190 | 09 |
| | Recuperative | 140 | 40 | 21 | 9 | 40 | 230 | 150 |
| | Cold-air | 140 | 40 | 21 | 9 | 41 | 1500 | 430 |
| 100 | Regenerative | 250 | 02 | 39 | 10 | 340 | 110 | 30 |
| | Recuperative | 250 | 70 | 39 | 10 | 120 | 320 | 08 |
| | Cold-air | 250 | 70 | 39 | 10 | 40 | 900 | 230 |
| 150 | Regenerative | 340 | 06 | 52 | 14 | 450 | 110 | 30 |
| | Recuperative | 340 | 06 | 52 | 14 | 160 | 320 | 06 |
| | Cold-air | 340 | 90 | 52 | 14 | 09 | 870 | 230 |



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CHAPTER 7

ENVIRONMENTAL AND ENERGY IMPACTS OF NO, CONTROLS

7.1 INTRODUCTION

This chapter discusses the environmental and energy impacts of the NO_x emissions control techniques identified in Chapter 5. The control techniques that have been applied or are potentially applicable to iron and steel mill process facilities are the following:

| <u>Facility</u> | Control technique |
|---------------------|--|
| Reheat furnace | LNB LEA LNB plus FGR |
| Annealing furnace | LNB SCR SNCR LNB plus FGR LNB plus SCR LNB plus SNCR |
| Galvanizing furnace | LNB LNB plus FGR |

Of these control techniques, LNB's, FGR, and LEA are combustion modification techniques, and SCR and SNCR are postcombustion control techniques. Potentially, all techniques can impact other air emissions in addition to NO_x , and all may have energy impacts. None have water pollution impacts. However, SCR may have a solid waste impact.

7.2 AIR IMPACTS

7.2.1 NO Emission Reductions

 ${
m NO_x}$ emission reductions for the emission control techniques are summarized in Table 7-1. Control efficiencies range from 13 percent for LEA on a reheat furnace to 90 percent for LNB plus SCR on an annealing furnace. Emission reductions range from 40 tons/yr for LNB control on a 150-MMBtu/hr, cold-air galvanizing furnace to 730 tons/yr for LNB plus FGR controls on a 300-MMBtu/hr regenerative reheat furnace. The cold-air galvanizing furnace reduction is low because the uncontrolled ${
m NO_x}$ emissions are low for this relatively low-temperature furnace.

TABLE 7-1. NO_X EMISSION REDUCTIONS - IRON AND STEEL MILL PROCESSES

| ION) NIR | | | | | | | | , | | | |
|---|--------|-----|-----------|-----------|-----------|------|-----|-------------|------------|-------------|------------|
| NO _X REDUCTION (TPY) COLD-AIR | 20 | 110 | 120 | 9 | 70 | 70 | 105 | 100 | 110 | 40 | 20 |
| NO _X REDUCTION (TPY) RECUPERATIVE | 30 | 160 | 180 | 160 | 200 | 200 | 270 | 250 | 280 | 120 | 140 |
| NO _x REDUCTION (TPY) REGENERATIVE | 120 | 620 | 730 | 380 | 450 | 450 | 640 | 009 | 089 | 340 | 420 |
| MID-SIZE CAPACITY (MMBtu/hr) | 300 | 300 | 300 | 200 | 200 | 200 | 200 | 200 | 200 | 150 | 150 |
| CONTROL | LEA | LNB | LNB + FGR | LNB | LNB + FGR | SNCR | SCR | LINB + SNCR | LINB + SCR | LNB | LINB + FGR |
| FURNACE TYPE | REHEAT | | | ANNEALING | | | | | | GALVANIZING | |

7.2.2 Air Impacts of Combustion Modifications

Combustion modification techniques applied to process facilities at iron and steel mills are LNB's, LNB's with external FGR, and LEA. LNB's incorporate one or more of the following combustion modification techniques: LEA, off-stoichiometric or staged combustion (either staged air or staged fuel), and FGR. Any of these combustion modification techniques have the potential to increase carbon monoxide and unburned hydrocarbon The NO_x reduction mechanisms inherent in these emissions. modification techniques are the reduction of peak flame temperatures that are exponentially related to the formation of thermal NO, and the reduced availability of excess oxygen needed to form NO. Reducing the availability of oxygen to the combustion process increases the likelihood that some HC will not be burned and that some CO will not be oxidized to CO2. However, it is not necessarily true that CO or HC emissions will increase if combustion modification techniques are used to limit NO, emissions. If the control is properly designed and applied, NO, control can be achieved without increasing CO or HC emissions. Experimental evidence from tests with process heaters, for example, indicate that decreases in excess oxygen levels begin to impact CO emissions below about 3 percent excess oxygen. Also, data from glass melting furnaces indicate that CO emissions begin to increase at excess oxygen levels of 3.2 percent. Limited data for ICI boilers indicate that HC emissions do not change due to the implementation of combustion modifications. Data in the utility boiler ACT show that CO emissions increase for some boilers and decrease for some boilers when implementing combustion modifications.4

For the steel reheat furnace with LEA for NO_x control, CO emissions of 39 ppm at 3 percent O_2 and 26 ppm at 3 percent O_2 are reported for the uncontrolled and controlled tests, respectively. These results indicate that CO emissions do not necessarily increase when LEA is implemented for NO_x control. It should be noted that, in this example, LEA is actually implemented using a PID control loop that functions to satisfy a CO ppm setpoint input. As the furnace operates independently to achieve individual zone temperature setpoints, the CO control loop continuously adjusts zone oxygen setpoints to minimize excess oxygen via the air-to-fuel ratio in each zone without violating the CO controller setpoint.

Other available sources report CO emissions from LNB-controlled reheat furnaces to be in the range of 20 to 30 ppm at 3 percent O_2 . Further, laboratory and field tests on a galvanizing furnace yielded NO_x emissions of 550 to 1,200 ppm at 3 percent O_2 and, concurrently, negligible CO emissions. Modifications to the burners reduced NO_x emissions to 350 to 430 ppm at 3 percent O_2 and, concurrently, increased CO emissions to

30 to 60 ppm at 3 percent O_2 . The purpose of the modifications was to reduce NO, and further modifications were planned.

No data are available relevant to the impact of NO_x control techniques on HC emissions from these iron and steel facilities. In general, controls that reduce NO_x by reducing the availability of excess oxygen in the high-temperature regions of a furnace would tend to increase both CO and HC emissions if the control were not properly designed and applied. In each case, given the availability of oxygen, available CO and HC molecules could be further oxidized according to the following reactions:

$$2CH_4 + 3O_2 \rightarrow 2CO + 4H_2O$$
 (7-1)
 $2CO + O_2 \rightarrow 2CO_2$ (7-2)

The reaction rates for HC to $\rm H_2O$ + CO and CO to $\rm CO_2$ differ; thus, they are competing reactions. Nevertheless, reducing the availability of oxygen to reduce $\rm NO_x$ can also inhibit these reactions, resulting in an increase in both CO and HC emissions if the oxygen availability is reduced excessively.

Reheat, annealing, and galvanizing furnaces predominantly use natural gas as a fuel. Natural gas does not contain sulfur, and thus, SO_2 is not a pollutant of concern. Gaseous fuels, including natural gas, can produce soot and carbon black when burned if insufficient oxygen is present. However, no information on the effect of NO_x controls on particulate emissions in iron and steel facilities is available.

7.2.3 Air Impacts of SCR and SNCR

As described in Chapter 5, SCR units are add-on, flue gas treatment facilities that reduce NO_x by injecting ammonia upstream of a catalyst reactor. Within the catalyst, NO_x reacts with the NH_3 and is reduced to N_2 and H_2O . There is a potential for unreacted NH_3 to escape with the flue gas from the SCR unit. Any such emissions are referred to as ammonia slip.

Section 114 respondents cite two instances of SCR controls on annealing furnaces at iron and steel mills. One of these units is operational with more than 3 years' operating history, and one is still under construction. In the case of the former, the NH $_3$ slip was guaranteed to be less than 10 ppm initially and less than 12 ppm after 1 year. The observed NH $_3$ was initially less than 10 ppm. Subsequent observations are not reported. The typical NH $_3$ /NO $_x$ molar ratio for this unit is 0.9.11

For the unit under construction, a NO_x reduction of 90 percent is guaranteed. The anticipated NH_3/NO_x molar ratio is 1.0. There is no NH_3 slip quarantee. The construction permit

requires 80 percent NO_x reduction and a minimum NH_3/NO_x molar ratio of 0.8. There are no requirements relevant to NH_3 slip.

Other reports indicate that NO_x removal rates of 70 to 90 percent can be achieved with SCR using NH₃/NO_x molar ratios between 0.9 and 1.0, and that the NH₃ slip will be between 5 and 10 ppm. These levels are considered to be well below health and odor thresholds. The Occupational Safety and Health Administration (OSHA) standard for NH₃ in the workplace is 25 to 30 ppm, and in the atmosphere it tends to form nonhazardous compounds and disappear within 2 weeks. In other applications in the United States, permitted NH₃ slip levels are often on the order of 5 to 10 percent. In Europe, 5 ppm is typically specified and achieved, and levels as low as 0.5 to 2.0 ppm have been achieved; and in Japan, levels as low as 4 ppm are specified. The specified of the specified of the specified of the specified of the specified.

No examples of SNCR applications to iron and steel mill process facilities have been found. In other SNCR applications, ammonia slip is controlled to acceptable levels by controlling the ammonia or urea to NO, molar ratio. These levels are similar to ammonia emissions from SCR applications, e.g., 10 ppm.

Pilot-scale testing and chemical kinetic modeling of SNCR processes have shown that nitrous oxide emissions are a byproduct of both ammonia and urea injection. The N_2O formation resulting from these processes has been shown to be dependent on the reagent used, the amount of reagent injected, and the injection temperature. ¹⁵

Full-scale tests on fossil-fuel-fired boilers have shown that direct emissions of $\rm N_2O$ are less than 15 ppm and do not generally correlate with NO $_{\rm x}$ emissions. Results from tests on a small pilot-scale combustor using NH $_{\rm 3}$ injection and encompassing a range of test conditions show a maximum N $_{\rm 2}O$ production of about 45 ppm corresponding to an initial NO level of 700 ppm, an NH $_{\rm 3}$ injection rate corresponding to a NH $_{\rm 3}/NO$ molar ratio of 2, and a temperature of 880 °C (1,620 °F). The corresponding NO $_{\rm x}$ reduction was 75 percent. The peak NO $_{\rm x}$ reduction corresponding to an initial NO level of 700 ppm and an N/NO ratio of 2 was about 95 percent at 980 °C (1,800 °F). The corresponding N $_{\rm 2}O$ production was about 21 ppm or 3 percent of the NO $_{\rm x}$ reduction. 15

 N_2 O production is higher for urea injection than for NH_3 injection. Given the same initial NO level (700 ppm) and reactant-to- NO_x ratio (corresponding to a NH_3/NO molar ratio of 2), the peak N_2 O production was about 160 ppm at 980 °C (1,800 °F) and the corresponding NO_x reduction was at a peak value of about 82 percent. Thus the N_2 O production was about 28 percent of the NO_x reduction. 15

Other pilot-scale tests have shown that, with urea injection, the level of CO present affects the NO_x removal efficiency and the NO_x removal temperature dependency. The presence of CO also affects N_2O by-product emissions. In the temperature range of 820 to 870 °C (1,500 to 1,600 °F), for example, increasing CO from 0 to 1,000 ppm caused an increase in N_2O emissions from 10 to 35 ppm. The initial NO_x level was 125 ppm and the NH_3/NO ratio was 2.16

7.3 SOLID WASTE IMPACTS

Combustion modifications do not have solid waste environmental impacts. There is a potential for SCR to have solid waste impacts in the disposal of spent catalyst materials.

Titanium dioxide and "vanadia/titania" have been identified as the catalysts in the two SCR annealing furnace applications cited. Other commonly used materials are vanadium pentoxide, tungsten trioxide, platinum, zeolites, and ceramics. Of these, vanadium pentoxide is a toxic compound and a cause for concern. However, worker safety precautions adequately prevent any increased risk to workers handling the catalyst, and stack emissions of vanadium pentoxide are 1 million times less than industrial worker exposure.

Most catalyst manufacturers arrange to recycle and reactivate the catalyst. When that is not practical, the spent catalyst can be disposed in an approved landfill in accordance with the Land Disposal Restrictions in 40 CFR Part 268, Subpart D. The volume of catalyst materials has been low and their useful lives are 4-5 years for coal-fired boilers, 7-10 years for oil-fired boilers, and more than 10 years for gas-fired boilers.¹³

7.4 ENERGY IMPACTS

All of the combustion modification control techniques have the potential to impact energy requirements by affecting the thermal efficiency of the process. No data are available to quantify the impact of these controls on iron and steel mill process facilities. A lack of discussion of these issues in the literature suggests that these impacts, if any, are not a major concern in installations using combustion modifications.

In the case of the SCR, the pressure drop across the catalyst requires additional electrical energy for the flue gas fan. Typical flue gas velocities over the catalysts are about 20 ft/s, and the pressure drop is about 3 inches of water. The volume flow of one typical unit is 1,550 ft³/m. Given these parameters and assuming an efficiency of 0.65 for the motor and fan, the additional power demand is 0.84 kW, which corresponds to

\$540/yr assuming 8,000 hours of operation per year and electricity at 8¢/kWh. 17

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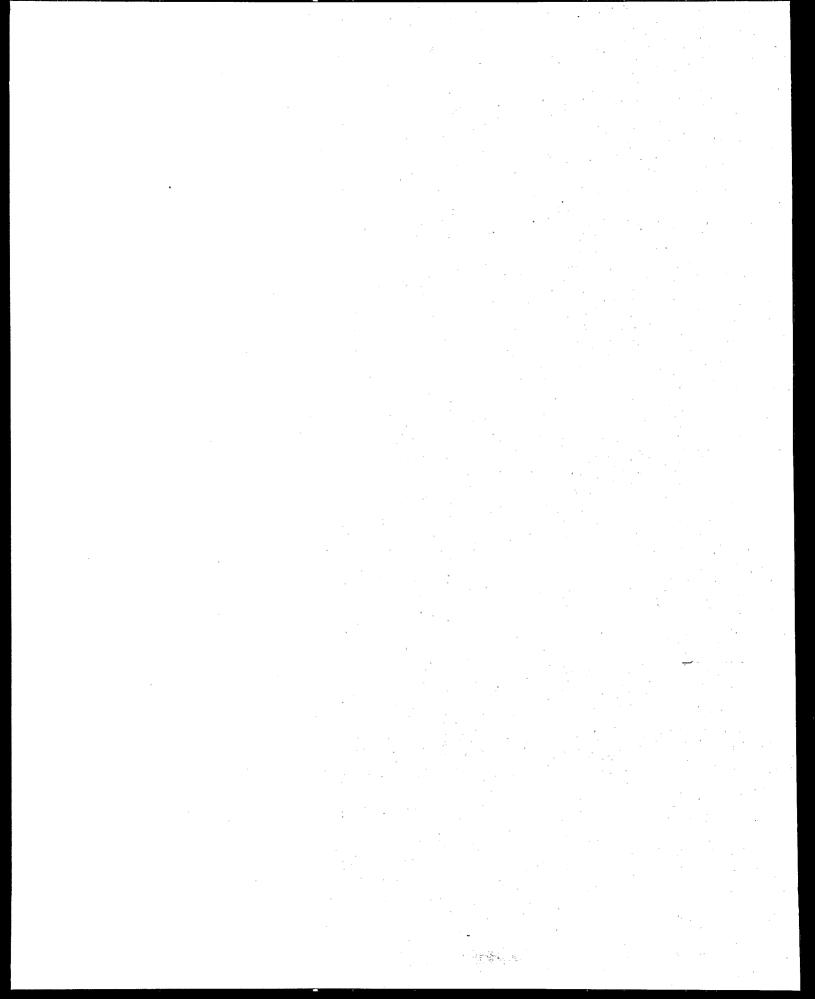
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APPENDIX A.

TABULATION OF UNCONTROLLED $\mathrm{NO}_{\mathbf{x}}$ EMISSIONS DATA

- Coke Ovens (underfiring) A-1
- Sinter Plants
- A-2 A-3 Blast Furnace Stoves
- A-3 Blast Furnace Stoves
 A-4 Basic Oxygen Furnaces
 A-5 Electric-Arc Furnaces
 A-6 Soaking Pits
 A-7 Reheat Furnaces
 A-8 Annealing Furnaces
 A-9 Galvanizing Furnaces



APPENDIX A-1. UNCONTROLLED NO EMISSIONS FROM IRON AND STEEL MILL PROCESS FACILITIES

Coke Ovens (Underfiring)

| Heat in Heat in Noy | | | | | | | | |
|--|------|-----------------------|------------------------------|--|-------------------------|--------------|---------|----------|
| BPG 141 193. ppm dry 0.59 1b/hr (ss N0 ₂) 1b/hmBtu 33 6/84 3 Note BPG 110 1.20 1b/hmBtu 29 8/84 3 Note BPG 110 112. ppm dry 0.39 29 8/84 3 Note 110 42.3 1b/hm 0.39 1b/hm 0.39 ppm dry 0.150 125 5/87 1,9(1) Note 160. ppm (peak) 0.151 1b/mRtu (avg) 0.151 100 4/89 4,9(B) 7 160. ppm (peak) 0.151 ppm (avg) 0.151 100 4/89 4,9(B) 7 160. ppm (peak) 0.151 1b/hr < | Fuel | Heat in (MMBtu/hr) | NO _x emissions | Emissions units | Production (tons/hr) | Test date | Ref.(*) | Comments |
| BFG 110 112. ppm dry 29 8/84 3 Note 10. | 18 | 141 | 193. 83.3 0.59 1.90 | ppm dry 1b/hr (as NO ₂) 1b/MMBtu 1b/ton coal | 33 | 8/84 | м | Note 1 |
| 356 100. ppm (avg) 125 5/87 1,9(I) 160. ppm (peak) 0.151 1b/milbtu (avg) 1.00 1b/milbtu (avg) 1.00 1b/milbtu (avg) 1.00 4/89 4,9(B) 1.00 1.51 1b/hr 3 0.2 1.00 4/89 4,9(B) 1.00 1.01. ppm 3 1 0.2 29.8 1.111. ppm 3 1 0.2 2.9(0) 1.00 2.9(0) 1.00 1.00 1.00 1.00 1.00 1.00 1.00 1. | 1 | 110 | 112. 42.3 0.39 1.10 | ppm dry lb/hr lb/MMBtu lb/ton coal | 2.9 | 8/84 | м | Note 1 |
| Fig. 8 in the control of the control | 500 | 356 | 100. 160. 0.100 | ppm (avg) ppm (peak) lb/MMBtu (avg) lb/ton (avg) | 125 | 5/87 | 1,9(I) | |
| 74.3 ppm @ 3* 0 ₂ 100 4/89 4,9(B) 782.3 ppm @ 3* 0 ₂ 100 4/89 4,9(B) 73.5 ppm @ 3* 0 ₂ 100 4/89 4,9(B) 1,012.0 ppm @ 7.2* 0 ₂ 11/90 2,9(O) Note , BFG 363.4 1,111. ppm @ 3* 0 ₂ 11/90 2,9(O) Note , BFG 385 1,119. ppm @ 6.6* 0 ₂ 3/91 2,9(O) Note , BFG 385 1,119. ppm @ 3* 0 ₂ 3/91 2,9(O) Note | 500 | | 93.0 616.6 37.7 | ppm ppm @ 3% 0 ₂ 1b/hr | 100 | 4/89 | 4,9(B) | |
| FIG. 363.4 1,111. ppm @ 3* 0 ₂ 11/90 4/89 4,9(B) Note 1,111. ppm @ 7.2* 0 ₂ ppm @ 3* 0 ₂ 11/90 2,9(O) Note 1,119. ppm @ 6.6* 0 ₂ 3/91 2,9(O) Note 1,400. ppm @ 3* 0 ₂ 3/91 2,9(O) Note 2.06 1b/MMBtu | 500 | | 74.3 782.3 30.1 | ppm ppm @ 3% 0 ₂ 1b/hr | 100 | 4/89 | 4,9(B) | • |
| BFG 363.4 1,111. | 500 | | 73.5 1,012.0 29.8 | ppm ppm @ 3% 0 ₂ 1b/hr | 100 | 4/89 | 4,9(B) | |
| BFG 385 1,119. ppm @ 6.6% 0 ₂ 3/91 2,9(0) 1,400. ppm @ 3% 0 ₂ 2.06 lb/MMBtu | 1 | | ,111 ,452 | ppm @ 7.2% 0 ₂ ' ppm @ 3% 0 ₂ lb/MMBtu | | 11/90 | 2,9(0) | Note 2 |
| | 1 . | 385 | 1,119. 1,400. 2.06 | ppm @ 6.6% 02 ppm @ 3% 02 lb/MMBtu | | 3/91 | 2,9(0) | Note 2 |

APPENDIX A-1 (continued)

Coke Ovens (Underfiring)

| | | | | 1 Cara = = = = = = 1 1 | | | |
|----------|-----------------------|---------------------------------------|--|-------------------------|--------------|-------------|----------|
| Fuel | Heat in (MMBturnr) | NO _x emissions | Emissions units | Production (tons/hr) | Test date | Ref.(*) | Comments |
| COG, BFG | 300 | 281. 474. 0.59 | ppm @ 10.3% 0 ₂ ppm @ 3% 0 ₂ lb/MMBtu | | 11/90 | . (0) 6 ' 2 | |
| COG, BFG | 345 | 323. 428. 0.432 149. | ppm @ 7.4% 0 ₂ ppm @ 3% 0 ₂ lb/MMBtu lb/hr | | 7/88 | 2,9(N) | |
| 500 | 106 | 102. 254. 0.258 27.4 | ppm @ 13.7% 0 ₂ ppm @ 3% 0 ₂ lb/MMBtu lb/hr | | 8/88 | 2,9(N) | |
| 500° | 135.6 | 87.8 95.0 0.239 32.4 0.46 | ppm (avg) ppm (peak) lb/MMBtu lb/hr | 70.5 | 2/90 | 9 (A) | |
| 900 | 135.6 | 87.7 95.0 0.236 31.9 0.41 | ppm (avg) ppm (peak) lb/MMBtu lb/hr | 77.3 | 2/90 | 9 (A) | |
| 500 | 135.6 | 82.2 95.0 0.244 33.1 0.53 | ppm (avg) ppm (peak) lb/MMBtu lb/hr lb/ton | 62.5 | 2/90 | 9 (A) | 4 · . |
| 502 | | 90.0 14.4 0.48 | ppm (avg) lb/hr lb/ton | 29.8 | 7/90 | (B) 6 | |

Coke Ovens (Underfiring)

| Fuel | Heat in (MMBtu/hr) | NO _x emissions | Emissions units | Production (tons/hr) | Test date | Ref.(*) | Comments |
|--------------|-----------------------|------------------------------|------------------------------|-------------------------|--------------|---------|-------------------------------------|
| ೨೦೦ | | 80.0 12.8 0.429 | ppm (avg) lb/hr lb/ton | 29.8 | 06/L | 6 (G) | |
| ಶಿ ಂಎ | | 100.0 16.0 0.536 | ppm (avg) 1b/hr 1b/ton | 29.8 | 06/L | 9 (G) | |
| ಶಿ ಂಎ | | 111.0 62.5 0.983 | ppm (avg) lb/hr lb/ton | 63.6 | 06/6 | (H) 6 | |
| ಶಿಂಬ | | 113.6 99.5 1.56 | ppm (avg) lb/hr lb/ton | 63.6 | 06/6 | (н) 6 | |
| 900 | | 125.0 137.0 2.15 | ppm (avg) lb/hr lb/ton | 63.6 | 06/6 | (н) б | |
| 500 | | 146.7 115.2 1.81 | ppm (avg) lb/hr lb/ton | 63.6 | 06/6 | (н) б | |
| BFG | | 200.0 34.6 1.09 | ppm (avg) 1b/hr 1b/ton | 31.8 | 8/90 | 6 (G) | 3 tests yielding same results |

Plant code, if applicable.

Avg. of results of 4 grab sample: 2-samples with all doors closed, 1-sample during push on one oven, 1-sample during charge on a second oven.

Data from same battery at different times : (*) Note 1:

Note 2:

APPENDIX A-2. UNCONTROLLED NOX EMISSIONS FROM IRON AND STEEL MILL PROCESS FACILITIES

Sinter Plants (Windbox Stacks)

| Fuel | Heat in (MMBtu/hr) | NO _x emissions | Emissions units | Production (tons/hr) | Test date | Ref.(*) | Comments |
|-----------------------|-----------------------|--|--|-------------------------|---------------------------|---------|----------|
| Coke, NG | 243.7 | 45.0 0.213 0.308 48.5 | ppmv (avg) 1b/MMBtu (avg) 1b/ton 1b/hr | 157.4 | 5/87 | 1, 9(D) | |
| Coke, NG | 174.4 | 62.0 55.0 0.495 0.439 86.3 | ppmv (peak) ppmv (avg) lb/MMBtu (avg) lb/ton (avg) | 180.0 | | 1, 9(I) | Note 1 |
| Coke, GOG | 439.5 | 89.0 284 0.589 233.2 | ppmv @ 15.3% 0 ₂ (avg) ppmv @ 3% 0 ₂ (avg) 1b/MMbtu (avg) 1b/hr | | 9/89 or 9/90 (?) | 2, 9(0) | |
| Coke, COG | 413.5 | 95.0 395 0.564 233.2 | ppmv @ 16.6% 0 ₂ (avg) ppm @ 3% 0 ₂ 1b/MMbtu 1b/hr | | 7/88 | 2, 9(N) | |
| eri Verie Verie | | 5.5 6.5 14.5 0.097 | ppmv (avg) ppmv (peak) 1b/hr 1b/ton | 150 | 1/90 | 9 (A) | |
| l | | 6.3 6.7 17.1 0.118 | ppmv (avg) ppmv (peak) lb/hr lb/ton | 144 | 1/90 | 9 (A) | |
| coke, cog | • | 7.2 7.7 19.4 0.117 | ppmv (avg) ppmv (peak) 1b/hr 1b/ton | 166 | 1/90 | 9 (A) | |

APPENDIX A-2 (continued)

Sinter Plants (Windbox Stacks)

| | | 3 | | | | | |
|----------|-----------------------|------------------------------|-------------------------------|-------------------------|--------------|---------|----------|
| Fuel | Heat in (MMBtu/hr) | NO _x emissions | Emissions units | Production (tons/hr) | Test date | Ref.(*) | Comments |
| Coke | l | 0.54 1.16 0.007 | ppm (avg) 1b/hr 1b/ton | 167 | 7/91 | 9 (A) | |
| Coke | 1 | 0.86 1.86 0.0112 | ppm (avg) lb/hr | 166 | 7/91 | 9 (A) | |
| Coke | | 1.23 2.66 0.0159 | ppmv (avg) lb/hr lb/ton | 167 | 7/91 | 9 (A) | |
| Coke, NG | | 1.30 1.50 0.0115 | ppmv (avg) 1b/hr 1b/ton | 130 | 5/89 | 9 (B) | |
| 1 | | 44.0 86.25 0.549 | ppmv (avg) lb/hr lb/ton | 157 | 10/88 | 9 (医) | |
| | | 40.3 78.6 0.501 | ppmv (avg) lb/hr lb/ton | 157 | 10/88 | 9 (E) | |
| | | 48.0 93.9 0.598 | ppmv (avg) lb/hr lb/ton | 157 | 10/88 | 9 (E) | |
| • | | 48.0 93.3 0.595 | ppmv (avg) 1b/hr 1b/ton | 157 | 10/88 | 9 (E) | |
| 1 | 1 | 56.0 106.6 0.697 | ppmv (avg) 1b/hr 1b/ton | 153 | 5/92 | 9(E) | |
| 1 | | | | | | | |

APPENDIX A-2 (continued)

Sinter Plants (Windbox Stacks)

| Fuel | Heat in (MMBtu/hr) | NO _x emissions | Emissions units | Production Test (tons/hr) date | Test date | Ref.(*) | Comments |
|------|-----------------------|------------------------------|-------------------------------|-----------------------------------|--------------|---------|----------|
| · | . 1 | 55.0 105.8 0.691 | ppmv (avg) lb/hr lb/ton | 153 | 5/92 | 9 (E) | |
| 1 | • | 57.0 106.7 0.698 | ppmv (avg) lb/hr lb/ton | 153 | 5/92 | 9 (E) | |

(*) Plant code, if applicable

(*) Plant code, if applicable

APPENDIX A-3. UNCONTROLLED NO_X EMISSIONS FROM IRON AND STEEL MILL PROCESS FACILITIES

Blast Furnace Stoves

| Fuel | Heat in (MMBtu/hr) | NO _x emissions | Emissions units | Production (tons/hr) | Test date | Ref.(*) | Comments |
|--------------------|-----------------------|--|---|-------------------------|--------------|---------|----------|
| BFG | | | ppm (low) ppm (peak) | 160 | 5/87 | 1,9(D) | |
| | | 25. 0.057 0.072 11.6 | ppm (avg) 1b/MMBtu (avg) 1b/tøn 1b/hr. | | | | |
| BFG, cog, NG | 820 |)55 | ppm @ 1.4% 0 ₂ ppm @ 3% 0 ₂ lb/MMBtu lb/hr | 1 | 7/88 | 2,9(N) | |
| BFG, | 702 | 7 0 0 1 3 8 9 0 2 4 | ppmv (avg) ppmv (peak) lb/MMBtu lb/hr lb/ton | 375 | 1/90 | 9 (A) | |
| BFG, COG | 792 | | ppmv (avg) ppmv (peak) lb/MMBtu lb/hr lb/ton | 375 | 1/90 | 9 (A) | |
| BFG, COG | 780 | 20.2 23.0 0.0210 16.4 0.04 | ppmv (avg) ppmv (peak) lb/MMBtu lb/hr lb/ton | 375 | 1/90 | 9 (A) | |
| BFG, COG | 745 | 6.7 0.016 12.16 0.0325 | ppmv (avg) 1b/MMBtu 1b/hr 1b/ton | 374 | 4/81 | 9 (A) | |

Blast Furnace Stoves

| Fuel | Heat in (MMBtu/hr) | NO _x emissions | Emissions units | Production (tons/hr) | Test date | Ref.(*) | Comments |
|-------------|-----------------------|----------------------------------|---|-------------------------|--------------|---------|----------|
| BFG | 436.6 | 1.2 0.0016 0.694 0.0033 | ppmv (avg) lb/MMBtu lb/hr lb/ton | 207 | 10/88 | 9 (E) | |
| BFG | 436.6 | 1.5 0.0023 1.01 0.0049 | ppmv (avg lb/MMBtu lb/hr lb/ton | 207 | 10/88 | 9 (E) | |
| BFG, COG | 500.5 | 8.50 0.011 5.6 0.040 | ppmv (avg) lb/MMBtu lb/hr lb/ton | 140 | 3/93 | (0) 6 | |
| BFG, COG | 500.5 | 10.3 0.014 6.790 0.04§ | ppmv (avg) lb/MMBtu lb/hr lb/ton | 140 | 3/93 | (Ŏ) 6 | |
| BFG, COG | 500.5 | 11.0 0.014 7.25 0.052 | ppmv (avg) lb/MMBtu lb/hr lb/ton | 140 | 3/93 | (Ŏ) 6 | |

(*) Plant code, if applicable

APPENDIX A-4. UNCONTROLLED NOX EMISSIONS FROM IRON AND STEEL MILL PROCESS FACILITIES

Basic Oxygen Furnaces (BOF)

| Fuel | Heat in (MMBtu/hr) | NO _x emissions | Emissions units | Production (tons/hr) | Test date | Ref.(*) | Comments |
|------|-----------------------|-------------------------------|--|-------------------------|-----------------|---------|---------------------------------------|
| 02 | | | ppm (avg) ppm (peak) lb/hr lb/ton | 610 | 5/87 | 1,9(D) | |
| 02 | | 26 0.064 | ppm @ 12.1% 0 ₂ lb/ton | | 10/90, 11/90 | 2,9(0) | |
| 0.2 | | 12.3 | ppm @ 8.9% 0 ₂ lb/ton | | 7/88 | 2,9(N) | Some inconsistency |
| 02 | | 12.7 24. 0.13 | ppm @ 16.6% 0 ₂ lb/hr lb/ton | | 10/91 | N | Average emissions over 6 cycles |
| 02 | | 21.4 | mdd | | 11/91 | Ŋ | Average emissions over 8 cycles |
| 02 | | 21.2 | ppm @ 18.8% 0 ₂ | | 6/92 | 2 | Average emissions over 5 cycles |
| 02 | | 13.3 | ppm @ 16.4% 0_2 | | 6/92 | 2 | Average emissions over 6 cycles |
| 02 | | 17.9 65.0 62.8 0.150 | $egin{array}{c} egin{array}{c} \egin{array}{c} \egin{array}{c} \egin{array}{c} \egin{array}{c} \egin{array}{c} \egin{array}$ | 418 | 8/92 | 9 (E) | |
| 02 | | 13.6 63.0 42.2 0.101 | ppm (avg) ppm (peak) lb/hr lb/ton | 418 | 8/92 | 9 (E) | |
| H | | | | | | | |

Basic Oxygen Furnaces (BOF)

| (avg) | | | | Jan Tanita ing Jun order | ידוומרכי וחרים ו | | | |
|---|------|-----|------------------------------|--|-------------------------|--------------|---------|--|
| 16.3 ppm (avg) 418 8/92 9(B) 52.5 1b/hr 10.0 ppm (avg) 326 3/93 9(Q) 10.034 1b/hr 1b/hr 6.0 ppm (avg) 326 3/93 9(Q) 8.2 1b/hr 1b/ton 326 3/93 9(Q) 7.0 ppm (avg) 326 3/93 9(Q) 8.53 1b/hr 1b/ton 9.026 1b/m @ 3 % 0_2 225 6/92 4,9(B) 9.00 9.00 9.00 3 % 0_2 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00 9. | Fuel | űr) | NO _x emissions | Emissions units | Production (tons/hr) | Test date | Ref.(*) | Comments |
| 11.0 1b/hr 1b/hr | 02 | | 16.3 52. 52.5 0.126 | ppm (avg) ppm (peak) 1b/hr 1b/ton | 418 | 8/92 | 9 (E) | |
| 6.0 ppm (avg) 326 3/93 9(Q) 8.2 1b/hr 1b/ton 326 3/93 9(Q) 7.0 ppm (avg) 326 3/93 9(Q) 8.53 1b/hr 1b/ton Assic Oxygen Furnaces (QBOP) Basic Oxygen Furnaces (QBOP) 4,9(B) 20.5 ppm @ 3\$ 02 225 6/92 4,9(B) 14.3 ppm @ 3\$ 02 225 6/92 4,9(B) 14.5 ppm @ 3\$ 02 225 6/92 4,9(B) 14.5 ppm @ 3\$ 02 225 6/92 4,9(B) 14.5 ppm @ 3\$ 02 225 6/92 4,9(B) | | | | ppm (avg) lb/hr lb/ton | 326 | 3/93 | (0)6 | |
| 14.5 Ppm (avg) 326 3/93 9(Q) Basic Oxygen Furnaces (QBOP) 29.3 Ppm @ 3% 0 ₂ 225 6/92 4,9(B) 14.3 Ppm @ 3% 0 ₂ 225 6/92 4,9(B) 14.5 Ppm @ 3% 0 ₂ 225 6/92 4,9(B) 14.5 Ppm @ 3% 0 ₂ 225 6/92 4,9(B) 14.5 Ppm @ 3% 0 ₂ 225 6/92 4,9(B) 14.5 Ppm @ 3% 0 ₂ 225 6/92 4,9(B) 14.5 Ppm @ 3% 0 ₂ 225 6/92 4,9(B) | | | 6.0 8.2 0.025 | ppm (avg). 1b/hr 1b/ton | 326 | 3/93 | (0)6 | |
| Basic Oxygen Furnaces (QBOP) 29.3 ppm @ 3% 02 225 6/92 4,9(B) 20.5 ppm @ 3% 02 225 6/92 4,9(B) 14.3 ppm @ 3% 02 225 6/92 4,9(B) 14.5 ppm @ 3% 02 225 6/92 4,9(B) 200. ppm @ 3% 02 225 6/92 4,9(B) | | | 7.0 8.53 0.026 | ppm (avg) 1b/hr 1b/ton | 326 | 3/93 | (0) 6 | |
| 29.3 ppm @ 3\$ 02 225 6/92 4,9(B) 20.5 ppm @ 3\$ 02 225 6/92 4,9(B) 14.3 ppm @ 3\$ 02 225 6/92 4,9(B) 14.5 ppm @ 3\$ 02 225 6/92 4,9(B) 200. ppm @ 3\$ 02 225 6/92 4,9(B) | | | | Basic Oxygen Fur | rnaces (QBOP) | | | |
| 14.3 ppm 3* 02 225 6/92 4,9(B) 14.3 ppm 3* 02 6/92 4,9(B) 14.5 ppm 3* 02 225 6/92 4,9(B) 200. ppm 3* 02 225 6/92 4,9(B) | 02 | | | ppm @ 3% 0 ₂ | 225 | 6/92 | 4,9(B) | During O ₂ Blow Period |
| .3 ppm @ 3% 0 ₂ 225 6/92 4,9(B) .5 ppm @ 3% 0 ₂ 225 6/92 4,9(B) | 02 | | | ppm @ 3% 0 ₂ | 225 | 6/92 | 4,9(B) | During O ₂ Blow Period |
| .5 ppm @ 3% 0 ₂ 225 6/92 4,9(B) | | | | @ | 225 | 6/92 | 4,9(B) | During Non-0 ₂ Blow Period |
| H | | | | | 225 | 6/92 | 4,9(B) | During Non-0 ₂ Blow Period |

APPENDIX A-5. UNCONTROLLED NO_X EMISSIONS FROM IRON AND STEEL MILL PROCESS FACILITIES

Electric Arc Furnaces

| ı t | | | 1 | | | |
|--------------------------------|---|---|---|---|---|---|
| Net heat time(min) | 185 | 160 | 130 | 140 | 145 | 145 |
| Comments | Notes 1,2 | Notes 1,2 | Noter 1,2 | Notes 1,2 | Notes 1,2 | Notes 1,2 |
| Ref.(*) | 1,9(L) | 1,9(L) | 1,9(L) | 1,9(L) | 1,9(L) | 1,9(L) |
| Test date | 8/87 | 8/87 | 8/87 | 8/87 | 8/87 | 8/87 |
| Production (tons/heat) | 165 | 165 | 165 | 165 | 165 | 165 |
| Emissions ions units | ppm (avg) ppm (peak) lb/heat lb/ton lb/kW | ppm (avg) ppm (peak) 1b/heat 1b/ton 1b/kW | ppm (avg) ppm (peak) lb/heat lb/ton lb/kW |
| NO _x emissions | 380. 97. 82.5 0.50 | 102. 330. 99.1 0.60 | 110. 380. 85.4 0.518 | 101. 310. 99.7 0.604 | 96. 320. 84.0 0.509 | 80. 340. 82.5 0.500 |
| Quantity NO _x emiss | 769kW 60.0MCF | 625kW 52.5MCF | 693kW 40.0MCF | 708kW 55.5MCF | 646kW 32.5MCF | 682kW 40.0MCF |
| Fuel ' | Electricity 0 ₂ | Electricity 02 | Electricity 02 | Electricity 02 | Electricity 02 | Electricity 02 |

Electric Arc Furnaces

| | | | | | | | 1 | |
|------|------------|------------------------------|-----------------------------------|---------------------------|--------------|---------|-------------------------------|-----------------------|
| Fuel | Quantity | NO _x emissions | Emissions units | Production (tons/heat) | Test date | Ref.(*) | Comments | Net heat time(min) |
| t | ŝ | 14. 82. | ppm @ 21% 0 ₂ lb/hr | 100 tons/hr 8/91 | 8/91 | 2 | | |
| ŧ | • | 12. 67. | ppm @ 21% 0 ₂ 1b/hr | 100 tons/hr 8/91 | 8/91 | 2 | | |
| 1 | 1 | 7. | wďď | 100 tons/hr 10/91 | 10/01 | 2 | 0 ₂ burners off | - |
| l | 1 . | 17. | wdd | 100 tons/hr 10/91 | 10/01 | 7 | 0 ₂ burners off | , |

Plant code, if applicable. Emissions in lb/ton based on an average production of 165 tons/heat. Longitudinal, radially fired oxy-fuel burners were used during meltdown. Note 1. Note 2. *

APPENDIX A-6. UNCONTROLLED NOX EMISSIONS FROM IRON AND STEEL MILL PROCESS FACILITIES

Soaking Pits

| Comments | lb/ton (cycle avg) based on 240 tons/day typical charge (Pit No. 3) Cold charge | j | lb/ton (cycle avg) based on 240 tons/day typcial charge. (Pit No. 5) | | lb/ton (cycle avg) based on 240 tons/day typical charge Cold charge No comb. air | (Pit No. 4) |
|------------------------------|--|--|---|---|---|---|
| Ref.(*) | 1,9(I) | | 1,9(I) | | 1,9(I) | |
| Test date | 8/871 | | 8/87 | | 8/87 | |
| Emissions Units Test | ppm (peak) 1b/MmBtu (avg) 1b/hr (avg) ppm (peak) 1b/mMbtu (avg) 1b/mMbtu (avg) 1b/hr (avg) | <pre>lb/MMBtu (cycle avg) lb/hr (cycle avg) lb/ton (cycle avg)</pre> | ppm (peak) 1b/MMBtu (avg) 1b/hr (avg) ppm (peak) 1b/MMBtu (avg) ppm (peak) 1b/MMBtu (avg) | lb/MMBtu (cycle avg) lb/hr (cycle avg) lb/ton (cycle avg) | ppm (peak) 1b/MMBtu (avg) 1b/hr (avg) ppm (peak) 1b/MMBtu (avg) 1b/hr (avg) | lb/MMBtu (cycle avg) lb/hr (cycle avg) lb/ton (cycle avg) |
| NO _x emissions | 280. 0.27 6.50 95. 0.065 | 0.137 1.86 0.186 | 270. 0.261 6.26 110. 0.110 44. | 0.148 1.94 0.194 | 88. 0.075 1.845 75. 0.065 | 0.069 1.04 0.104 |
| Comb. Air Temp | 505 515 | - | 450 450 450 | | 70 | |
| Mode Time (hrs) | 8 15 | | 12 3 | | 15 8 | |
| Heat in (mode) | 24 (heating) 8 (soaking) | | 24 (heating) 8 (soaking) 8 (soaking) | | 24.6 (heating) 10 (soaking) | |
| Fuel | COG (Note 1) | | COG (Note 1) | | COG (Note 1) | |

Soaking Pits

| | | | | SOGNE | SOAKIIIG FILE | | | |
|-----------------|---------------------------------|-----------------------|---------------------------|---|---|--------------|-----------|--|
| Fuel | Heat in (mode) (MMBtu/hr) | Mode Time (hrs) | Comb. Air Temp (°F) | NO _x emissions | Emissions Units | Test date | Ref.(*) | Comments |
| COG (Note 1) | 24 (heating) 10 (soaking) | 7 | 7.0 | 87. 0.085 2.04 65. 0.055 0.064 | ppm (peak) lb/MMBtu (avg) lb/hr (avg) ppm (peak) lb/MMBtu (avg) lb/hr (avg) | 8/87 | (I) 6 'I) | lb/ton (cycle avg) based on 240 tons/day typical charge No comb. air preheat (Pit No. 4) |
| | - | | | 0.0913 | lb/ton (cycle avg) | | | |
| NG | 24 (heating) 9 (soaking) | 7 | 490 | 212. 0.191 4.58 105. 0.090 | ppm (peak) lb/MMBtu (avg) lb/hr (avg) ppm (peak) lb/MMBtu (avg) lb/hr (avg) | 8/87 | 1,9 (I) | lb/ton (cycle avg) based on 240 tons/day typical charge Hot charge (Pit No. 3) |
| | | | | 0.121 1.64 0.164 | lb/MMBtu (cycle avg) lb/hr (cycle avg) lb/ton (cycle avg) | | | |
| COG/NG | | | | 57.7 689 4.5 0.155 | $\begin{array}{llllllllllllllllllllllllllllllllllll$ | 5/89 | 4,9(B) | lb/ton based on 29 tons/hr production |
| COG/NG | | | | 54.3 49.1 4.2 0.145 | ppm @ 1.1% 0 ₂ ppm @ 3% 0 ₂ 1b/hr 1b/ton | 5/89 | 4,9(B) | lb/ton based on 29 tons/hr production |
| COG/NG | | | | 65. 181.8 5.1 0.176 | ppm @ 14.5% 0 ₂ ppm @ 3% 0 ₂ 1b/hr 1b/ton | 5/89 | 4,9(B) | lb/ton based on 29 tons/hr production |
| BFG/COG | | | | 35. 0.361 | ppm @ 16.4% 0 ₂ lb/ton | 7/88 | 2,9 (N) | |

Plant code, if applicable. The COG supply line is pressure stabilized with a natural-gas/air blend.

(*): Note 1:

APPENDIX A-7. UNCONTROLLED NOX EMISSIONS FROM IRON AND STEEL MILL PROCESS FACILITIES

| Fuel | Heat in (MMBtu/hr) | NO _x emissions | Emissions units | Production (P) or capacity (C) (tons/hr) | Test date | Ref.(*) | Comments |
|-----------------|-----------------------|-------------------------------|--|--|-----------|---------|--|
| NG (608MCFH) | | 326. | ppm @ 3% 0 ₂ 1b/MMBtu | | 10/79 | E | Furnace Temp = 2127°F(avg) Recuperator temp = 1619°F(avg) Recuperative fired |
| NG | 1 L | 193. | ppm @ 3% 0 ₂ lb/MMBtu | | 06/9 | ഹ | Flue gas temp = 900-1200°F = 500-600°F beyond Rec. Recuperative fired |
| COG, NG | 412.2 | 326. 315. 0.387 | ppm @ 2.4% 0 ₂ ppm @ 3% 0 ₂ lb/MMBtu | _ | 10/90 | 8 | 80" Hot Strip Mill Recuperative fired |
| NG | 115.9 | 105. 219. 0.269 33.1 | ppm @ 12.3% 0 ₂ ppm @ 3% 0 ₂ lb/MMBtu lb/hr | ı | 11/90 | 7 | 110" Plate Mill Recuperative Fired |
| COG, NG | 256.8 | 133. 233. 0.287 79.1 | ppm @ 10.7% 0 ₂ ppm @ 3% 0 ₂ lb/MMBtu lb/hr | . | 11/90 | N | 160" Plate Mill, continuous Recuperative fired |
| cog, oil | 174 | 125. 185. 0.227 | ppm @ 8.8% 0 ₂ ppm @ 3% 0 ₂ lb/MMBtu | 1 | 8/88 | 2 | 160 " Plate Mill Recuperative fired |

| Fuel | Heat in (MMBtu/hr) | NO _X emissions | Emissions units | Production (P) or capacity (C) (tons/hr) | Test date | Ref.(*) | Comments |
|----------------|-----------------------|--------------------------------|--|--|-----------|---------|---|
| NG | 162.3 | 69. 65. 0.080 | ppm @ 1.9% 0 ₂ ppm @ 3% 0 ₂ lb/MMBtu | | 8/88 | 2 | 68" HSM Recuperative fired Has been replaced |
| NG | | 740. 0.909 | ppm @ 3% 0 ₂ lb/MMBtu | 1 | 7/91 | 7 | Billet Reheat furnace Regenerative fired Avg. of 2 rung |
| NG | 390 | 260. 0.31 122. | ppm @ 3% 0 ₂ lb/MMBtu lb/hr | | 4/89 | 6,9(E) | st st |
| #6 Fuel Oil | 94.85 | 23. 0.0327 3.1 0.114 | ppmv 1b/MMBtu 1b/hr 1b/ton | 27.2 | 1/78 | 9 (A) | 1 |
| #6 Fuel Oil | 135.5 | 23. 0.0229 3.1 0.0543 | ppmv 1b/MMBtu 1b/hr 1b/ton | 57.1 | 1/78 | 9 (A) | I |
| #6 Fuel Oil | 124.6 | 39. 0.0442 5.5 0.1104 | ppmv 1b/MMBtu 1b/hr 1b/ton | 49.8 | 1/78 | 9 (A) | ı |
| , . | | | | | | | |

| Comments | ı | 1 | 1 | Ejector Stack | Ejector Stack | ı | | ı |
|--|---------------------------------------|--|--|--|-------------------------------|-----------------------|--|--|
| Ref.(*) | 9 (F) | 9(L) | 9 (L) | 4,9(B) | 4,9(B) | 6,9(E) | 6,9(E) | 4,9(E) |
| Test date | 5/87 | 5/87 | 5/87 | 2/90 | 1/90 | 4/89 | 4/89 | 4/89 |
| Production (P) or capacity (C) (tons/hr) | 1 | 1. | 1 | ť | 1 | 190(C) | (C) | 190(C) |
| Emissions units | ppmv (avg) ppmv (peak) lb/MMBtu lb/hr | ppmv (avg) ppmv (peak) lb/MMBtu lb/hr | ppmv (avg) ppmv (peak) 1b/MMBtu 1b/hr | ppm @ 18.3% 0 ₂ ppm @ 3% 0 ₂ 1b/br | ppm @ 15.6% 02 ppm @ 3% 02 | 0027 | ppm @ 8.25% 0 ₂ ppm @ 3% 0 ₂ 1b/MMBtu 1b/hr | ppm @ 7.25% 0 ₂ ppm @ 3% 0 ₂ lb/MMBtu lb/hr |
| NO _x emissions | 38. 62. 0.0430 | | 54 94 | 63.1 434. | 42.5 | 192.5 266. 0.32 | 180.0 255. 0.31 | 196.5 258. 0.31 125.5 |
| Heat in (MMBtu/hr) | 43.9 | 46.7 | 57.3 | | .1 | 392.9 | 372.6 | 404.9 |
| Fuel | NG | NG | NG | NG, COG, Fuel Oil | NG, COG, | NG NG | NG | NG |

| Fuel | Heat in (MMBtu/hr) | NO _x emissions | Emissions units | Production (P) or capacity (C) (tons/hr) | Test date | Ref.(*) | Comments |
|------|-----------------------|--|--|--|-----------|---------|--|
| NG | 1 | 550. | ² 0 %E ® mďď | 83 (C) | | 8 | Regenerative |
| | | | | | | | LNBs with FGR disabled. Spot check |
| 500 | 48.8 | 104. 227. 0.276 13.5 | ppm @ 12.7% 0 ₂ ppm @ 3% 0 ₂ lb/MMBtu lb/hr | 1 | 11/90 | 2,9(0) | Recuperative fired |
| NG | 281.6 | 125. 165. 0.140 39.4 0.237 | ppmv (avg) ppmv (peak) lb/MMBtu (avg) lb/hr | 166.6(P) | 5/87 | 1,9(I) | Note 1 480°F (Note 2) |
| 900 | 256.5 | 165. 225. 0.166 42.6 0.244 | ppmv (avg) ppmv (peak) lb/MMBtu lb/hr | 174.5(P) | 5/87 | 1,9(I) | Note 1 490°F (Note 2) |
| 500 | 190.4 | | ppmv (avg) ppmv (peak) lb/MMBtu lb/hr lb/ton | 78.7(P) | 5/87 | 1,9(1) | Note 1 450°F (Note 2) |
| 500 | 245.9 | 125. 158. 0.126 31.0 0.197 | ppmv (avg) ppmv (peak) lb/MMBtu lb/hr lb/ton | 157.6(P) | 5/87 | 1,9(I) | Note 1 450°F (Note 2) |

| Fuel | Heat in (MMBtu/hr) | NO _x emissions | Emissions units | Production (P) or capacity (C) (tons/hr) | Test date | Ref.(*) | Comments |
|------|-----------------------|--|--|--|-----------|---------|---|
| 500 | 243.5 | 175. 250. 0.176 42.9 0.327 | ppmv (avg) ppmv (peak) lb/MMBtu lb/hr lb/ton | 130.9(P) | 5/87 | 1,9(1) | Note 1 515°F (Note 2) |
| Đ00 | 254.8 | 140. 195. 0.141 35.9 0.290 | ppmv (avg) ppmv (peak) lb/MMBtu lb/hr lb/ton | 123.7(P) | 2/87 | 1,9(I) | Note 1 420°F (Note 2) |
| 500 | 302.4 | 100. 150. 0.100 30.2 0.176 | ppmv (avg) ppmv (peak) lb/MMBtu lb/hr lb/ton | 171.8(P) | 5/87 | 1,9(I) | Note 3 460°F (Note 2) |
| 500 | 313.7 | 95. 105. 0.095 29.8 0.157 | ppmv (avg) ppmv (peak) lb/MMBtu lb/hr lb/ton | 190.1(P) | 5/87 | 1,9(I) | Note 3 420°F (Note 2) |
| 500 | 160.5 | 1.9 0.0083 1.34 0.0258 | ppmv (avg) lb/MMBtu lb/hr lb/ton | 52 (P) | 3/93 | 9 (R) | Recuperative fired 447°F (Note 2) |
| විටට | 160.5 | 0.90 0.0038 0.61 0.012 | ppmv (avg) lb/MMBtu lb/hr lb/ton | 52 (P) | 3/93 | 9 (R) | Recuperative fired 463°F (Note 2) |

Reheat Furnaces

| Fuel | Heat in (MMBtu/hr) | NO _x emissions | Emissions units Production (P) or capacity (C) (tons/hr) | | Test date Ref.(*) | | Comments |
|------------|-----------------------|----------------------------------|--|--------|-------------------|-------|---|
| 900 900 | 160.5 | 0.30 0.0013 0.210 0.004 | ppmv (avg) 1b/MMBtu 1b/hr 1b/ton | 52 (P) | £6/£ | 9 (R) | Recuperative fired 455°F (Note 2) |

Plant code (if applicable) *****

Recuperative-fired in heating and charging zones. Note 1:

Note 2: Note 3.

Cold-air-fired in soaking zones.
Refers to combustion air preheat temperature.
Recuperative-fired in heating, charging, and bottom soak zones.
Cold-air-fired in top soak zone.

APPENDIX A-8. UNCONTROLLED NOX EMISSIONS FROM IRON AND STEEL MILL PROCESS FACILITIES

Annealing Furnaces

| Fuel | Heat in (MMBtu/hr) | NO _x emissions | Emissions units | Production (tons/hr) | Test date | Ref.(*) | Comments |
|------|---------------------------------------|------------------------------|-------------------------|-------------------------|--------------|------------|--------------------------------|
| NG | 16 | 550 | ² 0 %E @ mdd | ı | | 8 | Estimated emissions |
| | • | 0.675 | 1b/MMBtu | | | | Regenerative fired |
| NG | 186 | 1000. | ppm @ 3% 02 | ı | 68/ | 8. | Regenerative fired |
| | · · · · · · · · · · · · · · · · · · · | 1.23 | 1b/MMBtu | 1 | , | | Emissions based on lab data |
| NG | 182 | 1000. | ppm @ 3% 0 ₂ | 1 | /92 | ' ω | Regenerative fired |
| | | 1,23 | 1b/MMBtu | 1 | | | Emissions based on lab data |

(*): Plant code, if applicable.

APPENDIX A-9. UNCONTROLLED NO_X EMISSIONS FROM IRON AND STEEL MILL PROCESS FACILITIES

Galvanizing Furnaces

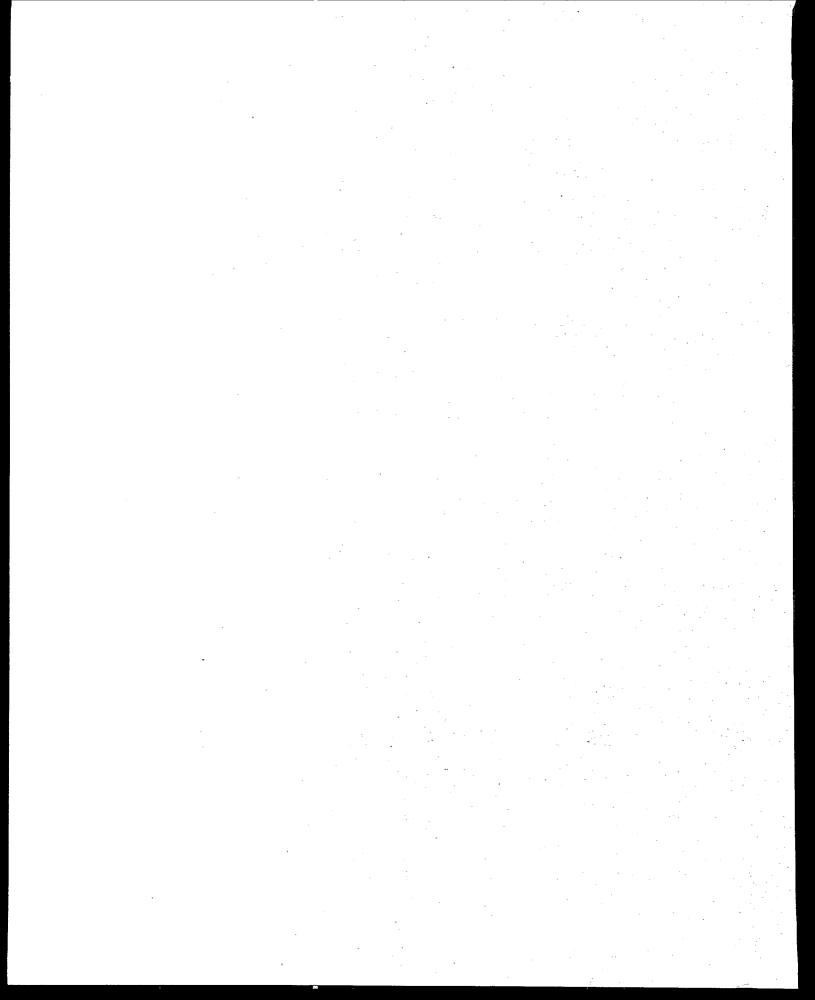
| Fuel | Heat in (MMBtu/hr) | NO _x emissions | Emissions units | Production (tons/hr) | Test date | Ref.(*) | Ref.(*) Comments |
|------|-----------------------|------------------------------|-------------------------|-------------------------|--------------|---------|---|
| NG | 179 | 1000. | ppm @ 3% 0 ₂ | 1 | /91 | 8 | Regenerative- |
| | | 1.23 | lb/MMBtu | | | | cired Galvanizing/ galvannealing Lab-based data without NO _x |
| NG | 38 | 875. | ppm @ 3% 0 ₂ | 4 | /89 | 8 | Regenerative- |
| | | 1.07 | lb/MMBtu | . 1 | | | fired Aluminizing |

): Plant code, if applicable.

References for Appendix A

- Letter and attachments from Felton, S. S., Armco Steel Company, L. P., to Jordan, B. C., EPA/OAQPS. June 26, 1992. Response to Section 114 letter on iron and steel mills.
- Letter and attachments from Anderson, D. M., Bethlehem Steel Corporation, to Jordan, B. C., EPA/OAQPS. July 13, 1992. Response to Section 114 letter on iron and steel mills.
- 3. Letter and attachments from Keeney, L., Rouge Steel Company, to Jordan, B. C., EPA/OAQPS. June 30, 1992. Response to Section 114 letter on iron and steel mills.
- 4. Letter and attachments from Starley, J. R., Geneva Steel, to Jordan, B. C., EPA/OAQPS. July 6, 1992. Response to Section 114 letter on iron and steel mills.
- 5. Letter and attachments from Lee, D., Cascade Steel Rolling Mills, Inc., to Jordan, B. C., EPA/OAQPS. July 6, 1992. Response to Section 114 letter on iron and steel mills.
- 6. Letter and attachments from Harmon, M. L., LTV Steel Company, to Jordan, B. C., EPA/OAQPS. July 2, 1992. Response to Section 114 letter on iron and steel mills.
- 7. Letter and attachments from Postlethwait, W., Nucor Steel, Darlington Division, to Jordan, B. C., EPA/OAQPS. December 2, 1992. Response to Section 114 letter on iron and steel mills.
- 8. Letter and attachments from Gilbert, F. C., North American Manufacturing Company, to Jordan, B. C., EPA/OAQPS.

 November 11, 1992. Response to Section 114 letter on low-NO, burners.
- 9. Letter and attachments from Steiner, B.A., American Iron and Steel Institute, to Neuffer, W. J., EPA/OAQPS/ESD. May 25, 1993. Comments on draft ACT document.



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15. SUPPLEMENTARY NOTES

16. ABSTRACT

This document describes available control techniques for controlling NO_x emissions from various processes at iron and steel mills. These processes include reheat furnaces, annealing furnaces, galvanizing furnaces, soaking pits, sintering, blast furnaces, basic oxygen furnaces, and electric-arc furnaces. Discussions of NO_x formation and uncontrolled emission levels are included. NO_x control techniques include low excess air, low NO_x burners, flue gas recirculation, selective noncatalytic reduction and selective catalytic reduction. Achievable NO_x emission levels, costs and cost effectiveness and environmental impacts for these controls are presented.

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