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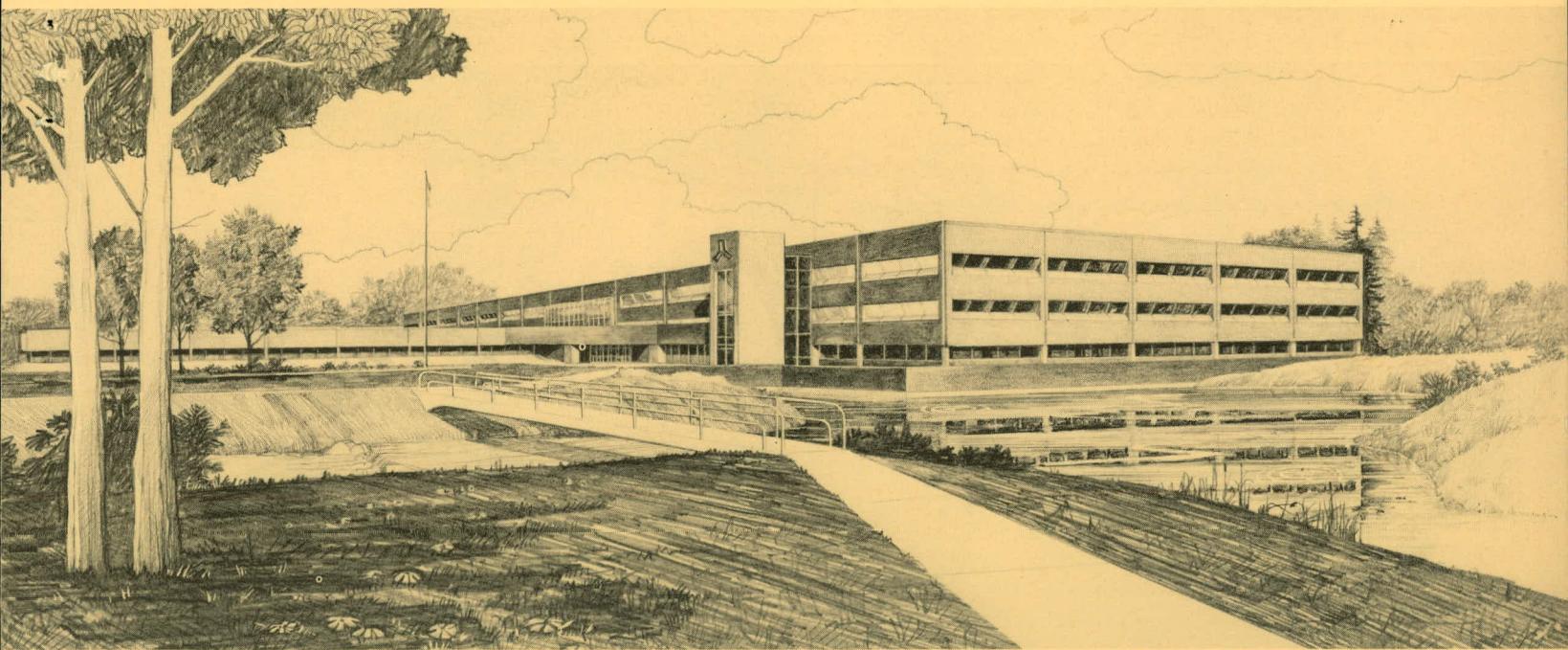
HIGH-TEMPERATURE WASTE-HEAT-STREAM
SELECTION AND CHARACTERIZATION

Penny M. Wikoff
Deborah J. Wiggins
Richard L. Tallman
Curt E. Forkel

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EC&G Idaho, Inc.
Idaho Falls, Idaho 83415

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ABSTRACT

Four types of industrial high-temperature, corrosive waste heat streams are selected that could yield significant energy savings if improved heat recovery systems were available. These waste heat streams are the flue gases from steel soaking pits, steel reheat furnaces, aluminum remelt furnaces, and glass melting furnaces. Available information on the temperature, pressure, flow, and composition of these flue gases is given. Also reviewed are analyses of corrosion products and fouling deposits resulting from the interaction of these flue gases with materials in flues and heat recovery systems.

SUMMARY

Background and Purpose

Effective recovery of energy from several major high-temperature industrial waste gas streams is limited by the high temperature and corrosive nature of these streams. To select and develop materials and waste heat recovery systems applicable to such industrial use, characterization of the waste heat streams is necessary. This report is a compilation and evaluation of available waste heat stream (flue gas) characterization information for four industrial high-temperature furnace processes: steel soaking and reheating, glass melting, and aluminum remelt. The flue gas characteristics chosen for their importance to the formation and composition of corrosion products and fouling deposits were temperature, flow rate, pressure, and chemical composition. Also important were the composition of fouling deposits from the flue gas in existing heat recovery systems, the composition of corrosion products in these systems, and the effects of process variables on flue gas composition. The types of furnaces and the processes for which the flue gases were characterized are also described.

Flue Gas Temperatures, Flow Rates, and Pressures

Except for glass melting, flue gas temperatures were generally not available and therefore were approximated by furnace temperatures. The temperature of steel soaking pits and reheat furnaces has a broad range: from 1300 to 2450°F. Part of this temperature variation is due to the batch method of operation for these furnaces. This method subjects the furnaces to large changes in temperature due to the addition or removal of materials. In addition, when a new batch is charged, an initial period of high fire (high air and fuel flow) brings the metal up to the maximum allowable surface temperature, after which lower firing conditions maintain a constant temperature to bring the bulk metal up to the desired finished temperature. Approximately half the reheat time is at or near low fire conditions. The required furnace temperatures are also determined by the size of the metal pieces charged and the type of alloy being heated.

Reheat furnaces nominally are operated at lower temperatures and with less temperature variation per charge than the soaking pits, primarily due to the smaller size of the pieces being heated. This temperature, however, was not established. The reverberatory remelt furnaces of the aluminum industry nominally operate continuously, at a much narrower temperature range of 2000 to 2800°F, while holding furnaces operate at 1290 to 1330°F. Glass melting furnaces are normally operated at 2800 to 3000°F, depending on the batch composition. The resulting temperature range of the flue gases is 1200 to 3000°F; the lower temperature occurring after the gas has passed through a regenerator for heat recovery.

Flue gas pressures were taken to be essentially the same as furnace operating pressures. The furnace types reviewed normally operate at pressures that prevent backflow of stack gases, i.e., slightly above atmospheric pressure. The pressure of the furnace may be slightly less than this at times, however, especially in batch furnaces. Nominally then, the furnace pressures range from -0.98 to 0.1 in. (water gauge).

The flow of the waste gas of both the steel soaking pit and reheat furnace is dependent on the furnace firing rate. A flow of 250,000 scfh corresponds to an average of the maximum fire rate used. The flow may decrease to 50,000 scfh when the burner is operated at low fire conditions. The average flue gas flow rate for aluminum remelt furnaces varies depending on furnace capacity and fuel input. For a continuous glass melting furnace, the flow rate of the waste gases ranges from 440,000 to 1,200,000 scfh, but will vary with furnace (production) size.

Flue Gas Constituents

Flue gas composition was generally found to be a main area of deficiency in the literature. Flue gas analyses for steel soaking pits and reheat furnaces were not available beyond the combustion products of the fuel. Fuel contaminants, topping compounds, oxidation of the metal surface, and furnace floor constituents will contribute to the composition of this waste gas stream, and include calcium, iron, potassium, sodium, sulfur, and magnesium. A partial analysis of the waste gas stream was

available for aluminum remelt furnaces. The analysis, however, did not include combustion products or particulates. Fluxes, degassing agents, and the batch composition will contribute to the composition of this waste gas stream, and include aluminum, calcium, chlorine, iron, potassium, magnesium, sodium, sulfur, fluorine, and vanadium. The waste gas streams for the glass melting furnace are the best characterized, probably due to the common use of regenerative furnaces in this industry and the problems encountered with the use of the flue gas in these regenerators. Glass melting furnace flue gas constituents have been analyzed thoroughly by the Environmental Protection Agency and the glass industry. The major components of this flue gas are the combustion products of the fuel. The critical corrosion/fouling substances introduced into the gas stream are usually fuel contaminants and batch components (such as carryover), and include aluminum, calcium, chlorine, fluorine, potassium, magnesium, sodium, sulfur, silicon, and vanadium.

Composition of Fouling Deposits and Corrosion Products

To some degree, constituents of a flue gas stream may be indicated by the corrosion products and fouling deposits on materials exposed to it. There are a limited number of studies that analyze the corrosion products and fouling deposits of the four candidate waste heat streams. However, data is lacking for many variations in operations, such as the broad ranges of steel and glass composition, fuel composition, and types of operation. Product and deposit analyses have not been accompanied by measurements of temperature, flow velocity, and stream composition. In general, the analyses are of a few small samples, without thickness measurement, without trace analysis of the substrate so that deposit constituents could be clearly differentiated, and without sufficient information for statistical evaluation. Consequently, predictions of deposition and corrosion in heat exchangers lack both empirical and theoretical bases. The most valuable information from corrosion product and fouling deposit analysis, for deducing problematic constituents of the waste gas stream, is the generally recognized contribution to fouling of fuel constituents such as sulfur, vanadium, sodium, potassium, and chlorine. Contributors to corrosion and

fouling from feedstock constituents, feedstock additives, and feedstock impurities can also be recognized in the analyses.

Additional Information Needed

As a result of the compilation and evaluation of available waste stream characterization information, it is concluded that additional waste stream characterization is necessary to adequately design advanced recuperator systems. The constituents and limiting flue gas conditions that cause heat recovery systems to have less than optimal performance and short lifetimes need to be identified for all the waste heat streams studied. The following information (listed in order of importance) is needed:

- Sizes of furnaces and correlating flue gas flow rates and temperature profiles
- The chemical composition of the flue gas from steel soaking and reheating and aluminum remelting. The effect on flue gas composition of reduced flow rates and temperatures in the heat recovery systems.
- The effects of the above variables on flue gas constituent deposition rates and the composition of scale and corrosion products formed in the heat recovery systems.

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HIGH-TEMPERATURE WASTE HEAT STREAM SELECTION AND CHARACTERIZATION

1. INTRODUCTION

In the United States, ~73 quadrillion Btu (quad) of fuels and electricity are purchased yearly. Approximately one-third of these fuels and electricity are purchased by the industrial sector. EPA estimates, however, that 23% of the major or energy intensive industrial energy consumption is discharged as waste heat in flue gases.¹⁻¹ For any single high-temperature (>1500°F) direct heating process, as much as 67% of the furnace energy consumed is lost with the flue gas; the higher the furnace temperature, the greater the percentage of energy lost.¹⁻² Thus, the potential for recovering energy from high-temperature (>1500°F) flue gases is large.

Industry has attempted to address the problem of loss of usable heat in flue gases by using waste heat recovery systems. These systems save energy by preheating furnace combustion air with heat recovered from the flue gases. Two major types of heat recovery system are discussed in this report: regenerators and recuperators. (Furnaces that have one of these types of heat recovery are termed regenerative or recuperative, respectively). In regenerators, combustion air is preheated by passage through brick checkerworks that have been previously heated by contact with hot flue gases. Recuperators preheat combustion air by passing it through a heat exchanger in which the hot stream is flue gas.

The high temperatures and sometimes corrosive constituents in flue gas waste heat streams affect the durability of the materials of construction and limit the use of heat recovery systems. Not many materials can structurally survive the high temperatures involved. Corrosion also has debilitating effects on nearly all materials, causing premature failures or excessive leakages. Failure of a heat recovery system not only disables waste heat recovery but can also severely impact process operation. In addition to causing corrosion, flue gas constituents can also foul heat exchanger surfaces. Fouling impacts process operation and heat recovery by

decreasing heat transfer rates and increasing pressure drop; these impacts increase costs by requiring (a) cleaning and refurbishing of heat exchangers and (b) increased heat exchanger surface area in installed systems, to compensate for expected fouling.

As shown in Figure 1-1, adequate design and development of advanced heat exchangers and heat recovery systems for severe flue gas environments requires a fundamental understanding of the corrosion and fouling mechanisms in these environments and their effects on the candidate materials. These mechanisms and their effects on materials are not well understood. The Department of Energy realizes this need and is developing a technical information base for corrosion, fouling, and other areas critical to the further technological advancement of high-temperature waste heat recovery.

The first step in understanding the high-temperature corrosion and fouling of materials is to identify the waste stream characteristics that cause the corrosion or fouling. These characteristics are temperature, flow rate, pressure, chemical constituents (flue gas composition), and as indicated in Figure 1-1, the effects of process variables on these constituents. As indicated in the figure, if the flue gas composition is not directly available from flue gas analysis, it might be deduced by knowing what is fed into the process and how this feed behaves chemically under the given operating conditions. It might also be deduced from the corrosion and fouling deposits on materials that have been exposed to the waste stream, if sufficient knowledge is available about (a) gas and particulate reaction mechanisms that produce these deposits and (b) the influence of system configuration and operating parameters on these mechanisms. The process variables that can affect flue gas composition include process feed composition, fuel type, operating schedule, and furnace materials.

The purpose of this document then, is to select processes for which large amounts of heat are lost in the off-gas streams because state-of-the-art heat recovery systems cannot be used due to fouling, corrosion, or other degradation of the systems by the excessively high temperatures and chemical constituents in the streams. The purpose of this document is also to begin to identify the characteristics of high-temperature flue

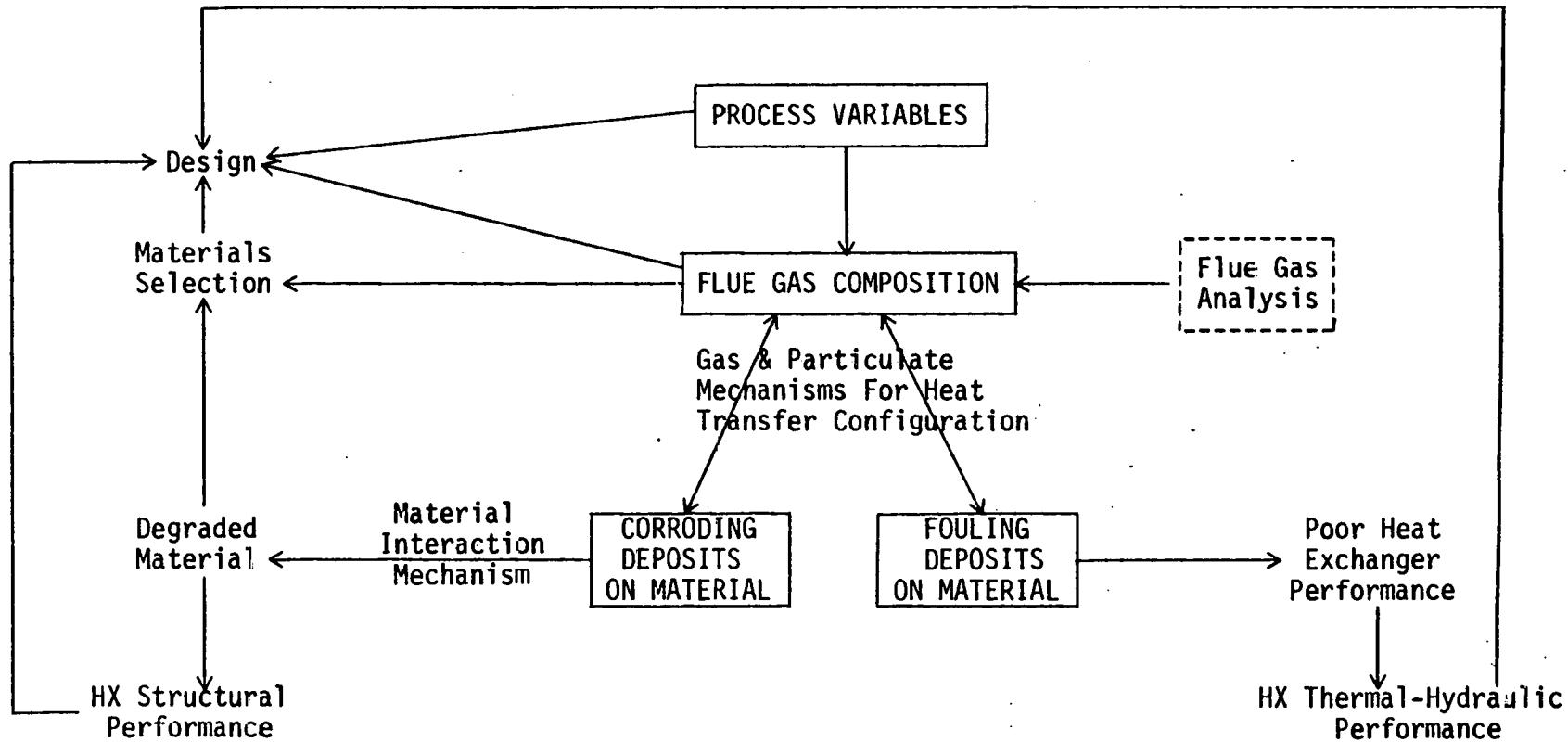


Figure 1-1. Relationship of design to waste heat stream characterization.

gases that cause corrosion or fouling of heat recovery systems. Available characterization information from the open literature, reports issued for government contracts, and industry sources are compiled and evaluated for the four major industrial high-temperature waste heat streams selected. Process variables, stream analyses, and analyses of deposits on materials exposed to these streams are presented. The research and development needed to obtain missing information is also discussed. Materials behavior and selection of materials is the topic of another report.

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- 1-1. S. R. Latour and J. G. Menningmann, Waste Heat Recovery Potential in Selected Industries, PB82-25927b, February 1981.
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2. PROCESS SELECTION

References 2-1 through 2-12 give available waste heat stream characterizations for the major types of industrial processes that have high-temperature off-gases. Several of these references also present a selection of process waste streams that would be primary potential candidates for waste heat recovery. As discussed below, based on this information, waste heat streams associated with four industrial furnace processes were selected for investigation in the current study of candidate streams for heat recovery. The processes are glass melting, steel soaking, steel reheating, and aluminum remelting. The criteria used for the current selection reflect the potential for fuel savings if the state-of-the-art technology for heat recovery from furnace flue gas were improved. These criteria were

1. Large amounts of fuel oil or gas are consumed by the furnace. The furnace has the greatest potential for discharging substantial quantities of waste heat to the environment.
2. A large amount of fuel savings is anticipated with the use of an advanced, high-effectiveness recuperator.
3. Initial flue gas temperatures are greater than 1900°F, the maximum acceptable temperature of the majority of state-of-the-art recuperators. (The flue gas temperature is measured at the base of the flue stack, before the gas passes through any existing recuperators.)
4. The furnace can be easily adapted to incorporate a high-temperature heat recovery system.
5. The flue gas at any time during furnace operation is too corrosive to use a state-of-the-art recuperator.

As shown in Table 2-1, the furnace flue gas from all four selected processes--glass melting, steel soaking or reheating, and aluminum

TABLE 2-1. SUMMARY OF POTENTIAL ENERGY SAVINGS AND FLUE GAS CHARACTERISTICS FOR SELECTED FURNACE TYPES

Furnace Type	Flue Gas Temperature (°F)	Energy Consumption (10^{12} Btu/yr)	Estimated Potential Fuel Savings (10^{12} Btu/yr)	Flue Gas Corrosiveness (Source)	Comment
Steel soaking	2200-2500	152	34.8	Corrosive (topping compounds, residue and particulates)	Unknown future; depression of industry and advent of continuous casting may eliminate steel soaking ^a
Steel reheating	2200-2500	335	135.5	Corrosive	Reluctance of industry to accept heat recovery systems
Aluminum remelt	1900-2300	49	27.5	Corrosive (fluxing compounds)	--
Glass melting	2600-2800	228	24.0 ^b	Highly corrosive (glass constituents)	Currently used regenerators have >70% effectiveness, but last only three years. ^c

a. From References 2-2 and 2-3.

b. Fuel savings were calculated assuming current regenerators are replaced by higher effectiveness, longer lasting recuperators; waste heat recovery upstream of regenerator is not considered.

c. From Reference 2-1.

remelting--meets the above selection criteria. Steel forging (using box and slot furnaces), copper processing (using reverberatory furnaces), and aluminum billet heating and annealing were also considered initially, but are not included here because of the cleanliness of their flue gases.

To make the present selection, yearly energy consumption, potential energy savings, and flue gas temperatures were reviewed for potential candidate processes and furnaces. Table 2-2 summarizes this information. The references used included two AiResearch Manufacturing Company studies^{2-4,2-5} that had previously selected glass melting, steel soaking, steel reheating, steel forging, and aluminum remelting as primary candidates for flue gas heat recovery. These two studies were part of a series of comprehensive, DOE funded studies to aid development of high-temperature recuperators. The study in Reference 2-4 was based on a mail survey of southern California industries and Department of Commerce (DOC) statistics for energy use in industrial sectors that were categorized according to standard industrial classification (SIC) numbers.²⁻¹³ The DOC statistics were used to preliminarily identify high-energy-consuming industrial sectors. Nationwide fuel oil and natural gas consumption were projected for each identified sector and potential fuel savings were calculated for the use of 85% effectiveness recuperators. In the study in Reference 2-5, a telephone survey and market assessment determined data that included flue gas temperature, ability of the process system to incorporate a recuperator, and annual fossil fuel consumption for a variety of furnace types.

Based on "...the applicability of the furnace to high temperature recuperation...," a similar Midland Ross study²⁻⁶ selected the same candidate processes and furnaces as the AiResearch studies, except the Midland Ross study did not select aluminum remelting. The sources of data used for this selection were not cited. In a Drexel University study,²⁻¹¹ all the above processes and furnaces were selected as candidates for energy recovery, based on high energy consumption, but the selection process used was not described. It should be noted that the flue gas temperatures given in this and in an EPA funded study²⁻¹² are lower than those given in the AiResearch and Midland-Ross studies. The lower temperatures were probably measured upstream of inplace recuperators or regenerators, or at the top of the flue stack, therefore this data is not included in Tables 2-1 or 2-2.

TABLE 2-2. LITERATURE ESTIMATES OF POTENTIAL ENERGY SAVINGS FOR HIGH-TEMPERATURE FLUE GASES

<u>Furnace Type</u>	<u>Reference</u>	<u>Flue Gas Temperature (°F)</u>	<u>Energy Consumption</u>		<u>Potential Energy Savings (10¹² Btu/yr)^a</u>
			<u>(10¹² Btu/yr)</u>	<u>Year</u>	
Steel soaking					
	2-5	1500-2500	152.0	1979	34.8
	2-6	2100-2400	160.0	1979 ^b	80.0
	2-4,2-8,2-9	--	295.0	1971,1979	--
Steel reheating					
	2-4	2200	861.7	1974,1977	191.7
	2-5	1500-2500	335.0	1979	135.0
	2-6	2000-2200	281.0	1979 ^b	140.5
Steel forging					
	2-4	2100	34.1	1974,1977	12.5
	2-5	1500-2600 ^c	85.0	1980	44.3
	2-6	2000-2100	50.0	1979 ^b	25.0
Aluminum remelt					
	2-4	1700-1900	166.7	1974,1977	28.4
	2-5	1400-2300	49.0	1978	27.5
	2-5	2000-2800	21.2	1979 ^b	--
	2-10		54.6	1980	--
Copper heating ^d	2-5	2400-2600	17	1976	--
Glass melting					
	2-4	1000-1600	234.0	1974,1977	28.6
	2-5	2600-2800	180.0	1979	19.0
	2-6	2600-3000	>200.0	1979 ^b	120.0
	2-4,2-7,2-8	--	191.2	1981	--

a. Assumed recuperator effectiveness for current installations was none in References 2-4 and 2-6; 40% for aluminum and steel processes and 70% for glass processes in Reference 2-5. Assumed effectiveness for future installations was 85% in References 2-4, 2-5, and 2-6.

b. Year of publication of data rather than year of energy consumption.

c. Temperatures were 2400 to 2600°F for slot forge furnaces and 1500 to 2600°F for carbottom and box forge furnaces.

d. Reverberatory furnace; type of processing was not specified.

The energy consumption and potential fuel savings were also calculated independently for the above selected processes to confirm the selection. Raw energy consumption numbers were obtained from References 2-7 and 2-8. Raw potential fuel savings were then calculated from the projections in Reference 2-4 for percent fuel savings for given temperatures.

Of the processes and furnace types selected in the present study, steel reheating furnaces and soaking pits exhibit the highest potential for fuel savings with the use of advanced recuperators. However, the uncertain future of the steel industry and the increased use of continuous casting operations might reduce or eliminate the use of the soaking pit. Heat recovery systems for glass melting furnaces and tanks will require the most advances in the state-of-the-art technology, because materials and configurations must be developed that can withstand the highly corrosive, high-temperature flue gas stream.

The following sections describe the processes for which the selected furnaces are used and discuss the available flue gas characterization information for each furnace type, including temperature, pressure, flow rate, chemical constituents, and fouling and corrosion of materials for heat recovery systems.

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3. STEEL SOAKING PITS AND BILLET REHEAT FURNACES

3.1 Process Characterization

In the steel industry, soaking pits and billet reheat furnaces are used to produce a metal of uniform temperature for rolling and shaping in steel finishing. Following pouring, the solidified ingot is stripped from its mold and placed in a soaking pit where it is heated to the uniform temperature required for rolling to produce slabs, blooms, or billets (Figure 3-1). The rolled product is subsequently heated in a reheat furnace to allow further shaping and treatment to produce the finished steel product. If continuously cast steel is used instead of ingots, the soaking pits may be bypassed.

Several types of soaking pits and billet reheat furnaces exist that accept different shapes of ingots or billets, allowing specific metal arrangements and heating temperatures.^{3-1,3-2} These pit types are outlined briefly below; all use high-temperature air or combustion gases to heat the ingots or billets.

3.1.1 Soaking Pits

The regenerative soaking pit is the oldest of the modern types of soaking pits. The ingot is heated by alternate operation of burners on the side walls of the pit. Control of the timing and intensity of firing of each burner (firing and dampering) equalizes the temperature on both sides of the ingot. The products of combustion pass horizontally across the pit and exit through the regenerator flues and stack to the atmosphere.

One of the most common types of soaking pit is the one-way fired pit, especially in conjunction with recuperative heat recovery (Figure 3-2). One-way pits are continuously fired; the combustion space is above the ingots and thus is unaffected by the number of ingots charged. The flow of gases through this type of pit is vertical, in accordance with hydrostatic principles.

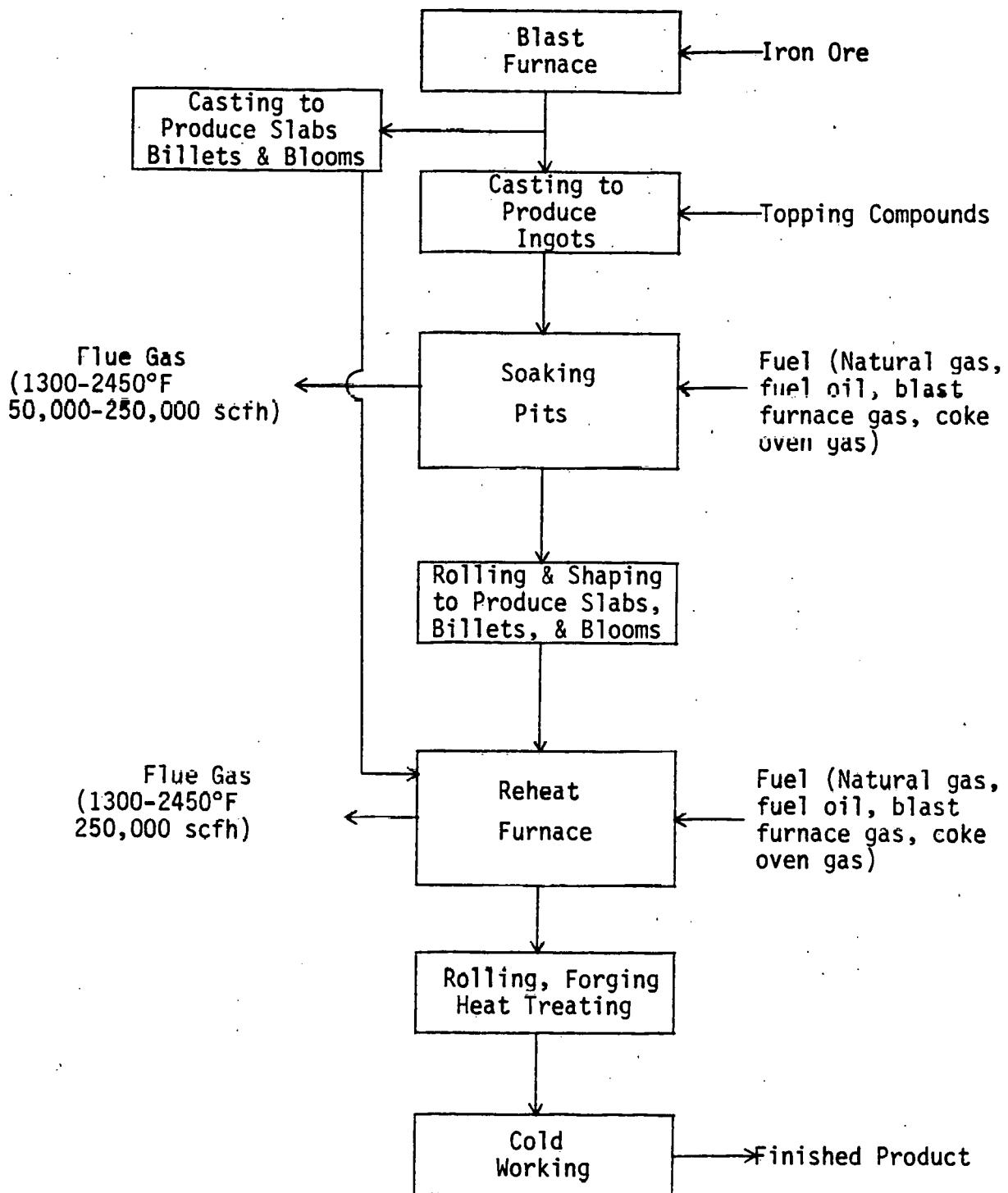


Figure 3-1. Steel production.

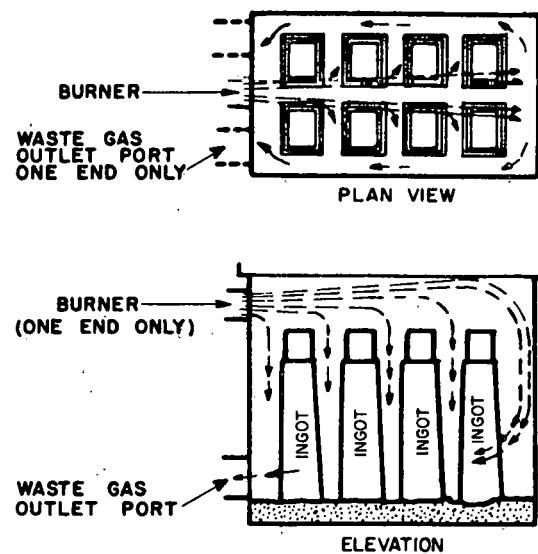


Figure 3-2 One-way fired soaking pit (from The Making, Shaping, and Treating of Steel, 3-2 copyright 1971 by U.S. Steel Corporation; used by permission).

In the bottom center fired (vertically fired) pit (Figure 3-3) the fuel is vertically fired through a port in the bottom center of the pit. This burner location promotes circulation of the gases around the ingots to aid heat distribution and the removal of combustion products. These pits may be recuperative.

In a circular pit (Figure 3-4), burners located in the lower periphery of the inclined side walls of the pit are fired tangentially. This burner arrangement permits recirculation and a long travel path for the combustion gases. The gas circulation ensures a uniform temperature in the pit. Normally, in a circular pit, high-Btu-content fuel and cold air are mixed in premix or nozzle-mix burners to insure complete combustion of the fuel before the hot combustion gases contact the ingots.

Bottom two-way fired pits (Figure 3-5) are fired by burners located at the center bottom of opposite end walls. Four flue gas ports are located in the same end walls, but at each corner. Combustion takes place in the center aisle. Spent gases flow from the flue gas ports to a recuperator located at each end of the pit. The position of the burners and the waste gas ports increases the turbulence of gases in the pit and improves the heating of the bottom of ingots.

In a top two-way fired pit (Figure 3-6), the burners are fired horizontally at an angle to the centerline of a deep pit. Firing occurs above the ingots, resulting in a swirling motion of the gases. The flue gas ports are located in the end wall just above the centerline. As in the one-way fired pits, the overall flow of gases is vertical. The shape of the pit depends on the desired coverage of the ingots; the sides and end walls are sometimes elliptical.

Electric soaking pits are used when a controlled atmosphere is required, such as for metals that require control of scaling. Electric soaking pits are divided into a number of cells that each hold one or more ingots.

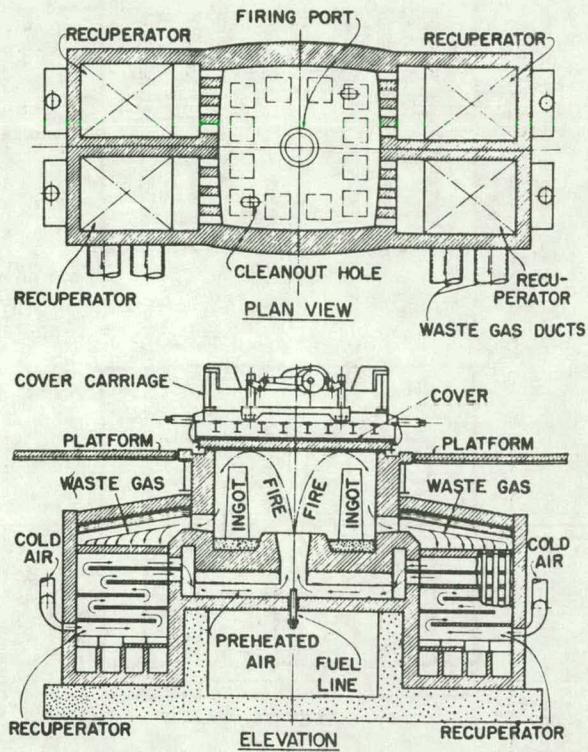


Figure 3-3. Vertically fired soaking pit (from The Making, Shaping, and Treating of Steel,³⁻² copyright 1971 by U.S. Steel Corporation; used by permission).

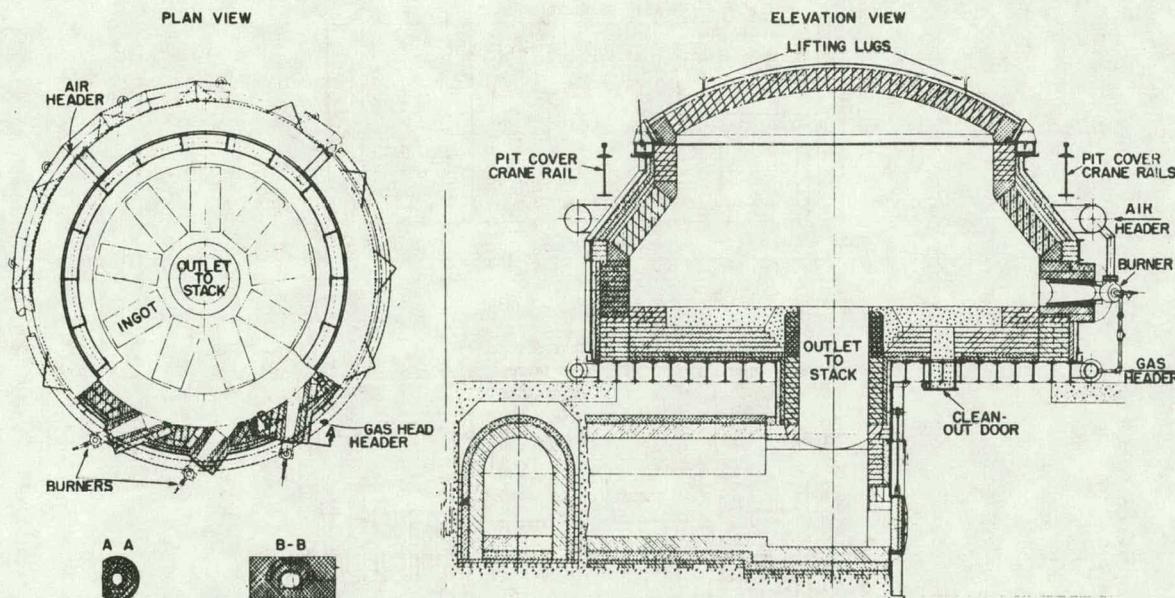


Figure 3-4. Tangentially fired soaking pit (from The Making, Shaping, and Treating of Steel,³⁻² copyright 1971 by U.S. Steel Corporation; used by permission).

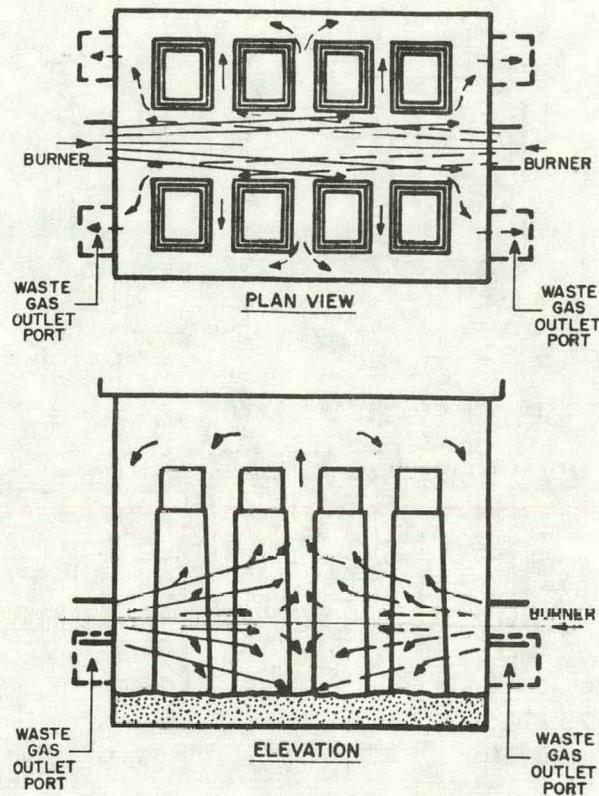


Figure 3-5. Bottom two-way fired soaking pit (from The Making, Shaping, and Treating of Steel,³⁻² copyright 1971 by U.S. Steel Corporation; used by permission).

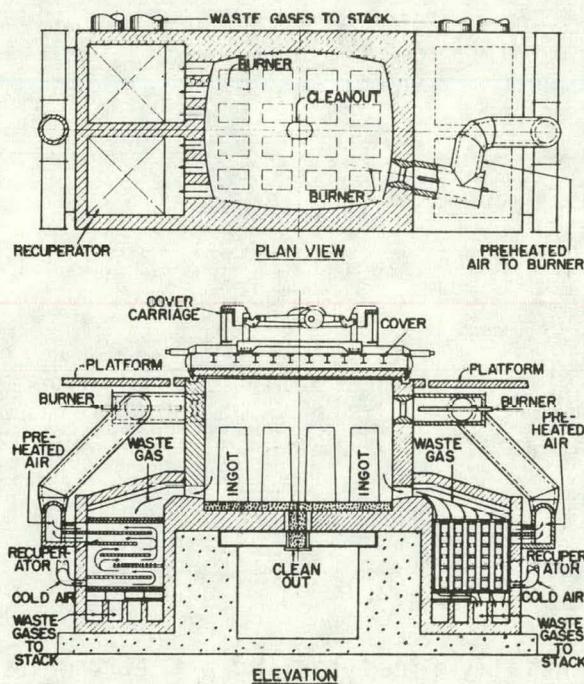


Figure 3-6. Top two-way fired soaking pit (from The Making, Shaping, and Treating of Steel,³⁻² copyright 1971 by U.S. Steel Corporation; used by permission).

3.1.2 Billet Reheat Furnaces

There are two types of billet reheat furnaces--batch and continuous.^{3-3,3-4} The batch furnace (Figure 3-7) is designed to heat the material to rolling temperature in a fixed position on the hearth. Although the batch furnace is generally less productive than the continuous reheat furnace, it can attain a higher temperature, be more closely controlled, and handle a wider variety of steel types, shapes, and sizes.

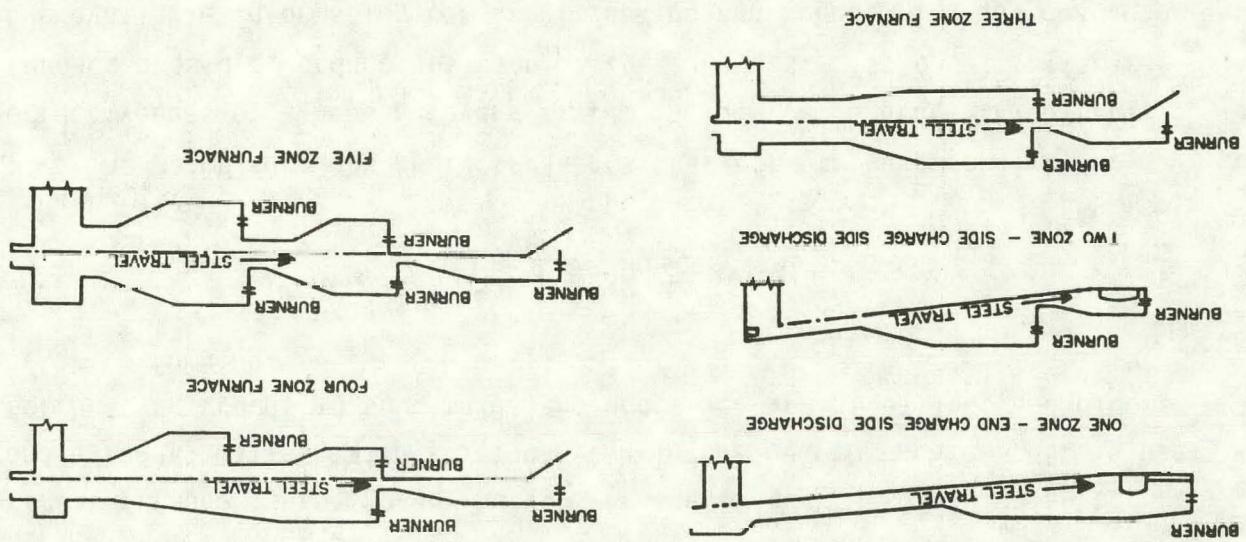
Continuous reheat furnaces are generally of two types--pusher and walking beam. The pusher type (Figure 3-8) consists of up to five heating zones, each with its own set of burners. There are many older furnaces with only two zones, however, and a newer design includes an unfired preheat zone that is heated by the exiting flue gases. In a pusher type furnace, the slab, bloom, or billet is charged (from the end or a side door) against a previously charged piece, forcing it further into the heating path of the furnace. The walking beam furnace (Figure 3-9), a relatively new design, uses water cooled beams to convey the material through the furnace. Generally the flow of steel in the continuous furnace is countercurrent to the flow of gases. A third, less common, continuous reheat furnace is the rotary hearth furnace (Figure 3-10) in which the roof and external walls remain stationary while the hearth rotates. It is used for heating rounds in tube mills and short lengths of billets and blooms prior to forging.

3.2 Flue Gas Characterization

The major flue gas characteristics that affect the durability or effectiveness of a heat recovery system include temperature, flow rate, furnace pressure, and composition of the flue gas. Table 3-1 summarizes the available information for steel soaking and reheat flue gas characteristics, including the factors that influence or control these characteristics. Although the flue gas temperatures are known, information is limited for flow and pressure, and the composition of the waste gases is not available. The flue gas characteristics are dependent on the reheating conditions in the furnace; the reheating conditions in turn are largely

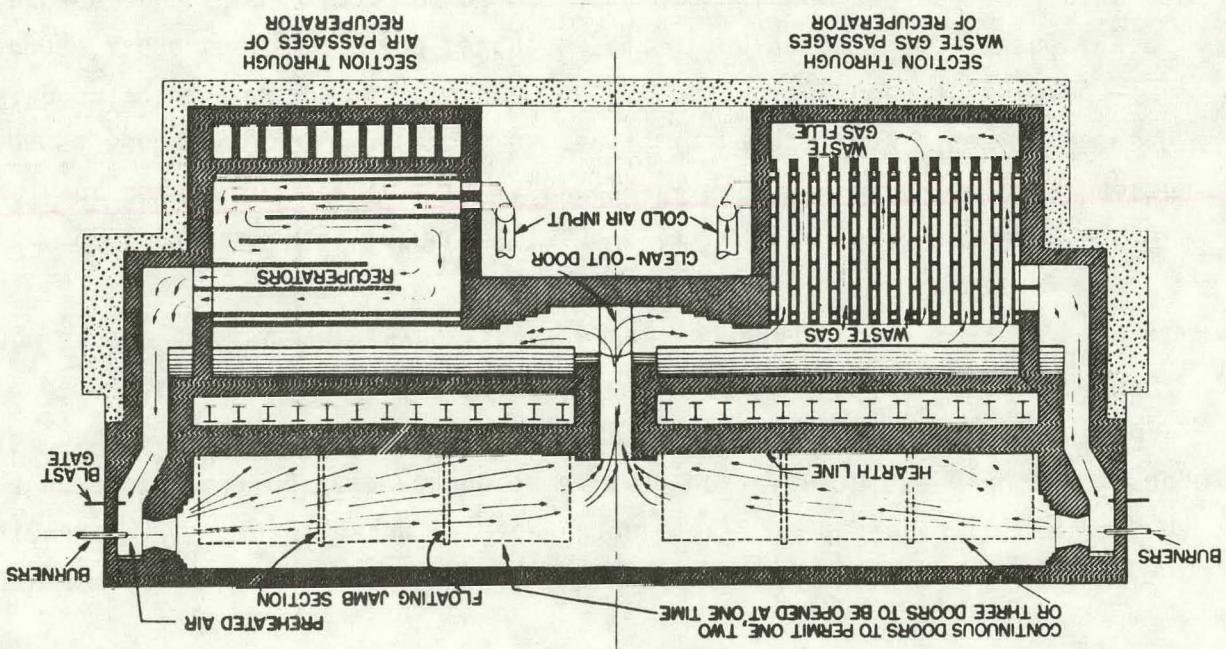
Shaping, and Treating furnaces (pusher type) (from The Making Steel Corporation; used by permission).

Figure 3-8.



Shaping, and Treating furnaces (reheating type) (from The Making Steel Corporation; used by permission).

Figure 3-7.



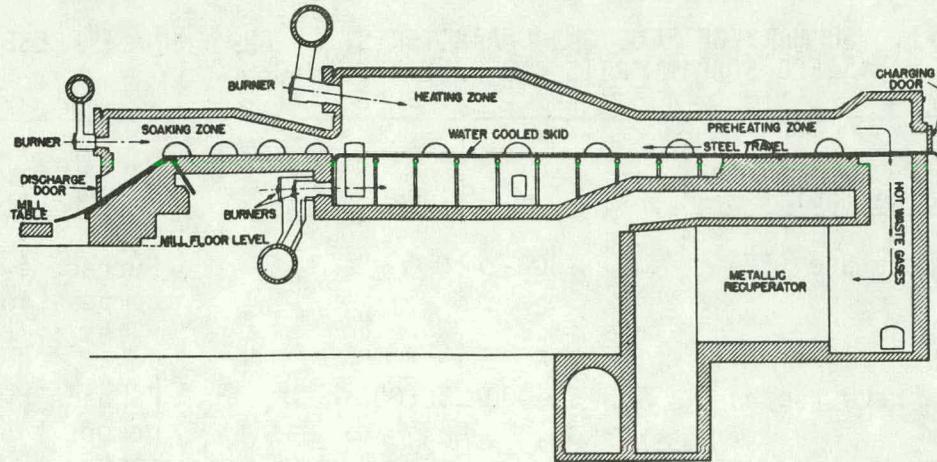


Figure 3-9. Counter-current continuous reheating furnace (walking beam type) (from *The Making, Shaping, and Treating of Steel*,³⁻² copyright 1971 by U.S. Steel Corporation; used by permission).

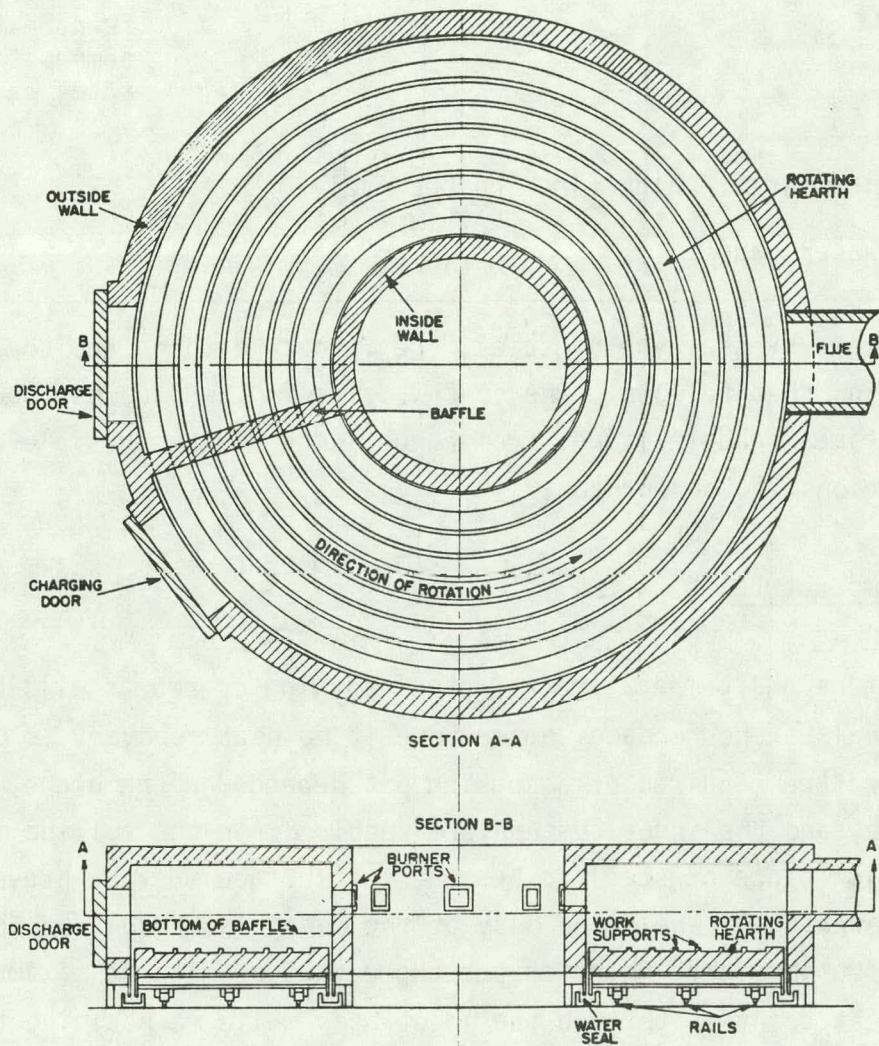


Figure 3-10. Continuous rotary hearth heating furnace (from *The Making, Shaping, and Treating of Steel*,³⁻² copyright 1971 by U.S. Steel Corporation; used by permission).

TABLE 3-1. SUMMARY OF FLUE GAS CHARACTERISTICS AND FURNACE PRESSURE FOR STEEL SOAKING PITS AND REHEAT FURNACES

Characteristic	Value	Variables That Affect Characteristics
Gas temperature (°F)	1300-2450	Furnace type, alloy composition, firing rate
Gas flow rate (scfh)	50,000-250,000 ^a	Furnace type, alloy composition, firing rate
Furnace pressure (in., wg) ^b	Slightly positive	Damper setting, firing rate
Gas composition	Not available	Topping compounds, fuel composition, furnace floor composition, firing rate.

a. From low fire to high fire, respectively.

b. wg = water gauge.

predetermined by the type of steel, the furnace design, and the type of metalworking that follows. The constituents in the flue gas stream can also sometimes be determined, from a knowledge of the possible constituents and conditions in the furnace.

3.2.1 Temperature

The flue gas temperature for steel soaking or reheat will be approximately equal to the furnace temperature if no heat recovery is provided. The temperature required of a soaking pit depends on the grade of steel, ingot size, and the ingot temperature required for the rolling mill.³⁻¹ When a thick piece of steel is heated, the surface must be prevented from melting (sweating), while the body of the metal is brought up to temperature.³⁻² Optimum heating rates are those that permit the maximum conductive heat transfer through the ingot body while maintaining the surface of the ingot just below the sweating point. Thus, to heat an ingot, the

burner is put on high fire to quickly bring the furnace temperature to just below the sweating point. The burner is then put on low fire to maintain the maximum heating temperature until the entire ingot is up to the required working temperature. The flue gas temperature for a soaking pit thus cycles from an initially high temperature to a constant lower temperature; with about half the reheat time at low fire. The maximum heating temperature is determined by the ingot composition and the specific furnace. For chrome nickel alloys in a double-chamber billet heating furnace, the maximum temperature is 2350°F, while for a high-carbon steel in an end fired soaking pit, it is 2450°F.³⁻³ Table 3-2 lists the maximum heating temperature of several grades of steel in the soaking pit of the TISCO Blooming Mill No. 2.³⁻⁴

TABLE 3-2. MAXIMUM SOAKING TEMPERATURES FOR SELECTED STEELS³⁻⁴

a Grade	b Temperature (°F)
Semi-killed and killed; up to 0.4% C	2340
Rimming quality strip bar	2340
0.4 to 0.6% C	2340
SWR with 0.6% C; 65 Si 7 spring steels	2280-2300
42 quality Hi Si HR	2230-2260
AMD-21, AMD-22A, Tata A; ball bearing steel	2230
Tata Special A	2150-2190

a. Steel grades are as listed in Reference 3-4; no explanation of these grades was given.

b. Temperatures are for the soaking pit of TISCO Blooming Mill No. 2.³⁻⁴

Reheat furnaces operate at a lower nominal temperature than soaking pits because of the smaller size of the charged pieces and the different requirements for final rolling. The temperature of the waste gases from a continuous reheat furnace will be essentially constant. If the furnace is recuperative with countercurrent flow, the waste gas temperature will approach the minimum reached in the heating zone but will also depend on the temperature of the material charged and maximum temperature attained by the furnace. Specific temperatures for reheat furnaces were not found in the search conducted for this report.

For a soaking pit or batch reheat furnace, the minimum temperature occurs when the furnace is charged. Normally this minimum is between 1300 and 1700°F,³⁻⁵ and depends on whether the material is charged cold or hot.

3.2.2 Flow Rate

The flow rate of the waste gases from a soaking pit or reheat furnace depends on the flow rate of fuel required by the furnace to attain the desired temperature. The maximum flow rate can be calculated from the maximum rating (installed input) of the burner. For example, for the Lone Star Steel soaking pit furnace, the installed input is 22 mm-Btu/h maximum at ambient temperature.³⁻³ For natural gas, having a calorific value of 1000 Btu/scf, the maximum natural gas flow rate would therefore be 22,000 scfh. For this pit, 10 ft³ of excess air is added for 1 ft³ of gas to ensure complete combustion; the maximum total flow rate would therefore be about 240,000 scfh. For the Babcock & Wilcox soaking pit, the flue gas flow rate is 230,000 scfh at the maximum acceptable temperature to the recuperator of 1750°F.³⁻⁶ For the Cyclops in-and-out billet reheat batch furnace, the maximum flow rate for each of four burners is 4000 scfh with 10% excess air.³⁻³ This would produce a total waste gas flow rate slightly lower than that for the Lone Star Steel and Babcock and Wilcox soaking pits. The average waste gas flow rate for these furnaces is ~250,000 scfh.

For a given furnace, the waste gas flow rate will also depend on whether the furnace is operated at high fire or low fire conditions. For example, the Lone Star Steel furnace is operated at the maximum flow rate during only part of the cycle. Figure 3-11 shows a typical heating curve for this soaking pit³⁻³ and includes a typical fuel curve for the pit. Figure 3-12 shows the fuel flow curve for the Cyclops in-and-out billet reheat furnace.³⁻³ The required fuel flow also depends on whether round or hexagonal billets are being heated, whether the combustion air is pre-heated, and the preheat temperature. If ingots and billets are charged hot, a lower flow rate will result than if they are charged cold. A continuous reheat furnace will have a more constant gas flow rate than a

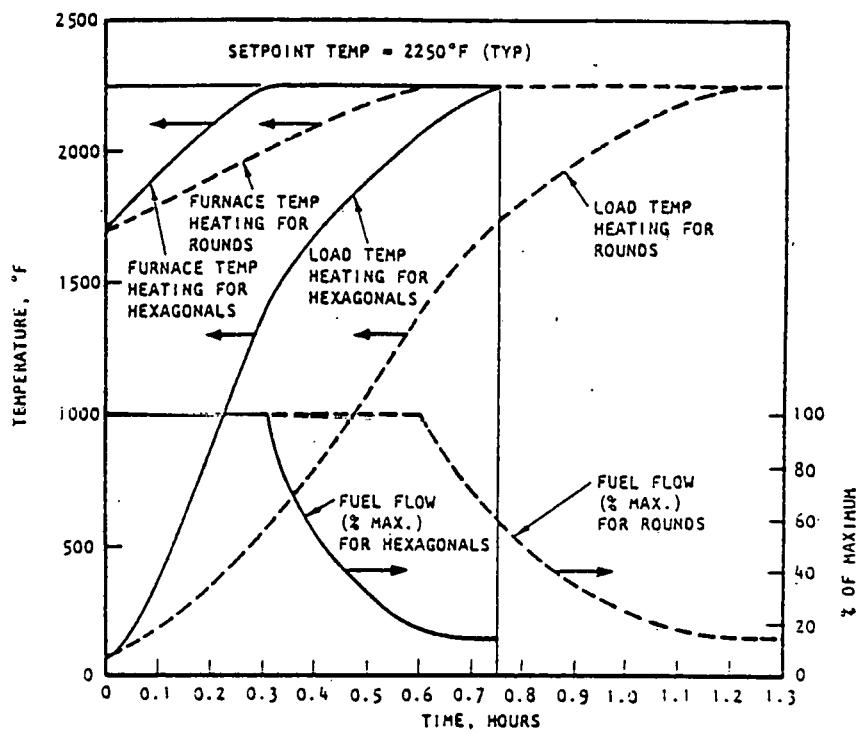


Figure 3-11. Typical heating curves for Lone Star steel soaking pit (from Reference 3-3).

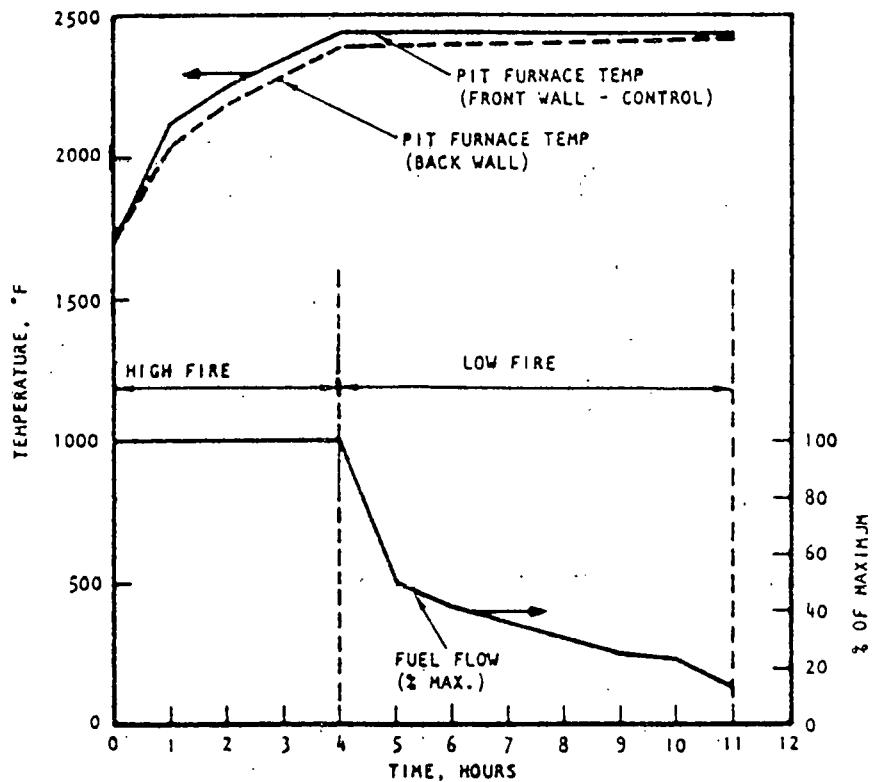


Figure 3-12. Typical heating curves for Cyclops in-and-out billet heating furnace (from Reference 3-3).

soaking pit or batch reheat furnace. Also, the flow rates and temperatures for a continuous reheat furnace should not reach the lows obtained from batch operations.

3.2.3 Pressure

Little information was found on operating pressures for soaking pits and reheat furnaces. The pressure is nominally slightly lower than atmospheric [within a few hundredths of an inch (water gauge)]. For the Lone Star soaking pit, the pressure is maintained at 0.06 in. (water gauge) during operation.³⁻³

3.2.4 Constituents

The composition of the waste gases from steel soaking and reheat furnaces was not available. As indicated in Table 3-1, there are four major variables that affect the rate of addition and types of particulate and gaseous species in the flue gas. These variables are the composition of topping compounds, fuel, and the furnace floor, and the rate of use of the combustion mixture (firing rate). Oxidation products of the ingot or billet can also contribute to flue gas contamination.

The major constituents of the flue gas will be the products of fuel combustion and will therefore depend on the type of fuel. Although the impurities in fuels can vary, Table 3-3 lists typical impurities in fossil fuels used for the high-temperature processes considered in this report. These fuels are natural gas, No. 2 fuel oil, and No. 6 fuel oil (residual oil). Natural gas is a relatively clean fuel; its combustion yields essentially no sulfur emissions, 6.4 to 6.7 vol% CO₂, 12 to 18 vol% H₂O, 70 to 75 vol% N₂, and 4.0 to 6.5 vol% oxygen.^{3-9,3-11,3-12} No. 2 fuel oil contains up to 1% sulfur and will increase the off-gas CO₂ to 10 vol% and SO₂ to 0.05 vol%. Although generally No. 6 fuel oil is not used in the soaking pits and reheat furnaces, it contains 2 to 3% sulfur and a vanadium additive that will be emitted in the flue gas as vanadium oxide.³⁻¹³ (The vanadium enhances the formation of sulfur trioxide and sulfate from sulfur dioxide).

TABLE 3-3. TYPICAL IMPURITIES IN FUELS

Fuel	Typical Impurity Elements ^a	Reference
Natural gas	S	--
No. 2 fuel oil	S, Si	3-7, 3-8
No. 6 fuel oil	S, V, Na, K, N	3-9
Coke oven off-gas	S, Na, K	3-9
Blast furnace off-gas	S, Na, K	3-10

a. This information was obtained incidental to the present search. A directed search, including fuel analyses and consultations, could provide a more complete listing of elements, and classifications of fuels by impurity content, such as "sour gas" and "Venezuelan oil" (said to contain seawater impurities).³⁻⁹

In about 10% of soaking and reheat furnaces, blast furnace off-gases supply a portion of the fuel requirements. Coke oven off-gas can also be used as fuel. These gases are cooled and scrubbed to remove particulates and sulfur.^{3-9,3-14,3-15,3-16} Table 3-3 lists the typical impurities recognized for blast furnace gas and coke oven gas. When scrubbed off-gas is used as a fuel for steel reheating, however, these constituents probably do not contribute significantly to the composition of the reheat furnace flue gases.

Because it transfers heat better than refractory would to the bottoms of ingots or billets, coke is used as a hearth floor material in soaking pits and reheat furnaces. This coke flooring is the major contributor of particulates to the flue gases from these furnaces. Two types of coke flooring are used. The most common is coke oven breeze (ashes)³⁻¹⁷ that is 1/2-in. mesh or smaller and can include dust. In the second (dry bottom), dolomite $[\text{CaMg}(\text{CO}_3)_2]$ or magnesite (MgCO_3) is mixed with the coke breeze. The constituents present in the coal feed (Table 3-4) to the coke making process are potential contaminants of the coke breeze.³⁻¹⁷ The hearth floor is also subject to the formation of calcium or magnesium oxide (scaling) and to abrasion.³⁻¹⁷ The resulting fine coke and scale particles can be carried out with the circulating gases.

TABLE 3-4. ANALYSIS OF COAL USED IN COKE MAKING³⁻¹⁷

	Coal Sample		
	A	B	C
Classification			
Rank (ASTM)	1vb	hvAb	mvb
International system	334	635	535
Specific volatile index	219	175	184
Carbon (%)	91.0	87.1	88.3
Proximate analysis (%)			
Ash	6.2	5.1	6.8
Volatile matter	17.5	32.1	28.7
Fixed carbon	76.3	62.8	64.5
Gross calorific value (Btu per pound)	14,735	14,625	14,500
Ultimate analysis (%)			
Carbon	84.7	82.2	81.7
Hydrogen	4.5	5.3	5.1
Sulfur	0.82	0.79	0.80
Nitrogen	1.2	1.6	1.6
Ash	6.2	5.1	6.8
Oxygen ^a	2.6	5.0	4.0
Ash analysis (%)			
SiO ₂	50.0	52.7	49.0
Al ₂ O ₃	30.1	28.4	29.1
Fe ₂ O ₃	11.5	10.0	9.7
TiO ₂	2.1	1.5	1.5
P ₂ O ₅	0.1	0.1	0.2
CaO	1.8	1.9	2.2
MgO	0.4	0.9	1.2
SO ₃	1.9	1.8	2.4
Na ₂ O	0.5	0.5	0.6
K ₂ O	1.2	1.5	2.4

a. By difference.

An additional source of flue gas contaminants is the oxidation of ingots or billets. The oxygen content of the fuel is controlled so that carbon does not become a scaling problem, however iron and some alloying elements are still oxidized, forming an iron-oxide--alloy-element-oxide scale on the metal. This scale is ~1 to ~2% of the ingot or billet. To remove surface defects, if present, this scale layer is burned off and a new scale layer is formed.³⁻¹⁵ Although some of the burned-off scale will remain on the hearth floor, some will be carried into the flue gas by the circulating gas. Scale oxides may be present in the flue gas as gas or as particulates.

A final source of flue gas contaminants is topping compounds added to the ingot surface following casting. These compounds react to prevent the surface from cooling too rapidly and have been indicated as a source of corrosion in systems using recuperators.³⁻¹⁴ No reported analyses were found for topping compounds, since the compositions are usually proprietary.

The topping compound residue, assumed to be largely refractory oxides, would also contribute particulates to the flue gas; these particulates would contain any impurities present in the residue. Information from the British Steel Corporation indicates that fluoride from hot topping compounds (residues on the ingots, presumably) contributes to corrosive deposits from soaking pit flue gases.³⁻¹⁸ Although this would indicate that the fluoride was present in the flue gases, oxidation of the calcium fluoride in hot topping compounds is expected to drive off the fluorine (probably as HF) before the ingots are placed in the soaking pits.³⁻¹⁰

3.2.5 Fouling and Corrosion

The elements found in flue gas system fouling deposits and corrosion products, and the identified sources of these elements, are summarized in Table 3-5. The critical flue gas constituents in the corrosion and fouling of recuperator materials can be postulated by evaluating the results of corrosion and fouling studies, discussed below.

TABLE 3-5. ELEMENTS IN FOULING DEPOSITS AND CORROSION PRODUCTS FROM FLUE GASES OF STEEL REHEAT FURNACES AND SOAKING PITS^{3-9,3-10,3-19}

Probable Source	Elements
Ingots and billets	Fe, Si, Mn, Cr, Pb ^a
Hot topping compounds ^b	Al, Ca, F, Mg, Si, Fe, Zn
Other ^c	K, Na, Al, Ca, Cu, Mg, Ti, S, V

a. Ni and Mo are present in some feedstocks but not identified by the references in this search as constituents of a deposit or corrosion product. Depending on the feedstock composition, additional elements may also be present.

b. Hot topping compounds are proprietary and variable, thus these elements could vary.

c. Other sources include, for example, fuels, refractory, and dust in air.

Glassy appearing deposits have been found on silicon carbide tubes placed in the waste gas flue of a soaking pit. The tubes, located near the pit and upstream from the dilution air, were exposed for 36 days while such alloys as 2 Cr-0.25 Mo, carbon steel, low Cr-Ni-Mo steel, and Ni-Mo steel were processed. During this time, the furnace temperature cycled from 1600°F after charging, to 2300°F during soaking. Semiquantitative emission spectrographic analysis of deposits from two of the tubes were essentially identical (Table 3-6).³⁻¹⁹ It appears from this analysis that overheating in the soaking pit results in the transport of FeO (as well as other elements of the alloy) as molten particulates (mist). Initial volatilization may be followed by reaction in the flue gas with water, carbon dioxide, or excess oxygen. Transport of iron as the FeO mist would be dependent on temperature, oxygen activity in the gas, and the gas velocity and flow pattern.³⁻²⁰

Analyzed deposits from flue gases from the Inland Steel soaking pit included 80 to 85% iron oxides (including large magnetite crystals), "small" percentages of SiO₂ and Al₂O₃, and a "tiny" percentage of CaO.³⁻¹⁰ Magnetite crystals are necessarily grown from molten or volatile material. The bulk of the deposits therefore appeared to consist of entrained particles of scale in cooled molten or condensed volatile material.

TABLE 3-6. ANALYSIS OF A SLAG DEPOSIT FROM STEEL SOAKING PIT FLUE GAS³⁻¹⁹

<u>Element</u>	<u>Composition (wt%)</u>
Fe	>10
Si	>10
K	5
Na	3
Al	3
Ca	0.7
Mn	0.3
Cu	0.3
Mg	0.1
Ti	0.08
Cr	0.07

Impurities in furnace fuel (Table 3-3) are also found in waste gas flue deposits and corrosion products (Table 3-5).^{3-9,3-10} These impurities can form volatile species at high temperatures. These volatilized impurities can then deposit at lower temperatures and subsequently cause corrosion. Information from U.S. Steel emphasizes sulfur and alkali (sodium and potassium) contributions from coke oven gas and No. 6 fuel oil and indicates that vanadium from the No. 6 fuel oil appears in deposits from flue gases.³⁻⁹

As discussed earlier, information from the British Steel Corporation indicates that fluoride from hot topping compounds (presumably residues on the ingots) contributes to corrosive deposits from soaking pit flue gases.³⁻¹⁸

Everything in the furnace or soaking pit, including the furnace materials, is a potential source of flue gas constituents that can form fouling deposits or contribute to corrosion. For example, unfiltered combustion air can include particulates,³⁻¹⁰ and if water rather than air is used to cool the flue gas to temperatures that a metallic recuperator can tolerate, then sulfate and other impurities can be introduced.³⁻¹⁸

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4. ALUMINUM REMELT FURNACES

4.1 Process Characterization

The off-gas stream from aluminum remelt is also considered a prime candidate for heat recovery that could effect large energy savings. Following electrolytic reduction (smelting), molten aluminum is siphoned from the reduction pot directly into a holding or remelt furnace. Here it is alloyed and degassed, then cast into an ingot of the proper metallurgical structure and size for metal working. The molten aluminum may also be cast into ingots prior to remelt.⁴⁻¹ Electrolytic reduction, remelt, alloying, and the final casting of new aluminum are called the primary aluminum process (Figure 4-1). The primary process can include the remelt of scrap from rolling and machining of the aluminum metal. When aluminum is being recycled, however, this sequence of steps is called the secondary aluminum process.⁴⁻² In the remelt step, recycled aluminum is treated in the same manner as new metal, however its higher level of contamination can lead to greater levels of impurities in the remelt furnace off-gas. The recycled aluminum in this step can include such contaminants as stainless steels, magnesium and other alloying agents, and dirt (hydrocarbons from oily residues and paints).

Remelting of the aluminum generally takes place in a continuous reverberatory furnace--a furnace in which the flame is developed some distance above the hearth and heat is reflected onto the hearth by an arched or sloped roof (Figure 4-2).^{4-3,4-4} To burn off any hydrocarbons or volatiles and bring the metal up to temperature, the ingot or baled scrap is allowed to remain on the forehearth of the remelt furnace before being pushed into a bath of molten metal.⁴⁻¹ Following melting and the addition of alloying agents, the molten metal is skimmed to remove oxide and dross that have risen to the surface. The metal is then run to a holding furnace, generally also a reverberatory furnace, and the temperature is adjusted for casting. (The steps of the remelt and holding furnace may also be combined in one furnace.) Any fluxing and degassing agents are added and there may be a quiescent period to allow any particulate matter to settle. The metal is then cast by a semicontinuous or direct chill process.⁴⁻¹

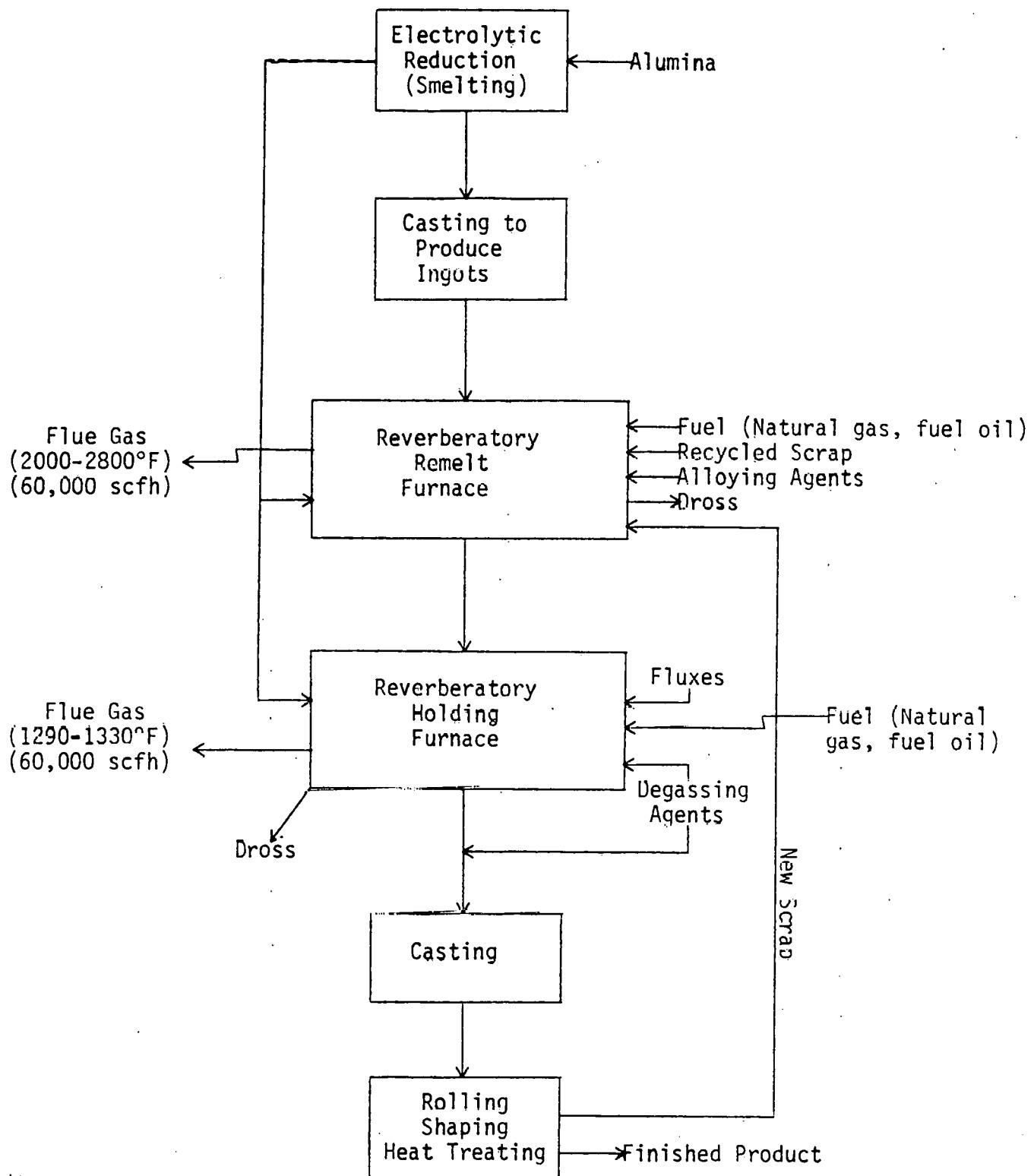


Figure 4-1. Aluminum production.

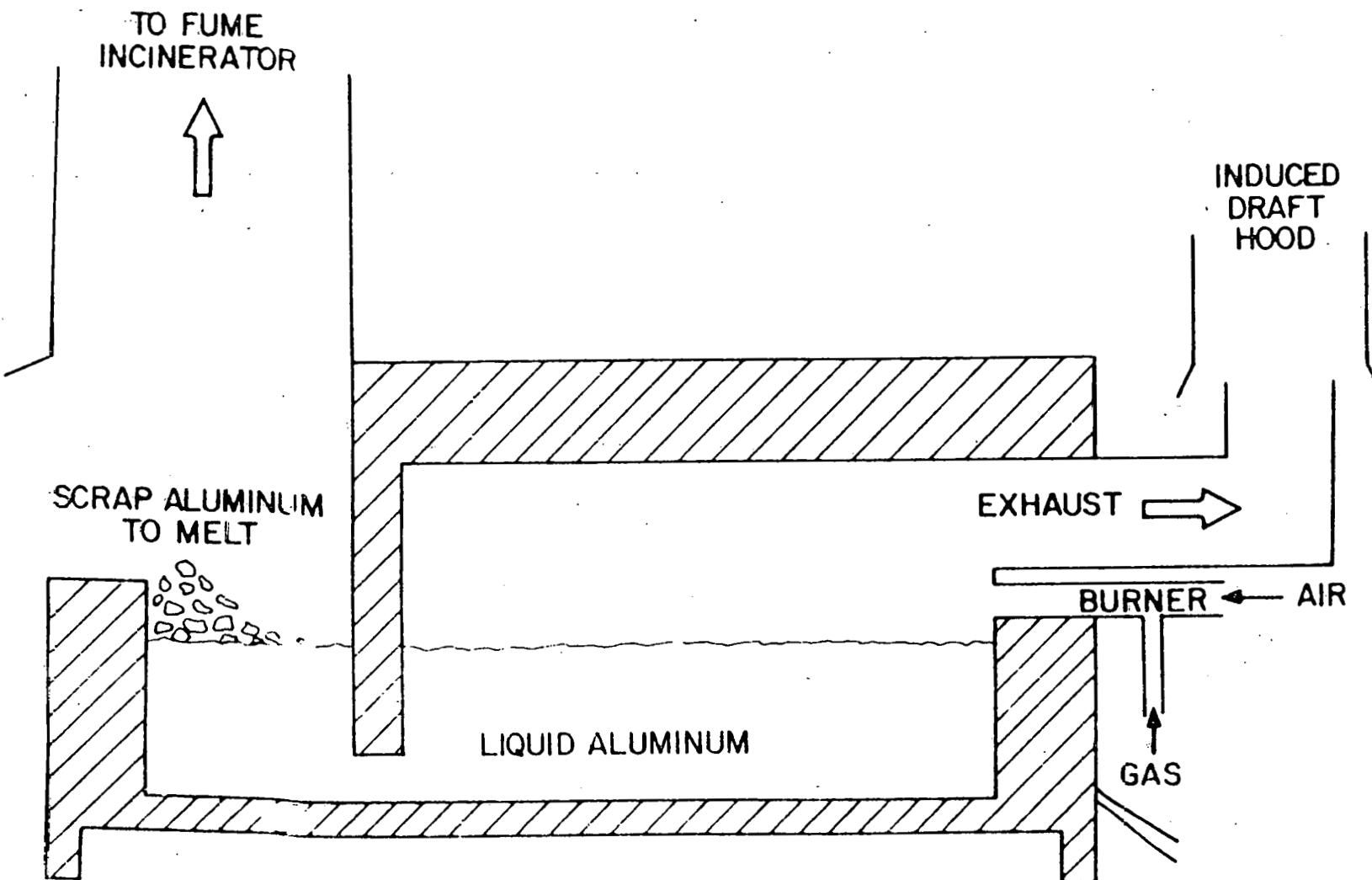


Figure 4-2. Aluminum smelting furnace (from Reference 4-5).

4.2 Flue Gas Characterization

Table 4-1 summarizes the available temperature, pressure, and flow rate information for aluminum remelt flue gas, and indicates the variables that can affect these parameters and flue gas composition. The compositions of the waste gas streams, however, could not be adequately characterized from the available information. For example, EPA analysis of industrial waste gas streams includes the off-gas stream for the electrolytic reduction process for aluminum, but not the remelt process.⁴⁻⁵ Limited information was available, however, on postulated and analyzed flue gas constituents. Scattered information was also available on the melt temperature, fluxes, degassing agents, and fouling and corrosion of materials in off-gas systems. The available information on flue gas characterization for aluminum remelt is discussed below.

TABLE 4-1. SUMMARY OF FLUE GAS CHARACTERISTICS AND FURNACE PRESSURE FOR ALUMINUM REMELT FURNACES.

<u>Characteristic</u>	<u>Value</u>	<u>Variables That Affect Characteristic</u>
Gas temperature (°F)	1100-2800	Furnace type, alloy composition, firing rate
Gas flow rate (scfh)	50,000-250,000 ^a	Furnace type, alloy composition, firing rate, degassing rate
Furnace pressure (in., wg) ^b	-0.02-0.09	Damper setting, firing rate
Gas composition	Partial analysis is available; see Tables 4-3, 4-7, and 4-8	Feed, alloying elements, fuel composition, fluxes, degassing agents

a. From low fire to high fire, respectively.

b. wg = water gauge.

4.2.1 Temperature

Conventional reverberatory furnaces depend on radiant heat transfer to melt and superheat the aluminum.⁴⁻⁶ Aluminum remelt furnaces operate at a molten bath temperature of 2000°F, with an ambient temperature of 2156°F above the bath.⁴⁻⁶ Therefore, flue stack temperatures are nominally in excess of 2100°F. Holding furnaces generally operate at a lower temperature--1290 to 1330°F.⁴⁻¹ The temperature of the flue gas from aluminum remelt furnaces therefore ranges from 1100 to 2200°F. One source, however, lists the temperature range as 2000 to 2800°F.⁴⁻⁷

4.2.2 Pressure

Only one source was found that listed aluminum remelt furnace operating pressure; the pressure range was -0.02 to -0.09 in. (water gauge).⁴⁻⁷ In general, it is desirable to have an operating pressure that maintains a positive flow of gas.

4.2.3 Flow Rate

The average waste gas flow rate from the aluminum remelt furnaces has been reported to be 60,000 scfh in one report,⁴⁻⁸ and 50,000 to 250,000 scfh in a second.⁴⁻⁷ The flow will depend on the furnace size and the fuel input.

4.2.4 Constituents

Flue gas constituents from aluminum remelt furnaces have not been analyzed thoroughly. The constituents will be determined, however, by the type of fuel used to fire the furnaces, and by fluxes, degassing agents, alloying agents, and contaminants from any recycled aluminum added to the furnace. The fuel is generally natural gas or fuel oil and can include No. 6 fuel oil, in contrast to the steel soaking pits and billet reheat furnaces, which use primarily No. 2 fuel oil. The flue gas constituents resulting from these fuels were discussed in Section 3.2.4 (flue gas constituents for steel soaking pits and reheat furnaces). As stated there,

the major contaminants from the No. 6 fuel oil would be sulfur compounds and vanadium oxide.^{4-9,4-10}

To remove aluminum impurities that would be detrimental to the quality of the fabricated product, flux is mixed with the molten metal. The flux assists in the separation and flotation of impurities such as metallic inclusions (principally aluminum oxide) and alkali metals (for example sodium)⁴⁻¹¹ to form dross, which is then skimmed off. Table 4-2 gives a typical flux analysis. If the alloy contains more than 1% magnesium, a sodium-chloride-free flux, such as a mixture of magnesium chloride and potassium chloride, is preferred and enhances sodium removal.⁴⁻¹¹

TABLE 4-2. TYPICAL FLUX COMPOSITION⁴⁻¹

<u>Chemical Species</u>	<u>Amount (%)</u>
NaCl	40
NaF	25
CaF ₂	6
AlF ₃	6
Na ₂ SO ₄	23

Flux can be a degassing agent as well. In this case, the flux is generally 45% KCl, 35% NaCl, and 20% NaF.⁴⁻¹ The degassing flux is held deep in a tank and the constrained metal forced to flow through it.⁴⁻¹ The degassing tank can be between the melting furnace and the holding furnace, or after the holding furnace. Another degassing flux is a mixture of an inert gas (nitrogen or argon) with 3 to 5% Freon 12 (CCl₂F₂).⁴⁻¹¹ The Freon 12 eliminates any further degassing in the process because it decomposes completely into carbon, fluorine, and chlorine. The fluorine and chlorine then react with aluminum and other elements, such as magnesium, to form compounds that are generally solid (AlF₃ and MgF₂) or liquid (MgCl₂) at the molten aluminum temperature. These compounds remain on the surface of the melt; however a small amount of AlF₃ and MgF₂ is hydrolyzed to form minute amounts of hydrogen fluoride (HF). Aluminum chloride (AlCl₃), which has a low sublimation temperature, is also formed. It enters the gaseous phase and reacts with moisture to form hydrated aluminum oxide and hydrogen chloride.

Although fluxes are reasonably effective at removing hydrogen, sufficient hydrogen gas may remain in the molten aluminum to cause porosity in the cast metal.⁴⁻¹ Although the metal will slowly lose hydrogen if held at 1330°F, the time for equilibration is long. If it is necessary to further degas the melt, chlorine and hexachloroethane (C_2Cl_6), which are also cleansers, can be used, as can an inert gas such as nitrogen or argon. Chlorine is generally used for recycled aluminum and reacts with the magnesium impurity to form $MgCl_2$. The constituents of the flue gas for a specific aluminum remelt system degassed with chlorine are listed in Table 4-3. The method of analysis was not indicated, nor were particulates discussed. The use of Freon 12, however, eliminates this degassing step and reduces the hydrogen chloride emission.

TABLE 4-3. ANALYSIS OF FLUE GAS FROM AN ALUMINUM MELT DEGASSED WITH CHLORINE⁴⁻¹¹

<u>Chemical Species</u>	<u>Amount (lb/h)</u>
Al_2O_3	21.6
$AlCl_3$	0.4
AlF_3	0.01
HCl	42.3
HF	0.01
Others	8.8

Alloying agents, usually as scrap or bar of the pure metal, are also added in the remelt furnace and are potential contaminants of the off-gas. The compositions of common aluminum alloys are shown in Table 4-4.

The major off-gas contaminants in the recycle of aluminum would be from paint and oil residue burned off as the charge is heated on the furnace forehearth. Another major source of contaminants is stainless steel in the recycled metal. Since the steel results in a problem in purification of the aluminum, however, most is removed by a crushing and separation procedure prior to remelt.

TABLE 4-4. COMPOSITION LIMITS OF SOME ALUMINUM WROUGHT AND CASTING ALLOYS⁴⁻¹²

Aluminum Association Designations	Composition Limit ^a (%)					
	Aluminum	Copper	Manganese	Magnesium	Silicon	Other Constituents
Wrought alloy series						
1000	99.00-99.75	0.2	0.05	0.05	1.0 ^b	0.1 Zn, 0.05 Ti
2000	Balance	1.9-6.8	1.2	1.8	0.1-2.5	1.3 Fe, 0.15 Ti, 2.3 Ni
3000	Balance	0.3	0.3-1.5	1.3	0.6	0.4 Zn, 0.1 Ti
4000	Balance	0.25-1.3	0.1	1.3	4.5-13.5	1.3 Ni
5000	Balance	0.2	1.0	0.5-5.6	0.5 ^c	0.35 Cr, 0.2 Ti
6000 ^c	Balance	1.2	1.1	1.5	1.8	2.4 Zn, 1.0 Fe
7000	Balance	2.6	0.7	3.7	0.7 ^b	0.3 Cr, 8.0 Zn
Die-casting ingots^d						
A380.1	Balance	3.0-4.0	0.5	0.1	7.5-9.5	0.5 Ni, 1 Zn,
	Balance	0.1	0.1	0.07	11.0-13.0	1.1 Fe
Sand and permanent mold casting ingots^d						
201.2	Balance	4.0-5.2	0.2-0.5	0.2-0.55	0.1	0.1 Fe, 0.35 Ti
242.2	Balance	3.5-4.5	0.1	1.3-1.8	0.6	0.6 Fe, 2.3 Ni, 0.1 Zn, 0.2 Ti
295.2	Balance	4.0-5.0	0.3	0.03	0.7-1.2	0.8 Fe, 0.3 Zn, 20 Ti
356.2	Balance	0.1	0.05	0.3-0.4	6.5-7.5	0.25 Fe, 0.05 Zn, 0.2 Ti
A390.1	Balance	4.0-5.0	0.1	0.5-65	16.0-18.0	0.4 Fe, 0.1 Zn, 2 Ti

a. Maximum weight-percent of the casting ingot or of at least one of the wrought alloys in the series unless a range is given, in which case the upper and lower limits do not necessarily apply to the same alloy in the series.

b. Including iron.

c. Alloy 6262 may contain 0.4 to 0.7% each of lead and bismuth.

d. Composition of castings may differ from that of ingots.

Aerojet Energy Conversion Company has postulated the composition of the off-gases from aluminum remelt.⁴⁻¹⁰ Table 4-5 lists the calculated gas composition for a melter using No. 6 fuel oil burned in excess air. The postulated chemical species in the off-gas particulates are listed in Table 4-6. Melting temperatures are included to indicate the approximate temperatures at which these species would form sticky deposits and potentially lead to fouling or corrosive deposits.

Limited flue gas analyses have been performed for aluminum remelt. Table 4-7 lists flue gas chloride, fluoride, and sulfur analyses for aluminum remelt furnaces that use No. 2 fuel oil, natural gas, or a mixture of these two fuels. Table 4-8 gives the flue gas particulate analyses for a furnace using No. 2 fuel oil or a mixture of No. 2 fuel oil and natural gas. The samples were taken with a water jacketed sample probe; neither the sampling location nor the method of analysis were discussed. The analyses in Tables 4-7 and 4-8 are not complete because they do not consider the products of combustion or the amount of particulates present.

4.2.5 Fouling and Corrosion

Only limited information was available on fouling and corrosion caused by the waste heat stream of an aluminum remelt furnace. Table 4-9 summarizes the elements that have been identified in fouling and corrosion deposits in aluminum remelt waste gas flues and lists the sources that can contribute these elements.

TABLE 4-5. PREDICTED COMPOSITION OF ALUMINUM MELTER FLUE GAS⁴⁻¹⁰

Species	Composition (vol %)
N ₂	77.1
O ₂	2.0
S ₀ 2	1.4
C ₀ 2	15.1
H ₂ O	4.0
Cl, AlCl ₃ , SO ₃ , HCl	Trace

TABLE 4-6. POSTULATED PARTICULATE SPECIES IN ALUMINUM MELTER FLUE GAS⁴⁻¹⁰

<u>Species</u>	<u>Melting Point (°F)</u>	<u>Species</u>	<u>Melting Point (°F)</u>
Aluminum oxide	3713	Sodium carbonate	1564
Aluminum sulfate	1418	Potassium carbonate	1636
Vanadium pentoxide ^a	1200	Potassium oxide	1662
Sodium sulfate	1623	Sodium chloride	1474
Potassium chloride	1429	Sodium oxide	2327
Potassium sulfate	1956		

a. Other vanadium oxides are also postulated.

TABLE 4-7. C1, F, AND S ANALYSIS OF FLUE GASES FROM ALUMINUM REMELT⁴⁻¹³

<u>Element</u>	<u>Flue Gas Analysis for Different Fuels</u> (mg/ft ³)		
	<u>Natural Gas</u>		
	<u>No. 2 Fuel Oil, Furnace A</u>	<u>Furnace B</u>	<u>Furnace A</u>
C1	1.4-6.0	3.6-4.6	0.4-3.9
F	0.03-0.4	0.10-0.16	0.01-0.12
S	6.8-12.8	0.12-0.13	0.01-0.003

TABLE 4-8. ANALYSIS OF PARTICULATES IN FLUE GASES FROM ALUMINUM REMELT⁴⁻¹³

<u>Element</u>	<u>Flue Gas Particulate Analysis (%)</u> for Different Fuels	
	<u>No. 2 Fuel Oil</u>	<u>Natural Gas with No. 2 Fuel Oil</u>
V	<0.003	--
Al	6.3	0.5
Ni	0.006	--
Fe	0.097	--
C1	23.6-31.4	53-57
Na	9.3-11.3	20-22
K	12.6-18.2	17-26
S	--	0.005

TABLE 4-9. ELEMENTS IN DEPOSITS AND CORROSION PRODUCTS FROM ALUMINUM REMELT FURNACE FLUES^{4-13, 4-14}

Probable Source	Elements ^a
Major feedstock components	Al
Feedstock impurities	
In new metal	(F) ^b
On scrap surface	Cl, S,
In bulk scrap	Cu, Zn, Mg, Si, Cr, Ti, Mn
Flux	K, Na, Cl, Ca, (F) ^b
Other (such as fuel)	S, Fe, Ca, Mo, W, Co, Si, (P), ^b V

a. Other elements may exist in the deposits, particularly for systems different than those studied.

b. Potential constituent; present in source material but not identified (by a reference in this search) in a deposit or corrosion product.

Although several fouling and corrosion tests have been reported, control failures in some make a thorough interpretation of the data difficult. In one of these tests, a radiant metal recuperator containing a reradiant insert was demonstrated on an aluminum remelt furnace at the Alabama Reclamation Plant of Reynolds Metals Company.^{4-13, 4-14, 4-15} During an initial 30-day testing period, no gaseous chlorine was used. The flux mix was 50% NaCl, 45% KCl, and 5% Na₃AlF₆.⁴⁻¹⁴ Control failure during the test resulted in excessive fuel burning in the recuperator.^{4-13, 4-14} As a result, the highest temperatures in the recuperator exceeded the normal furnace operating temperature of 1400°F.⁴⁻¹⁴ The lowest temperature was greater than 1000°F (the approximate "combustion" air temperature at the exit of the recuperator). The exact temperatures are uncertain.

Five samples of corrosion product from the 30-day test were analyzed spectrographically at the Oak Ridge National Laboratory (ORNL), with an accuracy "to within one-half to two times the reported value."⁴⁻¹⁴ These samples were taken from the recuperator wall, at 9.8 and 38 ft from the bottom; on the reradiant insert, at 5.9 and 24 ft; and on the damper near the dome, at 44.6 ft. Only four elemental constituents--K, Na, S, and

Cl--were clearly identified as deposited. The K, Na, and S concentrations in the corrosion products were listed as "Major" (>1%) for all five samples. The Cl concentrations, with increasing height in the recuperator, were >1000, 600, 400, >1000, and >1000 ppm.

After another year of operation, specimens of scale from the reradiant inserts were again taken for analysis by the ORNL.⁴⁻¹⁵ Temperatures at the inlet to the recuperator, measured over a few days of operation during the year, ranged from 1670 to 1815°F.⁴⁻¹⁵ The scale specimens were taken at roughly 0, 2, and 6 ft from the bottom of the inserts. The concentrations of elements, excluding the elements in the Type 446 and 309 stainless steels used for the inserts, are listed in Table 4-10. (Neither aluminum nor silicon were found, even though ~1% Si was present in the aluminum alloys.) At the heights studied, increasing concentrations with increasing height (decreasing temperature) were noted for Na, Mo, W, and Cu. The data accuracy is again expected to be within a factor of two.

TABLE 4-10. ANALYSIS OF CORROSION PRODUCT FROM AN ALUMINUM REMELT FURNACE RECUPERATOR⁴⁻¹⁵

Element ^b	Concentration at Given Height ^a (wt%)		
	0 ft ^c	2 ft ^c	6 ft ^d
K	>1	>1	>1
Cl	~1	~1	~1
S	~0.4	~0.1	~0.4
Na	~0.1	~0.1	~0.4
Ca	~0.2	0.005	0.01
Mo	0.02	~0.1	~0.2
W	0.05	0.07	~0.1
Cu	0.005	0.05	~0.1
Co	0.02	0.03	0.03
V	0.02	0.02	0.01
Ti	0.04	<0.001	0.01

- a. From bottom of reradiant insert in recuperator.
- b. Major stainless steel elements not included in reported results.
- c. On Type 446 stainless steel (SS).
- d. On Type 309 SS.

In separate tests, coupons of Incoloy 800, both uncoated and coated with an aluminum diffusion coating, have been exposed to flue gases at 1600 to 1800°F for 360 h of operation of a Vulcan Materials Company aluminum scrap remelt furnace.⁴⁻¹⁶ Natural gas was used as the fuel. A flux, predominately CaCl_2 , included some NaCl . Fluxing with gaseous chlorine is also common in this operation. Analysis by the ORNL of the material deposited in 1/16-in. holes in the uncoated coupon showed 22.4% Zn, 19.7% Ca, 2.6% Si, 1.9% Al, and 1.5% Mg--apparently from the flue gas--in addition to the contributions of 21.9% Ni, 15.8% Fe, and 8.6% Cr from the Incoloy 800. Analysis by EG&G Idaho, Inc. of the material in ~5- μm -diameter spots on the surfaces and cross sections of a coupon specimen revealed further elements,⁴⁻¹⁷ but the 15 energy-dispersive spectroscopic (EDS) analyses (in the scanning electron microscope) varied widely. Each element did not occur in every deposit. The concentration range (atomic %) was 0.1 to 83% Mg, 1.1 to 78.9% Al (or 1.1 to 5.6%, eliminating the largest value), 0.5 to 5.4% Ca, 4.6 to 24.2% Zn, 0.4 to 7.2% Si, 0.2 to 1.1% Cl, 0.4% K (one area), and 0.2 to 1.8% P. Only Fe, Ni, and Cr were found in every analysis. Material from a waste gas duct that had been in operation before this test was shown to include K, Na, and Cl as the only "major" elemental constituents.⁴⁻¹⁶ Apparently, either previous operations involved more Na and K, or the much longer period of deposition at the lower temperatures of the duct (600-1000°F) resulted in Na and K deposition.⁴⁻⁹

4.3 References

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5. GLASS MELTING FURNACES

5.1 Process Characterization

The glass melting process, illustrated in Figure 5-1, can be carried out in one of three types of melting tank: regenerative furnace, day pot, or day tank. Most glass tonnage is melted in continuously operating regenerative (or recuperative) furnaces. The regenerative furnaces (Figures 5-2 and 5-3) have two chambers of refractory checkerwork for heat recovery from the waste gas stream. While the combustion flue gases heat the refractory in one checkerwork, the other checkerwork preheats air. The operation is reversed every 10 to 30 min. Regenerative glass melting furnaces are divided into two classes--side port and end port, according to the burner firing pattern and the type of glass being produced. Regenerative furnaces can maintain a larger production rate than recuperative furnaces, which have one continuously operating tube-and-shell heat exchanger to preheat the combustion air. For smaller batches of glass, for example in the production of special compositions of glass, the day pot or day tank is used. Day pot capacities range from 20 lb to 2 ton, while day tanks are larger, but both are used to melt 24-h production batches. The major difference is the material of construction of the vessel walls.

5.2 Flue Gas Characterization

Plugging and other problems in operation of regenerator brick checker-works caused the waste gas stream from glass melting tanks to be studied more thoroughly than the flue gases of the other processes considered in this report. The glass melting waste gas stream is thus the best characterized flue gas of the processes considered. Much of the characterization work was supported by the EPA.⁵⁻² Table 5-1 gives typical flue conditions for two representative types of glass: flint and amber. Table 5-2 summarizes the major characteristics of the waste gas stream for glass melters and lists the variables that affect these characteristics, which are discussed below.

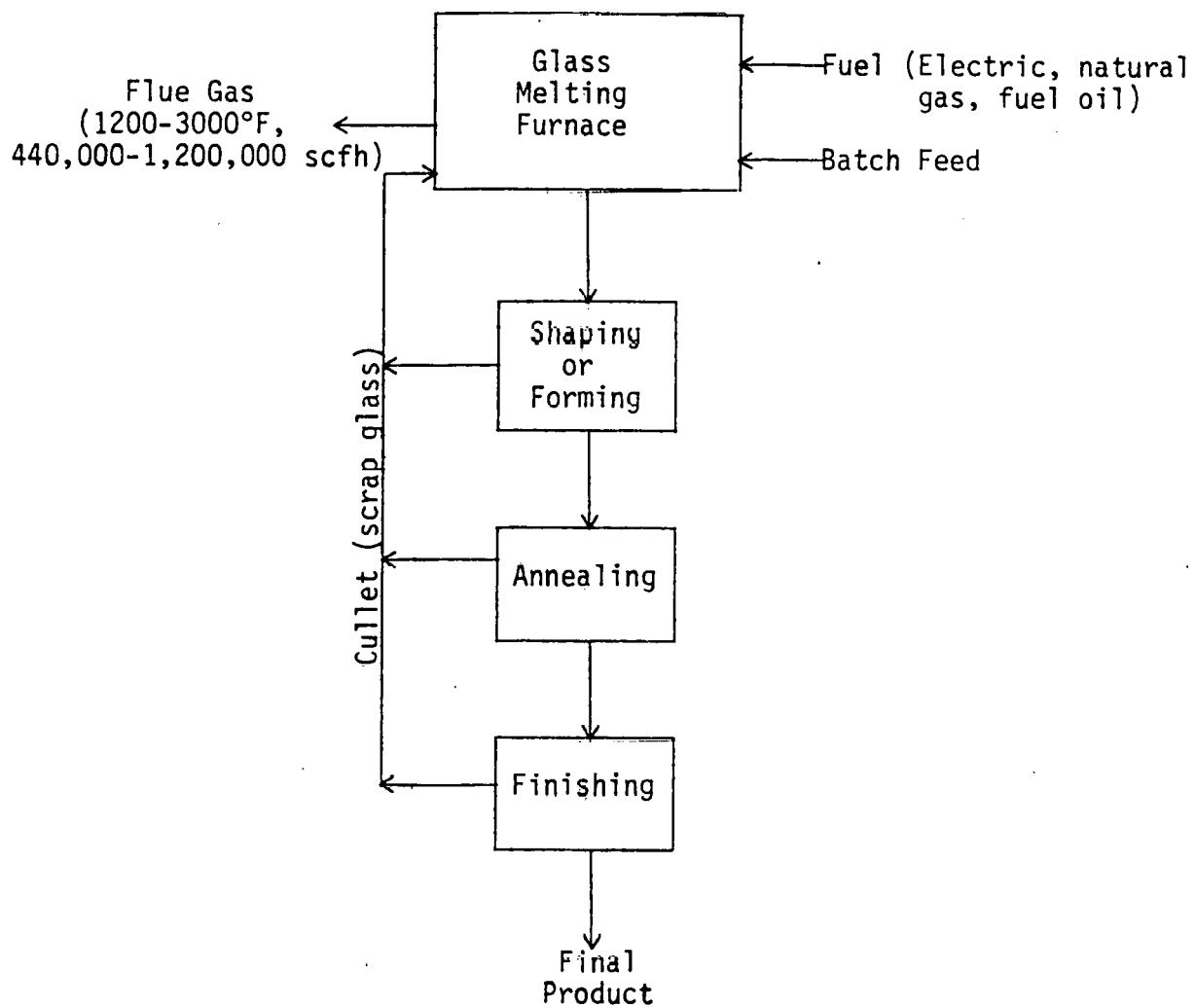


Figure 5-1. Glass production.

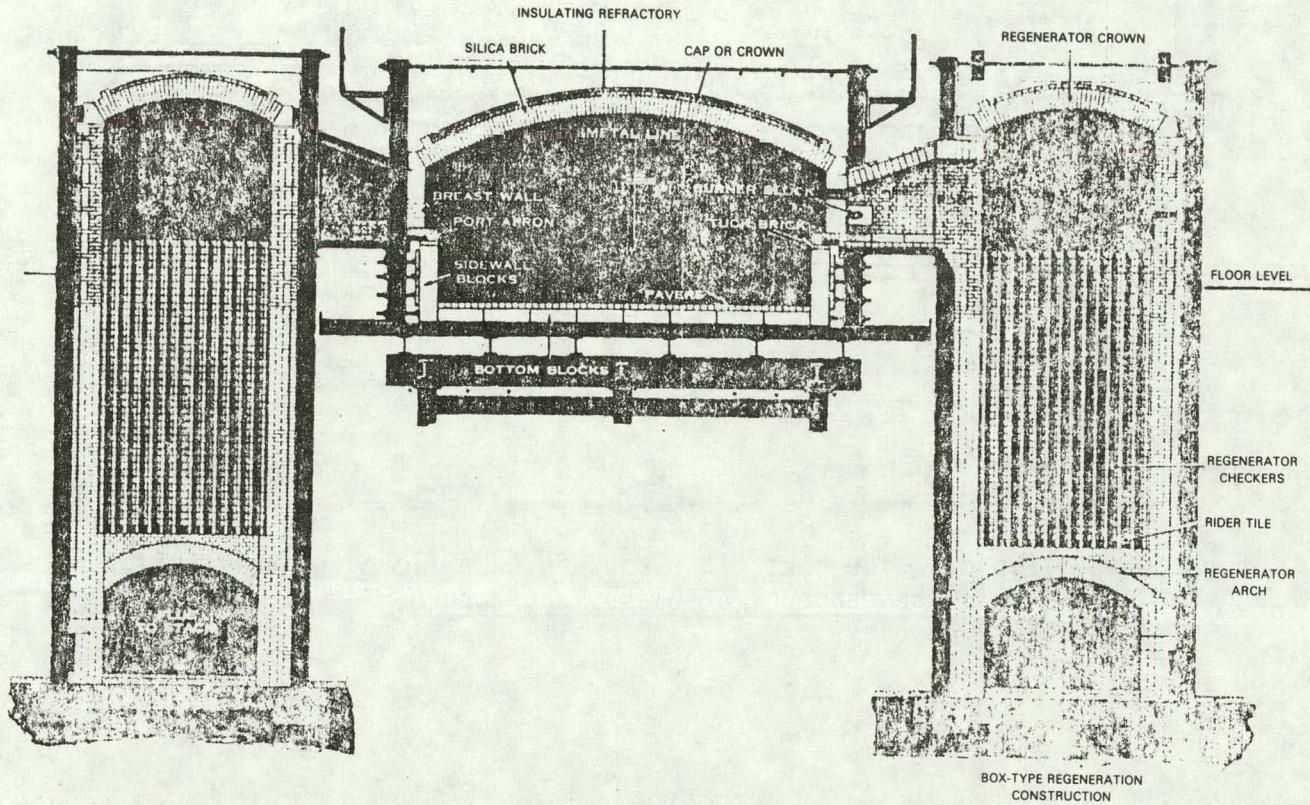


Figure 5-2. Typical side port glass tank furnace (end view) (from The Handbook of Glass Manufacture,⁵⁻¹ Vol. I, by F. V. Tooley).

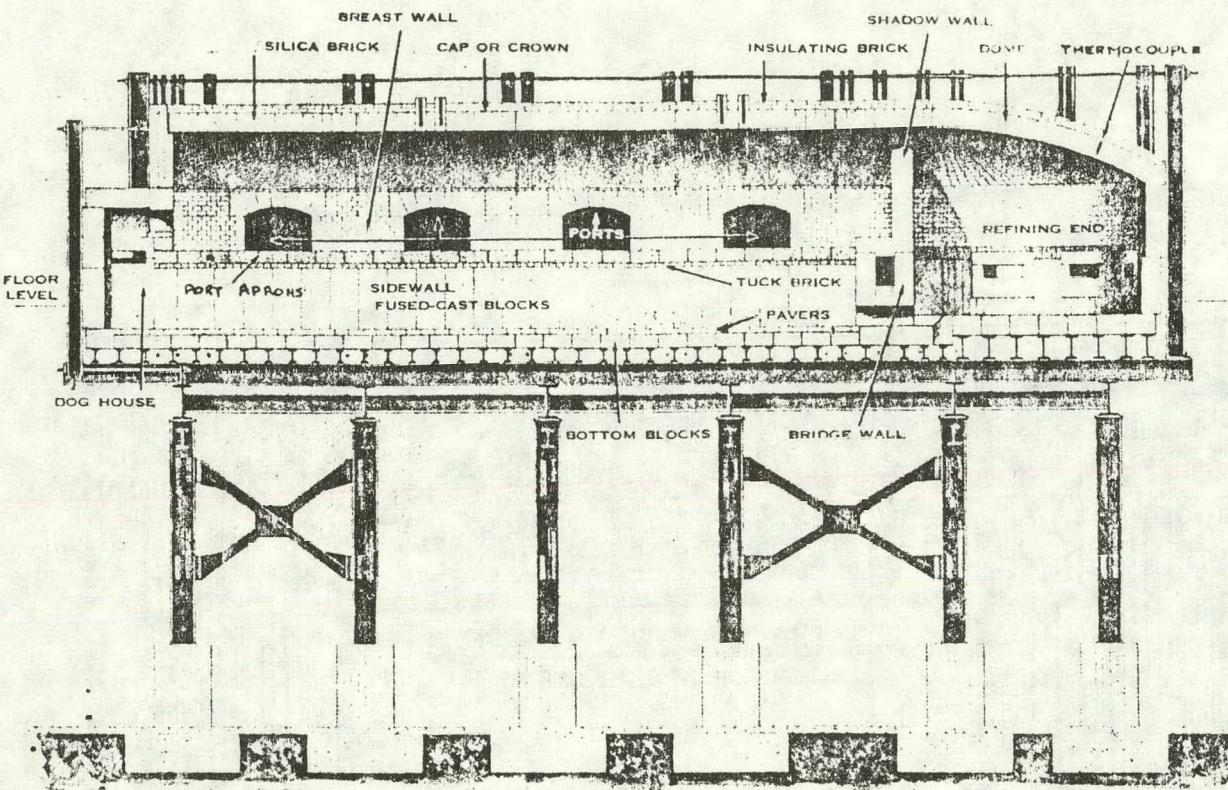


Figure 5-3. Typical side port glass tank furnace (longitudinal section) (from the Handbook of Glass Manufacture,⁵⁻¹ Vol. I, by F. V. Tooley).

TABLE 5-1. TYPICAL FURNACE FLUE CONDITIONS FOR FLINT AND AMBER GLASS MELTING⁵⁻³

Condition	Flint Glass	Amber Glass
Flue diameter (ft)	5	6
Average gas velocity (ft/s)	16	53
Average gas temperature (°F) ^a	1150	2090
Static pressure (in., wg) ^b	-0.44	-0.98
Gas flow rate (scfh)	495,000	1,008,000

a. Downstream of heat recovery system.

b. wg = water gauge.

TABLE 5-2. SUMMARY OF FLUE GAS CHARACTERISTICS AND FURNACE PRESSURE FOR GLASS MELTING FURNACES

Characteristic	Value	Variables That Affect Characteristic
Gas temperature (°F)	1200-3000	Furnace type, batch composition, firing rate
Gas flow rate (scfh)	440,000-1,200,000	Furnace type, batch composition, firing rate
Furnace pressure (in., wg) ^a	-0.98-0.02	Damper setting, firing rate
Gas composition	Available (see Tables 5-5 and 5-6)	Composition of batch, fuel, and brick checkerworks

a. wg = water gauge.

5.2.1 Temperature

The required operating temperature of a glass melting furnace depends on the composition of the batch (type of glass), which is in turn determined by the method that will be used to shape the final product (flat glass, container glass, pressed and blown glass, or wool fiber glass)⁵⁻² and by the type of use the product will be put to. Common types of glasses are:⁵⁻³

1. Fused silica or vitreous silica--a thermally resistant glass made by high-temperature pyrolysis of silicon tetrachloride
2. Alkali silicates--used only as solutions
3. Soda-lime glass--used for containers and plate glass
4. Lead glass--for decorative effects
5. Borosilicate glass--for optical, scientific work, and utensils

6. Glass ceramic--for cook-serve-freeze utensils
7. Alumino silica glass--20% or more alumina for higher temperatures
8. Fiber glass--for textiles and reinforcing
9. Special glass--colored glass, opal glass, translucent glass, safety glass, laminated and tempered glass, photo sensitive glass and specialties for chemical and industrial use.

The composition of these glasses is listed in Table 5-3.

The melting temperature (softening point) of a glass will determine the required operating temperature of the furnace in which it is melted. Softening points of several glasses are listed in Table 5-4. For soda lime glass, the softening point is 1285°F, while the corresponding furnace operating temperature is 2730 to 3000°F.⁵⁻⁵ The furnace operating temperature for the specialty glasses was not found, but would be higher.

For continuous operation furnaces with regenerative checkerwork, much of the sensible heat content of the waste gases is removed by the checkerwork, portions of which reach temperatures as high as 2800°F,⁵⁻⁶ while the exiting flue gas is only 1200°F (depending on the glass). Table 5-1 gives measured average flue gas temperatures downstream of the regenerator for two types of glass furnaces.⁵⁻³ During the start of production in these furnaces, the increments by which the furnace temperature can be raised are limited by the ability of the refractory to withstand the resulting thermal expansion. Thus large temperature transients, which could affect the generation of impurities that would appear in the off-gas stream, are not expected.

5.2.2 Pressure and Flow Rate

Table 5-1 indicates flue gas flow rate and pressure for continuous furnace melting of two types of glass. The flow rate ranges from 440,000 to 1,200,000 scfh.⁵⁻⁶ The pressures and flow rates are summarized in Table 5-2.

TABLE 5-3. COMPOSITION OF TYPICAL GLASSES⁵⁻⁴

Glass Type	Composition (%)										
	<u>SiO₂</u>	<u>B₂O₃</u>	<u>Al₂O₃</u>	<u>Fe₂O₃</u>	<u>As₂O₃</u>	<u>CaO</u>	<u>MgO</u>	<u>Na₂O</u>	<u>K₂O</u>	<u>PbO</u>	<u>SO₃</u>
Fused silica	67.8	--	4.4	--	--	4.0	2.3	13.7	2.3	--	1.0
Alkali silicates	69.4	--	3.5	1.1	--	7.2	--	17.3	--	--	--
Soda-lime	70.5	--	1.9	0.4	--	13.0	--	12.0	1.9	--	--
Lead	71.5	--	1.5	--	--	13.0	--	14.0	--	--	--
Borosilicate	72.88	-- ^a	0.78	0.78	--	12.68	0.22	12.69	--	--	--
Glass ceramic	72.9	--	0.7	0.7	--	7.9	2.8	15.0	--	--	--
Alumino silica	72.68	--	0.50	0.07	--	12.95	--	13.17	--	--	0.44
Fiber	70-74	--	2+2 ^a	0.09	--	--	10-13	--	13-16	--	--
Special	73.6	--	1.0	--	--	5.2	3.6	16.0	0.6	--	--
Special	73.88	16.48	2.24	2.24	0.73	--	--	6.67	trace	--	--
Special	74.2	0.4	--	--	0.2	4.3	3.2	17.7	--	--	--
Special	67.2	--	--	--	0.5	0.9	--	9.5	7.4	44.8	--
Special	69.04	0.25	--	--	--	12.07	--	5.95	11.75	--	--
Special	64.7	10.5	4.2	--	--	0.6	--	7.8	0.3	--	--
Special	80.5	12.9	2.2	--	--	--	--	3.8	0.4	--	--
Special	96.3	2.9	0.4	--	--	--	--	<0.2	<0.2	--	--
Special	70.3	--	7.15	0.47	--	4.93	--	12.75	4.97	--	--

a. As in Reference 5-4.

TABLE 5-4. GLASS SOFTENING TEMPERATURES⁵⁻⁴

Glass	Temperature (°F)
Common soda lime	1285
Pyrex borosilicate	1508
Vycar 96% silica	2732
Pyroceram	2282

5.2.3 Constituents

The flue gas composition will be determined by the glass batch composition, fuel composition, and furnace temperature. Generally the fuels used are natural gas, electricity, and fuel oil, with a trend toward the use of more electricity. The effects of the fossil fuels on flue gas composition are the same as those discussed previously for the steel and aluminum processing. Also, an increase of 50°C in the bridge wall (Figure 5-3) temperature will increase particulate emission by 85%.⁵⁻⁵ This may explain why the exhaust of the borosilicate glass furnace (which operates at a relatively high temperature of 2900°F) is the "dirtiest" compared to the exhaust of most other glass furnaces (which operate at ~2700°F).⁵⁻⁵

Tables 5-5 and 5-6 show the general constituents of glass melter flue gases. Flue gas analysis for melting flint and amber glass is shown in Table 5-5. Volumes and velocities were determined by an S-type pitot tube.⁵⁻³ Gases were collected by impinger tubes; particulates, by a teflon filter. A typical flue gas analysis for a soda lime glass melting system is also shown in Tables 5-5 (gas analysis) and 5-6 (particulate analysis). These tables give the total composition of the flue gas. The particulate composition was generally determined by x-ray diffraction, electron microscopy, and atomic adsorption spectroscopy.⁵⁻⁷ The method for the gas analysis was not given. The gaseous constituents of the flue gas arise from the fuel and the volatile components of the batch.

Typically, the concentration of particulates in the flue gas from glass melting is ~200 ppm. Most of the particulates are carried over

TABLE 5-5. ANALYSIS OF FURNACE FLUE GAS FROM GLASS MELTING

Constituent	Flue Gas Analysis for Flint, Amber, and Soda Lime Glass Melting		
	Flint ^a	Amber ^a	Soda Lime ^b
Solids			
gr/scf) (1b/h) (ppm)	0.029 2.1 --	0.041 5.4 --	-- -- <200
Sulfur trioxide (ppm)	17	--	
Sulfur dioxide (ppm)	250	315	271
Fluorine (ppm)	2.2	1.9	1.5 ^c
Chlorine (ppm)	4.9	4.1	15.8 ^d
Nitrogen oxides (ppm)	340	640	375
Carbon monoxide (ppm)	375	40	5.0

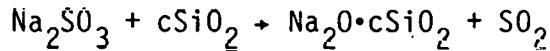
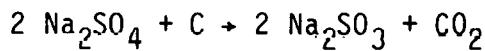
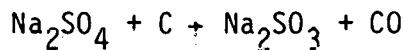
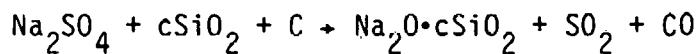
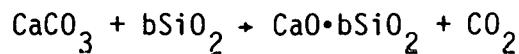
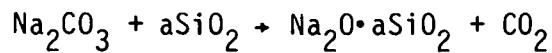
a. From Reference 5-3.
 b. From Reference 5-7.
 c. As HF.
 d. As HCl.

TABLE 5-6. ANALYSIS OF FLUE GAS PARTICULATE FROM SODA LIME GLASS MELTING⁵⁻⁷

Particulate Size Distribution		Chemical Composition	
(μ)	(%)	Species	(wt%)
>30	<1	SiO ₂	10.2
30 to 10.7	1.7 to 3.4	Al ₂ O ₃	8.3
10.7 to 3.1	4.3 to 8.6	Na ₂ SO ₄	63.0
3.1 to 0.3	94 to 86	K ₂ SO ₄	3.6
<0.3	<1	CaO	0.6
		MgO	2.0
		Fe ₂ O ₃	1.6
		Cr ₂ O ₃	0.6
		As ₂ O ₅	5.0
		B ₂ O ₃	5.0

from the glass batch, swept out by the hot gases passing over the molten glass surface. The glass batch is a mix of granular materials, which may be pelletized or otherwise treated to decrease losses by entrainment in the flue gas. This batch composition varies for different compositions of the desired product, and the entrained, volatilized, and deposited material in the flue gas varies accordingly. For example, any glass-coloring chemicals, such as minute amounts of oxides of nickel, iron, manganese, copper, cobalt, titanium, or vanadium, or elemental sulfur,⁵⁻⁴ can add impurities to the flue gas. The composition of the brick checkerworks also affects the composition of the particulates in the gas stream. For example, most of the chrome in the particulates is due to the attack of the brick checkerworks by batch carryover--through volatilization and entrainment of solids and liquids in the waste gases.

Carbon dioxide, carbon monoxide, and sulfur dioxide result from batch decomposition and fuel combustion. The applicable batch decomposition reactions are:⁵⁻⁴



The sodium sulfate becomes sticky below 1600°F and forms a hard scale on the surface of the regenerator. Frequently magnesium oxide is added with the fuel to form magnesium sulfate (MgSO_4), which is a soft scale that is more easily removed.⁵⁻⁵

5.2.4 Fouling and Corrosion

The flue gas from glass melting tanks has caused plugging of regenerators.⁵⁻⁵ Using information from the literature and a few glass plants, the deposit of material from the flue gas stream has been described as a function of distance from the furnace.⁵⁻⁵ With increasing distance, the waste stream is progressively depleted of particulates as they adhere to surfaces, while decreasing temperature results in progressive condensation of the gaseous materials from the flue gas stream. In the same study, it was shown that large amounts of entrained particulates from batch carry-over, and from condensed V_2O_5 , Fe_2O_3 , and NiO , are deposited in the top zone of the brick checkerworks. SiO_2 , Na_2SO_4 , and other compounds of SO_3 were also deposited in this zone and dusts of SiO_2 , V_2O_5 , CaO , Al_2O_3 , and eroded bricks contributed to blockage of the passages. Examination of degraded furnace and regenerator refractories from a glass furnace fired with residual oil for 3.5 years also showed the effects of Na_2SO_4 in the regenerator refractories, and Ni and V in the furnace refractories.⁵⁻⁸

The concentration of sodium sulfate particulates in the glass melter flue gas is 200 ppm, and over 85% of these particles are less than 2 μm . The sodium sulfate and other particulates are formed as follows:⁵⁻⁵ In the bottom zone of the brick checkerworks, the temperature decreases from 1900 in the lowest part of the zone to 1200°F in the upper portion of the zone. Sodium sulfate begins condensing (from Na_2O and SO_3 vapor species) at 1800°F and becomes a solid ("a fluffy white powder") below ~1600°F. Material that condenses or solidifies below ~1600°F would account for less than 10% of the total particulates. Immediately downstream of the brick checkerworks, the temperature is 1200 to 500°F, at which molten alkali pyrosulfates ($Na_2S_2O_7$ and $K_2S_2O_7$) condense with alkali vanadates; with B_2O_3 and As_2O_3 (possibly as alkali borates and arsenates); and with "sulfate of Se". At the cold end (500 to 100°F) sulfuric acid (H_2SO_4) can condense below 400°F. Remaining dusts continue to deposit, collected by the sticky sulfuric acid-alkali sulfate deposits. At the higher temperatures, more of the condensates, including sulfates, pyrosulfates, vanadates, borates, etc., would be sticky and promote deposition of particulates.

Information collected from others (especially Brockway Glass Co.,
Brockway, PA) by Terra Tek, Inc.⁵⁻⁹ shows that for melting of container
glass, "...there are approximately 2-1/2 lbs. of condensable volatiles
leaving the surface of the glass for every ton of glass melted....These
volatiles consist primarily of sodium sulfate and some sodium carbonate
[sic]. In addition to these variables, there is some amount of dust carry-
over from the batching operation. The quantity of this carryover varies
greatly from almost none near the firing end of a well run furnace to
several pounds per ton of glass melted near the charging end of a dirty
furnace."⁵⁻⁹ "Approximately 2-1/2 lbs. of sodium sulfate are produced
for every ton of glass melted. It is estimated that approximately 10 to
20% of this condenses in a standard regenerator. This fraction will be
greater for a system that cools the exhaust more than the 1100-1200°F out-
put of most regenerators. In addition to the condensate, over 50% of the
carryover dust settles out in the regenerator."⁵⁻⁹ The above estimates
of mass loss rates appear to be much less than the range of 10 to 18% of
batch "lost to emission" given by Webb and Kulkarni.⁵⁻⁵ However, if this
loss to emission refers to loss from the glass melt to the furnace rather
than to the atmosphere, the noncondensables (such as CO₂ and H₂O) could
be a large fraction of the loss.⁵⁻⁵

In work supported by the Department of Energy, the corrosion product (1.5 mm
thick) on the stainless steel (Type 321 SS) wall of an experimental recuper-
ator was analyzed semiquantitatively by emission spectroscopy.⁵⁻¹⁰ The
recuperator had operated for eight months at >1200°F in a borosilicate
glass melting furnace. Only a few percent of the corrosion products
analyzed could be identified as material deposited from the flue gases.
Table 5-7 lists the elements found in amounts >0.01%, but excludes ele-
ments likely to have come from the stainless steel. The sulfur was from
the natural gas fuel and constituents of the glass batch.⁵⁻² The very
low boron content of the corrosion product, >0.05%, does not reflect the
high boron content expected, according to Webb and Kulkarni,⁵⁻⁵ in flue
gases from borosilicate glass furnaces. The study also concluded that "The
low sodium-to-chlorine ratio of these elements in the corrosion product
does not support congruent vaporization as the principal means of trans-
porting chlorine to the corrosion product. Chlorine, therefore, probably

TABLE 5-7. GLASS BATCH COMPOSITION AND ANALYSIS OF GLASS MELTER FLUE GAS DEPOSITS AND CORROSION PRODUCTS

Soda Lime Glass		Analysis of Deposits and Corrosion Products Formed on Alumina, Mullite, and Stainless Steel		
Batch Composition, ^a for Alumina and Mullite Exposure		Amount (wt%)		
Element,	Amount			Stainless
As Oxide	(wt%)	Element	Alumina ^b	Mullite ^c
SiO ₂	50.64	Si	17.22	12.00
Na ₂ O	10.87	Na	10.62	17.38
CaO	10.30	Ca	0.67	--
Al ₂ O ₃	1.64	Al	22.43	10.94
MgO	1.56	Mg	0.11	--
BaO	0.44	Ba	--	--
F	0.43	F	--	--
B ₂ O ₃	0.38	B	--	>0.05
Total	76.26	Mo	--	0.2
		Cu	--	0.04
		Fe	1.82	2.18
		Ti	1.03	--
		K	0.85	4.26
		P	--	5.93
		S	--	3.36
		O	45.25	43.95
		Cl	--	--
		Co	--	0.05
		W	--	0.05
		V	--	0.01

a. This batch composition (Reference 5-11) is for the resulting deposits and corrosion products on alumina and mullite only. No batch composition was given for the borosilicate glass used in the stainless steel study (Reference 5-10).

b. Soda lime glass melting, exposed at 2650°F for 85 days (Reference 5-11).

c. Soda lime glass melting, exposed at 2100°F for 90 days (Reference 5-11).

d. Borosilicate glass melting, exposed at >1200°F for eight months (Reference 5-10).

evolved from the glass melt as some other specie (sic).⁵⁻² In apparent contradiction to this observation, it has been reported elsewhere that NaCl added to an experimental glass batch greatly increased the Na₂O content of the flue gas, and that 30 to 40% of the NaCl was volatilized.⁵⁻¹²

Deposits and corrosion products on refractory specimens exposed in the flue of a small experimental furnace, charged four times daily with a representative soda lime glass, have also been studied.⁵⁻¹¹ Table 5-7 lists the glass batch composition (calculated from the components in the charge) and representative analyses of corrosion products formed on 99.8% Al₂O₃ and on mullite (ideally Al₆Si₂O₁₃). The alumina was exposed 85 days at 2650°F; the mullite, 90 days at 2100°F. For silicon carbide refractory, the authors associated increased alkali deposition (Na, K) at lower temperatures with significantly greater corrosion. Table 5-7 also shows greater deposition of Na, K, P, and S (presumably as sulfate) on mullite at the lower temperature than on alumina at the higher temperature. Titanium and iron found at levels of 1 to 2% on refractory specimens exposed with no glass in the furnace were associated by the authors with titanium and iron contamination in the furnace.

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6. SURVEY TO DETERMINE CHARACTERISTICS OF TYPICAL FURNACES AND FLUE GAS STREAMS

To provide the basis for the most-typical functional and operational requirements and the possible benefits of furnace recuperators, associations and societies of the steel, aluminum, and glass industries were surveyed by telephone.^{6-1 through 6-7} The purpose of the survey was to determine the following information on steel soaking pits, steel reheat furnaces, aluminum remelt furnaces, and glass melting furnaces:

1. Population of each type of furnace
2. Population of each type that is equipped for recuperation
3. Type of recuperator used
4. Identity, heating value, and rate of use (per furnace) of fuel(s) used
5. Operating parameters--such as inlet air temperature, pressure, and rate of flow; and flue gas temperature, volume rate of flow, and duct velocity at furnace and recuperator exit
6. Flue gas contaminants
7. Geometrical relationships of the flue and burner, and any space limitations that would restrict recuperator design or installation.

The telephone survey was unsuccessful. The general tenor of the responses was that this information has not been collected into a central location. Specific handbooks and directories were recommended, however, as a starting point for obtaining the more general information; EG&G is collecting these references.

The Midland Ross Corporation Technical Center--Thermal Systems conducted a rather extensive survey of the steel, and possibly other industries, in 1978,⁶⁻⁸ but the results are not reported in detail. The Midland Ross Corporation has agreed to try to locate the original questionnaires for future use by EG&G, Idaho, Inc.⁶⁻⁴

The most complete information found, shown in Tables 2-2 and 6-1, was compiled for the Gas Research Institute by AiResearch Manufacturing Company, a Garrett subsidiary.⁶⁻⁹

A direct survey of the steel, aluminum, and glass industries may be necessary. If so, it is recommended that representative candidate sites and companies be identified through publicly available documents, based on a set of selection criteria. Appropriate people in these companies would then be identified and personally contacted. This approach should yield the best possible data through the elimination of impromptu responses from persons who may not be the most knowledgeable or may be unwilling to release proprietary information.

TABLE 6-1. FURNACE AND RECUPERATOR POPULATION AND OPERATION DATA⁶⁻⁹

Type of Furnace	Year	Unrecuperated Furnaces			Estimated Energy Consumption ^a (10^{12} Btu/yr)	Recuperated Population (%)	Cyclic Operation	Average Firing Rate ^b (MBtu/h)
		Number of Furnaces	Number					
Steel soaking	1979	2275	273		18	85-90	Yes	25
Steel reheating	1979	--	--		190	--	--	--
Continuous Batch	--	310	124		--	60	No	250
	--	385	270		--	30	Yes	40
Iron and steel forging	1980	--	--		72	15	--	--
Slot	--	8000	6800		--	--	No	0.25, 7.5
Carbottom and box	--	4500	3825		--	--	Yes	5, 50
Glass melting	1979	800	40		9	95	--	--
Unit melter	--	75	--		--	--	No	40
Regenerative	--	725	--		--	--	No	65
Aluminum reverberatory	1978	800	760		47	5	Yes	10, 90
Copper reverberatory	1976	12	11		16	8	No	115

a. Based on Reference 2-5 data for total energy consumption, given in Table 2-2.

b. When two firing rates are given, the first is applicable to low fire and the second to high fire conditions.

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7. RESEARCH AND DEVELOPMENT NEEDS

The waste gas streams of aluminum remelt furnaces, steel reheat furnaces or soaking pits, and glass melting furnaces could be only partially characterized using available information. Although some good stream characterization information is available for glass melting furnaces, available characterization information for the other waste streams selected in this study is sorely lacking. Knowledge of the stream characteristics is not only necessary for material selection and recuperator design but would also be useful to select recuperator operating parameters. Although additional characterization information is needed to design advanced recuperator systems for any of the furnaces that produce the waste heat streams studied in this report, it is especially needed for the waste heat streams from aluminum remelt furnaces and steel soaking and reheat furnaces. Otherwise recuperators will continue to be designed on a case by case "build 'em 'n bust 'em" basis, which does not significantly advance the state-of-the-art technology.

The constituents and limiting flue gas conditions that cause heat recovery systems to have less than optimal performance and short lifetimes need to be identified for all the waste heat streams studied. The following information (listed in order of importance) is needed:

1. Sizes of furnaces and correlating flue gas flow rates and temperature profiles
2. The chemical composition of the flue gas from steel soaking and reheating and aluminum remelting. The effect on flue gas composition of reduced flow rates and temperatures in the heat recovery systems.
3. The effects of the above variables on flue gas constituent deposition rates and the composition of scale and corrosion products formed in the heat recovery systems.

Operating parameters and waste stream constituents for all the typical furnaces need to be determined and correlated with corrosion and fouling testing. Using this information, appropriate materials can be selected, recuperators designed, and operating parameters optimized. These needs are discussed in more detail below.

Space constraints for existing and new furnace flue gas systems also need to be defined as they apply to the design and installation of new or retrofitted heat recovery systems.

7.1 Furnace Operating Conditions

There is, in general, a lack of concise operating information for the types and sizes of furnaces used. The information needed includes flow and temperature profiles, and the composition of additives, feedstocks, and fuels used. These parameters are interrelated and are essential for design calculations. The variability of these parameters in response to changing operating conditions is especially needed to assess the adaptability of a given recuperator to different types of furnaces and operations.

7.2 Flue Gas Characterization

A limited number of flue gas stream analyses were found for the glass melting furnaces at furnace operating conditions. These analyses were further limited because the constituents were reported as elements or oxides of elements, rather than the specific compounds existing in the gas stream. Total waste gas stream analyses were not found for the aluminum remelt furnace, the steel soaking pits, or the steel reheat furnaces. Furthermore, placing a recuperator in line with a waste gas stream changes the values of the stream parameters. Information was not available for the effect these changes will have, although the parameters affected will be furnace fuel flow (concentration of combustion products in the flue gas), linear velocity, flow pathway, temperature, and the environment in contact with the flue gas stream. Changes in these parameters will change the composition and chemical behavior of the waste gas streams. This information is extremely important to the successful operation of a recuperator.

The necessary analyses should be obtained at the conditions (temperature, flow rate, etc.) the recuperator will experience and should reflect the actual compounds found in the waste gas stream.

7.3 Fouling and Corrosion

Corrosion and fouling tests are critical to the selection of materials if a recuperator is to be operated successfully for an extended length of time. Many materials behave differently in the presence of specific chemical species even when these species are present in minute concentration. Furthermore, the species present may only interact in the presence of a specific recuperator material. This information is important prior to construction of a recuperator, if debilitating effects to its performance and lifetime are to be minimized. Particularly needed are studies of candidate heat exchanger materials such as ceramics.

Although some corrosion and fouling tests have been reported, methods of sampling and analytical testing were not given. The variance and accuracy of the data also was not discussed. In addition, the corrosion test data often reflect upset conditions and a lack of proper operational control. Data is also lacking for many variations in operations, such as the broad ranges of steel and glass composition, fuel composition, and types of operations. Analyses have not been accompanied by measurements of temperature, flow velocity, and stream composition. In general, the product and deposit analyses are of a few small samples, without thickness measurement, without trace analysis of the substrate so that deposit constituents could be clearly differentiated, and without sufficient information for statistical evaluation. Consequently, predictions of deposition and corrosion in heat exchangers lack both empirical and theoretical bases.

Corrosion and fouling tests are needed that reflect the conditions that will be seen by the recuperator. These tests should reflect changes in temperature, velocity, and waste stream composition. Simple tests could isolate the specific corrosive species. Such tests would aid in the selection of materials and in recuperator design.