
Industrial Fouling: Problem Characterization, Economic Assessment, and Review of Prevention, Mitigation, and Accommodation Techniques

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INDUSTRIAL FOULING: PROBLEM CHARACTERIZATION,
ECONOMIC ASSESSMENT, AND REVIEW OF PREVENTION,
MITIGATION, AND ACCOMMODATION TECHNIQUES

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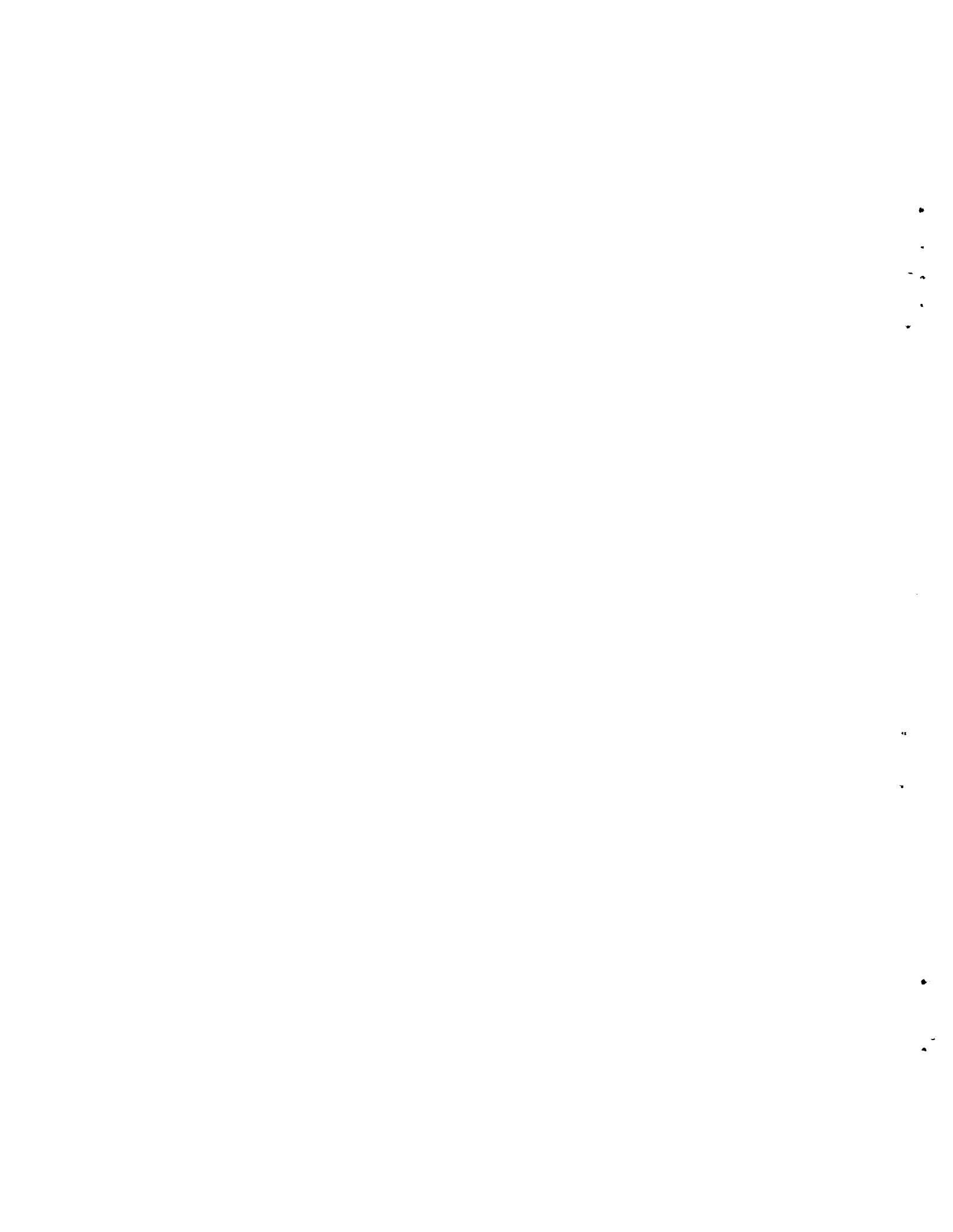


ABSTRACT

This report provides a comprehensive overview of heat exchanger fouling in the manufacturing industries. Specifically, this overview addresses:

- the characteristics of industrial fouling problems.
- the mitigation and accommodation techniques currently used by industry, and
- the types and magnitude of costs associated with industrial fouling.

A detailed review of the fouling problems, costs and mitigation techniques is provided for the food, textile, pulp and paper, chemical, petroleum, cement, glass and primary metals industries.



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SUMMARY

The following is a brief summary of the results of the Fouling and Corrosion study performed for the Department of Energy, Office of Industrial Programs.

- The cost of fouling and corrosion to the U.S. industrial sector is estimated to be between \$3 and \$10 billion per year. Of this, it is expected that one to four billion dollars per year can be attributed to gas-side fouling.⁽¹⁾
- Most of the fouling research conducted to date has been directed toward liquid-side fouling problems, with much less attention given to gas-side fouling. Reported research primarily deals with the electric utility industry, with relatively little published data addressing problems in the manufacturing industries.
- The most severe gas-side fouling problems are associated with burning coal, heavy oils, and waste fuels, which are seeing increasing use in industry.
- Temperature plays an important part in determining the type of deposit formed. In the high-temperature regime (above 500°F) fused-ash deposits are common. At low temperatures (below 500°F) condensation of acid and water vapor from combustion gas streams may lead to cold-end corrosion fouling. The latter is a particular concern with waste-heat recovery from low-temperature exhausts.
- A variety of mitigation techniques are available for liquid-side fouling; however, relatively few techniques are available for gas-side fouling.
- Patent activity in the area of fouling mitigation techniques has been relatively low with respect to other technologies. This lack of activity suggests that: 1) mitigation techniques that have been developed to date tend to be process specific and are protected as trade secrets, rather than by patenting, and/or 2) the private sector may believe that there are few opportunities for major profits in patentable fouling mitigation techniques.



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1.0 INTRODUCTION

The objective of this report is to provide a comprehensive overview of heat exchanger fouling problems as they occur in the industrial manufacturing sector. This information is intended to assist the U.S. Department of Energy (DOE), Office of Industrial Programs, in planning a long-term research and development program on fouling in the industrial sector. Specifically, this overview addresses:

- the types of fouling and conditions that influence fouling (Section 2.0)
- the characteristics of generic industrial heat exchanger fouling problems (Section 3.0),
- the mitigation and accommodation techniques currently used by industry (Section 4.0),
- mitigation technology trends (Section 5.0), and
- the types and magnitude of costs associated with industrial fouling (Section 6.0).

In addition, an overview of the characteristics, costs, and mitigation techniques associated with fouling problems in seven major manufacturing industries is provided in Appendix H.

The emphasis of this analysis is on problems that are generic in industry, with primary emphasis on gas-side fouling. Liquid-side fouling problems associated with cooling water are also discussed.

Increasing energy and raw material costs, declining availability of high-quality cooling water, and environmental restrictions limiting the use of certain additives that could be used to mitigate fouling have combined to increase the importance of understanding fouling phenomena in the design and operation of industrial heat exchangers. This increased interest in fouling is evidenced by the growth in the volume of published literature and in the number of conferences held on the subject in recent years.

Fouling literature has been classified in several bibliographies. The first of these, published in 1970 by Battelle Columbus Laboratories under the

sponsorship of the American Society of Mechanical Engineers (ASME) Ash Deposits and Corrosion Committee, provides an extensive bibliography on corrosion and deposits from combustion gases.⁽¹⁾ A second edition of the Battelle Columbus Bibliography is in press and should be available later this year.⁽²⁾ In 1979, AERE Harwell, in cooperation with Hemisphere Publishing Corporation, began publication of a quarterly awareness journal, "Fouling Prevention Research Digest". The journal provides an annotated bibliography of recent literature pertaining to fouling. Most recently, a bibliography on gas-side fouling, including a classification of references both by subject and by fuel type, was presented by Marner and Webb.⁽³⁾

Several review articles have documented the state of the art of fouling knowledge. In 1974, Taborek, et al.,⁽⁴⁾ provided a systematic treatment of fouling that has come to be recognized as a major contribution to the subject of fouling. Epstein⁽⁵⁾ presented an overview of fouling in which he proposed six basic types of fouling, an approach that has since been widely accepted. Recently, he presented a classification of fouling research in terms of a matrix in which the columns represent the types of fouling and the rows represent the sequential events in the fouling process.⁽⁶⁾ In 1977, Sujor, et al., presented a review of cooling water fouling that was published in the permanent literature in 1977.⁽⁷⁾ The most recent overall reviews of fouling were presented by Knudsen.^(8,9)

Numerous research reports have made significant contributions to the understanding of fouling. Some of these are highlighted here. In 1971, the now classic reference on deposits and corrosion in boilers and gas turbines by Reid⁽¹⁰⁾ was published. The ASME Research Committee on Corrosion and Deposits from Combustion Gases published a set of guidelines for coal fouling and slagging parameters in 1974.⁽¹¹⁾ In 1980, Battelle Columbus Laboratories completed a comprehensive review of fireside additives under contract to the Electric Power Research Institute (EPRI).⁽¹²⁾ The U.S. Department of Energy (DOE) commissioned surveys of gas-side fouling in the cement and glass industries that were completed in 1982 and 1983, respectively.^(13,14)

Many national and international conferences related to fouling have been held. These conferences have allowed researchers from all over the world to share their research findings and to formulate priorities for future research. Two conferences of major importance were organized by Bryers of the Foster-Wheeler Energy Corporation in 1978 and 1981 on ash deposits and corrosion from combustion gases.^(15,16) In 1979, Somerscales and Knudsen organized the first International Fouling Conference held at Rensselaer Polytechnic Institute in Troy, New York. The conference proceedings, published in 1981,⁽¹⁷⁾ contain several significant review articles on specific types of fouling as well as a number of recommendations for R&D investigations. The second International Fouling Conference, held at White Haven, Pennsylvania, in November 1982, was organized by R.W. Bryers.⁽¹⁸⁾

In 1981, Battelle Columbus and EPRI conducted a workshop on oil and gas additives that was attended by 116 representatives from industry, national laboratories, and electric utilities.⁽¹⁹⁾ That same year, DOE sponsored a workshop on the Assessment of Gas-Side Fouling in Fossil Fuel Exhaust Environments at Boulder, Colorado.⁽²⁰⁾ The 41 participants at that workshop, consisting primarily of representatives from industry, formulated a list of high-priority R&D recommendations for gas-side fouling.

In December 1982, Pacific Northwest Laboratory conducted a workshop in Seattle to gather information on industrial fouling and corrosion problems, costs and current mitigation techniques.⁽²¹⁾ This workshop provided a point of departure for the development of this document. In addition, a preliminary list of research priorities was developed by the workshop participants including representatives from industry, academia and government.

Currently, the most widely used data on fouling resistances is published by the Tubular Exchanger Manufacturers Association (TEMA).⁽²²⁾ TEMA provides a listing of experienced-based fouling resistances for various fluids, primarily liquids. These standards, which are defined for broad categories of equipment and heat duty, have several limitations: 1) they do not recognize the time-dependent nature of fouling, 2) they are not related to specific design

and operational characteristics of particular heat exchangers, and 3) information is only available for a limited number of fluids.⁽²³⁾ Recently, a committee has been formed to re-evaluate these fouling resistances. The committee consists of TEMA members and members of Heat Transfer Research, Inc. (HTRI). The committee is expected to complete its review in about two years.

Finally, it should be pointed out that HTRI has carried out a systematic study of fouling in cooling tower water during the past 15 years. Based on their research, HTRI has developed a proprietary relationship describing fouling resistance as a function of time for treated cooling water. The form of the equation is published in the open literature, however, the constant terms are currently available only to HTRI members.

It is clear that fouling is a subject of great interest and importance. However, in spite of the many efforts in this field few of the problems have been solved. The majority of research to date has addressed liquid-side fouling problems with significantly less information available on gas-side fouling. Applied research has largely focused on the electric utility industry. Research directed to the industrial sector deals largely with process-specific, rather than generic problems.

Heat exchanger designers are still faced with a great deal of uncertainty in specifying an appropriate fouling resistance for a given heat exchanger design. On the operations side, fouling problems are approached primarily in a reactive, rather than a preventative manner. In terms of oversized equipment, additional cleaning equipment, maintenance and energy losses, fouling is costing U.S. industry two to ten billion dollars each year. Thus, fouling must still be regarded as the "major unsolved problem in heat transfer."⁽⁶⁾

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2.0 OVERVIEW OF FOULING

Fouling is generally defined as the formation of deposits on heat transfer surfaces, which interferes with heat transfer and/or fluid flow. In order to include direct-contact heat exchange operations, the definition has at times been expanded to consider fouling as the accumulation of deposits at phase interfaces.⁽¹⁾ The present discussion will focus on fouling of heat transfer surfaces.

Fouling affects two aspects of heat exchanger performance. Typically, the fouling layer has a high thermal resistance with respect to other resistances in the system. This increases the resistance to heat transfer and reduces overall effectiveness. Also, as deposits occur, the cross-sectional flow area is restricted which causes an increase in the pressure drop across the exchanger. This requires additional pumping or fan power to achieve the same throughput.

Typically, allowance is made in the design of a heat exchanger for the added resistance due to fouling. That is, the thermal resistance due to fouling, R_f , is included in the equation for the overall heat transfer coefficient as follows:⁽²⁾

$$\frac{1}{U_o A_o} = \frac{1}{h_o A_o} + \frac{R_{fi}}{A_i} + \frac{R_w}{A_w} + \frac{R_{fo}}{A_o} + \frac{1}{h_i A_i}$$

where

U_o = overall heat-transfer coefficient based on outside area of tube wall

A = tube wall area

A_w = mean wall area

R_f = thermal resistance due to fouling

R_w = thermal resistance of wall

h = convective heat-transfer coefficient

and the subscripts i and o refer to the inside and outside of the tubes, respectively.

Fouling resistances of 0.001 to 0.002 $\text{hr}\cdot\text{ft}^2\text{-F/Btu}$ will normally add 20 to 50% more surface area beyond that required for a clean exchanger, depending

on the magnitude of other heat-transfer resistances. One approach used in designing steam-heated reboilers that may foul is to provide 50 to 75% more heat transfer area over that required for clean conditions.⁽³⁾

Selection of a fouling resistance is somewhat arbitrary and there are little data for accurate assessment of the degree of fouling that can be expected for a given exchanger and flow conditions. The Tubular Exchanger Manufacturers Association (TEMA) provides a listing of experience-based fouling resistances for various fluids. These "standards" are defined for broad categories of equipment and heat duty and provide little information on the variation of fouling resistance with temperature and velocity. No allowance is made for the time-dependent behavior of fouling resistance.

Since fouling deposits build up over time, the design fouling resistance typically represents a terminal value. That is, it represents the point at which some action should be taken to clean the exchanger.⁽⁴⁾ The exchanger is oversized for initial operation and care must be taken during startup operation to avoid overheating or cooling process streams.

The buildup of fouling deposits as a function of time may approximate one of the curves shown in Figure 2.1.^(5,6) If fouling resistance increases as a linear function of time, the exchanger can be operated for only a limited time before cleaning will be required. With the falling-rate mode, fouling resistance also increases with time, but the rate of increase decreases with time. The asymptotic mode is the most ideal case, because the fouling resistance eventually reaches a constant value. This mode is typical of industrial cooling water fouling.⁽⁶⁾

The remainder of this section discusses the fouling process, conditions that promote fouling, the types of fouling, the techniques used to mitigate fouling problems, and the costs associated with fouling.

2.1 TYPES OF FOULING

Fouling is generally classified into six categories: 1) precipitation, 2) particulate, 3) chemical reaction, 4) corrosion, 5) biological, and 6)

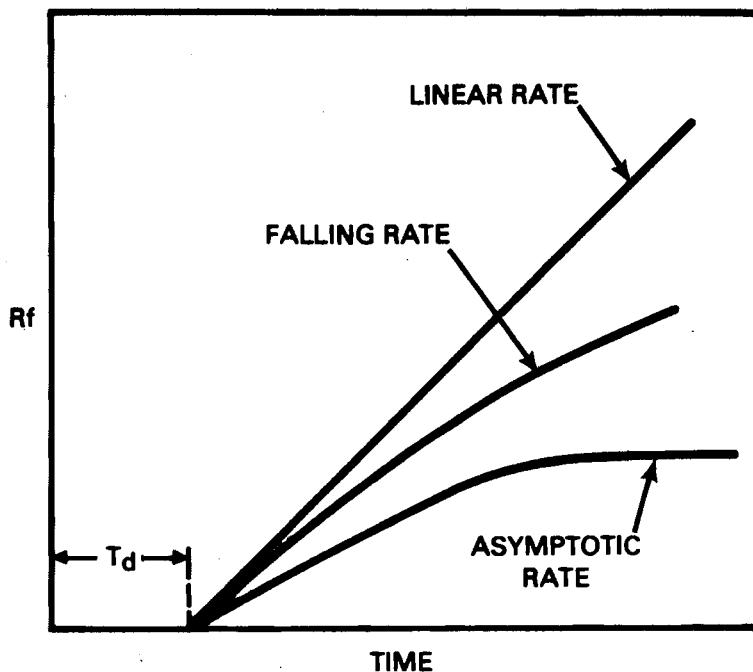


FIGURE 2.1 Fouling Resistance as a Function of Time

solidification fouling.⁽⁵⁾ However, this classification scheme was developed primarily for liquid-side fouling problems and is not completely satisfactory for classifying gas-side fouling problems. In particular, condensation of vapor species is not specifically addressed. In practice, the overall deposit accumulation process results from several fouling mechanisms acting sequentially or simultaneously.

2.1.1 Precipitation Fouling

Precipitation fouling involves the crystallization of dissolved species from solution onto the heat-transfer surface. Precipitation fouling occurs when process conditions lead to supersaturation of the dissolved inorganic salts at the heat-transfer surface. Process conditions that may lead to supersaturation include evaporation beyond solubility limits, cooling/heating beyond solubility limits, or mixing process streams.⁽⁷⁾

Some dissolved species exhibit inverse solubility versus temperature behavior. In this case, the substance tends to precipitate on a heated rather than

a cooled surface as is the case in cooling water applications. Salts with inverse solubility characteristics include CaSO_4 , CaCO_3 , Mg(OH)_2 , LiSO_4 and LiCO_3 , which are often found in brackish or sea water as well as most cooling tower waters.^(8,9)

The term "scaling" generally refers to hard crystalline deposits, well attached to the heat exchanger surface. Scaling often occurs when cooling water is used in condensers, in sea water evaporators, and on the waterside of steam-generating units.^(7,8)

Solutions containing a single salt tend to form hard, tenacious deposits that are resistant to removal. Solutions containing salt mixtures tend to precipitate in an irregular pattern on the surface. These deposits are softer and less adherent and the irregular surface promotes erosion by the fluid flowing across the deposit. Eventually an equilibrium is reached with the rate of deposition of new crystals equal to the rate of deposit removal.⁽²⁾

2.1.2 Particulate Fouling

Particulate fouling has been defined as the accumulation of particles suspended in liquid or gaseous streams onto heat-transfer surfaces.⁽¹⁰⁾ In a few cases, the deposition occurs as a result of gravity, in which case the process is referred to as sedimentation.

Suspended particles may include ambient pollutants, ex situ corrosion products, or products of chemical reactions occurring within the fluid.^(7,10) Ambient pollutants include sand, iron minerals or microbial organisms in cooling water, and airborne particulates in air-cooled exchangers. Corrosion product deposition is common in boiler waters and reactor coolants. Ex situ corrosion refers to corrosion products that originate from a source other than the heat-transfer surface and are subsequently deposited on the heat-transfer surface, as distinguished from corrosion fouling that is an in situ process.⁽¹⁾

2.1.3 Chemical Reaction Fouling

Chemical reaction fouling includes deposits that are formed as a result of chemical reactions within the process fluid. The heat exchanger surface material is not a reactant, although it may act as a catalyst. Chemical reaction

fouling is a common mechanism in petroleum refining, polymer production, and food processing.

2.1.4 Corrosion Fouling

In this case, the heat exchanger material reacts with the fluid to form corrosion products on the heat-transfer surface. This classification is restricted to *in situ* corrosion processes.⁽¹¹⁾ Corrosion products that are formed elsewhere and then deposited on the heat-transfer surface (*ex situ* corrosion) result in either precipitation or particulate fouling, depending on whether the corrosion products are soluble or insoluble at the bulk fluid conditions.⁽¹⁾

2.1.5 Solidification Fouling

Deposits are formed on the heat transfer surface by freezing a liquid or a high-melting point constituent of a multicomponent fluid onto the subcooled surface. Examples of this mechanism include ice formation in water cooling, deposition of paraffin waxes from hydrocarbon solutions, and deposition of ice from humid air in cryogenic plants.⁽¹²⁾ In addition, solidification fouling can also be important in gas-side fouling, for example in the deposition of sodium sulfate.

2.1.6 Biological Fouling

Biological fouling refers to the development and deposition of organic films consisting of microorganisms and their products (microbial fouling) and the attachment and growth of macroorganisms, such as barnacles or mussels (macrobial fouling).⁽¹³⁾ It has been postulated that microbial fouling always precedes fouling by macroorganisms, with the microorganisms acting as a nutrient source for the macroorganisms.⁽¹³⁾ The adsorption of microorganisms on the heat-transfer surface is a function of the surface roughness.

2.2 FOULING MECHANISMS

The overall fouling process can be viewed as consisting of five subprocesses: 1) initiation, 2) transport to surface, 3) attachment, 4) transformation or aging, and 5) removal or reentrainment.^(1,5)

As shown in Figure 2.1, there is a time interval (T_d) between the start up of a clean heat exchanger and the first detection of an increase in the heat transfer resistance due to fouling. During this time delay or initiation period, conditions that promote subsequent fouling are established. Among these are the establishment of a temperature, concentration, or velocity gradient, an oxygen-depletion zone, formation of crystal nucleation sites, or formation of a sticky film on the heat exchanger surface. In some cases, an initial enhancement in heat transfer may actually occur because the rough initial deposits may act as turbulators to break up the viscous sublayer.⁽¹⁴⁾

Of the five stages in the fouling process, the transport of the foulant to the heat exchanger surface has been the most widely studied phenomenon. A number of mechanisms have been identified that promote foulant migration to the heat-transfer surface. These transport mechanisms are described briefly below:

- **Diffusiophoresis:** A concentration gradient acts as the driving force in moving a foulant from the area of high concentration in the bulk of the fluid to the area of low concentration at the heat exchanger surface. The rate of arrival of particles at the surface is inversely proportional to particle size for this diffusion-controlled transport mechanism.⁽¹⁵⁾
- **Turbulent Diffusion:** Particles become entrained in eddies of turbulent boundary layers and are swept toward the surface. The arrival rate at the surface has been found to be directly proportional to the free stream velocity at the edge of the boundary layer and to the particle size. The arrival rate is inversely proportional to the boundary layer thickness.
- **Reaction-Rate Controlled:** Material accumulation at the surface is dependent upon a chemical reaction rate at the surface. The rate of deposition on the surface is dependent upon both the rate of diffusion to the surface and the chemical reaction rate at the surface. If the chemical reaction rate at the surface is high compared to the diffusion rate, the deposition is chemical reaction controlled.
- **Inertial Impaction:** The inertia of a particle relative to the bulk of the stream causes its trajectory to deviate from the flow streamlines, particularly where the stream encounters directional changes due to bends or

elbows. The arrival rate at the surface is a function of the particle diameter. (16)

- Thermophoresis: Particles move to a cold surface under the influence of a temperature gradient. Thus, the arrival rate is a function of both the thermal gradient and the particle size. (16,17) Thermophoresis is significant for particle diameters below 5 microns and becomes dominant at about 0.1 micron. (18)
- Brownian Diffusion: Particles randomly impact agitated molecules and are propelled to the heat transfer surface. The arrival rate is inversely proportional to particle size. (15) Brownian diffusion is negligible for particle diameters over about 0.01 micron. (18)
- Electrophoresis: Statically-charged particles are attracted to the heat exchanger surface. Electrical forces become increasingly important on charged surfaces at particle sizes below about 0.1 micron. (18) Very strong electrical fields would be required to influence deposition of larger particles.
- Gravity: In relatively static systems, particles larger than about 1.0 micron may settle on horizontal surfaces. (18)

The third step in the fouling process is the actual attachment of the foulant to the heat exchange surface. Little is known about this process. However, some of the factors that are thought to contribute to foulant adhesion are van der Waals forces, electrostatic forces, the surface tension of the adsorbed surface film, and external force fields. (15)

Once the foulant is deposited, physical or chemical changes may occur. For example, physical changes may include changes in the crystal structure arising from dehydration. In situ chemical reactions may occur within the deposit or between the deposit and constituents in the stream or in the heat exchanger material. The changes that occur after deposition are often referred to as deposit aging. (15)

Removal of fouling layers may begin as soon as an initial layer is deposited. Removal may occur as a result of spalling, erosion or dissolution. With

dissolution, the material detaches in ionic form. The material detaches in particulate form with erosion and in a large mass with spallation.⁽¹⁹⁾ Several removal models have been proposed.⁽⁵⁾ The models have related the rate of removal to the velocity, the shear stress of the fluid, and the strength of the deposits. Cleaver and Yates have postulated that removal is not simply a function of the shear stress, but rather it is due to the wall suction created by randomly distributed turbulent bursts.⁽¹⁾

2.3 CONDITIONS INFLUENCING FOULING

From an applications standpoint, conditions that influence fouling or that affect the impact of fouling on heat transfer or fluid flow can be classified as operating parameters, fluid properties, and heat exchanger design parameters.

2.3.1 Operating Parameters

Fluid velocity may be the most important parameter affecting fouling behavior. In addition, both the surface temperature and the bulk fluid temperature influence the rate of development of fouling resistance.

2.3.1.1 Velocity

Most reports indicate that for several types of fouling the rate of fouling decreases as the velocity increases.^(2,16,17) An increase in velocity may increase the rate of deposition but increase the removal rate to a greater extent so that the overall rate and the eventual equilibrium deposition thickness are decreased.⁽²⁾ Velocity influences mass diffusion-controlled deposition processes through convective mass transfer to the surface.⁽⁸⁾ This effect is only significant if the deposit mechanism dominates the removal mechanism. With biological fouling, attachment of microorganisms is promoted by low local fluid velocities. However, growth of the attached organisms may be dependent on higher velocities to enhance the diffusion of oxygen and nutrients to the surface. Growth is balanced by the shearing effect of higher velocities.⁽⁵⁾

The effect of velocity on the removal process is generally correlated in terms of wall shear stress and deposit mechanical strength.⁽⁸⁾

2.3.1.2 Surface Temperature

Surface temperature may increase, decrease or have no impact on the material deposited on the surface.⁽¹⁰⁾ The rates of chemical reaction and crystallization of inverse solubility salts are strongly dependent on surface temperature.⁽²⁾ Although the effects of surface temperature on the removal process have not been directly addressed, its effect in promoting additional crystallization in deposited materials suggests that there may be an indirect impact. Surface temperature influences the degree of in situ crystallization that will effect the strength of the deposit, thus indirectly affecting the removal process.⁽⁸⁾

2.3.1.3 Bulk Fluid Temperature

The bulk fluid temperature affects the rate of polymerization, the rate of chemical reaction, and the rate of crystallization. Thus, the rate of development of fouling resistance generally increases with temperature.

2.3.2 Heat Exchanger Parameters

Heat exchanger parameters have a significant effect on the potential for fouling to occur. Among these are surface material, surface structure, and type and geometry of exchanger.

2.3.2.1 Surface Material

The type of substrate material has been reported to be a major factor in the case of corrosion fouling. With biological deposits, copper alloys have a biocidal effect due to copper ion release at the surface.⁽⁸⁾ No differences are reported between material types for other fouling types. Indications that there is a difference in the induction period for carbon steel, stainless steel and admiralty steel exposed to brackish water are thought to be due to the surface roughness of the three materials rather than to the material composition.⁽⁸⁾

2.3.2.2 Surface Structure

For all types of fouling, the time delay is reported to decrease with increasing surface roughness.⁽¹⁾ Rough projections promote nucleation,

adsorption, or surface chemical activity. Surface indentations provide regions amenable to deposition because they are sheltered from the bulk velocity. Surface roughness may promote eddy diffusion deposition by decreasing the thickness of the viscous sublayer. This may also promote removal.

2.3.2.3 Exchanger Configuration

Properly designed plate-and-frame or spiral-plate heat exchangers are less prone to fouling than shell-and-tube exchangers.⁽²⁰⁾ These types of exchangers are characterized by higher velocities and higher turbulence levels than are encountered in shell-and-tube designs. Thus, low-velocity or stagnant areas that may promote settling of suspended solids are avoided.

In finned-tube heat exchangers, experience suggests that fin height does not have much influence on deposit buildup, but that fin density is an important parameter.⁽²¹⁾ A study of finned tubes in diesel engine exhausts indicates no differences in the propensity of foul between plain and segmented tubes.⁽²²⁾ However, segmented tubes are reportedly easier to clean.⁽²¹⁾

2.3.3 Fluid Properties

Both the nature of the fluid and the nature of the species dissolved or entrained in the fluid have a significant impact on fouling. With combustion gases, the quantity of volatile inorganics (e.g., sodium sulfate) and fly ash particles in the stream influences fouling behavior. In addition, trace elements such as vanadium may serve to catalyze fouling processes. The presence of sulfur may cause cold-end corrosion problems.

In cooling water systems and on the water side of steam generating systems, water quality is a key factor in fouling problems that might occur. Salts with inverse solubility may lead to scaling. Suspended solids in the raw makeup water or ex situ corrosion products may settle out on heat transfer surfaces. Dissolved gases influence corrosion of metal surfaces, and the presence of microorganisms and nutrients can lead to biological fouling.

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3.0 GENERIC INDUSTRIAL FOULING

This section focuses the discussion of fouling on generic problems experienced by the industrial manufacturing sector. A generic fouling problem is defined as one that cuts across most or all industrial sectors. The distinction between generic and process-specific fouling problems is best illustrated with the heat source-process-heat sink model shown in Figure 3.1. Industrial heat transfer processes can be viewed in terms of this three-part model. Heat is generated in a heat source, which is usually a boiler or a furnace. The heat is transferred to a process where a chemical or physical change in the product occurs. The heat is finally transferred to a sink, such as a cooling water or air-cooled system.

The heat-transfer surface represents the boundary between the product and either the heat source or sink. Fouling may occur on either side of this boundary. Clearly, the heat-source and heat-sink sides of the boundary is very similar among industries. Thus, the fouling that occurs on these sides of the heat-transfer process can be considered generic. The exception occurs with direct-heat processes, such as cement calcining, in which the combustion gases come in contact with the product. Here, the fouling that occurs in heat-recovery units is specific to the type of product.

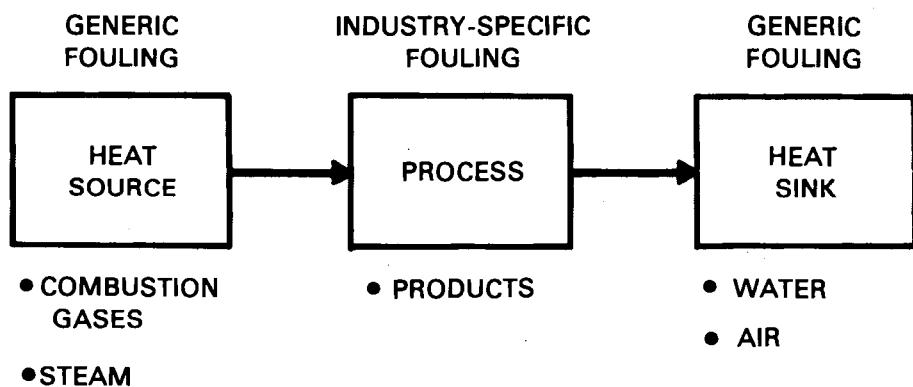


FIGURE 3.1 Heat Source - Process - Heat Sink Model

Heat-source fouling is generally associated with combustion gases (i.e., gas-side fouling). Generic fouling problems on the heat-source side include slagging in fire boxes, fouling of superheater sections and waste-heat boilers, and cold-end corrosion problems. In addition, fouling on the liquid-side of a steam generator (scaling) is a common problem in many industries.

Heat-sink problems generally involve cooling water (i.e., liquid-side fouling), although the use of air coolers may lead to gas-side fouling problems. Typical fouling problems associated with cooling water systems include scale formation and biological growth.

The generic fouling problems on the gas-side and liquid-side of industrial heat exchangers are discussed in the following sections. Particular emphasis is placed on gas-side fouling.

3.1 GAS-SIDE FOULING

Particulate fouling is the most common type of fouling associated with the gas-side, although chemical reaction, corrosion, and solidification fouling can also be important on the gas side. In general, much less is known about gas-side fouling than liquid-side fouling, particularly with respect to foulant attachment and removal processes.

Gas-side fouling related to the heat source occurs with primary and secondary heat recovery from combustion gases as they pass through a boiler, fired heater or a waste-heat recovery device. Gas-side fouling related to the heat sink involves air cooling in heat exchangers or condensers.

Fouling problems associated with air and with combustion gases in industrial heat transfer operations are discussed below. In general, fouling rates are much lower in air-cooled exchangers than in those recovering heat from combustion gases.

3.1.1 Air

Heat-transfer operations in which air is the fluid on the utility side include heat-recovery and heat-sink operations. Typically, in a heat-recovery operation the air is heated as it passes through a recuperator or regenerator

and serves as combustion air in the furnace or boiler. Air-cooled exchangers or air-cooled condensers are generally once-through systems that use the atmosphere as the heat sink.

Sources of potential foulants in air streams include particulates carried in the ambient air, ex situ corrosion products, fluids that leak from the process side of the exchanger, or in situ corrosion of extended surfaces. In process plant environments that are laden with airborne particulates (steel mills, textile mills, leather tanneries), air-cooled exchangers are particularly susceptible to fouling.⁽¹⁾ Units in coastal areas have been found to be fouled with salt from sea spray.

Bott and Bemrose⁽¹⁾ state that, in general, in the design of air-cooled exchangers no allowance is made for the increased thermal resistance that may result from deposition of these foulants. This is thought to be largely due to a lack of reliable information from which to estimate fouling resistances.

3.1.2 Combustion Gases

Fouling from combustion gases may occur in any of the following industrial heat-transfer equipment:

- Direct-fired boilers
- Superheaters
- Economizers
- Fired heaters and furnaces
- Waste-heat boilers
- Recuperators
- Regenerators
- Suspension preheaters

The degree of fouling that occurs in this equipment depends largely on the type of fuel burned. In addition, the operating conditions, and the geometry of the equipment each play an important role. The following sections discuss the types of fuels commonly used by the industrial sector, the fuel properties and operating conditions that influence fouling, and the characteristics of high-temperature and low-temperature gas-side fouling.

3.1.2.1 Industrial Fuels

The primary fuels used by industry are coal (primarily bituminous), natural gas, and fuel oil. In addition, rising fuel costs have encouraged

industries to burn waste products and to extract sensible heat from high-temperature exhaust gases to generate steam. The waste products include wood wastes, bagasse, digester liquor, blast-furnace gas, coke, petroleum coke, refinery gas, and carbon monoxide gas. With the exception of natural gas, refinery gas and carbon monoxide gas, which are relatively clean burning fuels, fouling problems are associated with burning these fuels. Table 3.1 designates the level of use of various fuels in specific manufacturing industries as high, medium or low.

Both the food processing and the textile industries rely heavily on natural gas as their primary fuel. In the food industry, gas, oil and solid fuels are used primarily to generate low-pressure process steam in boilers. A small portion of the gas is used directly in processes such as drying. Between 50 and 70 percent of the fossil fuels used in the textile industry are for steam production. A large portion of the natural gas is used in direct drying operations.

The pulp and paper industry and petroleum industry use large quantities of internally generated fuels. In the pulp and paper industry, large quantities of wood wastes (pulping liquor residue, hog fuel, and bark) as well as moderate amounts of gaseous and petroleum fuels are burned. The petroleum industry relies heavily on gaseous fuels, both process off-gases and petroleum fuels. The chemical industry also uses large quantities of gaseous fuels, especially heavy liquid feedstock and process fuels, which are used to produce chemicals such as sulfuric and phosphoric acid.

The glass and cement industries are characterized by their use of high-temperature direct heat operations. The glass industry uses primarily gaseous and petroleum fuels for melting, whereas the cement industry primarily uses coal for calcining operations. The primary metals industry relies primarily on natural gas with the exception of the iron and steel industry which obtains about three-quarters of its energy from coal and coal-derived fuels.

3.1.2.2 Influence of Fuel Type and Operating Conditions on Gas-Side Fouling

Both the characteristics of the fuel and the conditions under which it is burned influence the degree and type of fouling that may occur on the gas-side

TABLE 3.1 Use of Fuels in Various Industries
(adapted from Ref. 2)

Industry [SIC]	Fuel	Gaseous Fuels		Light Petroleum Fuels		Heavy Petroleum Fuels		Coal		Coal-Derived Fuels		Tar Sands and Shale-Derived Fuels		Agricultural Wastes		Miscellaneous Wastes		Process Fuels	
		H	M	L	H	M	L	H	M	L	H	M	L	H	M	L	H	M	
Food and Kindred Products 20		H		L		L		M						L					
Textile Mill Products [22]		H		L		H		M											
Paper and Allied Products [26]		M		M		L		L						H					
Chemicals and Allied Products [28]		H		M		L		L						L		L		M	
Petroleum Refining and Related Industries [29]		H		H		H		L		L				L		L			
Stone, Clay, Glass and Concrete Products [32]																			
Glass		H		H		L													
Cement		M		L		L		H					L		L				
Primary Metal Industries [33]																			
Aluminum		H		M		L		L											
Copper		H		M		L		L											
Iron and Steel		M		L		L		H		M									

of industrial heat exchangers. In general, gas-side fouling deposits reduce heat transfer and increase the pressure drop across the heat exchanger. In many cases, gas-side fouling deposits are accompanied by corrosion of the heat-transfer surface. The alkali-metal sulfates commonly present in coal-fired systems are particularly corrosive. In oil-fired systems, vanadium, sulfur, and chlorine compounds tend to be corrosive. Corrosive deposits are a major problem associated with burning miscellaneous wastes.

Impurities in fossil fuels react to form particulates and gaseous species upon combustion. These impurities include organically-bound sulfur in the carbon matrix of most fuels and organometallic alkali, alkaline earth or heavy metals in coals and oil.⁽³⁾ Inorganic impurities are also contained in coals and oil. These include minerals, such as clays, shales, micas, and pyrites, and salts, such as sodium chloride.⁽³⁾ Upon combustion, the impurities react to form oxides, sulfides, and sulfates and heavy, inert solids (ash) that tend to foul heat-transfer surfaces. In some cases, the quantity of ash is considerable. Table 3.2 categorizes industrial fuels as either containing ash or containing little or no ash. Of the common industrial fuels, coals generally have the highest ash content. The ash content of coal varies widely. For example, North Dakota lignites may contain from four to eight percent ash, whereas the ash content of Eastern bituminous coals may range from 6 to 20 percent.^(4,5) The ash content of residual oil is generally less than 0.2%.⁽⁴⁾

TABLE 3.2 Classification of Fuels by Ash Content⁽⁴⁾

<u>Fuels Containing Ash</u>	<u>Fuels Containing Little or No Ash</u>
Coal (all)	Natural gas
Residual fuels	Coke-oven gas
Refinery sludge	Refinery gas
Coke	Distillate (most)
Waste products	
Waste heat gases (most)	
Blast-furnace gas	
Cement-kiln gas	

Combustion gases contain a wide variety of gaseous species. Some of the gaseous species are condensable and some of them are corrosive. Knowledge of the behavior of the gaseous species present under various operating conditions is an important consideration in controlling gas-side fouling. For example, the dewpoints of various gaseous species present in combustion gases play an important role in gas-side fouling. If heat-transfer surface temperatures are below the dewpoint temperature, species may condense on the surface. Condensed acids may lead to corrosion fouling. In addition, surfaces wetted by the condensed species tend to attract particulate matter from the gas stream.

Natural gas and other fuels containing little ash produce relatively clean combustion gases, whereas heavy oil, and high-sulfur coals, and waste products produce dirty exhausts. For purposes of comparison, Table 3.3 lists recommended fouling resistances for heat exchangers in fossil fuel exhausts.

In addition to the combustion products, other contaminants may become entrained in the combustion gases. These potential foulants include entrained product if the operation is direct fired, or process fluids if they leak to the utility side of the heat exchanger. Other possible foulants are ex situ corrosion products or pollutants, such as dust, that are present in the ambient air.

Factors other than fuel composition that influence combustion product fouling include burner design, excess air, velocity, surface temperature, and fin

TABLE 3.3 Recommended Fouling Resistances for Fossil Fuel Exhausts⁽⁶⁾

	R_f (hr-ft ² -°F/Btu)
Natural gas	0.0005-0.003
Butane	0.001-0.003
Propane	0.001-0.003
No. 2 Fuel oil	0.002-0.004
No. 6 Fuel oil	0.003-0.007
Crude oil	0.004-0.015
Residual fuel oil	0.005-0.02
Coal	0.005-0.05

spacing. For example, the control of excess air is an important parameter in controlling gas-side fouling. In oil- and coal-fired systems, the excess air is kept at a minimum to minimize the reaction of SO_2 with oxygen to form SO_3 , which can react with water to form sulfuric acid. Conversely, in reciprocating engines, 200 to 300 percent excess air is common. Figure 3.2 shows the qualitative effects of some of these parameters on fouling resistance.

Particulate, chemical reaction and corrosion fouling are most commonly associated with gas-side fouling in combustion exhausts.⁽⁷⁾ The following sections discuss the characteristics of gas-side fouling at high and low temperatures.

3.1.2.3 High-Temperature Gas-Side Fouling

At elevated temperatures, compounds such as Na_2SO_4 , K_2SO_4 , P_2O_5 , Na_2CO_3 , and NaCl are deposited on heat-transfer surfaces. Various chemical reactions

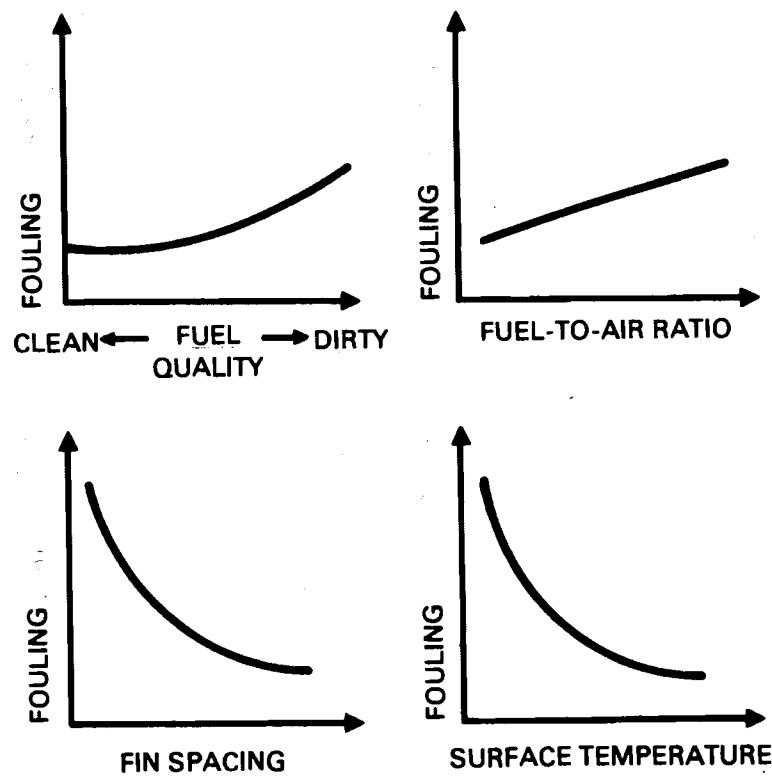


FIGURE 3.2 Qualitative Effects of Key Parameters on Combustion Gas Fouling⁽⁸⁾

and physical phenomena lead to ash deposition on cooled surfaces within boilers and waste-heat-recovery equipment. In the radiant section of boilers, molten or partially-fused ash particles may adhere to boiler surfaces (slagging). The strength of the slag is influenced by time, temperature, and the chemical and physical properties of the fuel. Fouling occurs in parts of the boiler where heat-transfer surface temperatures are below the dew point of volatile inorganics (e.g., sodium sulfate). These condensates react chemically with fly ash and with flue gas constituents to form deposits on the tubes. High-temperature deposits that occur in coal-fired boilers have been divided into two broad categories:⁽⁴⁾

1. Fused slag deposits, and
2. High-temperature bonded deposits.

Fused slag deposits generally occur in the radiant section of the boiler or furnace. Because of the complex composition of the coal ash, it tends to soften and melt over a wide temperature range. At the higher temperatures experienced in the radiant section, the ash is semi-molten and tacky, thus having a tendency to adhere to the surfaces it contacts. Ash deposits on the walls may act as an insulating layer, resulting in exit gas temperatures above the design point.⁽⁹⁾ This can cause slag deposits to advance into normally cooler parts of the boiler or furnace.⁽⁴⁾

High-temperature bonded deposits occur in the convective section of the boiler. These deposits are thought to be associated with the condensation of vaporized ash constituents onto the cooled tube surfaces. These deposits are often composed of three separate layers. The inner layer is composed of discrete particulates. The second layer, which is at a higher temperature than the inner layer due to the thermal resistance of the inner layer, tends to fuse, forming a sticky matrix. The outer layer is composed almost entirely of fly ash that adheres to the sticky surface of the second layer.⁽⁵⁾ Buildup of fouling in the tube banks lowers the effectiveness of heat transfer and may eventually lead to blockage of the gas passages.

The most significant impurities in fuel oil are vanadium, sulfur and sodium. These elements combine chemically with other constituents in the flue

gas to form complex compounds that melt over a wide temperature range. The low-melting constituents cause the particles to become sticky, resulting in a tendency to adhere to the surfaces that they contact. Dry ash particles may also adhere due to surface roughness and to attractive forces such as van der Waals forces.

Combustion of fuel oil droplets leads to the formation of minute, hollow spheres called cenospheres. Cenospheres are formed when droplets of volatile constituents vaporize, leaving the nonvolatile residue as a solid skeleton.⁽¹⁰⁾ If the particles are cooled promptly, the result is a dusty ash that may deposit on the surfaces in the boiler or may remain in suspension in the exhaust gases. If the cenospheres are insufficiently cooled, individual particles remain semi-molten and sticky and tend to agglomerate in large masses that readily adhere to boiler surfaces.⁽¹⁰⁾

3.1.2.4 Low-Temperature Gas-Side Fouling

Low-temperature deposits that occur in air preheaters and economizers are often associated with the condensation of acid or water vapor onto cooled surfaces. At low-temperatures (less than 500°F), the principal constituents of interest are H_2SO_4 , HCl, and water. When coal is burned, the sulfur compounds are converted to relatively stable mineral oxides and sulfur dioxide gas, SO_2 , is released.⁽⁴⁾ Some of the SO_2 is further oxidized to form sulfur trioxide, SO_3 . Vanadium, present in fuel oil, may act as a catalyst to promote the conversion of SO_2 to SO_3 at higher temperatures.⁽⁴⁾ Sulfuric acid may form if SO_3 combines with superheated water vapor at the acid dew point temperature. This reaction occurs between 240 and 280°F under normal boiler operating conditions depending on the amount of SO_3 in the gas.⁽³⁾

At lower surface temperatures, water will condense onto the surface in the range of 110 to 115°F. In this case, the water can combine with the SO_3 to form sulfurous acid, which like sulfuric acid, can be highly corrosive. The problem of low-temperature corrosion is frequently avoided by making certain that the surface temperature always remains above the acid dewpoint temperature of the gas stream.

3.2 LIQUID-SIDE FOULING

This section discusses fouling problems that occur in cooling water systems and on the water-side of steam generation equipment.

3.2.1 Steam

Water-side deposits in steam generation equipment can lead to reduced heat-transfer effectiveness, to equipment failure, or to contamination of industrial processes.

Boiler feedwater, despite chemical treatment, still contains measurable concentrations of impurities. In some plants, contaminated condensate introduces impurities to the boiler. Boiler water treatment chemicals may also increase the quantity of solids in the water. As water evaporates in the boiler, dissolved and suspended solids are left behind. These solids tend to concentrate as pure vapor is discharged from the boiler and feedwater containing impurities is added.

Scaling occurs when the concentration of dissolved solids in the boiler water exceeds solubility limits. The most common components of boiler scale deposits are calcium phosphate, calcium carbonate (in low-pressure boilers), magnesium hydroxide, magnesium silicate, iron oxides, silica and alumina.⁽¹¹⁾ In high-pressure boilers, deposits on tube walls may lead to overheating and to eventual tube failure. Scale may build up to a point at which boiler tubes become completely blocked, particularly in low-pressure boilers with low heat transfer rates.⁽¹¹⁾ Figure 3.3 shows potential boiler scale (pounds/year) as a function of steam rate and water quality.⁽¹²⁾

In addition to scaling in the boiler, over-concentration may result in carry-over of solids in the steam. These solids could result in scale formation in process heat transfer equipment (such as condensers, stage heaters, process heat exchangers, reboilers, evaporators or steam-jacketed process equipment), contamination of processes, or the return of contaminated condensate to the boiler. However, it is unusual to find deposits due to carry-over in most steam process equipment which operates continuously and at steady state. The most common cause of carry-over in industrial boilers is a sudden surge of boiler water due to a rapid change in the load.⁽¹²⁾ Thus, non-continuous

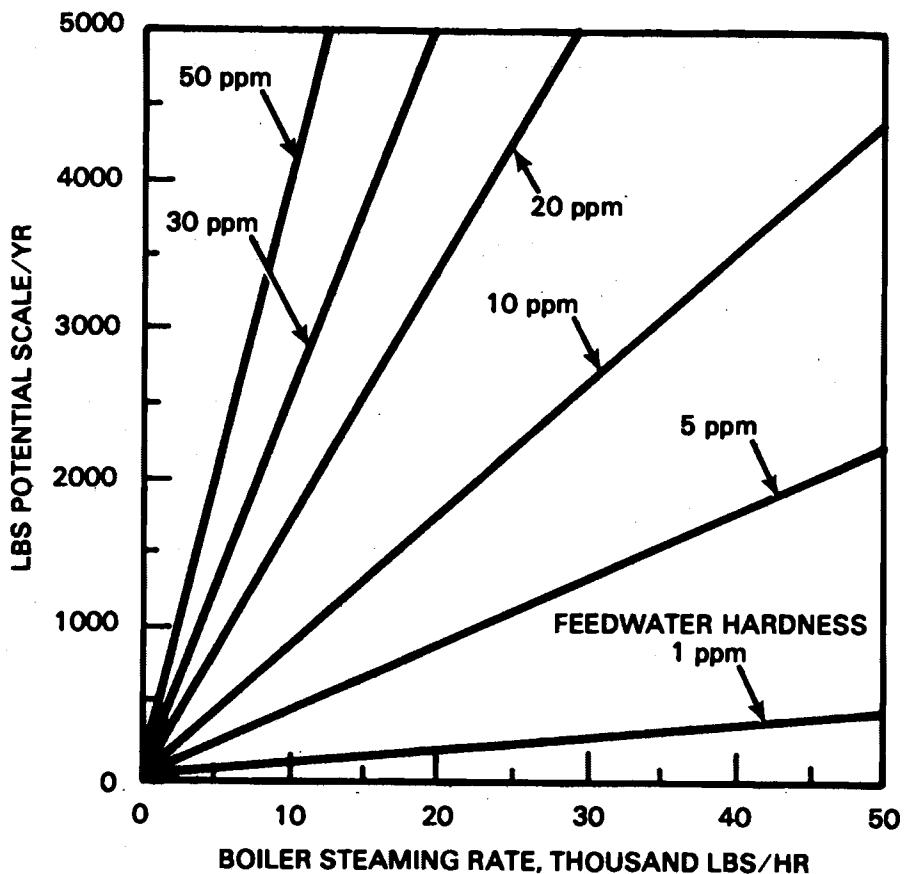


FIGURE 3.3 Potential Boiler Scale (Ref. 12)

operation can result in deposit formation as solids concentrate with intermittent wetting and drying of heat-transfer surfaces.

Deposits occasionally occur as a result of process fluid leakage to the steam side. Leakage is promoted during shutdown because a vacuum develops on the steam side, drawing process fluids through leaky tubes.

In-situ corrosion is the most common type of fouling on the steam side of process equipment. The main contributors to corrosion are dissolved gases (particularly carbon dioxide and oxygen), water pH, and excessive use of water treatment chemicals or over-concentration of treatment chemicals. Carbon dioxide is formed by the heat degradation of carbonates in the boiler feedwater. Oxygen may be introduced to the system in the feedwater or through

inleakage of air caused by a vacuum created during shutdown or under steam throttle conditions. Corrosion occurs when the protective layer of iron oxide (Fe_3O_4) is broken, exposing the metal to these constituents.

3.2.2 Cooling Water

Four types of fouling are most often associated with cooling water: precipitation, particulate, biological and corrosion. Rarely do these types of fouling occur independently of one another. Microbial deposits may trap suspended solids, further impeding heat transfer; microbes may alter water chemistry creating a tendency for scales to form or metal to corrode. The type and extent of fouling is influenced by the water chemistry, temperature, velocity and the type of cooling system. Fouling problems associated with three types of cooling systems are discussed below. These are open recirculating systems, closed recirculating systems and once-through systems.

3.2.2.1 Open Recirculating Systems

The open recirculating cooling system is the most common design for heat rejection. An open recirculating system takes water from a cooling tower basin or pond, circulates it through process equipment requiring cooling, and returns the water through the evaporation unit, where the water is cooled as a portion evaporates.⁽¹¹⁾ Makeup water must be added to balance the water evaporated and blow down is required to control the chemical composition of the water.

As water evaporates, the dissolved solids remain in the water. As evaporation continues, the concentration of total solids in the cooling water is increased. If the concentration were allowed to continue, deposition of salts would occur. Many of the salts normally present in natural water exhibit inverse solubility characteristics, tending to concentrate and precipitate at the heat-transfer surface. These salts include calcium carbonate, calcium sulfate, calcium phosphate, magnesium salts, silica and iron oxide.⁽¹³⁾ Deposits formed by these inorganic salts are referred to as "scale". Scaling is highly dependent on the surface temperature and the quality of water in the circulating system.⁽¹³⁾

In addition to the dissolved, inorganic salts, most natural waters contain a variety of suspended solids, such as silt or sand. Besides these natural contaminants, various other constituents may be introduced. Anti-foulants, corrosion inhibitors and other treatment chemicals are introduced intentionally. Other contaminants may include carryover from the treatment systems, corrosion products, inleakage from the process, and particulates from the ambient air.⁽¹³⁾ Airborne solids enter cooling systems through the natural scrubbing effect of the cooling tower.⁽¹⁴⁾ This is of particular concern in industries which, due to their processes, have a high concentration of ambient airborne particulates: textiles, tobacco, and steel for example. These suspended solids tend to settle out in the low-velocity or stagnant areas of the cooling system.

The contact between the cooling water and the air, combined with solar radiation stimulates the growth of algae and microorganisms.⁽¹⁵⁾ Common microorganisms that may cause problems are aerobic sulfate-reducing bacteria, aerobic sulfur-oxidizing bacteria, aerobic iron-oxidizing bacteria, algae and mold-like fungi.⁽¹³⁾ The various microorganisms may attach to heat transfer surfaces and grow, providing resistance to heat transfer.

In systems that require substantial makeup water, as do open recirculating systems, oxygen corrosion can present a serious problem.

3.2.2.2 Closed Recirculating Systems

In a closed recirculating system, the water is circulated through a closed loop with little evaporation or exposure to the atmosphere. Water losses are negligible and little makeup water is required. These systems are frequently used for critical cooling applications, such as continuous casters in the steel industry, where the slightest deposit could cause equipment failure.⁽¹¹⁾

Closed systems are less susceptible to fouling problems because little makeup water is required, concentration due to evaporation does not occur, and the water is not exposed to the atmosphere. Also, the quality of the water may be more closely controlled. Leakage of process fluids may be a source of fouling.

3.2.2.3 Once-Through Systems

The main characteristic of once-through cooling water systems is the large quantity of water that is used for cooling. The typical once-through cooling system draws water from the plant supply, circulates it through the cooling system and returns it to the receiving body of water. Water-side problems experienced by once-through cooling systems include corrosion, scaling, particulate fouling and biological fouling. However, these problems are not of the magnitude experienced in cooling tower systems. With once-through systems, design and water quality are the key factors influencing fouling.

Low-velocity areas, such as the shell-side of exchangers, reactor jackets and compressor jackets, tend to accumulate sludge as suspended solids settle. Fouling is directly related to the quality of the raw water. Surface waters may contain large quantities of suspended matter that can settle as flow rate decreases or can bake onto heat-transfer surfaces. Surface waters generally contain more microorganisms and nutrients than well or municipal water. Well water may be high in iron.

Scaling in once-through systems may be severe if the water is high in calcium hardness or if heat exchange rates or system temperatures are high.⁽¹⁶⁾ Calcium carbonate scale is the most frequent scale deposit in this type of system. Other scales (calcium sulfate, calcium silicate, and silica) are rarely a problem because they are more soluble than calcium carbonate and since the water is not concentrated, their solubility is rarely exceeded.

CHAPTER 3.0 - REFERENCES

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4.0 CURRENT FOULING MITIGATION, CONTROL AND REMOVAL TECHNOLOGIES

PNL assessed the fouling and corrosion mitigation strategies used in industry today and concluded the following:

- Many heat exchangers fail prematurely because of fouling and corrosion.
- Oversizing heat exchangers is probably the most frequently used strategy to mitigate fouling and corrosion.
- Oversizing heat exchangers frequently increases fouling.
- Chemical treatment (on- and off-line) and mechanical cleaning are the most frequent mitigation strategies used other than oversizing.
- Chemical treatment is a large, service-type business with custom treatments designed for each plant.
- Chemical treatment companies closely guard the formulations they use but rarely use patents to protect these formulations.

Many in the industry view fouling as inevitable and deal with it through conservation design, stream treatment and periodic cleaning of the exchangers. Some emphasize providing sufficient heat transfer surface either by having extra exchangers or excess surface in one exchanger to avoid unscheduled plant shutdown from exchanger fouling. Others emphasize fouling as a cleaning problem and believe that efforts should be focused on developing optimum cleaning methods.

Many strategies are possible for reducing, controlling or eliminating fouling and corrosion problems in heat exchangers. These strategies range from careful design and construction of the exchangers to techniques applied during installation and operation of the exchangers. Although many of these strategies can reduce or control fouling, their benefits are difficult to quantify and therefore they have found little commercial application. Other techniques, with established effectiveness, have gained wide industrial application.

In many cases, fouling and corrosion problems are being addressed by reactive rather than preventative solutions. Focusing on preventative solutions raises several issues:

- What alternatives are available for mitigating fouling and corrosion?
- What can be done during the plant design, heat exchanger fabrication and plant construction and operation to avoid fouling and corrosion?
- After startup, which options can be applied on-line and which don't require shutdown?
- Where can equipment, supplies or more information on preventative methods be obtained?

This section examines the current state of the technology in mitigation strategies available during heat exchanger design, construction, operation, and shutdown. Information on current mitigation approaches was gathered from a wide range of sources, including the following:

- contacts with process industry personnel
- contacts with heat exchanger designers and manufacturers
- contacts with suppliers of cleaning hardware, chemicals and cleaning services
- contacts with consultants to both the Waste Heat Recovery and the Fouling and Corrosion projects
- information from PNL's Heat Recovery Project
- a literature review
- a review of the trade press
- a review of supplier literature on cleaning equipment, chemicals and cleaning services

Table 4.1 lists the companies supplying information and indicates the scope of each company's product line. A data base was established and information was placed in the data base as received. The format and field descriptions (structure) of the data base are shown in Appendix A. Although information was not obtained for all of the fields of the data base, enough information was obtained to include the companies shown in the table in the lists of suppliers of specific equipment/material/services. (For additional product information, an alphabetical list of these companies is included in Appendix B.)

TABLE 4.1 Companies in Fouling Mitigation Data Base

COMPANY	ON-LINE MECHANICAL	OFF-LINE MECHANICAL	CLEANING CHEMICALS	WATER ADDITIVES	FUEL ADDITIVES	PROC FLUID ADDITIVES	CLEANING SERVICES	TESTING EQUIPMENT
ALCONOX, INC.	*							
AMERICAN AERO INC.	*							
AMERTAP CORPORATION	*							
AQUA-DYNE, INC.	*							
BARCO CHEMICAL PRODUCTS	*							
BARON BLAKESLEE MFG. CO.	*							
BEAVER ALKALI PRODUCTS CO	*							
BETZ LABORATORIES, INC.	*			*	*			*
BUTTERWORTH INC.	*							
CALGON CORPORATION	*		*	*				
CLEAN-FLO LABS., INC.	*		*					
CONCO SYSTEMS, INC.	*		*					
COPES-VULCAN	*							*
DAYTON CHEMICAL CORP.	*		*	*				
DEARBORN CHEMICAL CORP.	*		*	*	*			*
DIAMOND POWER SPEC. COMP.	*	*						*
DIONEX CORPORATION	*							*
DOBER CHEMICAL CORP	*		*					
DOWELL INDUSTRIAL SERVICE	*	*	*				*	
DREW CHEMICAL CORPORATION	*			*	*			
ELGENE CHEMICALS, INC.	*							*
ELLIOU COMPANY	*							
ENERCHEM INCORPORATED	*							*
EXPANDO SEAL TOOLS, INC.	*							*
EXXON CHEMICAL COMPANY	*							
FERGUSSON CO., ALEX C.	*							*
GLOBAL HEAT EXCHANGER INC	*							
GOODWAY TOOLS CORPORATION	*							
GREAT LAKES CHEMICAL CORP	*							
HALLIBURTON INDUST. SERV.	*							
HERCULES INC.	*							
KEM MANUFACTURING CORP.	*							
KVB, INC.	*							
MATESON CHEMICAL CORP	*							
MOGUL CORPORATION	*							
NALCO CHEMICAL COMPANY	*							
OAKITE PRODUCTS, INC.	*							
PENETONE CORPORATION	*							
PETROLITE CORPORATION	*							
PRIDE LABORATORIES, INC.	*							
SIOUX STEAM CLEANER CORP.	*							
TRITAN CORPORATION	*							
TURB-O-FLOW CORP	*							*
VICJET, INC.	*							
WATER SERVICES OF AMER.	*							
WILSON INC.	*							
WRIGHT CHEMICAL CO	*			*				

4.1 OVERVIEW OF CURRENT MITIGATION STRATEGIES

To accurately evaluate the information presented in this report, a description of the process used to select, specify, design, manufacture, and operate heat exchangers is needed. The process varies but typically follows the pattern below:

1. The potential customer specifies a fouling factor to the plant designer for each key application.
2. The heat exchanger is configured during an A&E design process.
3. A contract is let to the lowest bidder for fabricating the exchanger from the prints supplied.
4. The local contractor installs the heat exchanger.
5. The prime contractor starts up the heat exchanger.
6. After acceptance, the customer operates the heat exchanger.
7. A service company frequently uses chemical/mechanical methods to clean the heat exchanger (and associated system components, if required) after its performance degrades (usually regarded as inevitable) enough to warrant the expense and the time involved.

This process involves many people and complicates communication about potential improvements in techniques for dealing with fouling and corrosion. Some of the difficulties encountered are discussed below.

Fouling factors are difficult to predict and are controversial. Small increases in fouling factors cause the designer to make large changes in the heat exchanger's size. The heat exchanger's size and material becomes very important to its cost.

Because the heat exchanger user (buyer) is the one most concerned with the problems caused when the heat exchanger fouls, the user usually specifies to the designer the fouling resistances to be used in the design. The user is guided largely by previous experience or lacking that, depends on the TEMA⁽¹⁾ fouling resistances. The user wants the heat exchanger to perform at the required duty during the period between scheduled cleaning (usually at times of

general plant shutdown and maintenance). Unscheduled shutdowns are to be avoided because of excess cost from lack of production. As will be discussed, certain steps could be taken during the design process to mitigate fouling and these scheduled cleanings, but these are normally not done under current practice.

In the overall process of design, construction and operation, the heat exchanger fabricator has little opportunity or incentive to take steps to mitigate fouling and corrosion. First, the complete exchanger has already been designed and specified and thus must be built to specifications when the fabricator receives the prints. The fabricator does not change the design to help reduce fouling unless specifically requested to by the user.

The ultimate decision to select one or several of the available mitigation techniques depends upon the heat exchanger's application, the type of fouling and corrosion encountered, and the various economic parameters of the plant. Currently, most of the major efforts to mitigate, to prevent, or to remove fouling and corrosion occur during plant operation and shutdown. However, the mitigation of fouling and corrosion really needs to be addressed during four distinct phases in the life of a heat exchanger:

- design
- construction
- operation (on-line)
- shutdown (scheduled/unscheduled--off-line).

Table 4.2 shows these four phases and some of the items to be considered during each of them. These items represent opportunities by which fouling and corrosion may be prevented, mitigated, controlled, or removed from surfaces. They are discussed in the following subsections.

4.2 OPPORTUNITIES TO MITIGATE FOULING DURING THE DESIGN PHASE

During the design phase many opportunities exist to prevent or mitigate fouling and corrosion problems. However, as discussed below, some of the options solve one problem but create others. The potential options available to designers include the following:

TABLE 4.2 Spectrum of Fouling Mitigation, Prevention, Removal Strategies

<u>Design Phase</u>	<u>Construction Installation Phase</u>	<u>Operation (on-line) Phase</u>	<u>Scheduled (scheduled/unscheduled) Phase</u>
<ul style="list-style-type: none"> • Heat exchanger type 	<ul style="list-style-type: none"> • Manufacturing quality control 	<ul style="list-style-type: none"> • Maintaining appropriate temperature operating range 	<ul style="list-style-type: none"> *• Disassembly & manual cleaning
<ul style="list-style-type: none"> • Heat exchanger geometry & configuration 	<ul style="list-style-type: none"> • Protection in transport & storage 	<ul style="list-style-type: none"> • Maintaining appropriate flow operating range 	<ul style="list-style-type: none"> *• Mechanical removal • drilling • scraping
<ul style="list-style-type: none"> • Operating conditions <ul style="list-style-type: none"> • temperature • flow rate 	<ul style="list-style-type: none"> • Pre-operation cleaning & passivation 	<ul style="list-style-type: none"> *• Fluids pretreatment 	<ul style="list-style-type: none"> *• Lances <ul style="list-style-type: none"> • liquid jet • steam • air jet
		<ul style="list-style-type: none"> *• Use & control by appropriate additives <ul style="list-style-type: none"> • inhibitors • antiscalants • dispersants • acids 	<ul style="list-style-type: none"> *• Chemical cleaning*
		<ul style="list-style-type: none"> *• On-Line cleaning <ul style="list-style-type: none"> • Amertap (sponge balls) • MAN (brushes) • sonic horns • sootblowers • chains & scrapers • thermal shock 	

* Strategies that are commonly used by industry where applicable.

- selecting appropriate equipment for a given application
- specifying additional heat transfer surface area (the most frequently used option)
- designing for increased velocity of the fluids (This is limited, however, by excessive erosion of the heat exchanger if velocities are too high.)
- designing out hot-spot temperatures (In liquid heat exchanger equipment, higher temperatures are frequently associated with higher fouling and corrosion rates.)
- designing to avoid subsequent operation below the acid dew point temperatures in gas-side heat exchanger equipment (For some applications special equipment has, however, been developed that can survive below acid dew point temperature.)
- providing proper vent designs to purge trapped gases that can cause corrosion
- selecting corrosion- and fouling-resistant construction materials
- specifying special surface coatings or claddings in corrosive environments
- minimizing exposure of corrosion-sensitive areas such as tube-to-tube sheet crevices and heat-affected weld zones.

The following sections provide a discussion of the mitigation potential of alternative heat exchanger designs, design considerations for gas-side fouling control, and gas-side fouling factors.

4.2.1 Alternative Heat Exchanger Designs

In shell-and-tube designs, the most common mitigation strategy is to specify a sufficiently large fouling factor to produce a conservative design. Specifying larger fouling factors, however, can produce problems. For example, excess surface in the heat exchanger will reduce the flow rate causing fouling to occur during initial operation of the exchanger. An example of operational problems encountered during startup is given in Appendix C.

Several alternatives to shell-and-tube heat exchangers are available that may assure longer trouble-free operation of the plant. Initially, these special heat exchangers are frequently more expensive than shell-and-tube heat exchangers, but ultimately they may be more cost effective. Table 4.3 lists

TABLE 4.3 Special Heat Exchangers to Mitigate Fouling

PRODUCT	COMPANY	COMMENTS
GRAPHITE HX	ACTIVE CHEMICAL PRODUCE GRAPHITE HEAT EXCHANGERS FOR HIGH CORROSION APPLICATIONS SYSTEMS	
SPIRAL HEAT EXCHANGER	ALFA-LAVAL, INC.	SPIRAL HEAT EXCHANGERS FOR MANY APPLICATIONS, COUNTERFLOW AND CROSSFLOW UP TO 85% SOLIDS IN FLUID. SINGLE FLOW PATH.
CUSTOM FABRICATION	ALUMINUM-SCHWEISSWERK AG	CUSTOM FABRICATOR FOR CHEMICAL AND OTHER PROCESS INDUSTRIES. MAY HAVE SUPERIOR COATING TECHNOLOGY. LOCATED IN SWITZERLAND.
PLATE TYPE HEAT EXCH.	APV EQUIPMENT, INC	MANUFACTURER OF PLATE HEAT EXCHANGERS AND OTHER CHEM. PROCESS EQUIPMENT. WILL ASSIST IN DESIGN FOR HEAT RECOVERY APPLICATIONS
FINNED TUBE HX	ARMSTRONG ENGR. ASSOC.	ALSO PRODUCE SCRAPED SURFACE CRYSTALIZERS AND ELECTRIC HEAT EXCHANGERS
SHELL AND TUBE HX	ASTRO METALURGICA CO	SPECIALIZE IN CORROSION RESISTANT APPLICATIONS FOR THE CHEMICAL INDUSTRY
LATENT HEAT RECOVERY	BELTRAN ASSOCIATES INC.	THIS LATENT HEAT RECOVERY UNIT USES DIRECT CONTACT FLUID TO RECOVER LATENT HEAT IN WET EXH. GASES THEN TO NON-CONTACT HT EX
HOLLOW FLIGHT SCREW CONV	BEPEX CORPORATION	LARGE VARIETY OF PRODUCTS FOR HEATING AND COOLING SOLIDS. MOST INTERESTING IS HOLLOW FLIGHT SCREW CONVEYOR
HAIRPIN HEAT EXCHANG	BROWN FINTUBE COMPANY	HAS SOME USEFUL ADVANTAGES OVER SHELL AND TUBE TYPE EXCHANGERS
VISCOUS FLUID HEATER	BROWN FINTUBE COMPANY	MFR HEATERS FOR ASPHALT OR OTHER VISCOUS LIQUIDS.
BARE FINTUBE, CUSTOM	BROWN FINTUBE COMPANY	BASIC BUILDING BLOCKS FOR DESIGN OF HEAT EXCHANGE DEVICES FOR ANY HEAT RECOVERY APPLICATION, VISCOUS & DIFFICULT MEDIA
GRAPHITE HX EQUIP.	CARBONE USA CORPORATION	CARBONE MAKES A VARIETY OF BLOCK TYPE GRAPHITE HX IN ADDITION TO THE SHELL AND TUBE TYPES. ALL CAN BE USED WITH GASES ALSO.
GLASS LINED EQUIP.	CERAMIC COATING MFG. GLASS LINED PROCESS EQUIP., INCLUDING HEAT EXCH.	CO.
HEAT EXCH & MIXERS	CHEMINEER, KENICS	MANUFACTURES CUSTOM HEAT EXCHANGERS AND MIXERS, ESPECIALLY FOR VISCOUS MATERIALS
SCREW HT. EXCHR.	CHRISTIAN ENGINEERING	SCREW CONVEYORS USE HOLLOW FLIGHTS AND/OR CENTER TUBES TO TRANSFER HEAT TO/FROM BULK MATERIALS
COND. ECON SYSTEM	CONDENSING HEAT EX. CORP.	CHX UNITS TAKE OUTPUT GASES FROM OTHER ECONOMIZERS AND FURTHER COOLS THEM RECOVERING SENSIBLE AND LATENT HT--KEY IS TEFLON.
CORNING HT REC. SYS.	CORNING GLASS WORKS	CORNING GLASS SYSTEM HX EQUIP CAN SAVE UP TO 25% IN FUEL BILLS AND ARE AVAL IN VERY LARGE SYSTEMS FOR CORROSION APPLICATIONS
HEAT EXCHANGERS	CORNING PROCESS SYSTEMS	MANUFACTURER OF GLASS SHELL & TUBE HEAT EXCHANGERS HAS ABILITY TO DESIGN COMPLETE HEAT RECOVERY SYSTEMS.
TURNKEY SYSTEMS	CROSSE ENGINEERING LTD	THIS ENGLISH COMPANY PRODUCES COMPLETE HEAT RECOVERY SYSTEMS
HEAT EXCHANGERS	DENVER EQUIPMENT DIVISION	ALSO PRODUCE MINERAL PROCESSING EQUIPMENT, FILTERS AND PUMPS
MULTI TUBE COOLERS	DURCO	THE DURCO HX EQUIPMENT IS MADE ESPECIALLY SO THAT IT CAN BE DISSASSEMBLED FOR CLEANING AND THE GASKETS ARE RESISTANT PTFE ETC
HEAT EXTRACTOR	HEAT EXTRACTOR CORP.	THE DIRECT CONTACT LIQUID HEATER OPERATES IN THE TEMPERATURE REGION WHERE DEW POINT PROBLEMS CAN PRODUCE EXCESSIVE CORROSION!
HEAT EXCHANGERS	HUDSON PRODUCTS, INC	PERFORM CUSTOM DESIGN, PRODUCE AXIAL FLOW FANS AND GETTING INTO HEAT PIPES
HEAT RECOVERY SYSTEM	KVB, A RESEARCH-COTTRE	CONDENSING RECOVERY SYSTEM USES WATER SPRAY INTO FLUE GAS TO RECOVER SENSIBLE AND RESEARCH-COTTRE LATENT HEAT FROM WASTE GAS.

TABLE 4.3. (contd)

PRODUCT	COMPANY	COMMENTS
HT RECOVERY SYSTEMS	LUDELL MFG. CO.	DESIGNS AND MFG. COMPLETE SYSTEMS FOR RECOVERING WASTE WATER HEAT, ALSO COMPONENTS, TACKLES DIFFICULT LIQUID HT RECOVERY.
DIFFICULT LIQ HT EX	LUWA CO.	LUWA MAKES HEAT EXCHANGERS FOR VISCOSUS AND DIFFICULT FLUIDS--USES SPIRAL INSERTS IN TUBES TO PREVENT CHANNELING, STAGNATION
COOLING TOWERS	MARLEY COOLING TOWER CO.	MARLEY IS WELL KNOWN FOR CENTRAL STATION COOLING TOWERS ETC BUT ALSO HAVE A DIVISION EFCO WHICH CUSTOM FABRICATES HEAT REC EQ
GLASS HX	O-I/SCHOTT PROCESS SYSTEM	SCHOTT DIVISION OF OWENS ILLINOIS MAKES A WIDE VARIETY OF EQUIPMENT FOR RECOVERING HEAT USING GLASS COILS AND TUBES
SPIRAL FLOW TUBINTUS	PAUL MUELLER CO.	MUELLER TUBE IN TUBE SPIRAL FLOW HEAT REGENERATORS RECLAIM MUCH OF THE HEAT FROM PRODUCT ITSELF TO HEAT OR COOL PRODUCT.
REGEN. INCINERATER	REECO	MANUFACTURER OF REGENERATIVE INCINERATORS USING CERAMIC STONEWARE HEAT WHEEL REGENERATOR. CAN USE SHELL AND TUBE REGENERATION
CARTRIDGE HEAT EXCH	T.B.M. TECHNOLOGIES INC.	MFG. OF UNUSUAL HEAT EXCHANGER WHICH COMBINES FEATURES OF SPIRAL AND CONCENTRIC TUBE. POTENTIALLY USEFUL IN HEAT RECOVERY.

some of the available alternatives that were taken from the data base developed in the Waste Heat Recovery Equipment Analysis project. The various types are discussed in more detail in the source document. The names, addresses, and telephone numbers of manufacturers or suppliers are included in Appendix D.

Examples of alternative heat exchangers and their advantages for fouling and corrosion service include the following:

- plate heat exchangers for frequent cleaning requirements
- spiral heat exchangers for frequent cleaning requirements and more certain separation of fluids
- hollow flight conveyors for solids or liquids containing solids
- runaround heat exchangers for operating in the "acid dewpoint" region
- glass or glass-coated heat exchangers for handling corrosive and fouling materials
- graphite heat exchangers for handling even more difficult materials.

Although specialty design heat exchangers are available, shell-and-tube heat exchangers continue to dominate industrial applications with an estimated 80% market share. The low market share for specialty design heat exchangers is caused by their higher costs, limited service data and numerous problems associated with product information.

The key to properly designing heat exchangers is for the user to provide the designer with reliable information. If the designer knows the fouling characteristics of the fluids to be used, he can then consider numerous configurations and recommend operational techniques that could help reduce the rate of fouling. However, the user frequently does not have detailed quantitative data to adequately predict process fluid characteristics.

4.2.2 Design Considerations for Gas-Side Fouling Control

The specification of materials, configurations and operating conditions for industrial heat-transfer equipment is very important in designing for gas-side fouling control. The selection of these design considerations depend on the characteristics of the combustion gases, including temperature, velocity,

particle loading, particle composition, particle size distribution, vapor species composition and concentration, and dew-point temperatures. Some gas-side deposits are highly corrosive even at low temperatures. Exhausts laden with abrasive particles can erode heat-transfer surfaces if appropriate steps are not taken.

Temperature plays an important role in the deposition process in most cases of gas-side fouling. Both the combustion gas temperature and the surface temperature of the exchanger are important parameters. The following discussion of gas-side fouling considerations is divided into three combustion temperature regimes: 1) low-temperature, $<500^{\circ}\text{F}$, 2) intermediate-temperature range, 500 to 1500°F , and 3) high-temperature range, $>1500^{\circ}\text{F}$.

4.2.2.1 Low-Temperature Range

The most significant problem encountered in this temperature regime is dew-point condensation of corrosive vapors, such as sulfuric acid, or condensation of water vapor leading to the formation of sulfurous acid on the heat-transfer surface. Both of these acids are highly corrosive. In most applications, the surface temperature is maintained above the water dew-point temperature, but acid dew-point condensation remains a serious problem for waste heat recovery at low temperatures. In this case, the designer is faced with a critical dilemma: 1) the surface temperature should be above the dew-point temperature to avoid acid condensation problems, but 2) the gas temperature should be as low as possible to maximize energy recovery.

Some of the materials and design configurations that have been tried to deal with cold end corrosive problems, include plastics, glass and other ceramic materials, low-finned tubes and economizer preheat systems.

Tests carried out by Argonne National Laboratory and later confirmed with additional tests conducted by AiResearch Manufacturing Company of California indicated that Teflon^{®(a)}, Ryton^{®(b)}, and Kynar^{®(c)} would all be good

(a) Teflon is a registered trademark of the DuPont Company, Wilmington, DE.

(b) Ryton is a registered trademark of the Phillips Petroleum Co., Bartlesville, OK.

(c) Kynar is a registered trademark of the Pennwalt Corp., Philadelphia, PA.

candidates for coatings on heat exchanger surfaces for use in applications where cold end corrosion is a potential problem.⁽²⁾ To ensure successful application of these coatings, sharp edges, burrs, and other protrusions must be removed from the heat exchanger surface. Kentube applied a ceramic coating on finned tubes for a cold end corrosion application after mechanically cleaning and pickling the surface. The coating was found to be prone to chipping and to be ineffective in abrasive environments.⁽²⁾ Escoa Fintube has used hot-dip galvanizing on the outside of a carbon-steel finned-tube bundle to resist corrosion in an application where a water spray was used on the exterior of the tube bundle to enhance heat transfer via evaporative cooling.⁽²⁾

The operating experience of glass-tube heat exchangers shows considerable promise for low-temperature heat recovery where gas-side fouling and corrosion are potential problems. Most of the installations of glass-tube exchangers have been in Europe, although a few units have now been installed in this country. Glass-tube exchangers are typically limited to applications below 500 to 550°F because of limitations in current sealing techniques that use a special elastomer.⁽²⁾

Low-finned tubes have external, integral fins typically 0.030 to 0.040 inches in height with 19 to 30 fins/inch. As yet the fouling and corrosion service of this type of tube has not been critically tested. However, one flue gas desulfurization unit is currently using a steam heated, low-finned tube exhaust gas reheating system in hopes of overcoming earlier fouling and corrosion problems. In this case, the finned-tubes are made of Inconel 625.⁽²⁾

One common procedure used with boiler economizers is to preheat the feed-water to ensure that the surface temperature of the economizer remains above the acid dew-point temperature. A shell-and-tube heat exchanger is typically used with steam from the boiler supplying the heat to preheat the water. Thus, by means of an auxiliary heat exchanger, the designer is able to completely avoid cold end corrosion problems.

4.2.2.2 Intermediate-Temperature Range

In the intermediate-temperature range (500 to 1500°F) a major concern in coal-fired boilers is alkali and sulfur induced corrosion and fouling. In

general, carbon steels are reasonably resistant to scaling in combustion atmospheres up to about 1000°F, although accelerated oxidation may be experienced at lower temperatures under high stress conditions. Sulfur corrosion of heat recovery units in low-sulfur (less than one percent H₂ by weight) exhaust environments is a major concern at temperatures from 500 to 700°F. ENTEC recommends that "muffler" steel, which contains 11 percent chromium, be used in the tube bundles, and that the first two or three tube rows should consist of plain tubes to act as a shield for the finned tubes.⁽²⁾

There is some debate as to whether increasing the fin thickness should be considered as a solution to corrosion problems. Representatives at ENTEC believe that if a fin thicker than 0.05 inch is required, then the material should be changed. However, representatives of John Zinc Company suggest that fins should be as thick as possible because: 1) thicker fins are only slightly more expensive than thinner fins, 2) thicker fins are more erosion and corrosion resistant, and 3) increasing the fin thickness increases the fin efficiency and therefore the heat transfer.⁽²⁾

4.2.2.3 High-Temperature Range

Industrial exhausts at high temperatures (>1500°F) tend to have extreme fouling and corrosion characteristics, particularly those in the steel, aluminum and glass industries. These exhausts contain contaminants carried over from contact with the product. Currently waste heat recovery from these exhausts is impeded by the severe fouling potential of the exhausts. Research efforts sponsored by the DOE Office of Industrial Programs and by the Gas Research Institute (GRI) are aimed at developing heat exchangers that can withstand these environments. GRI contracted AiResearch to test various ceramic materials in several different industrial exhaust environments. Various silicon carbide ceramic materials were found to withstand the high temperature environments in reasonably good condition, with the exception of those tested in aluminum remelt furnace exhausts. In another study conducted by Solar Turbines for GRI, 21 different stainless steels, superalloys, and ceramics were corrosion tested in an aluminum remelt furnace environment. No evidence of reliably viable, intrinsic protection was seen with any of the materials at the temperatures tested.⁽²⁾

4.2.3 Gas-Side Fouling Factors

There are few published gas-side fouling factors and most of these are based on operating experience rather than on experimental data. In cases where gas-side fouling factors are available, there are often notable differences between data sources. Table 4.4 provides a summary of available gas-side fouling factors for combustion exhausts. Fouling factors are not available for many very important process-contaminated gas streams such as those in the cement, aluminum, and pulp and paper industries.

Of the entries in Table 4.4, only the Henslee-Bogue and the Rogalski fouling factors are based on experimental data. However, asymptotic conditions were not achieved in the Rogalski investigations. The remaining values in the table represent design values based on experience and are probably somewhat below the expected asymptotic values.⁽²⁾ The Weierman, Zink, and Henslee-Bogue values are all for finned tubes, while the Rogalski values were obtained using a smooth, cylindrical probe. It is likely that the TEMA values are also for smooth surfaces, although no specific mention is made of this fact in the literature.⁽²⁾

4.3 OPPORTUNITIES TO MITIGATE FOULING AND CORROSION DURING FABRICATION AND INSTALLATION

Heat exchanger equipment can be damaged during fabrication, shipping, or installation. Some of this damage may not be visible during the incoming inspection at the plant site and can therefore intensify fouling problems later. Some of the opportunities to prevent or mitigate fouling at this stage include the following:

- testing welds to assure the absence of leakage
- avoiding scratches on polished tubes that can initiate fouling and corrosion sites
- rolling tubes securely to avoid premature crevice corrosion
- sealing the heat exchanger thoroughly after drying during storage/shipment to prevent contact with corrosive materials
- following appropriate startup procedures.

TABLE 4.4 Comparison of Available Gas-Side Fouling Factors
(adapted from Ref. 2)

Gas Stream	R_f , Gas-Side Fouling Factor, $\text{hr}\cdot\text{ft}^2\text{-F/Btu}$				
	Weierman	Zink ^(b)	TEMA	Rogalski	Henslee-Bogue
<u>Clean Gas</u>					
Natural Gas	0.0005 - 0.003	0.001	--	--	--
Propane	0.001 - 0.003	--	--	--	--
Butane	0.001 - 0.003	--	--	--	--
Gas Turbine	0.001	--	--	--	--
<u>Average Gas</u>					
No. 2 Oil	0.002 - 0.004	0.003	--	--	--
Gas Turbine	0.0015	--	--	0.003 - 0.038	--
Diesel Engine	0.003	--	0.010	--	0.120 - 0.140
<u>Dirty Gas</u>					
No. 6 Oil	0.003 - 0.007 ^(a)	0.005	--	--	--
Crude Oil	0.004 - 0.015 ^(a)	--	--	--	--
Residual Oil	0.005 - 0.02 ^(a)	0.010	--	--	--
Coal	0.005 - 0.05 ^(a)	--	--	--	--

(a) Use of cleaning devices required to maintain fouling factor within range.

(b) Represent minimum recommended factors for service indicated.

4.4 OPPORTUNITIES TO MITIGATE FOULING AND CORROSION DURING PLANT OPERATION AND SHUTDOWNS

When heat recovery equipment is placed in operation, fouling and corrosion problems inevitably occur. The severity of the problems depends on the processes involved, where they occur, and the mitigation techniques that were applied during plant design, construction and operation. The options available for dealing with fouling after plant startup include on-line and off-line mechanical and chemical techniques. On-line techniques and equipment can be applied while the plant is operating. Off-line equipment and techniques require the plant to be shut down and may or may not require the equipment to be disassembled. Often a combination of techniques will be used.

Fouling and corrosion is not eliminated by proper selection and sizing of heat exchanger equipment. The trouble-free operation of the well-designed heat exchanger depends on an equally well-designed and controlled treatment program. A large amount of information is available on the effectiveness of various treatment chemicals and mechanical techniques for reducing or preventing fouling. The fouling resistances used by the designer may be based on subsequent treatment of the fluids, and the designer should be knowledgeable of the various treatment techniques that are used to mitigate fouling during operation.

The following first addresses gas-side opportunities, followed by a discussion of opportunities to mitigate fouling on the water side.

4.4.1 Mitigating Gas-Side Fouling During Plant Operation

Opportunities to mitigate gas-side fouling during normal operation are discussed below under four categories: 1) fuel and gas cleaning, 2) on-line chemical treatment, 3) on-line mechanical treatment, and 4) control of operating conditions.

4.4.1.1 Fuel and Gas Cleaning

Removal of contaminants that promote fouling, such as sodium, sulfur or vanadium, from fuels prior to combustion and contaminant removal from combustion gases are two approaches to mitigating gas-side fouling.

Water washing has helped to overcome some of the fouling problems experienced with residual oils in marine applications. However, it is expected that this technique will not see widespread use because only sodium and sediment are removed.⁽²⁾ Commercial and experimental methods are available for the mechanical and physical cleaning of coal, including gravity separation and froth floatation. However, these methods only remove the mineral matter (i.e., the inorganic sulfur) from the coal. These techniques are also not very successful in removing very fine, micron-sized mineral particles. Various chemical methods of cleaning coal are still in the conceptual and experimental stage.⁽²⁾

Electrostatic precipitators, mechanical collectors, fabric filters, or wet scrubbers can be used to remove the particles from combustion gas streams. Removal of gaseous constituents, which is much more difficult than particle removal, may involve limestone addition, wet scrubbing without sulfur recovery, MgO systems with sulfur recovery, or use of dry sorbent systems.⁽²⁾

4.4.1.2 On-Line Chemical Treatment

Under certain conditions, chemical fuel or flue gas additives can mitigate the effects of gas-side fouling and corrosion. Many proprietary additives have been marketed, with varying degrees of success in mitigating fouling.

Magnesium oxide has been used successfully to minimize fouling of coal-fired boilers, but the amount required, 0.4 to 3% of the fuel burned, makes the practice uneconomical. However, using fine, particle-size magnesia dispersions at rates of 0.015% of the fuel has reportedly reduced fouling. More investigation of this phenomenon may be warranted.

For oil-fired boilers, additives are used to control SO₃-related problems, high-temperature fouling, high-temperature corrosion, superheater temperature and stack plume color. For coal-fired boilers, additives are used for fly ash conditioning for electrostatic precipitation, convective tube fouling, coal-ash slag, SO₃-related problems and superheat control.⁽³⁾ In many cases, the evaluation of the effect of additives is qualitative and more fundamental information on their effect is needed.

Additives that have been used to control gas-side fouling in boilers include aluminum oxide, ammonium bicarbonate, magnesium oxide, magnesium carbonate, silica and zinc. Magnesium oxide has been used extensively. It acts as a catalytic inhibitor to retard the formation of SO_3 and it reacts with SO_3 to form MgSO_4 , which is inert and has a high melting point. Typical feed rates range from 0.005 to 0.013 weight percent of the fuel. Several proprietary formulations are available from various treatment chemical manufacturers including Betz Laboratories, Inc., Dearborn Chemical Corporation, Drew Chemical Corporation, Nalco Chemical Company, and Petrolite Corporation. These fuel additives are designed to improve combustion efficiency in boilers and to keep gas-side transfer surfaces clean by reducing soot and slag formation as well as controlling gas-side corrosion, cold-end corrosion and acid emission. (4,5,6,7)

4.4.1.3 On-Line Mechanical Techniques

In some cases, mechanical on-line equipment can dramatically increase the times between forced shutdowns. If the fouling deposits are sufficiently brittle, the energy that can be delivered to the fouling zone will be sufficient to break the bonds holding them to the heat transfer surface.

On-line mechanical techniques vary greatly, but soot blowers are the most popular for gas-side use. Some of the other techniques such as scrapers, rappers and chains work well in special applications but are not as readily available.

Two common types of soot blowers are sonic soot blowers and jet soot blowers. Sonic soot blowers operate best in the cooler regions of furnaces or in other apparatus where glassy phases of deposits are not encountered. They operate by emitting sound pressure waves that loosen the particulates and allow them to be carried away with the gas stream. Under normal operations, sonic horns need only isonate (or sound) for 15 to 30 seconds every 10 to 30 minutes. The horns are constructed of materials that can withstand temperatures as great as 1900°F , giving them a wide range of application.

According to KVB, which furnishes sonic soot blowers, the soot blower's overall costs, including both installation and operation, are only 10% as much

as jet soot blowers. Sonic soot blowers may not, however, be able to loosen the harder deposits that can be removed by the high velocity steam or air jets of conventional soot blowers (Figure 4.1).^(8,9) Diamond Power offers a system, the Infrasonic HZ-20, that emits sonic waves at a much lower frequency (20 Hz), which is in the infrasonic range, typically too low to be heard by the human ear. This sonic cleaner is not effective for wet deposits or slag but has proved to be effective in applications involving dusty deposits.⁽¹⁰⁾

The jet type of soot blower operates by emitting pulses of steam or air at programmed intervals. The kinetic energy of the gas stream breaks loose the particulate matter. These soot blowers work best if used frequently, thus avoiding any buildup of material. When buildup occurs, it insulates the surface from the coolant, allowing a temperature rise that can produce a glassy phase of the particulate. Particulates in the glassy phases are usually much harder to dislodge and frequently require shutdown for their removal.

Jet soot blowers can be of two types. The fixed position rotating type is installed inside the heat exchanger, and the retractable type periodically passes an externally mounted nozzle through the heat exchanger. The fixed position soot blowers require little additional floor space, but they usually cannot be used if the gas temperature is greater than 1800⁰F.

Diamond Power Co. has been producing soot blowers since 1903 and currently manufacturers electrically driven jet soot blowers of both types. Capes-Vulcan offers a complete line of air, water and electrically driven soot blowers including retractable units that are manually operated. Both of these companies support their soot blowers with a line of related electronic instruments and controls.^(11,12)

4.4.1.4 Control of Operating Conditions

The control of operating conditions is a very important consideration in the prevention of gas-side fouling. Some of the most important controls are:

- maintain surface temperatures above acid dew-point temperature,
- control amount of excess air, which governs the conversion of SO₂ to SO₃, and hence the amount of H₂SO₄ formed,

4.20

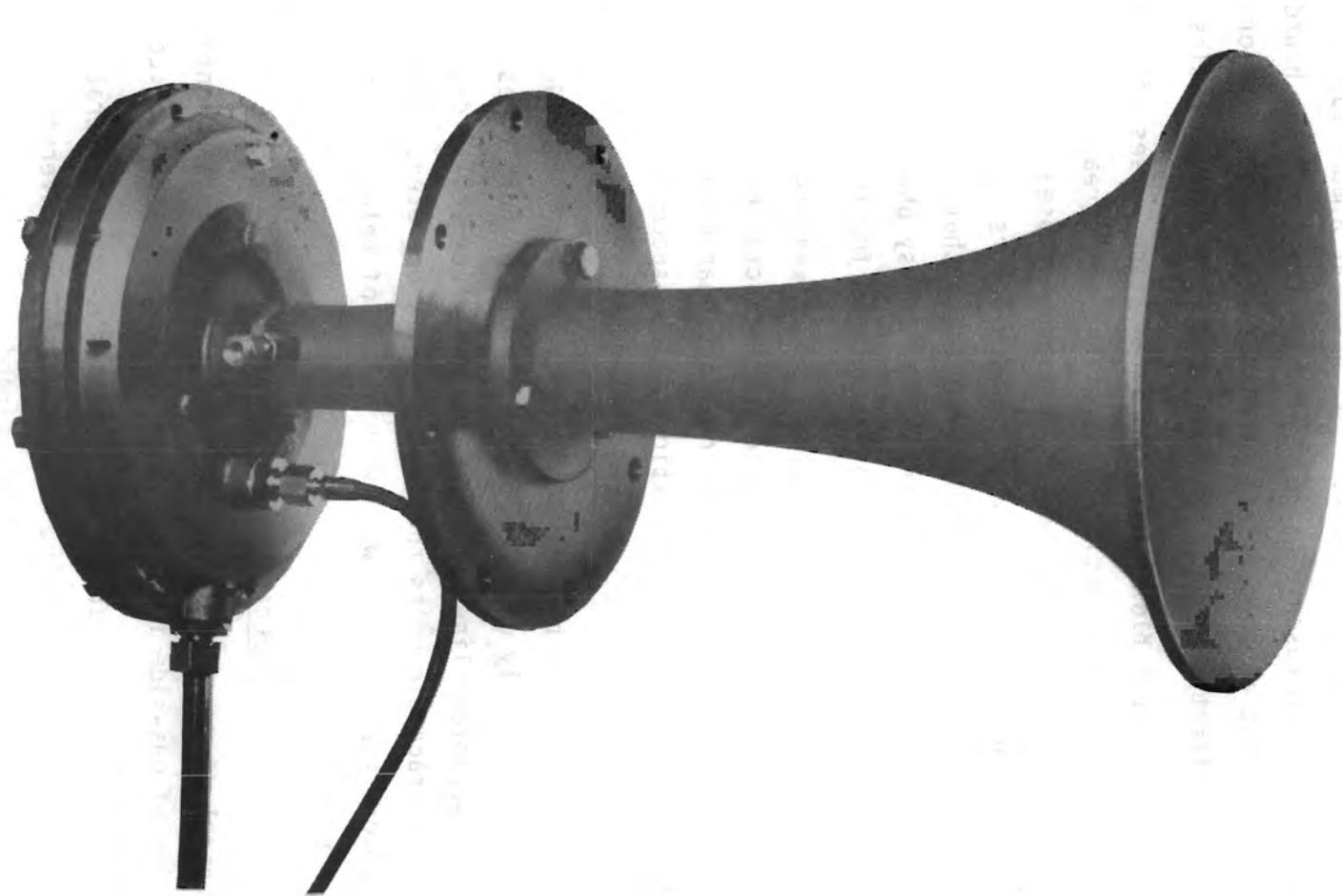


FIGURE 4.1. Sonic Sootblower (KVB, Incorporated)

- control combustion parameters such as fuel injection pattern, fuel injection schedule, and fuel viscosity,
- use fuel-air premixing to eliminate soot production, and
- quench hot flue gases to solidify molten and soft particles to prevent attachment at cooler heat transfer surfaces.

The control of combustion conditions is a difficult task due to great variability in the quality of fuel supplies. The quality of coal supplied to industrial installations is more variable than that supplied to electric utilities. Variability of fuel characteristics is a particular problem for those industries that burn waste products.

4.4.2 Mitigating Water-Side Fouling During Plant Operation

This section provides an overview of on-line chemical treatments and on-line mechanical techniques used to mitigate water-side fouling.

4.4.2.1 On-Line Water Treatment Chemicals

Several practical guides to water treatment are available.^(13,14,15) Because of environmental regulations and decreased water availability, the amount of water discharged from a cooling system often has been reduced. Therefore, systems are operating at more concentration cycles and any liquid discharge from the system is being eliminated if possible, except that which is carried out by entrainment in the effluent plume from the cooling tower.

Several alternatives are available to mitigate or to prevent scale deposition due to high concentrations of scale-forming ions (Ca^{++} , Mg^{++} , CO_3^{--} , SO_4^{--} , PO_4^{--} , SiO_3^{--}).^(16,17,18) These alternatives include removal of scaline species, pH control, use of scale inhibitors, biofouling control, corrosion control and boiler water treatment and are discussed more below. Other constituents that contribute to fouling are organics, clays, silts and metal oxides in untreated surface waters, corrosion products from the cooling system, oil, and process fluid from leaks and atmospheric pollutants such as dust, pollen, insects and gases.

Additives to inhibit or to reduce fouling and corrosion of water streams are used extensively in industry. These include pretreatment chemicals, acid

treatment, antiscalants, biocides, and corrosion inhibitors. These chemicals are manufactured by many companies including Betz Laboratories, Inc., Calgon Corporation, Dayton Chemical Corporation, Dearborn Chemical Corporation, Dowell Industrial Service, Drew Chemical Corporation, Exxon Chemical Company, Great Lakes Chemical Corporation, KEM Manufacturing Corp., Mogul Corporation, Nalco Chemical Company, Petrolite Corporation, Water Services of America and Wright Chemical Corp. The products of these companies are proprietary formulations that apparently are not widely patented (see Section 5.0 on the patent study). New or improved formulations appear on the market quite frequently as new compounds are developed and as environmental regulations change. For example, organic corrosion inhibitors are replacing chromate compounds, and organic (chlorine free) biocides are replacing chlorine to control biofouling. The major companies in the field have extensive research and development laboratories.

Removal of Scaling Species. Scaling species may be removed by ion exchange and lime soda treatments. Both treatments have high capital and operating costs.

pH Control. The solubility of scale-forming constituents increases with decreasing pH. Many treatment programs involve adding acid (H_2SO_4) to the system to maintain pH in the region of 6.5 to 7.5. If the system contains corrosion-resistant materials, a pH may be selected at which no scaling will occur. If the acidified water is slightly corrosive, a corrosion inhibitor must be added.

Scale Inhibitors. Many proprietary compounds are available for scale control:⁽¹⁹⁾

1. compounds that modify the crystal habit and reduce cohesive strength
2. threshold agents that retard precipitation of scale-forming salts while they remain in the system
3. dispersants that impart like charges to both the heat exchanger surface and to the particles of scale in suspension
4. chelating agents that complex strongly with scaling cations.

These additives can be as effective as pH control in reducing or preventing fouling without the risk of corrosion. Table 4.5 shows a list of antiscalants that are commonly used.

The effectiveness of antiscalant additives and dispersants has generally been determined by full-scale field tests. However, monitoring and testing of small side streams are being used to an increasing extent. Fouling tendency, conductivity, corrosion rate and pH of water can be monitored automatically on a real time basis both with and without the addition of fouling or corrosion inhibition additives.

Biofouling Control. An effective biofouling control program should be initiated at the outset of operation of a new heat exchanger. The environment in cooling towers and cooling systems is particularly conducive to the growth of microorganisms in the water and on the surfaces in the system. Microorganisms that attach and grow on surfaces produce polysaccharides that increase the sticking probability of the particles and crystals that come into contact with heat transfer surfaces. Biological growths may be controlled by destroying microorganisms with biocides. Chlorine has been the most widely used biocide to control biofouling. However, chlorine reacts with ammonia and other organics to form products that are potentially hazardous in the environment.

Various alternatives are available to control biofouling in cooling systems, although none are as cost effective as chlorine. The method of biofouling control selected by a plant operator will ultimately be based on economics and on environmental regulations. The organic biocides are nonoxidizing toxicants. Some of the more popular organic biocides are shown in Table 4.6.

TABLE 4.5 Antiscalants

Natural organics	- Organic acids, starch, tannin
Mineral sequestrant	- Polyphosphate
Synthetic organics	- Polyelectrolytes - ionic, phosphonates, polyacrylates
Functional groups	- Crystal distortion, adsorbants, dispersants, flocculants, chelants, emulsifiers

TABLE 4.6 Examples of Organic Biocides

Chlorinated phenolics
Organo-tin compounds
Quaternary ammonium salts
Organo-sulfur compounds
Acrolein

Corrosion Control. Corrosion control is necessary if the cooling system material is reactive with constituents in the water at the conditions in the system. When pH control is used to limit scaling, the system must be protected with a corrosion inhibitor. Corrosion inhibitors with a chromate base have long been used. This chromate-acid treatment involves adding acid to reduce pH and adding a chromate base compound to inhibit corrosion. The chromate is a highly efficient inhibitor and is cost effective. However, the toxicity of chromates in the environment has restricted their use and the development of other corrosion inhibitors. Zinc is also an effective corrosion inhibitor, but it also is toxic to organisms in the environment.

An alternative to high chromate treatment is the low chromate treatment using a combination of 5 to 10 ppm CrO_4 with a pH range of 7.5 to 9.0, and organic phosphorous compounds, such as aminomethylene phosphoric acid. Organic (nonchromate) compounds are being investigated as corrosion inhibitors.

Boiler Water Treatment. Boilers operate over a wide range of pressures and temperatures, and the composition of boiler water has specific limits. Boiler waters are subjected to various pretreatment processes ("polishing") to remove excess concentrations of unwanted species. Table 4.7 shows a list of various pretreatment processes.⁽²⁰⁾ In the boiler, phosphate and chelate treatments are the two major treatments used to prevent fouling on the tube side.

4.4.2.2. On-Line Mechanical Techniques

To prevent fouling in liquid systems, two on-line mechanical methods are gaining considerable acceptance: 1) sponge rubber balls (of special

TABLE 4.7 External Treatment Systems

Process	Results
1. Aeration	Reduces iron, manganese, hydrogen sulfide, carbon dioxide
2. Prechlorination	Reduces organic matter and microorganisms
3. Clarification	Reduces color and suspended matter
4. Cold process softening	Reduces suspended matter, iron, calcium, magnesium, bicarbonate and maybe some silica
5. Cation exchange sodium cycle	Reduces calcium and magnesium
6. "Split stream" cation exchangers sodium & hydrogen cycles with degasifier	Reduce calcium, magnesium, sodium and bicarbonate
7. Cation exchanger, sodium cycle followed by anion exchanger, chloride cycle for dealkalizing or hydroxide cycle for dealkalizing and desilicizing	Reduce calcium, magnesium, bicarbonate, and, if needed, silica
8. Hot lime followed by filters and cation exchanger, sodium cycle	Reduce suspended matter, iron, calcium, magnesium, bicarbonate and silica
9. Demineralization	Reduces all cations, anions and silica to very low concentrations

formulation) constantly circulating through the system, and 2) brushes that are periodically backflushed through the heat exchanger tubes.

The Amertap recirculating ball system (Figure 4.2) uses sponge rubber balls that constantly circulate throughout the heat exchanger. The balls are sized slightly larger than the inside diameter of the heat exchanger tube and are slightly compressed as they are moved through the tube by the pressure differential. Each tube "sees" a ball about once every 5 minutes, and the rubbing action of the ball cleans the inner walls by wiping away the deposits,

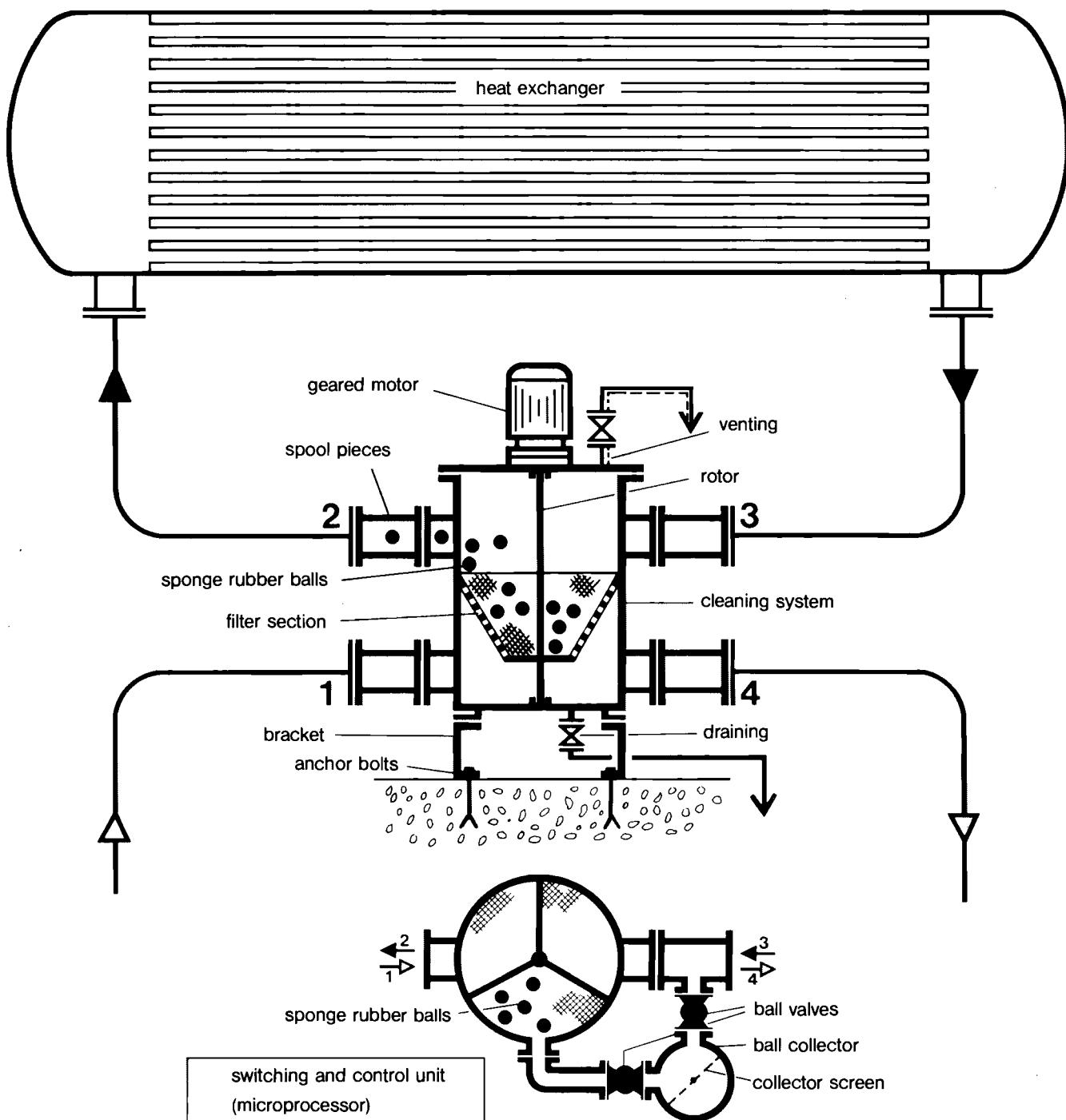


FIGURE 4.2 On-Line Sponge Rubber Ball System (Amertap)

scale, and biological fouling, which are then mixed in with the heat exchanger's fluid. For more corrosive systems, the balls may have an abrasive coating to aid the cleaning process.

Manufacturers claim that an added advantage of this cleaning system is that the balls interrupt the stagnant layer of fluid in the tube, thereby improving heat transfer. The exiting balls are screened, transported, and reinjected upstream to create a continuous operation. An automatic ball-counting-and-sorting system pulls out undersized balls (worn down from wear) and keeps a count for replacement.

Florida Power and Light Co. estimates a savings of \$2 million per year directly attributable to the use of the Amertap recirculating ball system. This estimate is based on operation of two similar nuclear power plants, one using the Amertap system and the other without any heat exchanger cleaning system.^(21,22,23) These balls are used almost exclusively in water systems for cleaning heat exchanger and condenser tubes. There are over 500 U.S. applications with the heaviest representation in utilities, petrochemical, and refinery operations.

The second on-line mechanical method for liquids, the Water Services of America (WSA) Superscrubber system, uses special brushes made to fit the specific tubes of the heat exchanger (Figure 4.3). The brushes are sent through the tubes by the fluid flow. A four-way valve returns the brushes for another trip through the tubes by temporarily reversing the flow of fluid in the heat exchanger tubes. Two innovations make this whole process practical: 1) to get enough force to propel the brush through the tube while it is in contact with the tube wall, a close fitting disc only slightly smaller than the heat exchanger tube is fitted to each end of the traveling brush; and 2) a special retaining basket is fitted to each end of each heat exchanger tube to retain the brush until the fluid flow is reversed. This basket retains the brush just far enough from the fluid stream so that normal flow is not seriously impeded, but it retains it close enough to the tube end so that when the flow is reversed, the brush will be inducted into the tube.

Both the Amertap and the WSA systems have advantages and disadvantages. Both require a substantial investment and routine replacement or renewal of the

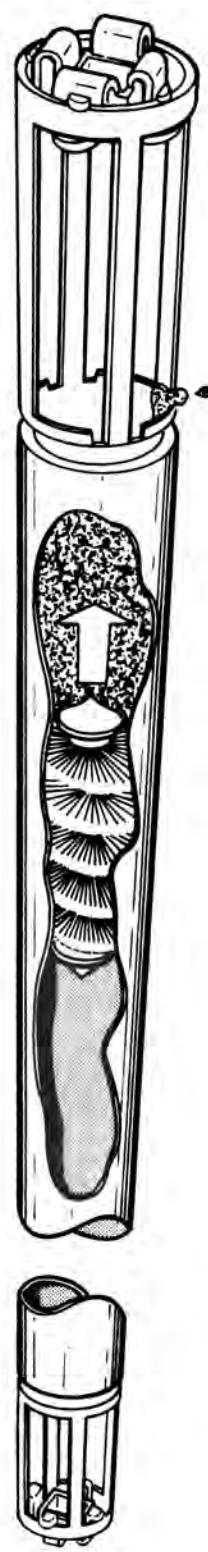


FIGURE 4.3 WSA Superscrubber System

sponges or brushes/retainers. The Amertap system requires special plumbing to install the ball insertion and downstream recovery equipment and special plumbing to avoid unwanted ball diversion or bunching. However, no flow reversal is required with the Amertap system. The WSA system requires no special upstream brush insertion or downstream recovery equipment because of the retainer baskets placed on each end of the heat exchanger tubes. The WSA system, however, does require flow reversal of the entire stream of cooling liquid, and valves, plumbing and controls to accomplish this flow reversal. One disadvantage of the WSA brush approach is that in some applications the brushes become fouled.

Considerable savings are possible using these two on-line mechanical cleaning systems for fluids. Better heat transfer coefficients are maintained and, in cooling tower applications, considerable savings can be realized in makeup water because the tubes can be kept clean with higher concentrations of impurities in the water.

Manufacturers of these devices claim they can reduce fouling factors to "nearly zero" allowing for savings in initial heat exchanger costs/reduced operating costs so that the initial investment can be regained in 6 to 24 months, depending on the severity of the operating conditions and the required energy costs. Both systems are limited to modest temperature operation because of the temperature limitations of the construction materials. All of the firms offering heat exchanger cleaning equipment and that sent information are shown in the data base printout in Tables 4.8, 4.9, and 4.10.

4.5 OPPORTUNITIES TO MITIGATE FOULING DURING PLANT STARTUP AND SHUTDOWN

This section provides a discussion of some startup and shutdown techniques used to minimize the effects of gas-side fouling. In addition, chemical and mechanical deposit removal techniques, used during plant shutdowns, which are applicable to both gas-side and water-side fouling are discussed.

4.5.1 Startup and Shutdown Procedures to Minimize Gas-Side Fouling

Heat-transfer equipment is generally designed for operation at some specified, steady-state operating condition. During plant startup and shutdown, the exchanger operates at conditions other than those for which it was designed.

TABLE 4.8 Manufacturers of Equipment for Cleaning Heat Exchangers

COMPANY	PRODUCT	COMMENTS
AMERICAN AERO INC.	WATER BLASTER	PROVIDE A LINE OF ELECTRIC AND DIESEL WATER CLEANERS WITH EITHER FLEXIBLE OR RIGID LANCE. SELLS MAINLY TO PETROLEUM INDUSTRY.
AMERTAP CORPORATION	SPONGE RUBBER BALLS	SLIGHTLY OVERRSIZED SPONGE RUBBER BALLS ARE SENT THROUGH HX TUBES WIPE AWAY DEPOSITS. BALLS ARE COLLECTED & RECYCLED. "ON LINE" PROCESS.
AQUA-DYNE, INC.	WATER JET	VARIOUS MODELS OF HIGH-PRESSURE WATER JET BLASTERS. UNITS OPERATE AT 3000-22,500 PSI ON DIESEL OR ELECTRIC POWER PACKAGES. \$14,000-50,000 PER UNIT.
BUTTERWORTH INC.	LIQUA BLASTER	PROVIDE A WATER JET WITH LANCES THAT CAN HANDLE ABRASIVE MATERIALS. UNITS ARE EITHER GAS DIESEL OR ELECTRIC POWERED.
CONCO SYSTEMS, INC.	WATER GUN	WATER POWERED GUN SHOOTS SPRING-LOADED SCRAPPING HEADS THROUGH TUBES. SCRAPPING HEADS ARE COLLECTED IN A TRAP AT THE EXIT END OF THE TUBE.
COPES-VULCAN	SOOT BLOWER	OFFER RETRACTABLE & ROTARY SOOT BLOWERS. INTERMITTENT BLAST OF AIR THROUGH A SERIES OF NOZZLES LOOSENS AND CARRIES AWAY PARTICULATES.
DIAMOND POWER SPEC. COMP.	SOOT BLOWER	OFFER STATIONARY, RETRACTABLE, AND ROTARY SOOT BLOWERS. ALSO OFFER A FEW SONIC DEVICES.
DIONEX CORPORATION	DIAGNOSTIC EQUIPMENT	MANUFACTURES ION CHROMOTROGRAPHY DIAGNOSTIC EQUIPMENT TO ANALYZE IMPURITY CONTENT IN HX FLUID. USED EXTENSIVELY BY UTILITY INDUSTRY.
ELLIOT COMPANY	LANCE	CHOICE OF BRUSHING, SCRAPPING, AND CUTTING HEADS THAT ROTATE ON THE END OF LANCE. AIR, WATER, OR ELECTRIC DRIVEN MOTORS ARE INTERNAL OR EXTERNAL TO TUBE.
EXPANDO SEAL TOOLS, INC.	CLEANING GUNS	EXPANDO SEAL PRODUCES TOOLS FOR CLEANING, PLUGGING, TESTING AND REPAIRING TUBE-TYPE HEAT EXCHGFRS. THEY WILL ALSO PROVIDE THESE SERVICES.
GLOBAL HEAT EXCHANGER INC	AIR LANCES	PROVIDE AIR-DRIVEN LANCES THAT OPERATE AT 8-10,000 PSI. PRIMARY INDUSTRY SERVED IS CHEMICALS AND PETROLEUM.
GOODWAY TOOLS CORPORATION	LANCE	"REAM-A-MATIC" LANCE WITH ROTATING HEAD AND WATER FLUSH. FLEXIBLE SHAFT TO RESIST STICKING & FOR CURVED TUBES. \$800-2000 PER UNIT.
KVB, INC.	SONIC HORN	LOW FREQUENCY AIR DRIVEN HORN. SOUND PRESSURE WAVE LOOSENS PARTICULATES. USED UP TO 1900F. \$1000-6000 PER HORN. 500 EMPLOYED IN U.S.
SIOUX STEAM CLEANER CORP.	WATER JETS/STEAMERS	SELL HIGH-PRESSURE WATER BLASTERS AND STEAM CLEANERS. UNITS MAY BE GAS, OIL, OR ELECTRIC POWERED.
TRITAN CORPORATION	WATER JET	"HYDRO LASER" IS HIGH PRESSURE WATER BLASTER(1000-15,000 PSI). GAS, DIESEL, ELECTRIC POWER PACKAGES. CAN INTRODUCE SAND, CHEMICALS, ETC INTO FLUID STREAM.
TURB-O-FLOW CORP	HX SCRAPERS	TUB-O-FLOW PRODUCES BLOW THROUGH SURFACE SCRAPERS WHICH UTILIZE METAL SCRAPERS PUSHED THROUGH THE HX TUBING BY WATER PRESSURE. REQUIRES HX SHUTDOWN.
VICJET, INC.	HOT SPRAY CLEANERS	THESE HOT WATER SPRAY CLEANERS ARE DESIGNED FOR GENERAL PURPOSE INDUSTRIAL CLEANING. NOT DESIGNED ESPECIALLY FOR SHELL AND TUBE HEAT EXCHANGERS.
WATER SERVICES OF AMER.	ON-LOAD BRUSH	NYLON BRUSH IS INSERTED IN EACH TUBE AND IS FORCED THROUGH THE TUBE BY WATER PRESSURE. BRUSHES ARE COLLECTED IN BASKETS.
WILSON INC.	ROTARY HX CLEANERS	WILSON PRODUCES ROTARY HX CLEANERS FOR USE WITH SHELL & TUBE TYPE HX. THESE UNITS UTILIZE HIGH PRESSURE STEAM TO CLEAN THE TUBES.

TABLE 4.9 Manufacturers of Chemicals for Cleaning Heat Exchangers

COMPANY	PRODUCT	COMMENTS
ALCONOX, INC.	DETERGENTS/SOLVENTS	ALCONOX PRODUCES DETERGENTS AND SOLVENTS TO MANY INDUSTRIES INCLUDING THE DAIRY, PETROLEUM AND ELECTRONICS INDUSTRIES.
BARCO CHEMICAL PRODUCTS	METAL DEGREASER	"TP-100" IS SOLVENT MIXTURE THAT REMOVES OIL, GREASE, WAX, ETC. OTHER CHEMICALS OFFERED, BUT THIS IS #1. VERY USEFUL IN FLUSHING TUBING IN HX EQUIPMENT.
BARON BLAKESLEE MFG. CO.	SOLVENT VAPOR DEGRSR	BARON BLAKESLEE PRODUCES SOLVENTS (AND RELATED EQUIPMENT) FOR GENERAL PURPOSE CLEANING OF INDUSTRIAL EQUIPMENT (METALS).
BEAVER ALKALI PRODUCTS CO	INDUSTRIAL CLEANERS	BEAVER ALKALI PRODUCES HOUSEHOLD AND INDUSTRIAL CLEANERS AND CAN DESIGN CUSTOM SOLVENTS. THEY PRIMARILY SERVICE THE STEEL INDUSTRY.
BETZ LABORATORIES, INC.	VARIOUS CHEMICALS	OFFER MANY CHEMICALS, BUT MOST ARE USED TO TREAT WATER SYSTEMS. CHEMICALS ARE MAINLY DESIGNED FOR ON-LINE USE.
CALGON CORPORATION	DESCALE AND ALK CLNR	CALGON PRIMARILY SERVES THE FOOD PROCESSING INDUSTRY. THEY WILL TEST WATER TO DETERMINE THE APPROPRIATE CLEANING REQ'D AND TRAIN COMPANY ENGINEER.
CLEAN-FLO LABS., INC.	DESCALER	MILDLY ALKALINE CLEANER WHICH REMOVES GREASE, ORGANIC DEPOSITS, LIME SCALE. BEST RESULTS WHEN APPLIED UNDER PRESSURE.
DAYTON CHEMICAL CORP.	CLEANERS & DESCALERS	THE DAYTON CORP PRODUCES MANY TYPES OF SOLVENTS AND CLEANERS INCLUDING SOME THAT ARE APPLICABLE TO HEAT EXCHANGER CLEANING.
DEARBORN CHEMICAL CORP.	WATER TREATMENT CHEM	DEARBORN PRODUCES WATER TREATMENT CHEMICALS.
DOBER CHEMICAL CORP	METAL CLEANING CHEMS	DOBER PRODUCES A VARIETY OF METAL CLEANING COMPOUNDS.
DREW CHEMICAL CORPORATION	ADDITIVES & CLEANERS	DREW CHEMICAL PRODUCES ADDITIVES FOR THE HEAT EXCHANGER WORKING FLUID TO PREVENT SCALING. ALSO PRODUCE CLEANING CHEMICALS.
ELGENE CHEMICALS, INC.	VARIOUS CHEMICALS	SOLVENTS, DEGREASERS, ETC. OFFERED. NOT SPECIFICALLY AIMED AT HX CLEANING. MAINLY AIMED AT CLEANING EXTERIOR SURFACES AND GENERAL PLANT CLEANUP.
EXXON CHEMICAL COMPANY	VARIOUS CHEMICALS	OFFER VIRTUALLY EVERY TYPE OF CLEANING CHEMICAL USED IN FOULING & CORROSION. SALES TO MOST EVERY INDUSTRY, BUT PETROLEUM IS #1 BY FAR.
FERGUSSON CO., ALEX C.	DESCALER	"DESCALER S" IS SULFAMIC ACID WITH INHIBITORS. ATTACKS CA & MG SALTS AND OXIDES. SOLUTION TURNS COLOR WHEN DONE.
GREAT LAKES CHEMICAL CORP	DI BROMIDE	PROVIDE A WIDE VARIETY OF CHEMICALS FOR WATER SYSTEMS MAINLY FOR CORROSION INHIBITORS. SELL TO OIL REFINERIES.
HERCULES INC.	CHEMICALS	SELL A VARIETY OF ANTIFOULANT CHEMICALS FOR ONLINE USE TO OIL REFINERIES, CHEMICAL PLANTS ETC.
KEM MANUFACTURING CORP.	CLEANING SOLVENTS	KEM HAS OVER 300 PRODUCTS OF WHICH APPROXIMATELY 12 TO 14 ARE RELATED TO HEAT EXCHANGER CLEANING, INCLUDING BOTH ADDITIVES AND DIRECT APPLICATION TYPES
MATESON CHEMICAL CORP	SOLVENTS/CLEANERS	PRODUCE SEVERAL CHEMICALS FOR CLEANING HEAT EXCHANGERS. MOSTLY FOR THE HVAC, REFRIGERATION AND MARINE SYSTEMS INDUSTRIES.
NALCO CHEMICAL COMPANY	VARIOUS CHEMICALS	WATER TREATMENT IS #1, BUT ALL MAJOR INDUSTRIES ARE THEIR CUSTOMERS. CHEMICALS OFFERED FOR MOST EVERY KIND OF FOULING & CORROSION.
OAKITE PRODUCTS, INC.	SCALE/RUST REMOVAL	OFFER 4 ACIDIC DESCALERS W/ INHIBITORS TO REMOVE LIME SCALE & RUST DEPOSITS. USED MOST IN WATER HANDLING EQUIPMENT. SOLUTIONS CAN BE HEATED.
PENETONE CORPORATION	VARIOUS CHEMICALS	OFFER MANY CHEMICALS AIMED AT CLEANING SOOT, OIL, AND CARBON BUILDUP.
PRIDE LABORATORIES, INC.	DEGREASER/CLEANER	NON-ACIDIC WATER SOLUBLE DEGREASER & CLEANER. MORE EFFECTIVE IF APPLIED UNDER PRESSURE.
WRIGHT CHEMICAL CO	CHEMICALS	PROVIDE SEVERAL CHEMICALS FOR WATER TREATMENT DEPENDING ON THE TYPE OF FOULING AND CORROSION.

TABLE 4.10 Companies Providing Heat Exchanger Cleaning Services

COMPANY	PRODUCT	COMMENTS
DOWELL INDUSTRIAL SERVICE	CHEM & MECH CLEANING	"COMPLETE" SERVICE--LABORATORY ANALYSIS, ENGINEERING ANALYSIS, CHEMICAL AND/OR MECHANICAL CLEANING. MOST OF THEIR CLEANS ARE VIA CHEMICALS.
ENERCHEM INCORPORATED	CONSULTING FIRM	ANALYZE COMBUSTION FOULING PROBLEMS THEN RECOMMEND CHEMICAL CLEANING APPROACH. THEY DO NOT CLEAN--JUST DISPENSE ADVICE. NOT A TRUE "SERVICE."
HALLIBURTON INDUST. SERV.	CHEM & MECH CLEANING	OFFER CHEMICAL AND/OR MECHANICAL CLEANING. MANY TYPES OF EQUIPMENT AND OVER 300 CHEMICALS USED. PERFORM LAB ANALYSIS. SALES AIMED AT ALL INDUSTRIES.
MOGUL CORPORATION	WATER TREATMENT	DEAL MAINLY WITH WATER TREATMENT. USE CHEMICAL CLEANING METHODS. THEY PROVIDE THE SERVICE AND THE CHEMICALS.
PETROLITE CORPORATION	CHEMICAL CLEANING	USE CHEMICAL CLEANING METHODS. PROVIDE THE SERVICE AND THE SPECIALIZED CHEMICALS. SALES TO PETRO INDUSTRY #1, BUT INDUSTRIAL SALES ARE GROWING.

During these periods, the propensity of the exchanger to foul is higher than under normal operating conditions. Because of the variability in design, fuels used, and operating conditions, startup and shutdown procedures must typically be developed on a trial-and-error basis.

Some techniques that have been used to minimize fouling during startup operations are:

- use a clean fuel for startup,
- maintain heat-exchanger surfaces above dew-point temperatures ,
- use bypasses to avoid low flow velocities.

During startup, combustion efficiency is low, which allows considerable quantities of unburned material to escape, especially with heavier oils, coal or waste fuels. It is recommended that a clean fuel such as natural gas, which has a low ignition temperature, be used for startup. Once the boiler or heat exchanger has reached steady state, it can be switched to coal, oil or other dirty fuels.

To avoid acid dew-point corrosion problems, heat-exchanger surfaces should be maintained above the dew-point temperatures. Hot air or other warm fluids can be used for this purpose. Once the exchanger has reached the proper temperature it can be brought on line.

Although bypasses are typically installed to control exit gas temperatures, they can also be used to control velocities during startup and shutdown operations. Because the heat exchanger is designed for a specific fouling factor at steady-state conditions, use of the unit under clean conditions requires a lower velocity (see Appendix C). The fouling tendencies at low velocity are greater because of the lower shear stress of the fluid. By using the temperature bypass, it is possible to minimize the use of low velocities without overheating the product stream.⁽²⁾

Experience with boilers has indicated that if deposits are not removed before the boiler is completely shutdown, they can act as a sponge to absorb acid and water condensate, leading to corrosion of heat-transfer surfaces. Deposits should, therefore, be removed as completely as possible before complete shutdown and the residual can be removed with air lances and scrapers after the unit has cooled.⁽²⁾

4.5.2 Off-Line Deposit Removal Techniques

This section discusses mechanical techniques and chemical cleaning procedures used for deposit removal during plant shutdown. In addition, a brief discussion of the heat exchanger cleaning industry is provided.

4.5.2.1 Off-Line Mechanical Techniques

Eventually, heat exchangers require cleaning or replacement either during scheduled or unscheduled shutdowns of the plant. If the shutdown is required because the heat exchanger fails, drastic measures may be used to return the equipment to service. The solution is to fix it quickly or to remove it.

Heat exchangers can be cleaned off-line by two ways: 1) flush out the deposits with liquid treatments, or 2) mechanically remove the deposits. The liquid, i.e., chemical treatments, has an advantage of being applied without physically disassembling the equipment. The disadvantage is that it is expensive and may require expensive disposal. Chemical treatments can be difficult to handle even with experienced personnel. In some cases, the treatment can eat away the heat exchanger as well as the deposit. Whereas the mechanical removal methods appear more straightforward, they require disassembly of the equipment and may require considerable time and expense to accomplish. One

advantage, however, is that any damaged tubes can be replaced or sealed off while the equipment is apart.

The type of equipment for off-line mechanical cleaning of heat exchangers most frequently offered appears to be high-pressure water jets. These devices use water under pressures as great as 20,000 psi to "blast" away deposits in heat exchanger tubes or on other heat transfer surfaces. Examples of both stationary and mobile water blasting machines offered by Tritan Corporation are shown in Figure 4.4. Units are available with gas, diesel, or electric power packages.⁽²⁴⁾ Some of the units operating at lower pressures allow chemicals, sand, etc. to be introduced into the water stream to assist in the cleaning process. Adding sand is extremely useful in removing stubborn silica scale. Predominance of this type of equipment among manufacturers of cleaning devices suggests that it is also the most frequently used equipment type.

Steam cleaners, such as those offered by Sioux Steam Cleaner Corporation and shown in Figure 4.5, are similar in design and operation to water jets and are offered by many of the same companies. These devices, which may be gas, oil, or electric power packages, inject steam into the tubes or shell of a heat transfer device. They have broad industrial application, but their greatest use in industry is for general plant cleanup--not heat exchanger cleaning. Their advantage is that they remove some deposits that require "thermal" loosening and that can't otherwise be removed by pressure forces alone.

Another commonly offered off-line mechanical device that has application predominantly in cleaning heat exchanger tubes is the lance. This device may be equipped with various cleaning and cutting heads that rotate on the end of the lance. Depending on the tube materials and the deposit, the heads may vary from a soft brush to a drill bit. The source can be air, water, steam, and electric drive and can be mounted either internal or external to the lance. Internal sources are used mainly for cleaning boiler tubes and heat exchangers with large tubes, whereas external drives are used in heat exchangers with small tubes. Manufacturers claim that these lances remove some of the residue that high-powered water jets leave behind and therefore, are more effective than the jets. Manufacturers also claim very minimal damage to the tube even when using the cutting and scraping head attachments. The lances, made by

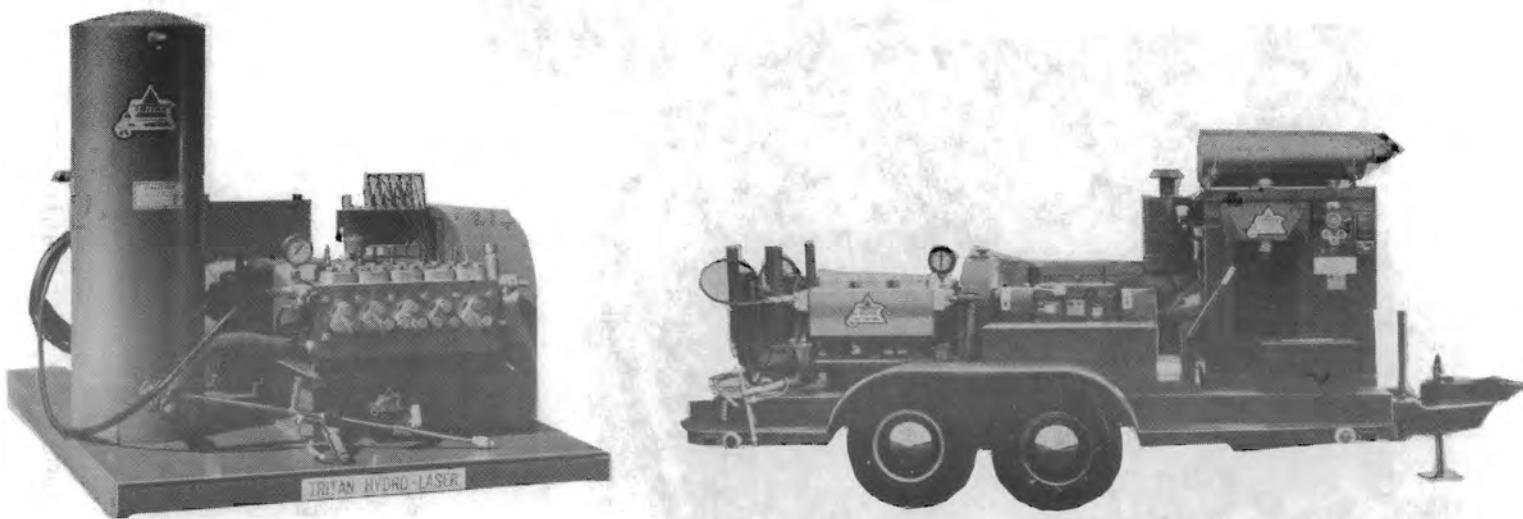


FIGURE 4.4. Stationary and Mobile Water Blasting Machines (Tritan Corporation)



FIGURE 4.5 Steam Cleaner (Sioux Steam Cleaner Corporation)

Goodway Tools Corporation, the Elliot Company, and Tritan Corporation, are modularly designed so that the users can select the cleaning head, power supply and shaft configuration separately. (24,25,26) Lances have applications in virtually every industry, but an exceptionally large number of sales seem to be made to central station power plants. (27)

A device that delivers the same type of cleaning as the lance, but is of different design, is the water gun. To clean with this device, the heat

exchanger rear header must be removed. Spring-loaded steel tube cleaners are then "shot" through the tubes with the gun at 200 to 300 psi water pressure. Tube cleaners travel through the tube, plowing off deposits and corrosion, while the water stream flushes the dislodged deposit. Cleaners exit the end of the tube and are collected in a tarp. Conco Systems water guns use a jet stream of water to propel multihead steel scrapers through fouled heat exchanger tubes. The Elliot Company water guns use a jet stream of water or air and water mixed to propel spiral wound nylon brushes through the heat exchanger tubes. ^(26,28)

4.5.2.2 Off-Line Chemical Cleaning

Chemical cleaning of heat exchangers is an off-line technique in that the exchanger must be taken out of service. The cleaning, however, can usually be accomplished in situ, so the exchanger does not have to be removed or opened. Chemical cleaning has several advantages: ⁽²⁹⁾

1. It is relatively rapid.
2. It is effective.
3. Heat transfer surfaces are not damaged mechanically.
4. Chemical solutions usually reach inaccessible areas.
5. Complete surface treatment is achieved.
6. It is not as labor intensive as mechanical cleaning.
7. Cleaning can be performed in situ.

An important factor in using acids as cleaning chemicals is the use of an inhibitor so the acid will remove the deposit and not dissolve the heat transfer surface. Modern inhibitors can be used under extremes of temperature, and flow rate and metal losses are less than 0.0025 in. for a 6-hour contact time.

Chemical cleaning operations generally use a circulation technique to ensure that the chemicals are always well-mixed and that fresh chemical contacts the heat transfer surfaces. With this technique, the deposits are dissolved as well as removed by mechanical scouring.

Table 4.11 lists the variety of deposits that can be removed by chemical cleaning. Table 4.12 lists deposits that are not susceptible to chemical

TABLE 4.11 Typical Deposits Removed by Chemical Cleaning

Organic	Inorganic
Oil	Rust
Grease	Magnetite
Fats	Calcium carbonate
Waxes	Calcium sulfate
Soft carbon	Magnesium hydroxide
Tars	Calcium phosphate
Silt	Silica
Vegetation	Magnesium silicate
Biological matter	Copper/Copper oxides
Polymers	Alumina
Resins	Nickel oxide
Paints	

TABLE 4.12 Deposits not Normally Removed by Chemical Cleaning

Glasses	Inert plastics (e.g., polythene)
Ceramics	Vulcanized rubber
Hard carbon	Rubber latex

cleaning, and Table 4.13 is a list of typical chemicals used for in situ chemical cleaning.

4.5.2.3 Heat Exchanger Cleaning Services

Many plants do not care to get involved in the heat exchanger cleaning process and therefore contract an outside agency to do the job. Plants without much capital (usually small plants) or plants with only minor fouling and corrosion problems often opt for a cleaning service since purchase of cleaning equipment and/or expensive chemicals may not be cost effective. Larger plants with adequate capital may also elect to purchase cleaning services from outside firms to take advantage of the specialized knowledge and most up-to-date equipment and chemicals.

TABLE 4.13 Common Types of Chemicals Used for In Situ Chemical Cleaning

Acids	Alkalies	Complexing Agents	Oxidants	Solvents	Others
Hydrochloric	Caustic Soda	EDTA	Potassium Permanganate	Aromatic	Inhibitors
Nitric	Ammonia	Gluconates	Sodium Bromate	Aliphatic	Surfactants
Sulfuric	Trisodium		Sodium Nitrite	Chlorinated	Antifoams
Hydrofluoric	Sodium Meta-silicate		Sodium Hypochlorite	Solvent Emulsifiers	Biocides
Citric	Soda Ash		Ammonium Persulfate	Dewatering Formulations	Dispersants
Formic Sulfamic					Hydrazine Ammonium Bifluoride

Cleaning service companies like Dowell Industrial Service⁽³⁰⁾ will supply just off-line cleaning equipment or chemicals, or they will do the cleaning, supplying all the equipment/chemicals needed. Companies offering chemical cleaning services include Enerchem Incorporated, Mogul Corporation,⁽³¹⁾ and Halliburton Industrial Services,⁽³²⁾ and companies offering mechanical and cleaning tube repair include Expando Seal Tools, Inc. Some of these companies, such as Dowell and Halliburton, offer complete laboratory analysis and engineering to determine the best cleaning methods.

More and more users of heat exchanger equipment are taking advantage of instrumentation designed to measure either fouling and degradation as it occurs or the conditions that produce the corrosion. The major companies that supply chemical treatments for on-line use also see improved instrumentation as an opportunity to improve the quality of their service. Drew Chemical Corporation manufacturers instruments that can actually measure the corrosion as it occurs in a circulating side stream. It then tailors water treatment to optimize heat exchanger life on a "real time" basis.

Many of the major suppliers of on-line and off-line equipment or chemicals offer testing equipment/services. These companies are excellent sources of information about suppliers of needed instrumentation/testing equipment even if they don't supply it themselves. In addition to Drew Chemical, other suppliers of chemical treatment materials who also supply instrumentation include Betz Laboratories,⁽⁴⁾ Dearborn Chemical,⁽⁵⁾ the Mogul Corporation,⁽³¹⁾ and Petrolite Corporation.⁽⁷⁾ Suppliers of mechanical on-line equipment, such as Copes-Vulcan,⁽¹¹⁾ also supply control and monitoring instrumentation. The Turboflow Corporation⁽³³⁾ supplies off-line cleaning equipment and instrumentation to monitor and control the operation.

4.6 CONCLUSIONS

Users of heat transfer equipment appear to react to fouling and corrosion problems rather than try to prevent them. This raises several important issues:

- Is fouling and corrosion an important area? (see Section 6.0 on the cost of fouling and corrosion.)

- Why isn't more being done if the problem is important? (See the following discussion for a partial answer.)
- Why not leave the problem to industry? (Also discussed below.)

Steps to mitigate and/or to prevent fouling can be taken in the design, construction and installation, operation, and the shutdown phases of heat exchanger use. However, little is done during the design and construction/installation phases to mitigate or to prevent fouling. By far, the greatest effort is in the operation (on-line) phase in which fluid additives are used. For fouling and corrosion not being prevented or mitigated by other means, off-line cleaning by mechanical or chemical techniques is used.

Several reasons explain these current practices.

1. Not enough is known about the effect of the several parameters on fouling to be able to quantify the benefits of mitigation/prevention opportunities. This is particularly true in the design and construction/installation phases. In the on-line fluids treatment phase, the effect of fluid additions is generally determined by full-scale field tests, although field monitoring and testing of small side streams is being used increasingly. The quantitative effects of changing process variables (flow rate and temperature) are generally not well enough known for a plant manager to make changes in the process.
2. A lack of communication exists among the heat exchanger user, the designer and the fabricator. The user normally provides the designer with a fouling resistance to be used in design to assure that the heat exchanger will perform to the desired capacity. The designer does not usually receive information on proposed treatment program, so the heat exchanger often is considerably oversized.

The fabricator has no incentive and cannot afford to take the initiative to reduce the potential for fouling, which may result from fabrication and installation practices. Often, the user and the fabricator do not communicate enough to consider fabrication and installation practices that would reduce the potential for fouling during the operation phase.

3. Generally, individual plants cannot economically investigate improved fouling or corrosion prevention/mitigation opportunities, the effects of which are quantitatively unknown/unmeasureable. This effort could involve a rather extensive research and development activity that is beyond the capacity of individual plants, particularly if cost-effective on-line or off-line techniques are available and are being used to prevent/mitigate/remove fouling. The plant manager is not likely to change plant operating conditions unless such changes can qualitatively be shown not to adversely impact production amount and quality.

The current philosophy results in considerable excess surface in the exchanger, followed by fouling problems. Subsequently, on-line or off-line prevention/mitigation methods are used to continue satisfactory operation. The overall result of the current practices is that, on a national basis, heat exchangers fail prematurely, considerable excess materials are used, and additional costs incurred in heat exchanger fabrication. These costs are detailed in Section 6.0 of this report. Considerable expenses are also incurred in on-line and off-line prevention/mitigation/removal techniques and from energy losses because of lowered efficiency of heat transfer. These factors increase the costs of waste heat recovery and much valuable energy is discarded because it is perceived as too costly to recover.

Because of the diversity of interests involved in design, fabrication, installation and operation of heat exchanger equipment, the private sector most likely will not undertake the program required to develop a fully integrated approach to prevention/mitigation techniques. For energy and materials conservation, as much quantitative information as possible should be obtained on all prevention/mitigation/removal strategies. Areas that should be addressed include the following:

1. research and development on the quantitative effect of heat exchanger geometry on fouling. This information would help the user and designer to accomplish optimal design for fouling mitigation.
2. systematic acquisition of reliable fouling data on existing operating exchangers. Such data could be used to relate fouling to heat exchanger geometry, fluid quality and fluid treatment methods.

3. research on the effect of fabrication practices on the potential for fouling when the heat exchanger is placed in service
4. encouragement of better communication among the heat exchanger users, designers, fabricator and researcher
5. a search for innovative concepts not presently being funded because the concept does not offer significant profit opportunity
6. studies of current instrumentation practices and the potential for transferring advanced monitoring techniques from other areas.

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5.0. MITIGATION TECHNOLOGY TRENDS

PNL has developed analytical procedures useful for tracking and for possibly predicting technological trends in fields of interest. Several of these procedures involve the use of patents.⁽¹⁾ Some of the issues addressed in the patent analysis include the following:

- Are technological developments occurring primarily in narrow areas of a field?
- Are the developments being carried out by many companies or only a few?
- Have the developments been primarily due to private initiative or have they been heavily influenced by federal support?
- Are the developments temporally well distributed or are there strong temporal trends or peaks?
- If there are peaks or strong trends, can they be correlated with economic or societal driving forces?
- Is there a cohesive body of patents in the field or are significant patents scattered among many different topics?
- What can be inferred about the amount of foreign interest in the field from the number of foreign-held patents?

One of the most important elements of any patent trend analysis is selecting relevant patents. Relevance, in turn, is tied to the concept of problem domains. A problem domain is a set of related problems having one or more technical approaches to a solution. For example, patents on fuel injection, stratified charge formation, and electronic ignition are all part of the problem domain of automotive fuel economy. The concept of problem domains can be interpreted in two ways. First, it represents an actual body of innovative activity directed toward a specific technical area. Second, it represents an intellectual framework, a filter used to select a meaningful subset of patents from the much larger patent system. Chosing an appropriate problem domain should be guided by both the area of technical interest and the specific questions and issues the analysis should address. Thus, for a patent trend analysis to be useful, the appropriate problem domain must be selected and the subsequent patent search must identify patents relevant to that domain.

All patent analysis is based on the working hypothesis that the number of patents issued in a particular field can be used as a quantitative measure of innovation. This hypothesis is based on four key assumptions about inventor and corporate perception of a particular problem domain:

- They recognize there is a problem.
- They believe the problem is amenable to technical solution(s).
- They believe the problem is worth solving (i.e., sufficient potential economic return).
- They believe that the solutions are patentable and that the patents are enforceable.

If any of these four conditions are not met, the interpretation of any patent statistics becomes difficult. For example, a very low level of patent activity may accurately reflect the efforts in a field that is widely perceived to offer little potential economic return to innovation. Or, a low level of patent activity may underestimate the actual amount of R&D efforts in a field where innovations are unpatentable or where patents are difficult to enforce. In such a problem domain, the economic returns to innovation may be better protected by proprietary information rather than by patents. When possibly confronted with this type of problem domain, interpretation of the patent data must be supplemented with knowledge and information gained from sources besides the patents.

5.1 PATENT SEARCH

In this study, PNL's initial search efforts for patents related to fouling and corrosion of heat exchangers encountered immediate difficulties. The U.S. Patent Office Manual of Classification is not indexed to directly identify patents in this area. Various key word searches conducted on a commercially available patent data base uncovered either a very small number of patents or literally thousands of patents, depending on the key words used. This suggests that probably no single well-defined body of technical effort exists in this area.

PNL then contacted the Office of Technology Assessment and Forecasting (OTAF) of the U.S. Patent and Trademark Office. Their staff, in consultation with Patent Office examiners familiar with the heat exchanger patent art, confirmed PNL's initial findings that the patents were scattered. With OTAF's assistance, several specific classes and subclasses that might contain relevant patents were identified. Appendix E contains a list of the classes and subclasses searched and the key words used. These subclasses were too broad to include all patents referenced or cross-referenced to them. PNL then conducted further key word searches specifically tailored to each group of subclasses. This resulted in an initial list of patents.

The initial list was screened for titles that were outside the scope of the study. Many patents that were obviously uniquely related to heat exchangers in the nuclear, desalinization, and automotive engine cooling fields were discarded as irrelevant to industrial heat exchanger fouling and corrosion. In some cases, the full patent abstract was analyzed before it was included or excluded. This process yielded 255 patents. Copies of these patents were then acquired and individually reviewed. Another 24 of these patents were then discarded as outside the relevant problem domain. Some automotive radiator patents were included when they contained a feature that made them relevant to broader industrial fouling and corrosion problems.

This screening and review left a final set of 231 patents for analysis, which represents a relatively small data set. Some patents that should have been included undoubtedly were not disclosed in this search procedure; however, we feel that such patents are few in number and their inclusion would not significantly change the findings and conclusions of this patent trend analysis. For example, we are aware of one recent patent (#4339945) that discloses a novel means of on-line measurement of the fouling characteristics of heat exchanger fluids. This patent was not identified by the search criteria and was therefore not included in the patent for the sake of consistency. This particular patent illustrates one of our main findings, that innovation in this problem domain is scattered. The patent was not identified because the patent examiner placed the patent in the broad Measurement and Testing class and it

was not cross-referenced to any of the Heat Exchanger subclasses as defined by the U.S. Patent Manual of Classification.

5.2 PATENT CODING

The final set of 221 patents were individually analyzed and coded according to the type of mitigation strategy used. The patents were grouped into five types of mitigation techniques:

1. process, cooling, and fuel additives and inhibitors
2. surface coatings
3. fouling/scale removal and cleaning techniques
4. materials considerations
5. design.

Categories 1, 2 and 4 are relatively straightforward. Category 3, removal and cleaning, includes both physical and chemical cleaning (on/offline). It also includes continuous mechanical stirring of the process fluid and scraping of the heat exchanger surface. Category 5, design, includes both inventions to prevent the problem (e.g., maintain minimum temperature or flow rate, anodic protection) and inventions that claim to minimize the problem through increased ease of cleaning (e.g., quicker disassembly or easier access). Following categorization, patent data for each patent were then entered into a computer data base. The following information was included for each patent:

● patent number	● assignee name
● issue date (DD/MM/YY)	● assignee sector
● filing date (DD/MM/YY)	● assignee country
● title (68 characters maximum)	● type of mitigation
● inventor name (up to 5 inventors)	

5.3 PATENT ANALYSIS AND FINDINGS

The fouling and corrosion patent data base was sorted by assignee name, country, and sector as well as by type of mitigation and inventor. The yearly patent activity (number of patents issued per year) for country, sector, and type of mitigation was individually analyzed.

5.3.1 Aggregate Trends

Figure 5.1 shows a plot of the total number of mitigation patents issued from 1969 through 1982. The general level of activity is low. Even in peak years, relatively few patents were being issued in this problem domain. Since 1973 the rate of innovation in this domain apparently has doubled. Because fouling affects heat exchange efficiency, this increase is not surprising, considering the rise in energy prices during this period.

A review of the data base listing of the patent titles (Appendix F) reveals several important insights. The titles seem to indicate that many of the patents are process specific and most of the companies have been issued only one or two patents. This suggests either a very limited application or a decision not to do the additional R&D needed to bring an initial invention to commercial introduction. Many well-known heat exchanger design, manufacturing, and cleaning firms are noticeably absent. Their absence may be due to their lack of invention effort in this area or to their decision to protect their innovations through nonpatent means (i.e., trade secrets).

5.3.2 Activity Disaggregated by Sector

Table 5.1 lists the number and percentage of patents issued to different types of assignees. It reveals that a large majority of the patents in this area were assigned to private firms or corporations. This is typical of the patent system as a whole. The independent inventor patents are those listing no assignee or an individual. Such patents suggest an independent inventor or that the employer does not chose to take title to the patent. In our analysis, the proportion of individually owned patents is relatively high, which is generally true of mechanical patents. A review of the patent data base for this study reveals that a disproportionate share of the individually owned patents were in mitigation categories three and five. These represent mostly mechanical mitigation approaches. Only three patents were assigned to the U.S. government, one to DOE and two to the Secretary of the Navy. This may indicate very little previous government funding for work in mitigation. Also, only three patents were assigned to universities, suggesting that their research has not resulted in many patents.

**Number Of
Patents**

Total = 231

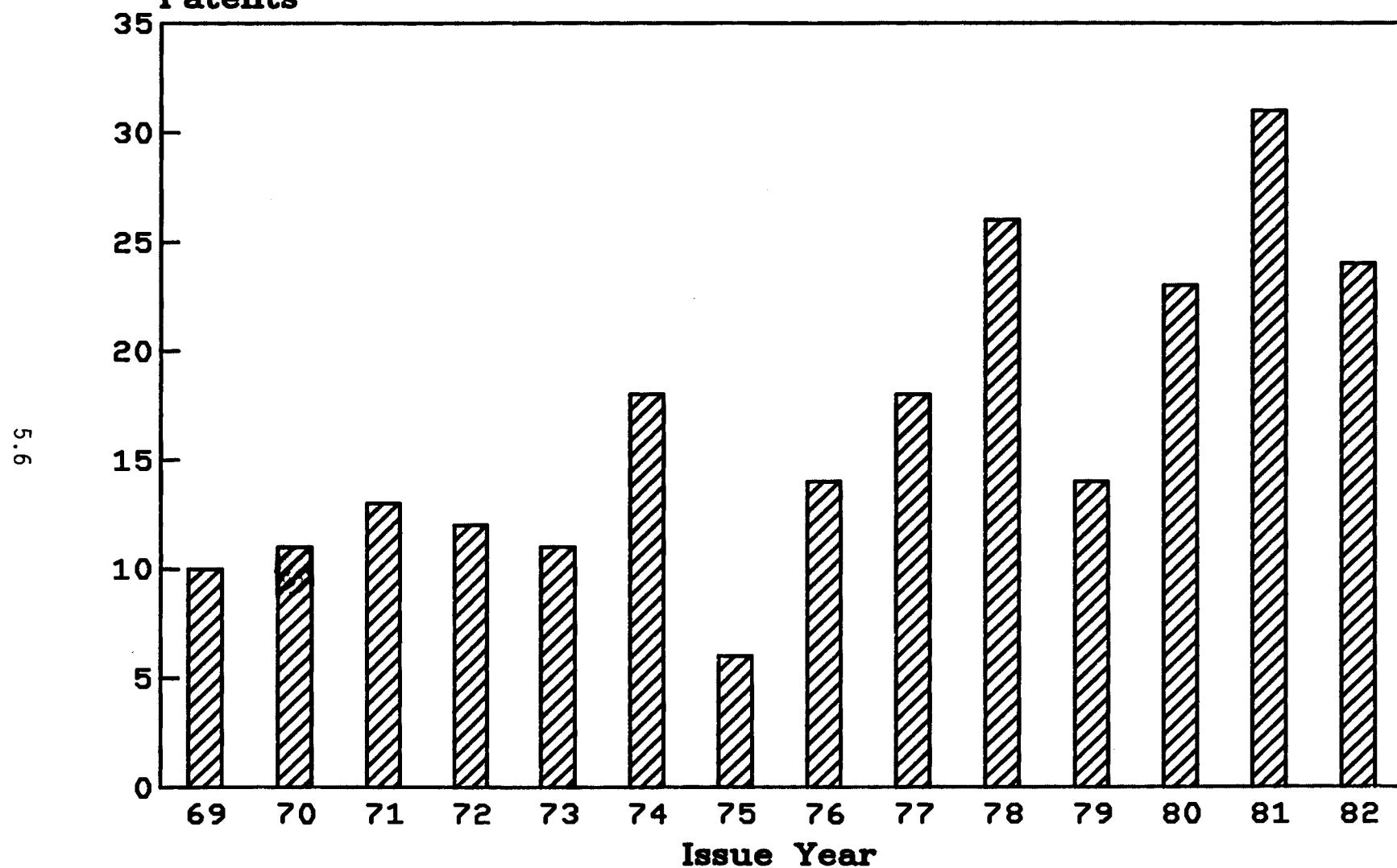


FIGURE 5.1. Fouling and Corrosion Patent Activity

TABLE 5.1 Activity by Sector of the Economy

<u>Sector</u>	<u>No. of Patents</u>	<u>% of Patents</u>
Private firm or Corporation	179	77.5
Independent (privately owned)	46	19.9
Government agency	3	1.3
University	3	1.3

Figure 5.2 is a plot of the yearly activity disaggregated by sector. The six university and government assigned patents were combined as "other" for ease of graphical interpretation. This figure reveals that the level of corporate activity in the post-1973 period was only slightly higher than the preceding years. Most of the overall increase in activity was due to the increased rate of patents issued to independent inventors (approximately three times higher after 1973). This suggests that corporations may not believe that the increased energy efficiency of better cleaned heat exchangers can be translated into increased profits. Independents, with perhaps a less critical view of the financial potential of innovation in mitigation, have been more active. Corporate activity does not show any significant indication of having followed up on some initial breakthrough pioneered by the independent inventors.

5.3.3 Activity Disaggregated by Country

Table 5.2 lists the number and percentage of patents by assignee country (inventor country, if unassigned). The U.S. received 63.6% of the patents on mitigation, which is very close to the proportion of U.S. assigned patents across all technologies in recent years.⁽²⁾ West Germany and Japan are the two most active foreign countries, as is common in many other technologies.

Figure 5.3 disaggregates the yearly patent activity by country. This can be useful in identifying late bursts of foreign competition in technologies historically dominated by the U.S. The figure shows that the number of foreign-assigned patents has remained relatively constant. Foreign-assigned patents have averaged about 6 per year over a 14-year interval. The level of U.S.

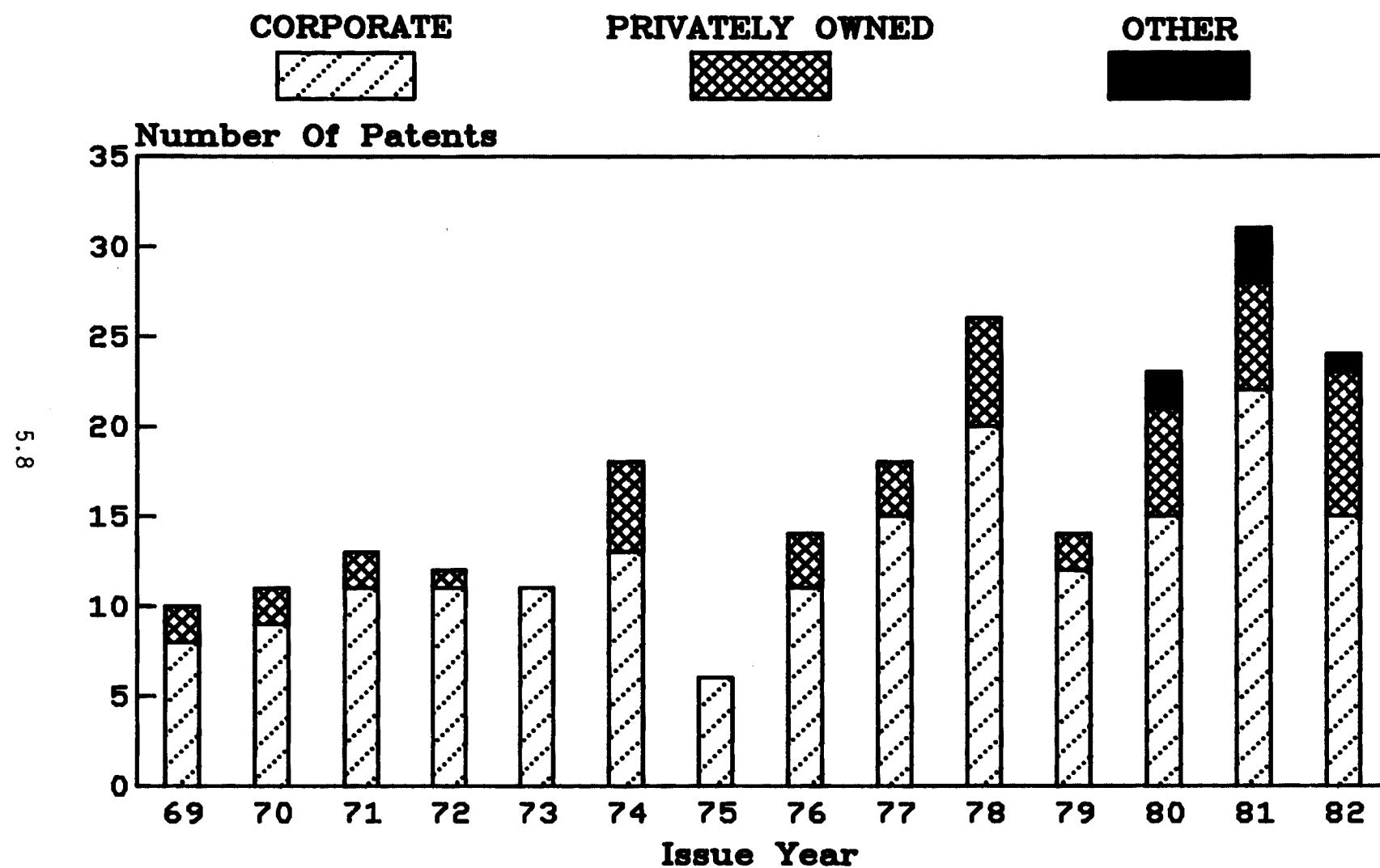


FIGURE 5.2. Time Series by Assignee Sector

TABLE 5.2 Activity by Country

<u>Country</u>	<u>No. of Patents</u>	<u>% of Patents</u>
United States	147	63.6
West Germany	22	9.5
Japan	21	9.1
Sweden	9	3.9
Switzerland	8	3.5
France	5	2.2
United Kingdom	4	1.7
USSR	4	1.7
Italy	3	1.3
Canada	2	0.9
Other	6	2.5

activity has shown more yearly variation. No single foreign country shows any late burst of activity, which suggests that the U.S. may not be in any immediate danger of falling behind technologically because of a foreign innovation in mitigation.

5.3.4 Activities Disaggregated by Type of Mitigation

Table 5.3 lists the number and percentage of patents by type of mitigation used. The largest category, removal & cleaning techniques, contains many patents on specific production processes that include some kind of continuous mechanical stirring of the process fluid or scraping of the heat exchange surface to prevent fouling. It also includes patents concerning various on- and off-line scale/fouling removal techniques (both physical and chemical). One of the more interesting scale-removal techniques disclosed in the patents was the use of sponge balls or brushes that scoured the heat exchanger tubes. Hitachi has been issued several patents on the use of sponge balls. This category also includes improvements on cleaning tools such as lances.

The second largest category, design, primarily consists of patents that claimed easier cleaning either due to better access or quicker disassembly. It also included patents that incorporated anodic protection as part of the heat

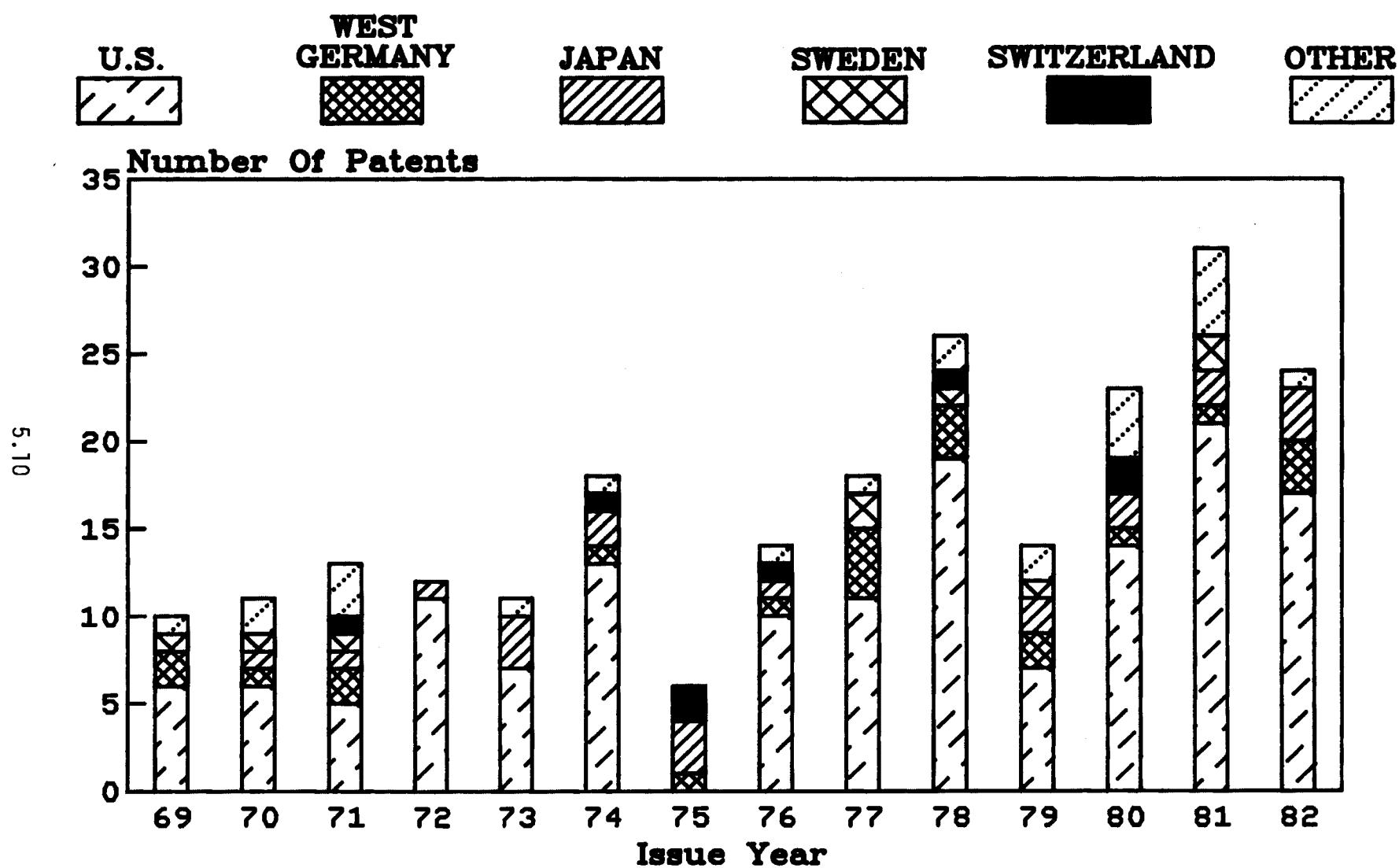


FIGURE 5.3. Time Series by Country

TABLE 5.3 Activity by Type of Mitigation

Type of Mitigation	No. of Patents	% of Patents
Process, cooling, & fuel additives/inhibitors	31	13.4
Surface coatings	8	3.5
Removal & cleaning techniques	117	50.6
Materials considerations	16	6.9
Design	59	25.5

exchanger design. Very few patents claimed reduced fouling or corrosion from some generic shape or unique operating conditions.

The third largest category, additives and inhibitors, includes patents on various chemicals intended to prevent corrosion and scale formation on heat exchanger surfaces and fuel additives to prevent soot buildup in boilers.

The two categories with the fewest patents concern patents that include the use of a particular surface coating or material intended to limit corrosion of the heat exchanger.

Figure 5.4 is a plot of the yearly patent activity disaggregated by the type of mitigation. Patents on cleaning techniques have been consistently the most common type of patent. Much of the modest increase in patent activity in recent years has been due to more frequent patenting of improved designs. However, since most of these patents claim easier cleaning rather than prevention of fouling and corrosion, it would seem safe to conclude that the dominant thrust of new mitigation innovations has consisted of incremental improvements in existing cleaning techniques.

Figure 5.4 does show a slight increase in the number of patents involving additives and inhibitors. However, those few patents seriously underestimate the amount of industrial R&D in this area. For example, Betz Laboratories, a leader in industrial water conditioning, had sales of over \$250 million in 1982 (Directory of Corporate Affiliations 1983).⁽³⁾ Yet, they have none of the

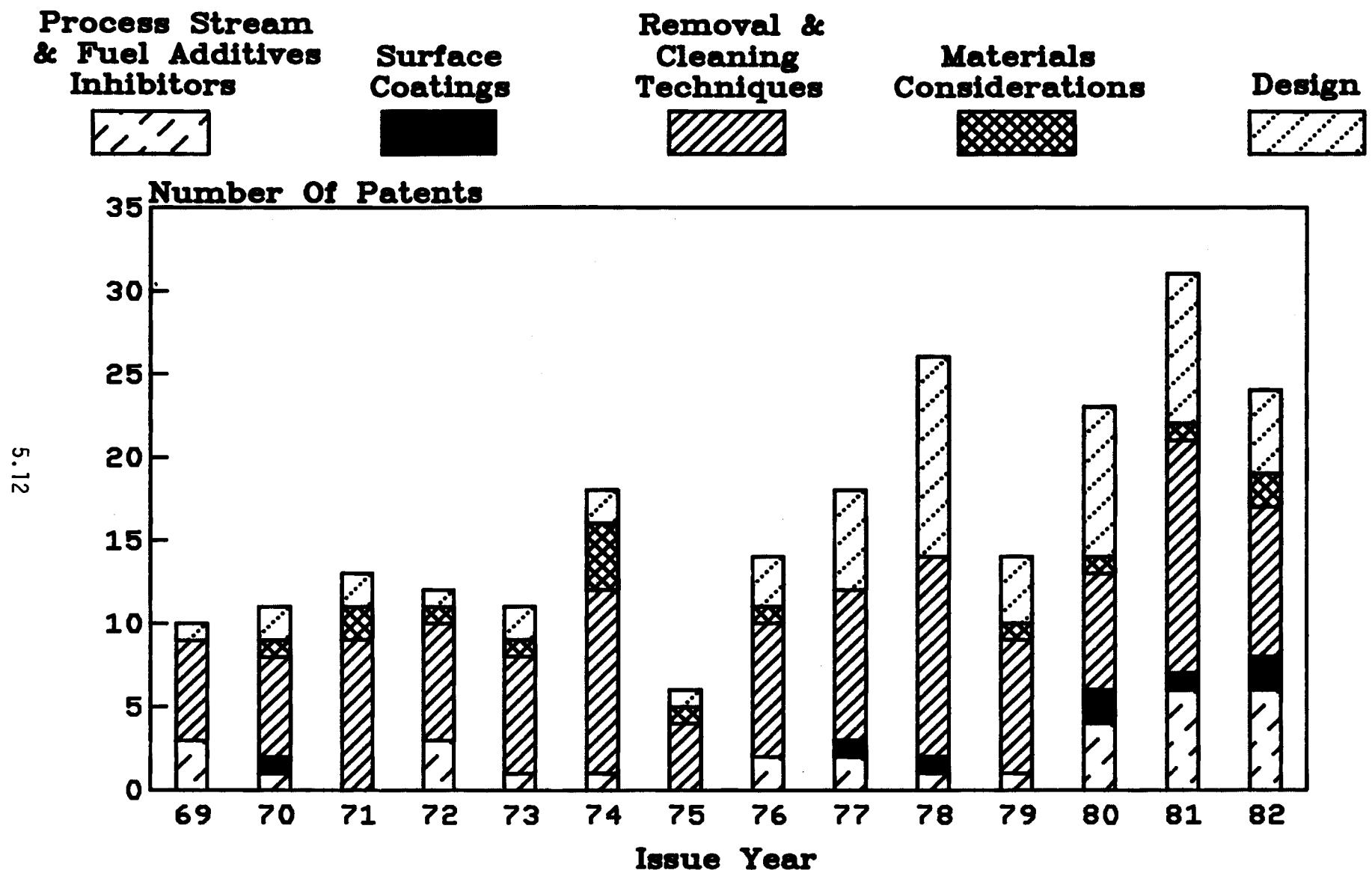


FIGURE 5.4. Time Series by Type of Mitigation

221 patents identified in this study, probably because of the specific and changing character of water conditioning problems. Commercial success in this field is tied more to the ability to analyze a particular water chemistry problem and to formulate a specific treatment, rather than to developing generic new chemical compounds. In such a business environment, patents on chemicals are of relatively less financial importance and protection is obtained through trade secrets.

Inventions of new materials and coatings, which would generally have a broader application, are more likely to be patented. Most of the patents in these categories concern the prevention of corrosion in aluminum heat exchangers. The relatively few patents uncovered in this study probably accurately reflect the limited amount of successful innovation to date on this type of mitigation approach.

5.4 SUMMARY AND CONCLUSIONS

Although the general level of patent activity in the area of fouling mitigation is relatively low, the rate of innovation in this area has roughly doubled since 1973, corresponding to the sharp increases in energy prices in this period. This low level of activity may imply a widespread conviction by the private sector that there were few patentable opportunities for major profits in designing equipment and techniques to prevent fouling and corrosion problems or it may suggest that industry prefers to protect its innovations through non-patent means.

The patent analysis indicates modest incremental improvements in mitigation techniques. These improvements are primarily focused on existing cleaning techniques scattered across many applications. The relative absence of major breakthroughs during what is a very long time in most technologies may be a function of the essential maturity of the area, the highly specific nature of fouling and corrosion problems, the absence of a strategically directed research program, or the inherent difficulty of the problem.

CHAPTER 5.0 - REFERENCES

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6.0 COSTS OF FOULING

Heat exchangers are used in many heat source, heat sink, and process applications throughout the U.S. industrial sector. In 1981, heat exchanger sales totaled \$1.5 billion (in 1982 dollars)⁽¹⁾ and sales are expected to grow at 6% per year between 1975 and 1985.⁽²⁾ The presence of fouling in heat exchanger equipment represents additional costs to the industrial sector in terms of additional capital, energy and labor. In an industrial setting free of fouling, these additional expenditures would not be as large, and resources previously used for fouling could be employed in more productive activities.

This section estimates the cost of fouling and corrosion to the entire industrial sector using two separate approaches. From this analysis, it is estimated that the cost is between \$3 and \$10 billion per year. Information on the cost of fouling to specific industrial subsectors is included in Appendix H. All costs are specified in constant 1982 dollars unless noted.

6.1 FOULING COST COMPONENTS

Specifically, the costs of fouling include:

- oversizing or redundant equipment - Since fouling reduces the rate of heat transfer, designers increase the heat transfer area of heat exchangers by specifying fouling resistances. In some industries, where uninterrupted production is required, duplicate heat exchangers may be installed. When one exchanger fouls and must be taken out of production for cleaning, the second exchanger is placed in production.
- specialty materials and geometric configurations - Highly corrosive fluids may require the use of high cost materials such as titanium, stainless steel, glass, or graphite. Also, various geometric configurations such as minimizing the baffle to shell clearances, reducing the number and size of crevices, and eliminating eddies and dead zones, help to reduce the impact of fouling. These special design considerations add to the final cost of the exchanger.
- additional downtime for maintenance and repair - Most firms schedule downtime for normal plant maintenance and repair. During these planned shut-

downs, heat exchanger equipment is also cleaned or replaced. If fouling were not present in heat exchangers, additional expenditures for labor, equipment and chemicals would not be required.

- lost production - If plant production levels are at or near capacity, and plant production is stopped due to fouling, this downtime results in the loss of valuable production. In some industries, such as the pulp and paper industry, plant shut-down and start-up result in products that do not meet normal product specifications. These products must either be discarded, or sold at a discount.
- cleaning equipment and services - Many industries use either on or off line heat exchanger cleaning equipment such as soot blowers, sonic horns, and vibrators, to help reduce fouling problems. The use of antifoulant chemicals has proven to be quite effective in reducing cleaning frequency in some industries but add to the cost of production.⁽³⁾
- additional energy and waste heat opportunities foregone - Since fouling reduces the rate of heat transfer from one fluid to another, additional energy may be required to bring stream temperatures to desired levels. Also, as fouling deposits build-up, the cross-sectional flow area is reduced, resulting in larger pressure drops across the exchanger. These pressure drops require additional pumping or fan power. In some industries, waste heat is not captured and reused due to severe fouling problems.

A few industry studies, such as those conducted by Battelle Columbus Laboratory⁽⁴⁾ for the National Bureau of Standards, and by the National Association of Corrosion Engineers (NACE)⁽⁵⁾ for their members, have attempted to estimate the costs of corrosion to the industrial sector. However, these studies estimate corrosion costs on an aggregate level and do not provide any detailed information on the costs of fouling in heat exchangers. A review of the literature and contact with industry experts indicates that no real attempts have been made to estimate these costs for the entire U.S. industrial sector. However, Thackery⁽⁶⁾ develops a series of "considered guesses" that he uses to make an order-of-magnitude estimate of fouling costs in the United Kingdom. The four basic cost components evaluated in his study are:

- increased capital costs
- energy losses
- maintenance costs
- lost production

Based on his considered guesses, and his knowledge of United Kingdom fouling problems, Thackery estimates that the annual costs of fouling in the U.K. were \$800 to \$1,000 million (in 1978 dollars) in 1978 (Table 6.1).

Although the information on the costs of fouling to the U.S. industrial sector is limited, a crude order-of-magnitude estimate of these costs can be made using the U.K. results and two separate approaches. The first approach assumes that U.S. fouling problems are similar to those experienced in the U.K., that the distribution of heat exchangers (by size) is the same for the U.S. and U.K., and that fouling problems increase with total industrial output. Such assumptions imply that an estimate of fouling costs can be made by multiplying U.K. fouling costs by the ratio U.S. and U.K. Gross National Product (GNP). In 1978, U.S. GNP was about seven times larger than the GNP of the U.K. Multiplying the U.K.'s fouling costs by seven, and inflating them to 1982 dollars yields a crude order-of-magnitude estimate for the U.S. of \$8 to \$10 billion.

A second approach uses some of the same logic that Thackery employed in making his estimate for the U.K., and is modified to better reflect the U.S. situation. These modifications are based on a detailed survey of the literature as well as contacts with heat exchanger manufacturers and industry (see

TABLE 6.1 Costs of Fouling and Corrosion in the U.K. Industrial Sector

<u>Cost Component</u>	<u>Annual Cost (millions of 1978 dollars, U.S.)</u>
Capital costs	190
Energy losses	290-480
Maintenance costs	130-170
Loss production	190
Total	\$800-\$1030

Appendix G). The following lists the various fouling cost components and the logic used in deriving U.S. cost estimates.

6.1.1 Special Design Considerations

Information from U.S. manufacturers indicates that oversizing of heat exchangers ranges from 10 to 500%, depending on the severity of the fouling problem. An average figure is 30 to 40% for the amount of additional surface area this represents. This additional surface area adds about 25% to annual heat exchanger sales. Thus, approximately 20% (i.e., 25/125) of the value of U.S. annual heat exchanger sales is due to the oversizing of heat exchangers to help lessen fouling problems. These data tend to correlate well with the information presented by Thackery on oversizing in the U.K.

The value of shipments of heat exchangers in the U.S. for 1982 is estimated to be \$1.6 billion. If 20% of these shipments were for oversizing equipment, that would represent an annual cost of \$320 million to the industrial sector. However, the sales price does not typically include the associated heat exchanger installation costs. As Thackery notes, these installation costs tend to increase with the size of the heat exchanger, and are usually 2 to 3 times the delivered cost. Adding the installation costs to the additional capital costs increases the costs of oversizing to \$640 to \$960 million per year.

In some highly corrosive applications, heat exchanger designers will specify that specialty materials such as titanium, stainless steel or graphite, be used in place of carbon steel. When these materials are recommended, occasionally no fouling factor is used. Discussions with heat exchanger manufacturers indicated that the use of these specialty materials increase the cost of the heat exchangers by 15 to 100% over the costs of carbon steel exchangers with 25% being the average. The use of specialty materials represents an additional cost to the industrial sector of \$320 million per year.

Figure 6.1 illustrates the relationship between fouling factors, materials of construction, and the initial capital cost of heat exchangers. These cost curves were generated using the B-JACS^(a) computer code. This code optimizes

(a) Developed by B-JACS Computer Services of Midlothian Virginia.

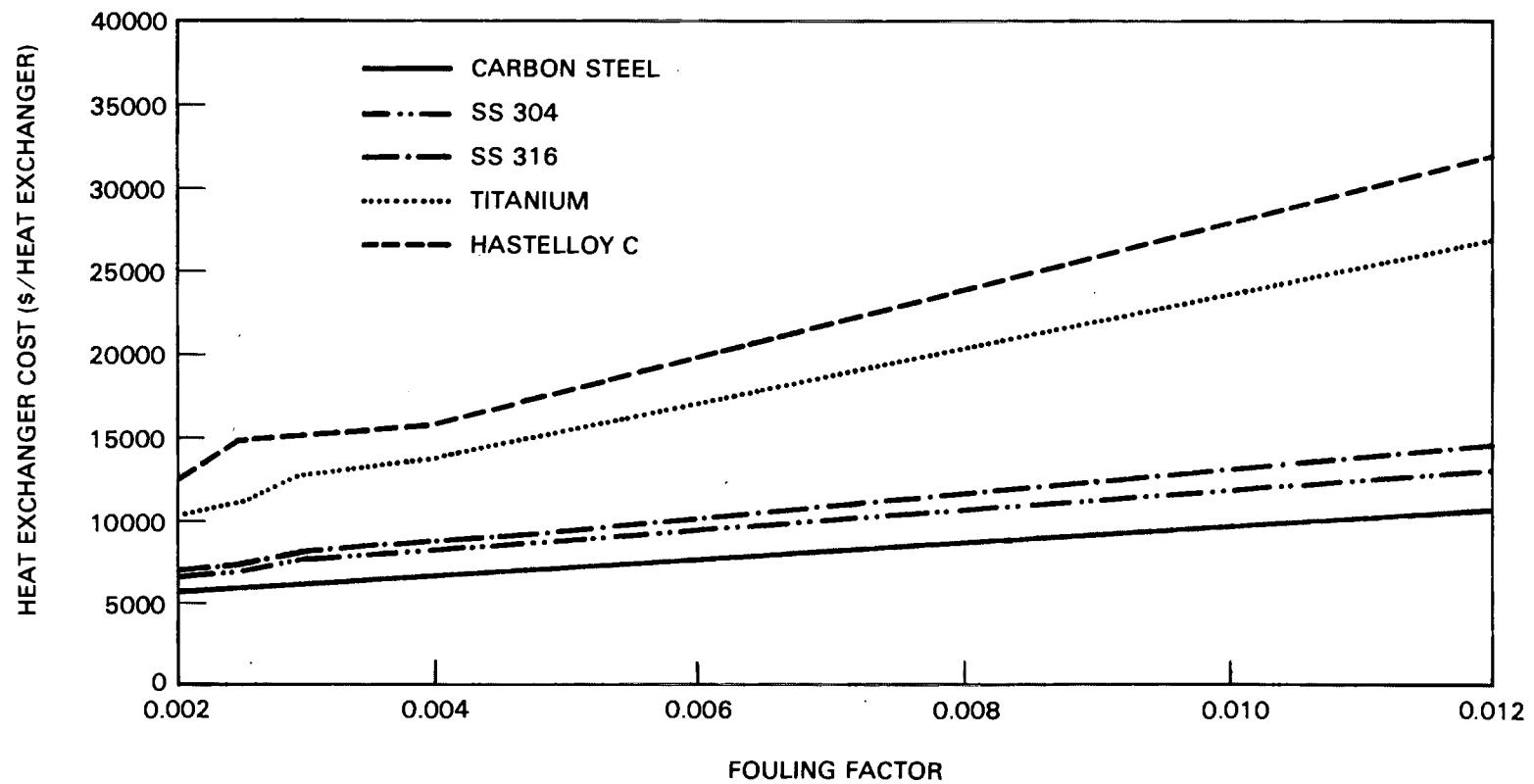


FIGURE 6.1 Heat Exchanger Cost Versus Fouling Factor and Construction Material

the design and estimates the initial cost of shell and tube heat exchangers given various user-supplied technical parameters.

For this analysis, it was assumed that the shell side fouling factor remained constant at 0.002. The tube side fouling factor was then varied for each material of construction from 0.00 to 0.01. The tube and tube sheet materials selected were carbon steel, 304 stainless steel, 316 stainless steel, titanium, and hastelloy c.

As illustrated in Figure 6.1, the cost of a heat exchanger increases as a larger fouling factor is used. This increase in cost is due to the additional surface area required. Also, heat exchangers constructed from "specialty" materials, such as titanium and hastelloy c are relatively more expensive than exchangers constructed from carbon or stainless steel. Furthermore, as the fouling factor increases, the cost of specialty material heat exchangers increases faster than does the cost of carbon or stainless steel exchangers.

It should be noted that the costs of heat exchangers presented in Figure 6.1 are only the initial capital costs and do not include the additional costs of installation.

Thus, the total cost of special design considerations due to fouling is \$960 to \$1280 million per year (Table 6.2).

6.1.2 Energy Loss

The presence of fouling and corrosion in heat exchangers requires the use of additional energy in many industrial applications. This additional energy is required since fouling tends to reduce the rate of heat transfer and fluid

TABLE 6.2 Costs of Special Design Considerations

Component	Percent of Heat Exchanger Sales (\$)	Cost to Industry (\$ M)
Oversizing	20	\$320
Additional install.	--	\$320-640
Specialty mat'l.	20	\$320
Total		\$960-\$1280

flows as well as decreasing the economic attractiveness of waste heat recovery opportunities.

In 1982, the industrial sector consumed approximately \$70 billion worth of coal, natural gas and petroleum.⁽⁸⁾ No detailed information is available on the amount of this energy that is required because of the presence of fouling and corrosion. However, a reasonable assumption would be that of the total value of the energy consumed by the industrial sector in 1982, about 1 to 5%, or \$700 million to \$3.5 billion is due to fouling problems.

6.1.3 Maintenance Costs

In the past, oversizing was the principal method of handling the fouling and corrosion of heat exchangers. When a heat exchanger fouled, and the rate of transfer fell below a minimum acceptable level, the heat exchanger was either replaced or cleaned.

With the discovery of effective antifouling and cleaning chemicals, the operating periods of many heat exchangers has been extended. As new chemicals are discovered and adopted by industry, maintenance costs may become more significant components in the costs of fouling. As discussed in Section 4.0, a variety of online and offline mechanical cleaning techniques are also available.

A detailed accounting is not available of the additional maintenance costs due to fouling and corrosion. Thackery estimates the costs of additional maintenance costs using fairly detailed data collected on the U.K. industrial sector. Unfortunately, similar data is not compiled for the U.S. However, contacts with companies that supply heat exchanger online and offline cleaning equipment, chemicals, and cleaning services indicates that total annual sales by these companies were about \$2 billion in 1982.

6.1.4 Lost Production

The severity of a plant shutdown due to fouling and/or corrosion depends on both the plant capacity and the length of the shutdown. If a plant is operating at only 60% capacity, and is shutdown for one day, the value of the lost production will be negligible (other than the costs associated with plant start-up and shutdown). However, as the plant capacity and/or the length of

the downtime increases, the value of the lost production also increases. If production is delayed, customers' orders may not be filled on time, or if the plant is down for an extended period of time, customers' orders may go unfilled. In either case customers will be forced to seek other manufacturers for the needed product.

The plant engineer will typically use all means available to keep the plant operating. For heat exchangers, this includes ordering properly sized exchangers, and installing cleaning equipment. Plant engineers will also establish a maintenance program that will minimize the amount of plant downtime. However, regardless of the precautions taken, many heat exchangers still foul and cause plants to lose product revenues.

No detailed information is available from the literature on the value of this lost production to the industrial sector. Contacts with industry indicate that it is one of the most difficult of the four fouling cost components to estimate, and often it is impossible to attribute lost production exclusively to the fouling of a heat exchanger. Also, the value of this lost production must be weighed against the reduction in operating expenses during the plant shutdown.

One method of estimating an upper limit of this cost is to assume that the present value of the lost production over the life of a heat exchanger must be less than the present value of the cost of adding redundant exchangers. If this were not true, it would be to the advantage of the firm to install redundant heat exchangers in most industrial applications.

The productive life of a heat exchanger can vary with 5 to 20 years. Assuming that the average life of a heat exchanger in the U.S. is 10 years, and assuming a real discount rate of 5%, the value of lost production due to heat exchanger fouling is implied to be less than 13% of annual heat exchanger sales. This result yields a crude, order-of-magnitude estimate of the cost of lost production of less than \$200 million per year.

6.2 CONCLUSION

The annual cost of fouling and corrosion to the U.S. industrial sector is estimated to be between \$3 and \$10 billion. The general lack of detailed

information on fouling and corrosion costs make a precise estimate extremely difficult. Therefore two approaches were used in this section to estimate these costs. The first approach is based on the methodology developed for the U.K., and assumes that fouling and corrosion problems are similar to those experienced in the U.S. This approach yields an order-of-magnitude estimate of \$8 to \$10 billion per year.

The second approach uses a similar logic to that applied to the U.K. experience and incorporates the limited amount of data available for the U.S. With this approach, all estimates tend to be somewhat conservative due to the assumptions made, and the lack of detailed information. This approach yields an order-of-magnitude estimate of about \$3.8 to \$7 billion per year (Table 6.3).

TABLE 6.3 Summary of Fouling and Corrosion Costs for U.S. Industrial Sector

<u>Component</u>	<u>Cost to Industry (\$M)</u>
Special design considerations	\$960-\$1280
Energy losses	\$700-\$3500
Maintenance costs	\$2000
Lost production	\$200
Total	\$3860-\$6980

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APPENDIX A
FORMAT AND FIELD DESCRIPTIONS OF DATA BASE

<u>Number</u>	<u>Name</u>	<u>Type</u>	<u>Width</u>	<u>Description</u>
001	COMPANY	C	025	
002	ADDRESS	C	060	
003	PHONE	C	014	
004	CONTACT	C	035	
005	PRODUCT	C	020	
006	PRODTYPE	C	012	equipment/chemicals/service
007	ONOFFLINE	C	003	
008	APPL1	C	015	
009	APPL2	C	015	product applications
010	APPL3	C	015	
011	SALESDOL	N	020	annual sales (\$)
012	SALESUNIT	N	020	annual sales (units)
013	COST	N	015	
014	INDPROB	C	030	industries facing most serious problems
015	LOCPROB	C	025	location of problems
016	TYPEPROB	C	025	type of problems
017	INSTTIME	C	020	installation time
018	DESNCHNG	C	025	design changes required
019	DOWNTIME	C	020	
020	PROBLEMS	C	040	possible problems with product
021	ADDBEN	C	030	additional benefits of using product
022	BARRIERS	C	025	barriers to product application
023	FUTMKT	C	025	future market trends
024	YRENTER	N	004	year that product entered market
025	AFFIL	C	020	company affiliations
026	COMMENTS	C	150	
027	UPDATED	C	008	latest update of file
028	SORT1	C	020	
029	SORT2	C	020	undesignated fields

Note: C denotes a comment (alpha field)
 N denotes a numeric field

APPENDIX B

LIST OF COMPANIES OFFERING CLEANING EQUIPMENT, CHEMICALS AND CLEANING SERVICES



APPENDIX B

LIST OF COMPANIES OFFERING CLEANING EQUIPMENT, CHEMICALS AND CLEANING SERVICES

COMPANY	ADDRESS	TELEPHONE	CONTACT
ALCONOX, INC.	217 PARK AVE S., NEW YORK, NY 10003	(212) 473-1300	MR. LEBOWITZ, TECHNICAL ADVISOR
AMERICAN AREO INC.	PO BOX 55343 HOUSTON TX 77255	(713) 896-0002	JOHN JACOBSON
AMERTAP CORPORATION	25381-G ALICIA PKWY SUITE 205 LAGUNA HILLS, CA 92653	(714) 855-2024	JOHN VALENS / REGIONAL SALES MGR.
AQUA-DYNE, INC.	2208 KARBACH HOUSTON, TX 77092	(713) 681-3581	BOB GROWER
BARCO CHEMICAL PRODUCTS	327 SOUTH LA SALLE CHICAGO, IL 60604	(312) 427-2916	RALPH R. BAREWIN / PRESIDENT
BARON BLAKESLEE MFG. CO.	2001 N JANICE, MELROSE PARK, IL 60160	(312) 450-3900	MS. ANN CARNEY, ADMINIS. ASSISTANT
BEAVER ALKALI PRODUCTS CO	NEW YORK AVE & WATER STREET, ROCHESTER, PA 15074	(412) 774-2649	HAROLD DAVIDSON, OWNER
BETZ LABORATORIES, INC.	SOMERTON ROAD TREVOS, PA 19047	(215) 355-3300	DANIEL W. YANKOVICH
BUTTERWORTH INC.	PO BOX 18312 HOUSTON TX 77223	(916) 622-1041	MIKE SCHIAVONE, SALES MANAGER
CALGON CORPORATION	P.O. BOX 2000 RAHWAY, NJ 07065	(800) 423-6577	TOM TENNIS
CLEAN-FLO LABS., INC.	4342 SHADY OAK ROAD HOPKINS, MN 55343	(612) 935-2137	ROBERT LIANG / PRESIDENT
CONCO SYSTEMS, INC.	135 SYLVAN STREET VERONA, PA 15147	(412) 828-5222	GEORGE E. SAXON / PRESIDENT
COPES-VULCAN	P.O. BOX 577 LAKE CITY, PA 16423	(814) 774-3151	JAMES T. DICARLO / SALES MGR
DAYTON CHEMICAL CORP.	1341 HAMBURG, TURNPIKE, WAYNE, NJ 07470	(201) 628-9303	PAUL LEAL, SALES MANAGER
DEARBORN CHEMICAL CORP.	300 GENEESE ST, LAKE ZURICH, IL 60047	(503) 657-5501	PETE SESING, VP SALES AND MKTG
DIAMOND POWER SPEC. COMP.	P.O. BOX 415 LANCASTER, OH 43130	(614) 687-6500	JAMES W. LOCKE
DIONEX CORPORATION	1228 TITAN WAY SUNNYVALE, CA 94086	(408) 737-0700	GREG FRANKLIN
DOBER CHEMICAL CORP	14461 S WAVERLY AVE. MIDLOTHIAN IL 60445	(312) 388-7700	JOHN DOBREZ
DOWELL INDUSTRIAL SERVICE	P.O. BOX 2710 TULSA, OK 74102	(918) 250-4200	HUGH C. ATCHISON
DREW CHEMICAL CORPORATION	ONE DREW CHEMICAL PLAZA BOONTON, NJ 07005	(201) 263-7682	JOHN STINGER, MANAGER OF COMMUN.
ELGENE CHEMICALS, INC.	327 NORTHRUP AVE. MAMARONECK, NY 10543	(914) 698-7800	WARREN W. CHRISTOPH
ELLIOT COMPANY	1809 SHERIDAN AVENUE SPRINGFIELD, OH 45501	(513) 324-4191	CARL STEVENS
ENERCHEM INCORPORATED	26917 BRAHMS DRIVE P.O. BOX 45246 CLEVELAND, OH 44145	(216) 835-3958	JERROLD E. RADWAY
EXPANDO SEAL TOOLS, INC.	P.O. BOX 368, SPRING HOUSE, PA 19477	(215) 643-7044	ROSEMARY TATTON, SEC'Y
EXXON CHEMICAL COMPANY	8230 STEDMAN STREET HOUSTON, TX 77029	(713) 870-6230	BRUCE IRWIN
FERGUSSON CO., ALEX C.	SPRING MILL DRIVE FRAZER, PA 19355	(215) 647-3300	BILL PYLE
GLOBAL HEAT EXCHANGER INC	PO BOX 1127-TR BEAUMONT TX 77704	(713) 833-6343	RALPH DELONG
GOODWAY TOOLS CORPORATION	404 WEST AVENUE STAMFORD, CT 06902	(203) 359-4708	BRUNO DENOYER
GREAT LAKES CHEMICAL CORP	PO BOX 2200 WEST LAFAYETTE IN 47906	(317) 463-2511	DR. DADGAR
HALLIBURTON INDUST. SERV.	P.O. BOX 297 DUNCAN, OK 73536	(405) 251-3360	JOHN KNOX / PRESIDENT
HERCULES INC.	6803 W 64 TH SUITE 100 SHAWNEE MISSION KANSAS 66202	(913) 384-2592	JOHN RHOADS
KEM MANUFACTURING CORP.	2075 TUCKER INDUSTRIAL RD., TUCKER, GA 30084	(404) 938-7980	BARRY KIEFABER, SALES CONSULTANT
KVB, INC.	18006 SKYPARK BOULEVARD IRVINE, CA 92714	(714) 641-6200	JOSEPH SCHWARTZ / MARKETING MGR
MATESON CHEMICAL CORP	1025 E MONTGOMERY AVE PHILIDELPHIA PA 19125	(215) 423-3200	MR. JEAN MATESON, PRESIDENT
MOGUL CORPORATION	6650 NORTH BASIN PORTLAND, OR 97217	(503) 285-0248	JACK L. JOHNSON / NW DIVISION MGR
NALCO CHEMICAL COMPANY	1801 DIEHL ROAD NAPERVILLE, IL 60566	(312) 887-7500	FRED ROENCH
OAKITE PRODUCTS, INC.	50 VALLEY ROAD BERKELEY HEIGHTS, NJ 07922	(201) 464-6900	DENNIS FORAN
PENETONE CORPORATION	72 HUDSON AVENUE TENAFLY, NJ 07670	(201) 567-3000	DENNIS ESPOSITO, SALES MANAGER
PETROLITE CORPORATION	369 MARSHALL AVE. ST. LOUIS, MO 63119	(314) 961-3500	DAVID A. GALLI / IND PRODUCTS MGR
PRIDE LABORATORIES, INC.	110 SCHMITT BLVD. FARMINGDALE, NY 11735	(516) 752-8600	JEFF MANN, SALES MANAGER
SIOUX STEAM CLEANER CORP.	P.O. BOX 192 BERESFORD, SD 57004	(605) 763-2776	GLENN A. LAWRENSON
TRITAN CORPORATION	9000 AIRPORT BLVD. HOUSTON, TX 77017	(713) 941-8941	L.R. HINESLEY
TURB-O-FLOW CORP	10 PEARY AVE NORWALK CONN. 06850	(203) 846-4455	MR. VAN WINKLE
VICJET, INC.	821 AUBREY AVE, ARDMORE, PA 19003	82159 688-7550	VICTOR SHERONAS, PRESIDENT
WATER SERVICES OF AMER.	PO BOX 23848 MILWAUKEE WISCONSIN 53223	(414) 354-6470	JANET ENDRIES
WILSON INC.	21-11 44TH AVE. LONG ISLAND CITY NY 11101	(212) 729-3360	MATT EWERLING, INSIDE SALES SPRVSR
WRIGHT CHEMICAL CO	4328 NORTH UNITED PARKWAY SCHILLER PARK IL 60176	(312) 678-4806	RON SCHULTZ



APPENDIX C
THE EFFECT OF EXCESS AREA ON HEAT EXCHANGER OPERATION

APPENDIX C
THE EFFECT OF EXCESS AREA ON HEAT EXCHANGER OPERATION

The specification of excess area in the exchanger leads to operational problems and may be the cause of fouling of the surface beyond that which was used in the design. Increase in velocity and reduction in surface temperature cause a reduction in the asymptotic fouling resistance for several of the fouling types. This behavior is shown schematically in Figure 1. Such a family of curves cannot yet be predicted for most fouling types. Point A represents design velocity and surface temperature and the corresponding fouling resistance which was used. At start-up, there is too much area in the exchanger for the required heat duty. Operating conditions must then be adjusted to point B corresponding to lower than design velocity and higher than design surface temperature. This is a region of higher fouling resistance than was used in the design, so conditions are present for the tendency to develop this higher fouling resistance.

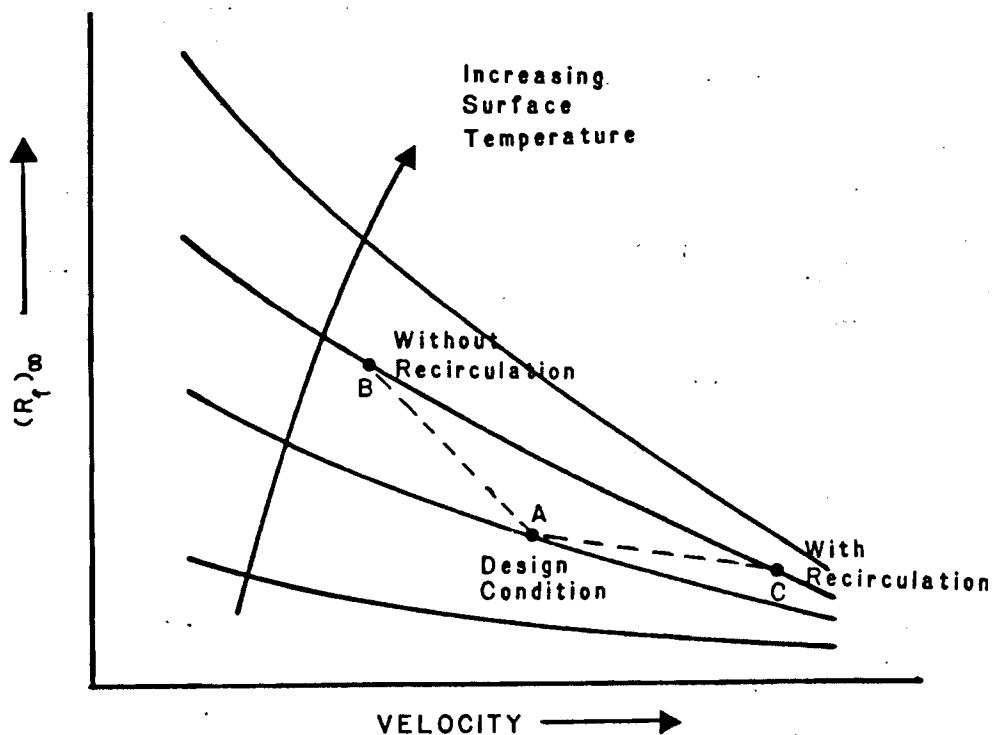


FIGURE 1. Effect of Velocity and Surface Temperature on the Asymptotic Fouling Resistance

A simple quantitative example will illustrate this point. Figure 2 shows a countercurrent heat exchanger designed to cool a process fluid with water. Water flows on the tube side.

The fouling resistance used in the design brings about a 50% increase in the surface area over that required if there was no fouling resistance.

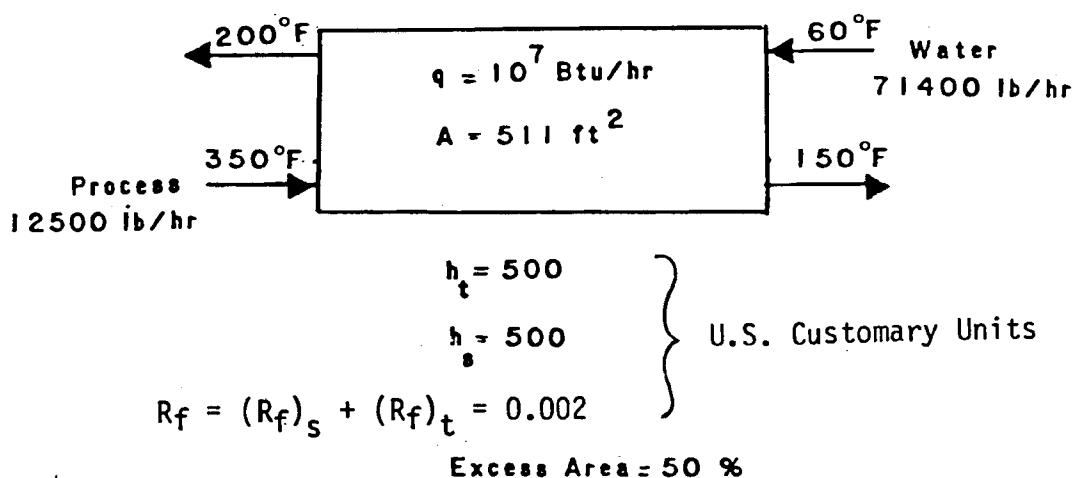
Consider the operation of the heat exchanger at any time when the total fouling resistance is R_f ($R_f = 0$ at start-up and the design value of R_f is 0.002). With the heat duty, the temperatures of the process stream, and the inlet water temperature remaining as specified, the outlet water temperature is not 200°F but $T_2^{\circ}\text{F}$. The water flow rate is \dot{m} and the water heat-transfer coefficient is proportional to the eight-tenths power of the flow rate, i.e.,

$$\frac{h_D}{h} = \left(\frac{\dot{m}_D}{\dot{m}} \right)^{0.8}$$

Inserting the design values $\dot{m}_D = 71400 \text{ lb/hr}$ and $h_D = 500 \text{ Btu/hr ft}^{20}\text{F}$,
 $h = 0.0655 (\dot{m})^{0.8}$,

the overall heat-transfer coefficient, U_0 , is expressed as

$$\frac{1}{U_0} = \frac{1}{500} + \frac{1}{0.0655(\dot{m})^{0.8}} + R_f \quad (1)$$



Neglect wall resistance

Neglect difference between inside and outside areas.

FIGURE 2. Illustrative Example

The log-mean-temperature driving force is

$$\Delta T_{LM} = \frac{(350-T_2) - (150-60)}{\ln \left(\frac{350-T_2}{150-60} \right)} \quad (2)$$

The water outlet temperature, T_2 , is related to the heat duty, \dot{q} , and water flow rate, \dot{m} , as follows

$$(\dot{m})(C)(T_2 - 60) = \dot{q}$$

from which (with $C = 1$)

$$T_2 = \frac{10^7}{\dot{m}} + 60 \quad (3)$$

The heat-transfer rate equation is

$$(U_0)(A)(\Delta T_{LM}) = 10^7$$

i.e.,

$$U_0 (511) \Delta T_{LM} = 10^7 \quad (4)$$

For given values of R_f , Equations 1 through 4 may be used with trial-and-error methods to obtain values of T_2 and \dot{m} .

The results are tabulated below for various fouling resistances

Total Fouling Resistance <u>hr - ft²°F/Btu</u>	Water Mass Flow Rate, 10^{-4} <u>lb/hr x 10⁻⁴</u>	Water Outlet Temperature, °F
0	5.1	258
0.0005	5.5	243
0.001	5.9	229
0.0015	6.5	215
0.002	7.14	200 (design value)
0.00025	8.0	185
0.003	9.2	169
0.0035	10.7	153

Therefore, when the heat exchanger is placed in operation in the clean condition ($R_f = 0$), 30% less water flow is required and the water outlet temperature is increased by 56°F to accomplish the required cooling of the process stream. The water flow rate and outlet temperature as a function of fouling resistance are shown in Figure 3. When the exchanger is clean ($R_f = 0$) conditions are such that the tendency for fouling is significantly increased. Figure 3 also shows that as fouling resistance becomes higher than the value used in the design, water usage becomes greater than the design value and a significant cost penalty is incurred due to increased friction losses. Friction loss is considered proportional to the square of the velocity.

It would be desirable if during the initial operating period, the water velocity could be maintained at a value equal to or greater than the design value. This can be accomplished by recirculation of the water as shown in Figure 4 so that initial start-up conditions correspond to point C in Figure 1.

The water inlet temperature is T_1 and the water outlet temperature is T_2 . Water is still supplied to the total system at 60°F . Assuming $R_f=0$, and maintaining design values of the heat duty and the temperatures of the process stream, the following equations apply. The quantity \dot{m} is the mass flow rate of water through the exchanger (it is the sum of the fresh water and the recirculating water). At this flow rate the water heat transfer coefficient is h .

The water heat transfer coefficient is assumed to vary as the eight-tenths power of the water flow rate. Thus

$$\frac{h_D}{h} = \left(\frac{\dot{m}_D}{\dot{m}} \right)^{0.8}$$

with $h_D = 500$ and $\dot{m}_D = 71400$ (design conditions)

$$h = 0.0655(\dot{m})^{0.8}$$

Thus the overall heat-transfer coefficient, U_0 , is

$$\frac{1}{U_0} = \frac{1}{500} + \frac{1}{0.0655(\dot{m})^{0.8}} \quad (5)$$

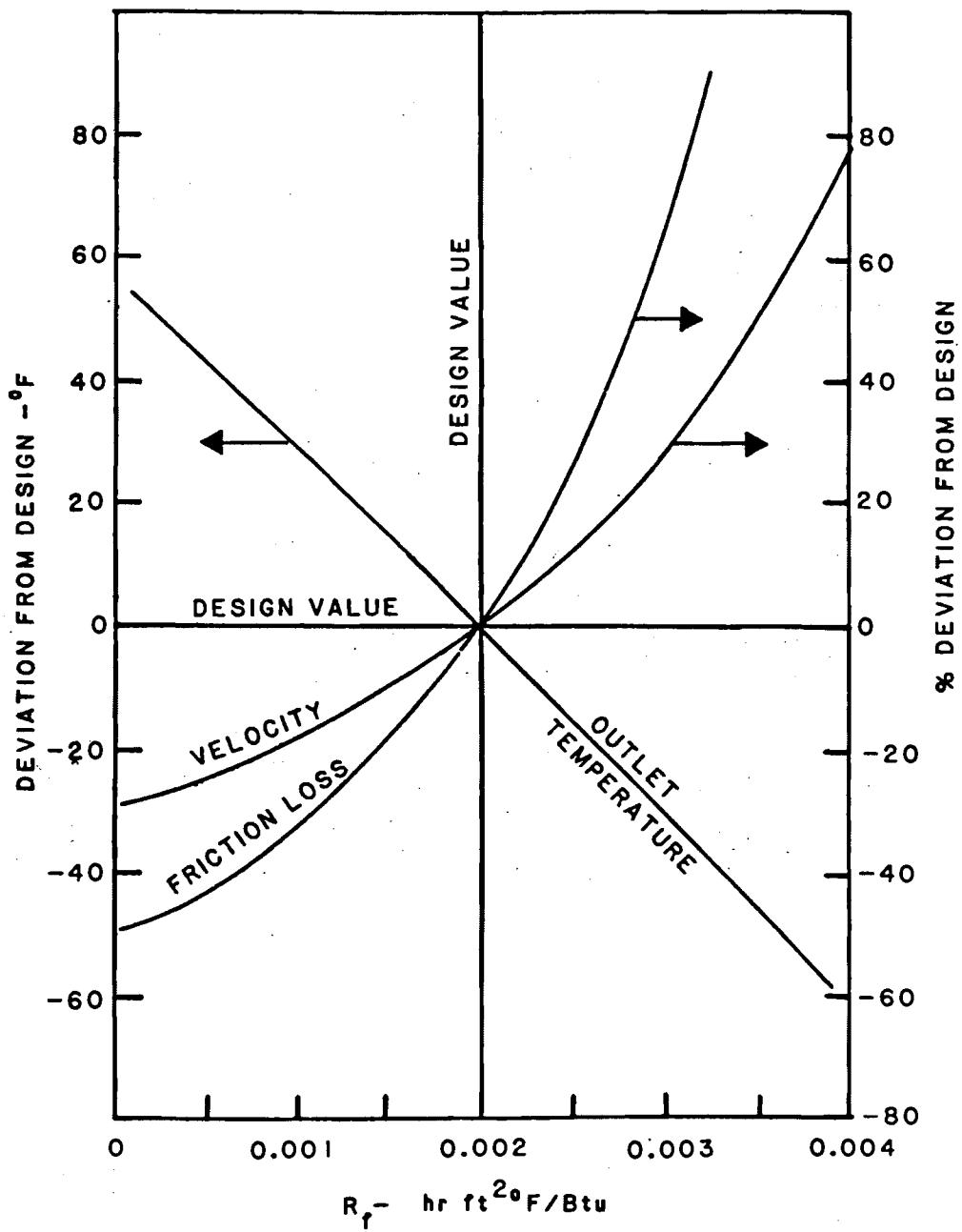


FIGURE 3. Effect of Fouling Resistance on Water Flow and Temperature for the Clean Exchanger in Figure 6

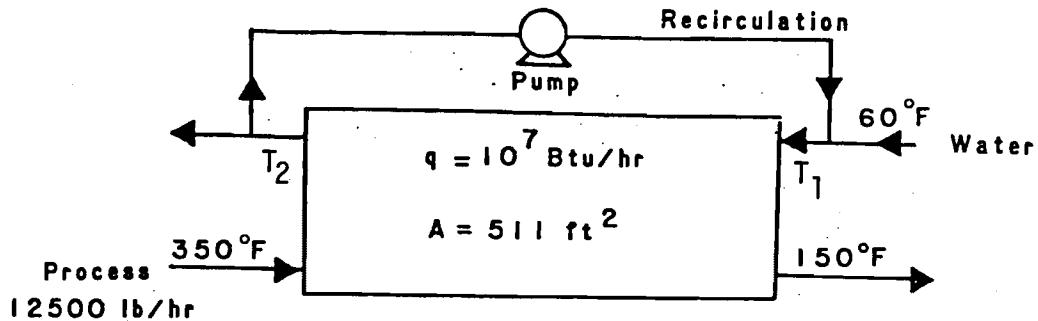


FIGURE 4. Illustrative Example of Figure 6 with Recirculation of the Water

Letting \dot{m}_R be the water recirculation rate and \dot{m}_F be the fresh water rate (at 60°F) entering the system ($\dot{m} = \dot{m}_R + \dot{m}_F$), then by an overall heat balance

$$\dot{m}_F C (T_2 - 60) = q$$

with $C = 1$

$$T_2 = \frac{10^7}{\dot{m}_F} + 60 \quad (6)$$

Likewise

$$(\dot{m}_F + \dot{m}_R)C (T_2 - T_1) = q$$

so

$$T_2 = \frac{10^7}{(\dot{m}_F + \dot{m}_R C)} + T_1 \quad (7)$$

Also with reference temperature of zero

$$\dot{m}_R C T_2 + \dot{m}_F C (60) = (\dot{m}_R + \dot{m}_F) C (T_1) \quad (8)$$

The log-mean-temperature driving force is

$$\Delta T_{LM} = \frac{(350-T_2) - (150-T_1)}{\ln\left(\frac{350-T_2}{150-T_1}\right)} \quad (9)$$

The rate equation is

$$q = U_0 A \Delta T_{LM}$$

Hence

$$U_0 (511) (\Delta T_{LM}) = 10^7 \quad (10)$$

Equations 5 through 10 may be solved by trial and error for various values of \dot{m}_R . The solution is more easily obtained by setting various values of T_2 and determining the values of T_1 , \dot{m}_R and \dot{m}_F . The results are tabulated below.

Recirculation Rate $16/\text{hr} \times 10^4$	Fresh Water Rate $1\text{b}/\text{hr} \times 10^{-14}$	Outlet Temperature $^{\circ}\text{F}$	Inlet Temperature $^{\circ}\text{F}$
0	5.1	258	60
1.2	5.6	240	75
2.3	5.9	230	108
3.6	6.3	220	119
5.3	6.7	210	127
7.8	7.1	200	133
11.5	7.7	190	138
17.9	8.3	180	142

The water flow rate, outlet temperature and average bulk temperature are shown in Figure 5 as a function of recirculation rate. It is noted that with recirculation, operation can be carried out at or above the design velocity, the result being that the average bulk temperature of the water is increased. The effect of maintaining velocity at or slightly above the design value may reduce the fouling tendency and results in slight increase in pumping power required. At high recirculation rates, the velocity is well above design value but a high cost penalty is paid for additional friction losses. The decision to use recirculation is an economic one that involves the additional capital cost of pumps and piping balanced against the advantage of perhaps significantly reducing the fouling in the heat exchanger.

Unfortunately, the quantitative effect of velocity and surface temperature on fouling are not well enough known that firm economic analyses can be made.

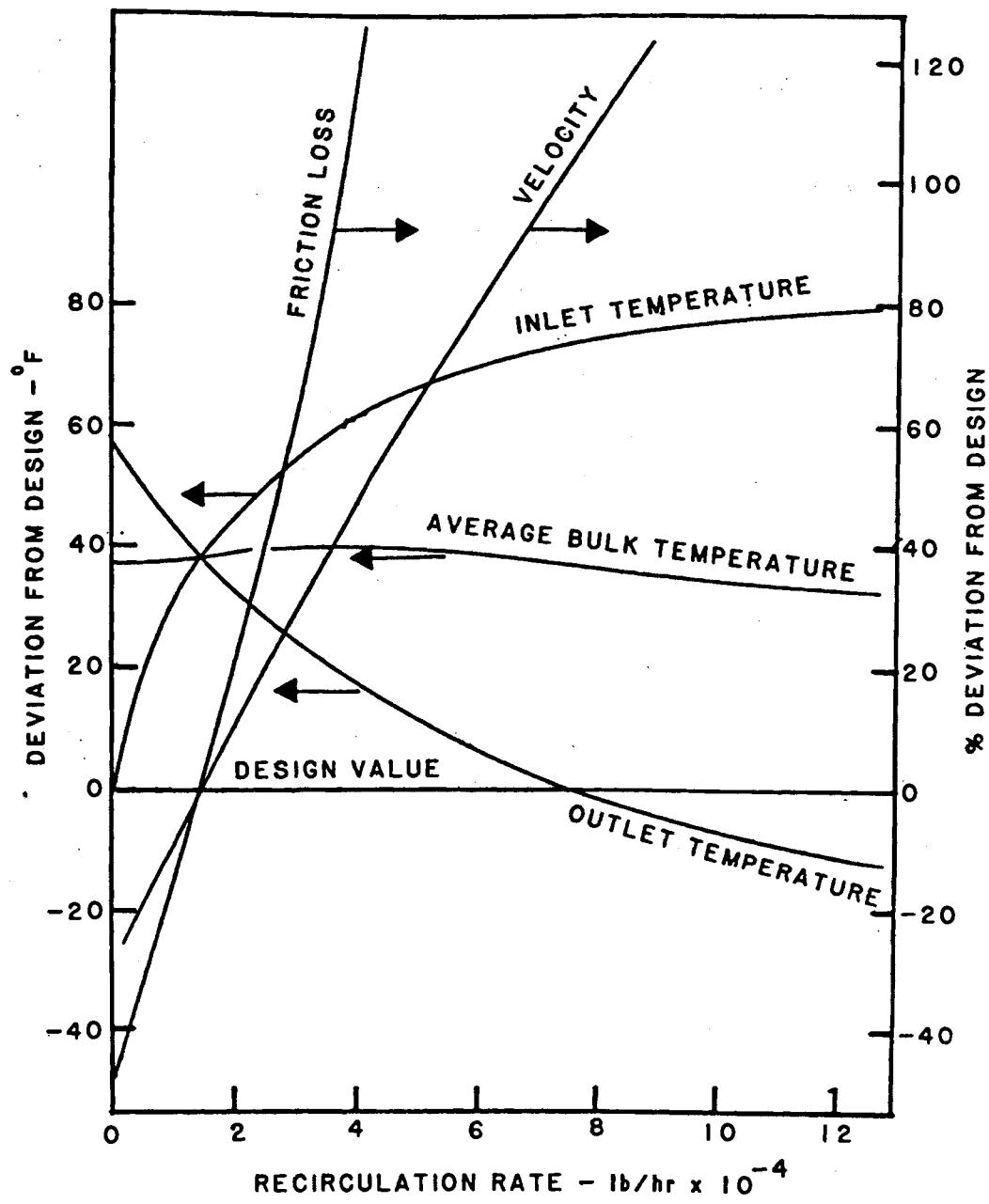


FIGURE 5. Effect of Recirculation Rate on Water Flow and Temperature for the Clean Exchanger in Figure 8

APPENDIX D

MANUFACTURERS AND SUPPLIERS OF EQUIPMENT FOR PREVENTING
AND MINIMIZING FOULING

APPENDIX D

MANUFACTURERS AND SUPPLIERS OF EQUIPMENT FOR PREVENTING AND MINIMIZING FOULING

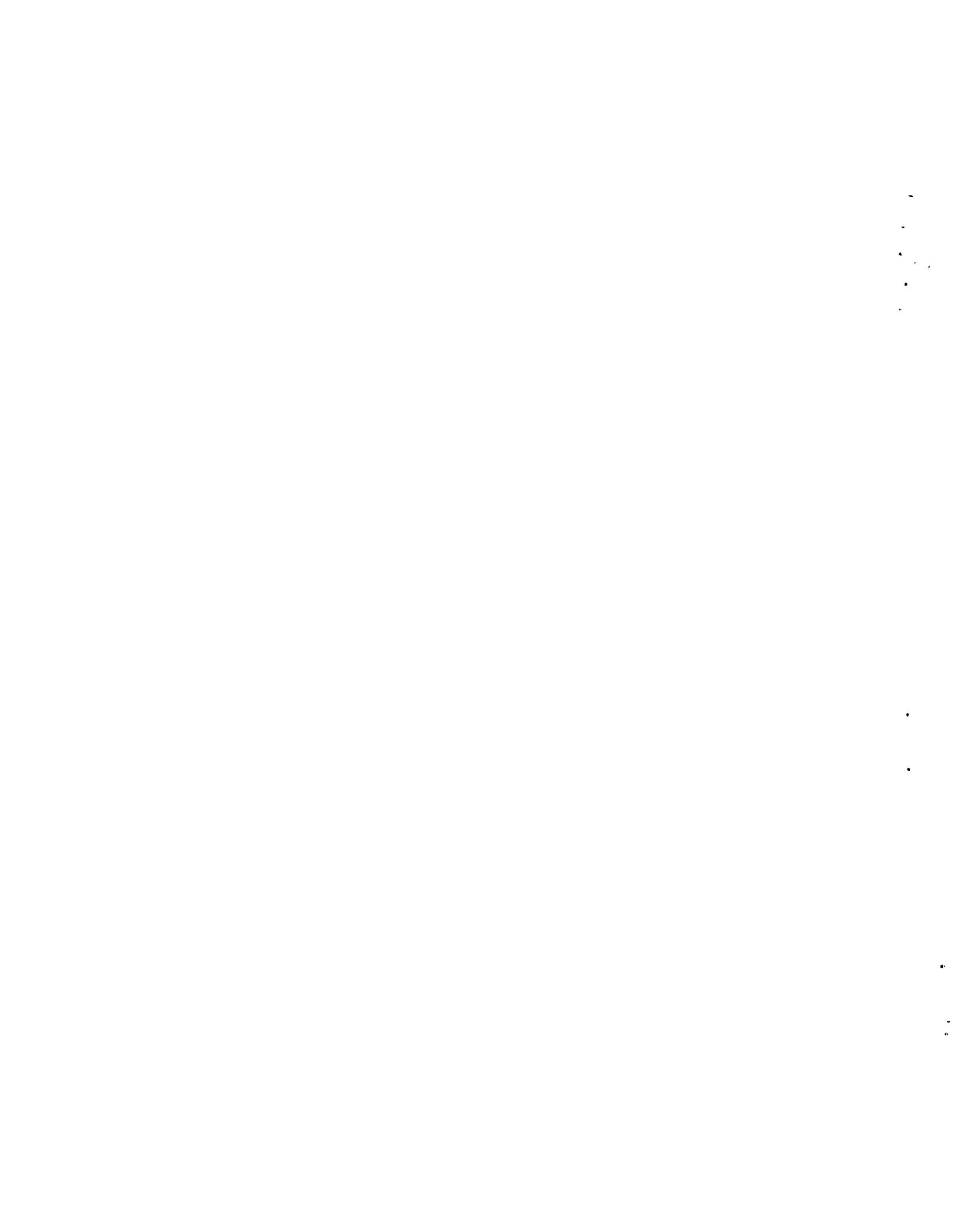
SPECIAL HEAT EXCHANGERS TO MITIGATE FOULING

09/26/83

COMPANY	ADDRESS	PHONE NUMBER
ACTIVE CHEMICAL SYSTEMS	16755 PARK CIRCLE DR., CHAGRIN FALLS, OH 44022	216-543-8197
AHLSTROM, ENG. WORKS DIV.	P.O. BOX 184, SF-78201 VARKAUS 20, FINLAND	358-72-211
ALFA-LAVAL, INC.	2115 LINWOOD AVE., FORT LEE, NJ 07024	201-592-7800
ALUMINUM-SCHWEISSWERK AG	BERNSTRASSE 63, CH-8952 SCHLIEREN, SWITZERLAND	01-730-88-44
APV EQUIPMENT, INC	395 FILLMORE AVE., TONAWANDA, NY 14215	716-692-3000
ARMSTRONG ENGR. ASSOC.	P.O. BOX 566, WEST CHESTER, PA 19380	215-436-6080
ASTRO METALURGICAL CO	3225 LINCOLN WAY W., WOOSTER, OH 44691	216-264-8639
BEPEX CORPORATION	333 NE TAFT STREET, MINNEAPOLIS, MN 55413	612-331-4370
BROWN FINTUBE COMPANY	PO BOX 2739, TULSA, OK 74101	918-584-2621
CARBONE USA CORPORATION	400 MYRTLE AVE. BOONTON, NJ 07005	201-334-0700
CERAMIC COATING CO.	P.O. BOX 370, NEWPORT, KY. 41072	606-781-1915
CHEMINEER, KENICS	45 SOUTH MAIN ST., DAYTON, OH 45401	513-229-7167
CHRISTIAN ENGINEERING	BLDG. 411, HUNTERS PT., SAN FRANCISCO, CA. 94124	415-822-1080
CORNING GLASS WORKS	CORNING, NY 14831	607-974-7221
CORNING PROCESS SYSTEMS	CORNING, NY 14831	607-974-9000
DENVER EQUIPMENT DIVISION	BOX 340, COLORADO SPRINGS, COLO 80901	303-471-3443
DURCO	9542 HARDPAN RD. ANGOLA, NY 14006	716-549-2500
LUDELL MFG. CO.	5200 WEST STATE ST., MILWAUKEE, WIS. 53208	414-476-9934
LUWA CO.	P.O. BOX 16348, CHARLOTTE, N.C. 28216	704-394-8341
O-I/SCHOTT PROCESS SYSTEM	1640 S.W. BOULEVARD, P.O. BOX T, VINELAND, NJ 08360	609-692-4700
PAUL MUELLER CO.	PO BOX 828, SPRINGFIELD, MO 65801	417-831-3000
T.B.M. TECHNOLOGIES INC.	778 CORNWALL, STATE COLLEGE, PA 16801	814-238-2663



APPENDIX E
FOULING AND CORROSION PATENT SEARCH SUMMARY



APPENDIX E

FOULING & CORROSION PATENT SEARCH SUMMARY

Class 106 COMPOSITIONS, COATING OR PLASTIC

Subclases 14.05-14.45: Corrosion Inhibiting Coating Composition

Search Dates: 1969-1982

Key Words: Heat Exchange

Class 110 FURNACES

Subclasses 341-345: Process for Treating Fuel Constituent or Combustion Product

Search Dates: 1969-1982

Key Words: Magnesium Oxide, Alumina Oxide, Ammonium Bicarbonate, Silica Oxide, Manganese Oxide

Class 148 METAL TREATMENT

Subclasses 6.11-6.35: Coating

Search Dates: 1969-1982

Key Words: Heat Exchange + (Fouling or Corrosion)

Class 165 HEAT EXCHANGE

Subclass 94: With Scraper Removing Product from Temperature Modifying Surface

Subclass 95: With Cleaning Means for Heat Exchanger

Search Dates: 1969-1982

Key Words: None (all patents in these subclasses)

Class 165 HEAT EXCHANGE

Subclass 133: With Coated, Roughened, or Polished Surface

Subclass 134R: With Protector or Protective Agent

Search Dates: 1969-1982

Key Words: Fouling or Corrosion

Class 252 COMPOSITIONS

Subclasses 71,73-79: Heat Exchange, Low-Freezing or Pour Point, or High Boiling Point Compositions (Organic Compounds)

Search Dates: 1969-1982

Key Words: Fouling or Corrosion

Class 252 COMPOSITIONS

Subclasses 80-87: Descaling Agent Containing

Search Dates: 1969-1982

Key Words: Heat Exchange

Class 252 COMPOSITIONS

Subclasses 387-396: Anti-Corrosion

Search Dates: 1969-1982

Key Words: Heat Exchange

**Class 422 PROCESS DISINFECTING, DEODORIZING, PRESERVING, OR
STERILIZING, AND CHEMICAL APPARATUS**

**Subclass 12-19: Maintaining Environment Nondestructive to
Metal (Aqueous acid, aqueous alkali, and
essentially pure water environments)**

Search Dates: 1969-1982

Key Words: Heat Exchange + (Fouling or Corrosion)

APPENDIX F

FOULING AND CORROSION MITIGATION PATENT LISTING AND DESCRIPTION OF DATA BASE



APPENDIX F
FOULING & CORROSION MITIGATION PATENT LISTING FIELD CODES

1. SECTOR FIELD

Sector	Interpretation
1	Private firm or Corporation
2	University, college, or medical school.
4	Government agency or laboratory
7	Individually owned patent - no assignee given. This suggests an independent inventor or that the employer does not chose to take title of the patent.

2. COUNTRY FIELD

01	UNITED STATES
54	WEST GERMANY
55	JAPAN
56	FRANCE
61	ITALY
67	SWITZERLAND
68	USSR
69	SWEDEN
72	HUNGARY
80	NETHERLANDS
85	UNITED KINGDOM
89	REPUBLIC OF SOUTH AFRICA
92	DENMARK
97	FINLAND
98	NORWAY

3. TYPE OF MITIGATION FIELD

TYPE	INTERPRETATION
01	Chemical Additives and Inhibitors used in either the process stream, cooling fluid, or fuel to prevent fouling or corrosion
02	Surface Coatings
03	Fouling/Scale Removal Techniques - continous or offline,physical/chemical
04	Materials Considerations - metallic or nonmetallic heat exchange components used to prevent fouling or corrosion
05	Design - Heat exchangers which operate in a manner to minimize theproblem or are designed for easier cleaning

FOULING & CORROSION PATENTS: ASSIGNEE ALPHABETICAL LISTING

PATENT#	ISSUED	FILED	TITLE	ASSIGNEE	SCOTTY EUNPE CTR TY O R
4279295	210781	141277	SCRAPED-SURFACE HEAT EXCHANGER	A.JOHNSON AND CO. LTD.	1 85 03
4207942	170680	260778	PLATE HEAT EXCHANGERS	A.P.V. COMPANY LIMITED	1 85 05
4194557	250380	040178	COOLER FOR MIXTURES OF CRYSTALS AND CRYSTALLIZING LIQUID IN THE PROD	AKTIESELSKABET DE DANSKE	1 92 03
4014383	290377	200175	METHOD OF HEATING HEAT EXCHANGER UNIT	ALFA-LAVAL AB	1 69 05
3805880	230474	240472	CIRCULATING COOLING SYSTEM	ALLIED CHEMICAL CORP.	1 01 03
3586487	220671	210469	APPARATUS FOR CONTINUOUSLY DIGESTING ALUMINA	ALUTERS ALUMINIUMIPARI TE	1 72 05
3463730	260869	050865	PREVENTION OF AND REMOVAL OF SCALE FORMATION IN WATER STREAMS	AMERICAN CYANAMID COMPANY	1 01 01
3585006	150671	061168	NON-PLUGGING REACTOR FOR TiO2 PRODUCTION	AMERICAN CYANAMID COMPANY	1 01 03
3706717	191272	010770	COPOLYMERS OF FUMERIC ACID AND ALLYL SULFONIC ACID	AMERICAN CYANAMID COMPANY	1 01 01
3842904	221074	150672	HEAT EXCHANGER	ARONETICS, INC.	1 01 05
4068709	170178	221075	DEVICE FOR CLEANING AND HEAT RECOVERY FROM THE EXHAUST GASES IN HEAT	ARTOS DR.-ING. MEIER WIND	1 54 05
4018262	190477	240275	HEAT EXCHANGE WITH GAS/SOLIDS MIXTURES	BAYER AKTIENGESELLSCHAFT	1 54 03
3951827	200476	031273	COMPOSITION AND METHOD FOR REMOVING INSOLUBLE SCALE DEPOSITS FROM SU	BORG-WARNER CORPORATION	1 01 03
4333516	080682	271178	CORRODIBLE CONTAINER FOR AUTOMATIC ADDITION OF CORROSION INHIBITOR T	BORG-WARNER CORPORATION	1 01 01
4338959	130782	291080	DEVICE TO AUTOMATICALLY ADD A CONTROLLED AMOUNT OF CORROSION INHIBIT	BORG-WARNER CORPORATION	1 01 01
4338997	130782	050181	HEAT EXCHANGER WITH BILAYERED METAL END CONTAINER FOR ANTICORROSION	BORG-WARNER CORPORATION	1 01 01
4347895	070982	050181	HEAT EXCHANGER WITH BILAYERED METAL END CONTAINER FOR ANTICORROSION	BORG-WARNER CORPORATION	1 01 01
3490926	200170	190766	CORROSION INHIBITION IN FUEL FIRED EQUIPMENT	CANADIAN PATENTS AND DEVE	1 59 02
4076072	280278	091075	MODULAR HEAT EXCHANGER WITH PIVOTAL CORES	CATERPILLAR TRACTOR CO.	1 01 05
4116265	260978	240677	HEAT EXCHANGER HAVING CONTROLLABLE CLEANING MEANS	CATERPILLAR TRACTOR CO.	1 01 05
4125147	141178	130677	METHOD FOR CONTINUOUSLY MAINTAINING A RADIATOR FREE OF DEBRIS	CATERPILLAR TRACTOR CO.	1 01 03
3666404	300572	051169	METHODS OF INHIBITING CORROSION IN AQUEOUS SYSTEMS WITH HIGH MOLECUL	CHEMED CORPORATION	1 01 01
3935125	270176	250674	METHOD AND COMPOSITION FOR INHIBITING CORROSION IN AQUEOUS SYSTEMS	CHEMED CORPORATION	1 01 01

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PATENT# ISSUED FILED	TITLE	ASSIGNEE	S CO TY E UN PE C TR T Y O R
4190421 260280 170778	FIRESIDE TREATING COMPOSITIONS	CHEMED CORPORATION	1 01 01
4245573 200181 151278	AIR HEATER CORROSION PREVENTION	CHEMED CORPORATION	1 01 01
4256703 170381 200978	FLY ASH COLLECTION	CHEMED CORPORATION	1 01 01
3430928 040369 030467	SCRAPING APPARATUS	CHEMETRON CORPORATION	1 01 03
4126177 211178 100377	DUAL SCRAPED SURFACE HEAT EXCHANGER	CHEMETRON CORPORATION	1 01 03
4185352 290180 100278	SCRAPED-SURFACE APPARATUS	CHEMETRON CORPORATION	1 01 03
3430451 040369 100767	COMPRESSION OF GASEOUS STREAMS CONTAINING CARBON MONOXIDE	CHEMICAL CONSTRUCTION COR	1 01 01
4308076 291281 090480	METHOD FOR CLEANING HEAT EXCHANGERS IN SITU	CHEVRON RESEARCH COMPANY	1 01 03
3835922 170974 210373	HEAT EXCHANGER FOR FLUENT MASSES	CHOCOLADE FABRIKEN LINDT	1 67 03
3633664 110172 081168	VERTICALLY ORIENTED SWEEP SURFACE HEAT EXCHANGER	CONITHERM CORPORATION	1 01 03
3476522 041169 161166	HIGH VISCOSITY REACTORS	CRAWFORD & RUSSELL INC.	1 01 03
4366003 281282 251180	APPARATUS AND PROCESS FOR THE PERIODIC CLEANING-OUT OF SOLIDS DEPOSITED ON HEAT EXCHANGER TUBES	DEGUSSA AKTIENGESELLSCHAFT	1 54 03
4018267 190477 100175	CLEANING HEAT EXCHANGER TUBES	DORR-OLIVER INCORPORATED	1 01 03
3526267 010970 120468	PROCESS FOR COOLING SUSPENDED TiO ₂ PARTICLES	E.I. DUPONT DE NEMOURS CO	1 01 03
3662817 160572 260570	PROCESS FOR ACCOMPLISHING HEAT EXCHANGE BETWEEN A CORROSIVE LIQUID AND A SOLID	P E.I. DUPONT DE NEMOURS CO	1 01 04
3801286 020474 031169	SLURRY POLYMERIZATION REACTOR	E.I. DUPONT DE NEMOURS CO	1 01 03
3545938 081270 160862	APPARATUS FOR PRODUCING AND PROCESSING VISCOS MATERIALS	EASTMAN KODAK COMPANY	1 01 03
4121656 241078 270577	HEADER	ECODYNE CORPORATION	1 01 05
4303122 011281 160879	FLUE HEAT RECOVERY DEVICE	ENTEC PRODUCTS CORP.	1 01 05
3587729 280671 290869	DOUBLE-WALLED TUBULAR HEAT EXCHANGER	ESCHER WYSS G.M.B.H	1 54 03
4075376 210278 110475	BOILER TUBE COATING AND METHOD FOR APPLYING THE SAME	EUTECTIC CORPORATION	1 01 02
3784676 080174 050668	REMOVING SULFUR FROM HYDROCARBONS	EXXON RESEARCH & ENGINEER	1 01 01
4002554 110177 081074	PROCESS OF MINIMIZING OR PREVENTING FOULING	EXXON RESEARCH & ENGINEER	1 01 03

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3884135 200575 090672 COOKING APPLIANCE		P. KUPPERBUSCH & SOHNE A	1 54 03
3549334 221270 261267 APPARATUS FOR FORMING A THIN FILM		FARBENFABRIKEN BAYER AKTI	1 54 03
3473896 211069 110866 APPARATUS FOR PREPARING ALKALI METAL SALTS OF AROMATIC HYDROXY COMPO	FAEWERKE HOECHST AKTIENG	1 54 03	
3827944 060874 240573 WAX CRYSTAL GROWTH CONTROL IN OIL DEWAXING PLANTS	FOSTER WHEELER CORP.	1 01 03	
3999600 281276 071074 HEAT TRANSFER SHIELDS	FOSTER WHEELER CORP.	1 01 05	
4282925 110881 260380 SCRAPED SURFACE HEAT EXCHANGER	FRANRICA MFG. INC.	1 01 03	
4279768 210781 040280 SERVICE DESCALER FOR AQUEOUS SYSTEMS	FREMONT INDUSTRIES, INC.	1 01 01	
4105066 080878 021176 HEAT EXCHANGER	FRYMA-MASCHINEN AG.	1 67 03	
4268586 190581 260675 CORROSION RESISTANT ZIRCONIUM ALLOY STRUCTURAL COMPONENTS AND PROCES	GENERAL ELECTRIC COMPANY	1 01 02	
4087371 020578 290774 METHOD OF PREVENTING INCRUSTATION ON HEATED SURFACES, AND COMPOSITIO	GRILLO-WERKE AKTIENGESELL	1 54 01	
4332295 010682 190580 COMPOSITE CERAMIC HEAT EXCHANGE TUBE	HAGUE INTERNATIONAL	1 01 04	
3639279 010272 010469 SCALE REMOVAL COMPOSITION AND METHOD USING SALT OF DIGLYCOLIC ACID A	HALLIBURTON COMPANY	1 01 03	
4098325 040778 060776 FLUID HEAT EXCHANGER	HAWLEY MANUFACTURING CORP	1 01 05	
3934857 270176 161173 MIXING AND HEAT TRANSFER APPARATUS	HEGE ADVANCED SYSTEMS COR	1 01 05	
3707442 261272 270270 MULTISTAGED FLASH EVAPORATOR AND METHOD OF OPERATING SAME WITH SPONG	HITACHI, LTD.	1 55 03	
3882931 130575 200373 MEANS FOR CLEANING HEAT CONDUCTIVE CONDUITS OF A HEAT EXCHANGER	HITACHI, LTD.	1 55 03	
4168743 250979 270177 HEAT EXCHANGING WALL AND METHOD FOR THE PRODUCTION THEREOF	HITACHI, LTD.	1 55 04	
4226283 071080 110877 MULTITUBULAR HEAT EXCHANGER	HITACHI, LTD.	1 55 05	
4304295 081281 180480 CLEANING BODY INTERCEPTING APPARATUS FOR TUBE-TYPE HEAT-EXCHANGER	HITACHI, LTD.	1 55 03	
4156617 290579 060575 PROCESS FOR PREPARING ORGANIC PIGMENTS OF HIGH TINTORIAL STRANO	HOECHST AKTIENGESELLSCHA	1 54 03	
4297236 271081 140978 WATER MISCIBLE CORROSION INHIBITORS	HOECHST AKTIENGESELLSCHA	1 54 01	
4033407 050777 020975 HEAT EXCHANGER CLEANING SYSTEM	HOOKER CHEMICALS & PLASTI	1 01 03	
3593781 200771 071169 DISTRIBUTING ARRANGEMENT FOR SHOT-FED SOOT CLEANING SYSTEMS	HUSQVARNA	1 69 03	

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3593779 200771 250869	HEAT EXCHANGER FOR QUENCHING THERMALLY CRACKED GAS	IDEMITSU PETROCHEMICAL CO	1 55 03
3818975 250674 130771	METHOD OF REMOVING CARBONACEOUS MATTER FROM HEAT EXCHANGE TUBES	IDEMITSU PETROCHEMICAL CO	1 55 03
4032748 280677 101075	SCALE DEPOSIT REMOVAL ARRANGEMENT FOR ELECTRIC WATER HEATERS AND VAP	INNOVATIVE PROCESS EQUIPM	1 01 03
4299272 101181 170579	INDUSTRIAL HEAT PIPE ENERGY RECOVERY PACKAGE UNIT	JAMES HOWDEN AMERICA, INC	1 01 05
3762464 021073 291271	HEAT EXCHANGER	JAPAN ENGIN. AND TRADING	1 55 03
4034803 120777 240775	CORROSION RESISTANT TUBULAR AIR PREHEATER	JOHN ZINK COMPANY	1 01 05
4244749 130181 241178	ULTRASONIC CLEANING METHOD AND APPARATUS FOR HEAT EXCHANGERS	JOHNS HOPKINS UNIVERSITY	2 01 03
4350202 210982 140879	EXTRACTOR FOR RECIRCULATING CLEANING BODIES IN A FLUID-CIRCULATION	S KLEIBER & SCHULZ, INC.,	1 01 03
4043758 230877 290673	APPARATUS FOR THE MANUFACTURE OF METALLIC CHLORIDES	LARCO SOCIETE MINIERE ET	1 56 03
4095307 200678 280676	SCRAPER FOR A VESSEL INTERIOR SURFACE	LOX EQUIPMENT COMPANY	1 01 03
3841397 151074 081173	HYDRODYNAMIC SORTING APPARATUS	LUDWIG TAPROGGE,REINIGUNG	1 54 03
4113008 120978 250377	APPARATUS FOR SEPARATING CLEANING ELEMENTS FROM A FLUID	LUDWIG TAPROGGE,REINIGUNG	1 54 03
4135574 230179 250377	DEVICE FOR RECOVERING CLEANING ELEMENTS FROM A HEAT-EXCHANGER STREAM	LUDWIG TAPROGGE,REINIGUNG	1 54 03
3590916 060771 210369	THIN FILM APPARATUS	LUWA AG	1 67 05
3628602 211271 130770	PROCESSING APPARATUS	MANNING'S INC.	1 01 03
4113890 120978 111275	METHOD OF COOKING A FLOWABLE FOOD PRODUCT IN A CONTINUOUS FLOW SCRAP	MARLEN RESEARCH CORP.	1 01 03
3722229 270373 291271	SMOOTH SURFACE CHILLER CRYSTALLIZER	MARUZEN OIL COMPANY	1 55 04
3473961 211069 310562	METHOD FOR CLEANING SURFACE CONDENSER AND HEAT EXCHANGER TUBES	MASCHINENFABRIK AUGSBURG-	1 54 03
4332143 010682 220180	DEVICE FOR COOLING A GAS TO BELOW ITS DEW POINT	MESSER GRIESHEIM GMBH	1 54 03
3602297 310871 220569	HEAT TRANSFER TUBE ASSEMBLY	METALLGESELLSCHAFT AG	1 54 04
3730486 010573 190471	HEAT EXCHANGING MIXER-REACTOR FOR HIGH VISCOSITY SUBSTANCES	MITSUBISHI JUKOGYO KABUSH	1 55 03
4257819 240381 230279	METHOD FOR FLUSHING OUT A NARROW GAP	MITSUBISHI JUKOGYO KABUSH	1 55 03
4173615 061179 240677	CHEMICAL APPARATUS FOR CORROSIVE MATERIALS	MITSUI TOATSU CHEMICALS	1 55 05

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4315541 160282 290879 DEVICE FOR SCRAPING OFF DEPOSITS FROM INTERNAL SURFACES OF ELONGATED MITSUI TOATSU CHAMICALS I	1 1 55 03		
3973623 100876 061274 HEAT EXCHANGE APPARATUS		MOBIL OIL CORPORATION	1 01 03
4095646 200678 100177 HEAT EXCHANGE STRUCTURE		MODINE MANUFACTURING CO.	1 01 05
4171722 231079 030277 HEAT RECOVERY SYSTEM		MODINE MANUFACTURING CO.	1 01 05
4175614 271179 010678 HEAT EXCHANGER DEVICE		MODINE MANUFACTURING CO.	1 01 03
3508882 280470 171167 STIRRED AUTOCLAVE		MONSANTO COMPANY	1 01 03
3634042 110172 240270 POLYMERIZATION VESSEL HAVING READILY REMOVABLE WORKING PARTS		MONSANTO COMPANY	1 01 05
3986950 191076 121274 RECOVERY OF CHROMATES BY MEMBRANE		MONSANTO COMPANY	1 01 03
4061695 061277 141175 PHOSPHATE ESTERS		NALCO CHAMICAL COMPANY	1 01 01
3974783 170876 220875 METHOD FOR IMPROVING SEWAGE SLUDGE INCINERATION		NALCO CHEMICAL COMPANY	1 01 01
4309297 050182 281180 HEAT STORAGE MATERIAL		NIPPON PETROCHEMICALS CO.	1 55 04
3726339 100473 131069 STEAM GENERATOR PROTECTOR		NORTH AMERICAN ROCKWELL	1 01 05
3789915 050274 070569 PROCESS FOR IMPROVING HEAT TRANSFER EFFICIENCY AND IMPROVED HEAT TRANSFER	OLIN CORPORATION		1 01 04
3809155 070574 020272 EROSION-CORROSION RESISTANT ALUMINUM RADIATOR CLAD TUBING		OLIN CORPORATION	1 01 04
3825443 230574 070672 COILED TUBE BLOWOUT PROCESS AND APPARATUS		OLIN CORPORATION	1 01 03
3850227 261174 070569 PROCESS FOR IMPROVING HEAT TRANSFER EFFICIENCY AND IMPROVED HEAT TRANSFER	OLIN CORPORATION		1 01 04
4182399 080180 151177 PROCESS FOR REMOVING HEAVY METAL IONS FROM AQUEOUS FLUIDS		OLIN CORPORATION	1 01 05
4246960 270181 260379 FAIL SAFE HEAT EXCHANGER		OLIN CORPORATION	1 01 05
4275784 300681 260379 FAIL SAFE HEAT EXCHANGER		OLIN CORPORATION	1 01 05
3809150 070574 160473 MINIMIZING CORROSION OF OVERFLOW RECEPTACLE EQUIPPED ENGINE COOLING	OPTI-CAP INC.		1 01 05
3627032 141271 120670 COOLING TOWER WATER TREATMENT SYSTEM		PARKER ENGINEERED CHEMICALS	1 01 03
3754741 280873 280971 WATER TREATMENT SYSTEM		PARKER ENGINEERED CHEMICALS	1 01 01
3521706 280770 220368 HEAT EXCHANGER WITH CLEANING MEANS		PHILLIPS PETROLEUM CO.	1 01 05

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3681308	010872	231266	STIRRED, SCRAPPED-SURFACE APPARATUS AND PROCESS FOR TREATING MATERIAL	PHILLIPS PETROLEUM CO.	1 01 03
4296800	271081	180480	WASTE HEAT RECOVERY	PHILLIPS PETROLEUM CO.	1 01 03
3777802	111273	100969	METHOD AND APPARATUS FOR TEMPERATURE CONTROL OF A ROTATING METAL OXI	PPG INDUSTRIES	1 01 03
3475258	281069	281266	REMOVAL OF ADHERING DEPOSITS FROM EXTERNALLY COOLED CONDUITS	PPG INDUSTRIES INC.	1 01 01
3544280	011270	250264	APPARATUS FOR THE PREPARATION IN MASS OF VINYL CHLORIDE POLYMERS	PRODUITS CHIMIQUES PECHIN	1 56 03
4176059	271179	080678	ANTI-CORROSION COMPOSITION FOR USE IN AQUEOUS SYSTEMS	QUATIC CHEMICALS LIMITED	1 59 01
3627488	141271	070769	CORROSION- AND EROSION-RESISTANT MATERIAL	RAYTHEON COMPANY	1 01 04
4193180	180380	020377	METHOD OF FORMING A HEAT EXCHANGER	RESISTOFLEX CORPORATION	1 01 02
4296804	271081	280679	CORROSION RESISTANT HEAT EXCHANGER ELEMENT AND METHOD OF MANUFACTURE	RESISTOFLEX CORPORATION	1 01 04
3629217	211271	280769	PROCESS AND APPARATUS FOR THE CONTINUOUS PREPARATION OF A SPINNABLE	RHONE-POULENC	1 56 03
3495951	170270	250766	SCREW REACTOR	SHIONOGI & CO. LTD.	1 55 05
3770252	061173	190670	APPARATUS FOR TREATING VISCOS LIQUIDS	SNAMPROGETTI S.P.A.	1 61 03
4317787	020382	111280	DEVICE FOR DISTRIBUTING A LIQUID IN THIN-FILM FORM IN VERTICAL HEAT-	SNAMPROGETTI S.P.A.	1 61 05
4231422	041180	240478	METHOD FOR PROTECTING HEAT EXCHANGER TUBES MADE OF ALUMINUM AGAINST	SOCIETE ANONYME DES USINE	1 56 02
4232729	111180	010678	AIR-COOLED HEAT EXCHANGER FOR COOLING INDUSTRIAL LIQUIDS	SOUTH AFRICAN COAL, OIL & I	1 89 05
3480404	251169	290466	APPARATUS FOR REACTING POLYMERIC MATERIAL	STANDARD OIL CO., INDIANA	1 01 03
4258018	240381	261279	PROCESSING ELEMENTAL PHOSPHORUS (P4) CONTAINING GAS STREAMS	STAUFFER CHEMICAL COMPANY	1 01 01
3647687	070372	020770	PROCESS OF CONDITIONING SEWAGE SLUDGE IN SYSTEM WITH BY-PASS VALVE	S STERLING DRUG, INC.	1 01 03
4139461	130279	271277	REMOVAL OF SOLIDS FROM A WET OXIDATION REACTOR	STERLING DRUG, INC.	1 01 03
4143702	130379	270875	REVERSE FLOW HEAT EXCHANGERS	STERLING DRUG, INC.	1 01 03
4217218	120880	271277	REMOVAL OF SOLIDS FROM A WET OXIDATION REACTOR	STERLING DRUG, INC.	1 01 03
4203490	200580	201078	HEAT EXCHANGER CORE HAVING FIN MEMBERS SERVING AS SACRIFICIAL ANODES	SUMITOMO LIGHT METAL IND.	1 55 05
4317484	020382	120680	HEAT EXCHANGER CORE	SUMITOMO LIGHT METAL IND.	1 55 05

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3731339 080573 290971 SCRAPPER ASSEMBLY FOR PROCESS VESSELS		SUN OIL COMPANY	1 01 03
4025362 240577 310376 APPARATUS FOR CLEANING THE HEAT EXCHANGING SURFACES OF THE HEAT TRAN SVENSKA ROTOR MASKINER AK	1 69 03		
4141754 270279 100577 APPARATUS AND METHOD FOR CLEANING THE HEAT EXCHANGING SURFACES OF TH SVENSKA ROTOR MASKINER AK	1 69 03		
3878871 220475 121173 CORROSION RESISTANT ALUMINUM COMPOSITE		SWISS ALUMINUM LTD.	1 67 04
3960208 010676 131274 PROCESS FOR PROVIDING HEAT TRANSFER WITH RESISTANCE TO EROSION-CORRO	SWISS ALUMINUM LTD.	1 67 04	
4209059 240680 111278 CREVICE-CORROSION RESISTANT ALUMINUM RADIATOR TRICLAD COMPOSITE		SWISS ALUMINUM LTD.	1 67 04
4283807 180881 280979 CLEANING OF HEAT EXCHANGERS COMPOSED OF TUBES		TECHNOS	1 56 03
4291753 290981 070279 SCRAPER ASSEMBLY FOR USE WITH A FLUIDIZED BED CONDENSER		TELEDYNE INDUSTRIES, INC.	1 01 03
3714979 060273 250871 CLEANING ALUMINUM HEAT EXCHANGE SURFACES		TEXACO, INC.	1 01 03
4178758 181279 210676 PARTIAL OXIDATION PROCESS		TEXACO, INC.	1 01 05
4184322 220180 210676 PARTIAL OXIDATION PROCESS		TEXACO, INC.	1 01 05
3730259 010573 020372 HOT-SPOT DETECTOR FOR HEAT EXCHANGER		THE AIR PREHEATER COMPANY	1 01 03
4054174 181077 180374 METHOD OF INHIBITING DEPOSITION OF INTERNAL CORROSION PRODUCTS IN TU	THE BABCOCK & WILCOX CO.	1 01 02	
4120350 171078 270871 TUBE SUPPORT STRUCTURE		THE BABCOCK & WILCOX CO.	1 01 05
4158387 190679 240478 BLOWDOWN APPARATUS		THE BABCOCK & WILCOX CO.	1 01 05
4209028 240680 290579 LANCE CONSTRUCTION FOR BOILER CLEANING APPARATUS		THE BABCOCK & WILCOX CO.	1 01 03
3955617 110576 091274 SWEPT SURFACE HEAT EXCHANGER WITH DUAL HEAT EXCHANGE MEDIA		THE DE LAVAL SEPARATOR CO	1 01 03
4073339 140278 061276 SWEPT SURFACE HEAT EXCHANGER		THE DE LAVAL SEPARATOR CO	1 01 03
4324757 130482 020779 HALOGENATED HYDROCARBONS INHIBITED AGAINST DENICKELIFICATION WITH LO	THE DOW CHEMICAL COMPANY	1 01 01	
4299562 101181 290579 HEATED CHAMBER WALLS		THE ENERGY EQUIPMENT CO.	1 85 05
4079782 210378 141174 SELF CLEANING HEAT EXCHANGER CIRCUIT		THE LESLIE COMPANY	1 01 03
4208220 170680 150578 METHOD AND APPARATUS FOR CLEANING HEAT EXCHANGER TUBES MOUNTED TRANS	THE RESEARCH CORP. OF U.H	2 01 01	
4338363 060782 170281 METHOD FOR INHIBITING THE FORMATION OF SCALE		THE RESEARCH FND OF U.N.Y	2 01 02

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4276927	070781	040679	PLATE TYPE HEAT EXCHANGER	THE TRANE COMPANY	1 01 05
3872920	250375	250274	DESCALING SYSTEM FOR THE COOLING TUBES OF A STEAM CONDENSER	TOKYO SHIBAURA ELECTRIC C	1 55 03
3919732	181175	241074	DESCALING SYSTEM FOR CONDENSER COOLING TUBES	TOKYO SHIBAURA ELECTRIC C	1 55 03
3978917	070976	050974	DESCALING SYSTEM FOR THE COOLING WATER TUBES OF A STEAM CONDENSER	TOKYO SHIBAURA ELECTRIC C	1 55 03
4351277	280982	230181	SOOTBLOWER FOR ECONOMIZER	TRANTER, INC.,	1 01 05
4029142	140677	191175	HEAT EXCHANGER	U.S. PHILLIPS CORPORATION	1 01 05
4237090	021280	151178	METHOD FOR INHIBITING CORROSION IN AQUEOUS SYSTEMS	U.S.A. DEPT. OF ENERGY	4 01 01
4253408	030381	240879	METHOD OF PROTECTING INCINERATOR SURFACES	U.S.A. SEC. OF THE NAVY	4 01 01
4266601	120581	130979	HEAT EXCHANGER FOR CONTAMINATED WATER	U.S.A. SEC. OF THE NAVY	4 01 03
3426838	110269	210267	DRYING APPARATUS FOR DRYING MOIST ORGANIC OR INORGANIC MATERIALS	UNASSIGNED OR INDIVIDUAL	7 98 03
3434532	250369	230367	HEAT EXCHANGER FOR WASTE HEAT RECOVERY	UNASSIGNED OR INDIVIDUAL	7 69 05
3489209	130170	180566	HEAT EXCHANGER HAVING PLASTIC AND METAL COMPONENTS	UNASSIGNED OR INDIVIDUAL	7 01 04
3534805	201070	170668	METHOD OF CLEANING THE GAS-SWEPT HEATING SURFACES IN HEAT EXCHANGERS	UNASSIGNED OR INDIVIDUAL	7 69 03
3588061	280671	200669	APPARATUS FOR THERMAL TREATMENT OF FREE-FLOWING MATERIALS AND SLURRY	UNASSIGNED OR INDIVIDUAL	7 68 03
3621506	231171	141069	SCRAPER BLADE MOUNTING ARRANGEMENT	UNASSIGNED OR INDIVIDUAL	7 01 03
3641783	150272	290770	SCRAPER ASSEMBLY AND MATERIAL RETARDER FOR A CYLINDRICAL CONTINUOUS	UNASSIGNED OR INDIVIDUAL	7 01 03
3799746	260374	060268	APPARATUS FOR MANUFACTURING ANHYDROUS ALUMINUM CHLORIDE	UNASSIGNED OR INDIVIDUAL	7 01 03
3825064	230774	261262	HEAT EXCHANGER	UNASSIGNED OR INDIVIDUAL	7 55 04
3827343	060874	120571	GREASE-COLLECTING HEAT EXCHANGER INSTALLATION	UNASSIGNED OR INDIVIDUAL	7 01 03
3835817	170974	210872	APPARATUS FOR OUTSIDE CLEANING OF BOILER TUBES	UNASSIGNED OR INDIVIDUAL	7 97 03
3846986	121174	270871	GEOTHERMAL PLANT CLEANING SYSTEM	UNASSIGNED OR INDIVIDUAL	7 01 03
3957110	180576	160175	CONTINUOUS PROCESS DRYER	UNASSIGNED OR INDIVIDUAL	7 85 03
3982588	280976	120572	GREASE-COLLECTING HEAT EXCHANGER INSTALLATION	UNASSIGNED OR INDIVIDUAL	7 01 03

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3997001 141276 170475 HEAT ENERGY RESERVOIR USING SOLID REMOVAL AND GRAVITATION SETTLING	UNASSIGNED OR INDIVIDUAL	7 01 03	
4008758 220277 170475 INTERMITTENT ENERGY INPUT SALT BATH CHAMICAL PROCESSOR	UNASSIGNED OR INDIVIDUAL	7 01 03	
4054175 181077 131273 GEOTHERMAL POWER SYSTEM	UNASSIGNED OR INDIVIDUAL	7 01 01	
4064931 271277 240975 FUSION-TYPE THERMAL STORAGE ACCUMULATOR WITH DISCHARGING APPARATUS	UNASSIGNED OR INDIVIDUAL	7 54 05	
4095349 200678 081076 HEAT EXCHANGER FOR CLOTHES DRYER	UNASSIGNED OR INDIVIDUAL	7 01 05	
4098095 040778 210576 REFRIGERATION APPARATUS FOR VISCOUS PASTE SUBSTANCE	UNASSIGNED OR INDIVIDUAL	7 01 03	
4100887 180778 191176 IMPROVEMENTS IN OR RELATING TO BOILERS	UNASSIGNED OR INDIVIDUAL	7 69 05	
4105042 080878 290377 SOLAR HEATING METHOD AND APPARATUS	UNASSIGNED OR INDIVIDUAL	7 01 05	
4112702 120978 130177 FREEZE DESALINATION AND CONCENTRATION APPARATUS	UNASSIGNED OR INDIVIDUAL	7 68 03	
4119139 101078 170576 HEAT-EXCHANGER COMPRISING A SYSTEM OF GRANULATE CONTAINING VERTICAL	UNASSIGNED OR INDIVIDUAL	7 80 05	
4120699 171078 071174 METHOD FOR ACOUSTICAL CLEANING	UNASSIGNED OR INDIVIDUAL	7 01 03	
4135534 230179 010877 MULTI-NOZZLE MULTIPLE LANCE FOR WASHING ROTATING HEAT EXCHANGERS AND	UNASSIGNED OR INDIVIDUAL	7 61 03	
4174750 201179 180478 TUBE CLEANER HAVING ANCHORED ROTATABLE SPIRAL MEMBER	UNASSIGNED OR INDIVIDUAL	7 01 03	
4185080 220180 020878 METHOD OF REDUCING THE SULFUR OXIDE CONTENT OF COMBUSTION GASES RESU	UNASSIGNED OR INDIVIDUAL	7 54 01	
4206742 100680 170578 HEAT EXTRACTOR AND SHIELD FOR ROOM STOVES AND THE LIKE	UNASSIGNED OR INDIVIDUAL	7 01 05	
4215741 050880 030878 HEAT EXCHANGER	UNASSIGNED OR INDIVIDUAL	7 01 05	
4224982 300980 081178 TUBULAR HEAT EXCHANGER	UNASSIGNED OR INDIVIDUAL	7 67 05	
4225362 300980 090977 METHOD FOR CLEANING THE INTERIOR OF TUBES	UNASSIGNED OR INDIVIDUAL	7 01 03	
4234993 251180 270178 CONDENSER CLEANING SYSTEM USING SPONGE BALLS	UNASSIGNED OR INDIVIDUAL	7 01 03	
4237962 091280 110878 SELF-CLEANING HEAT EXCHANGER	UNASSIGNED OR INDIVIDUAL	7 01 03	
4274845 230681 120778 AIR-CLEANING HEAT-EXCHANGE APPARATUS	UNASSIGNED OR INDIVIDUAL	7 01 03	
4287938 080981 070979 METHOD FOR EXCHANGING HEAT AND A DEVICE FOR CARRYING OUT SAID METHOD	UNASSIGNED OR INDIVIDUAL	7 69 05	
4295519 201081 131179 HEAT RECLAIMER	UNASSIGNED OR INDIVIDUAL	7 01 03	

FOULING & CORROSION PATENTS: ASSIGNEE ALPHABETICAL LISTING

PATENT# ISSUED FILED	TITLE	ASSIGNEE	S CO TY E UN PE C TR T Y O R
4296780 271081 280280 APPARATUS INCLUDING THROTTLING DEVICE FOR USE IN VENTILATION DUCT	UNASSIGNED OR INDIVIDUAL	7 69 05	
4300625 171181 211076 PREVENTING DEPOSITION ON THE INNER SURFACES OF HEAT EXCHANGE APPARAT	UNASSIGNED OR INDIVIDUAL	7 68 03	
4305455 151281 280279 MULTIPASS CORROSION PROOF AIR HEATER	UNASSIGNED OR INDIVIDUAL	7 68 05	
4308990 050182 170180 FLUE GAS HEAT RECOVERY SYSTEM	UNASSIGNED OR INDIVIDUAL	7 01 05	
4310029 120182 270278 EXPANDABLE TUBE PLUG	UNASSIGNED OR INDIVIDUAL	7 01 05	
4312919 260182 160180 PROCESS OF PRODUCING A NON-AGGLOMERATING VANADIUM COATED PARTICLE	UNASSIGNED OR INDIVIDUAL	7 01 01	
4314604 090282 200979 APPARATUS FOR THE SEGREGATION OF WORN-OUT CLEANING BODIES	UNASSIGNED OR INDIVIDUAL	7 54 03	
4330032 180582 120381 SELF-CLEANING SCREW CONVEYOR	UNASSIGNED OR INDIVIDUAL	7 01 03	
4332292 010682 090580 COIL CLEANING DEVICE AND SYSTEM	UNASSIGNED OR INDIVIDUAL	7 01 03	
4341262 270782 050580 ENERGY STORAGE SYSTEM AND METHOD	UNASSIGNED OR INDIVIDUAL	7 01 02	
4351387 280982 080780 SIEVE ASSEMBLY FOR CLEANING BODIES AND HEAT EXCHANGER SYSTEM INCLUDI	UNASSIGNED OR INDIVIDUAL	7 01 03	
3505244 070470 300465 ENCAPSULATED CORROSION INHIBITOR	UNION CARBIDE CORPORATION	1 01 01	
3773651 201173 240172 CRUDE OIL HEAT EXCHANGE	UNIVERSAL OIL PRODUCTS CO	1 01 05	
4102393 250778 230975 HEAT EXCHANGE APPARATUS	UOP INC.	1 01 05	
4036594 190777 161274 APPARATUS FOR RECOVERING HIGHER MELTING ORGANIC MATERIALS VIA FRACTI	VERBA-CHEMIE AG	1 54 05	
3705766 121272 231170 CORROSION INHIBITION WITH METHYLENE BIS-BENZOIC ACID	VENTRON CORPORATION	1 01 01	
4055218 251077 230874 METHOD AND ARRANGEMENT FOR CHANGING THE TEMPERATURE OF FLUIDS WHICH	VEREINIGE ALUMINUM-WERKE	1 54 05	
3679477 250772 200870 CHAMBER CLEANING DEVICE AND METHOD	W.R. GRACE & CO.	1 01 03	
4124065 071178 041176 APPARATUS FOR CLEANING HEAT EXCHANGER TUBES	WATER SERVICES OF AMERICA	1 01 03	
4269264 260581 030778 CLEANING OF HEAT EXCHANGER TUBING	WATER SERVICES OF AMERICA	1 01 03	
4353414 121082 210880 HEAT EXCHANGER TUBE CLEANING	WATER SERVICES OF AMERICA	1 01 03	
4047972 130977 230976 METHOD FOR THERMALLY DE-SOOTING HEAT TRNSFER SURFACES	WESTINGHOUSE ELECTRIC COR	1 01 03	
3921708 251175 071070 HEAT EXCHANGER AND MEHTOD OF OPERATION THEREOF	YGNIS S.A.	1 67 05	



APPENDIX G
INFORMATION FROM HEAT EXCHANGER MANUFACTURERS



SUMMARY OF HEAT EXCHANGER MANUFACTURERS

COMPANY	INDUSTRY	MOST SERIOUS	PROBLEM TYPE	FOULIN G FACTOR	OVERSI ZING	SPECIAL MAT'L'S	CLEANING EQUIP.	SPECIA L COSTS	CLEANI NG COSTS	OVERSI ZE COSTS	DESIGN CONSIDERATIONS	COSTS OF DESIGN	TEMA ST'D
AIR PREHEATER CO.	UTILITY, STEEL, ALUM., GLASS	ALUM., GLASS	PARTICULAT E, CORROSIO	VARIABLES	20%	STAINLESS STEEL	SOOTBLOWER S	50-100	50%	15-20%		5-50%	
ALPHA LAVAL	CHEM, HVAC	CHEM, HVAC	PART. BIOLOGICAL	0	10-20%	STAINLESS STEEL	BACK FLUSH	50%	25-50%		SPIRAL - INCREASE CHANNEL SPACING TO INCREASE VELOCITY.		ASME
AMERICAN SCHACK CO	CHEMICAL, STEEL	CHEMICAL, STEEL	PARTICULAT E, CORRO.	.001	5-10%	NI, SS	SOOTBLOWER S	VARIABLES	5%	5-10%	FLUE GAS THRIUGH TUBE SIDE VS. OUTSIDE.		YES
AMERICAN STANDARD HEAT TR	NAVY, COOLERS	OIL COOLERS	SCALING, PARTICULAT E	.001	10-20%	NO				5-10%	NO		YES
APV CO. INCORPORATED	CHEM. FOOD	FOOD	PART., CORROSION	PLATE	10-20%	SS, TITANIUM	CHEMICALS	VARIABLES	VARIABLES				YES
BABCOCK & WILCOX	COAL & OIL	COAL & OIL	CORROSION								BALANCE FLOW.		
BABCOCK & WILCOX	STEEL, PULP & PAPER, PETRO	FUEL DEPENDENT COAL	PARTICULAT E, CORRO.	VARIABLES	10%	SS, CR, NI	VIBRATION	10%	10%		MODULARIZED CONSTRUCTION		ASME
CHEMETRON PROCESS EQUIP.	FOOD, CHEMICALS	FOOD, CHEMICALS	FREEZING	USE "U"	NONE	CS, SS, NI	SCRAPERS		80%				ASME
CHESTER JENSEN CO.	DAIRY	DAIRY	BURN ON	NONE	5%	STAINLESS STEEL	CHEM CLEAN						
COMBUSTION ENGINEERING	PETRO CHEM, PHARM	REFINING	PARTICULAT E	.002	30%	NO	NO			30%	REMOVABLE TUBES VS. FIXED TUBES	20%	YES
CORNING GLASS WORKS	CHEM PROCESS, PHARM.	FOOD	PARTICULAT E, CORROSIO	NONE	NONE	GLASS	SPRAY WASH	30%>	5-10%				NA
DELTAK CORP.	PETRO CHEM, STEEL, CHEM	CHEM	PART., CORROSION	.001-.05	30%		SOOT BLOWERS		5-15%	VARIABLES	REMOVABLE BUNOLES THAT DOUBLE THE PRICE OF THE SYSTEM.		ASME
DUPONT DE NEMOURS	SULFURIC ACID	SULFURIC ACID	CORROSION, PARTICULA	0	?	TEFLONS	NO CLEANING						
ECODYNE CORP. MRM DIVISION	REFINERIES, CHEM	CHEMICALS	PART. CORR. SCALE	.002	25-30%	CU, TITANIU M	SOOT BLOWERS	100%	VARIABLES		REDUCE FOULING BY KEEPING FLUID VEL. AT 6-7 FT/SEC.		API

SUMMARY OF HEAT EXCHANGER MANUFACTURERS

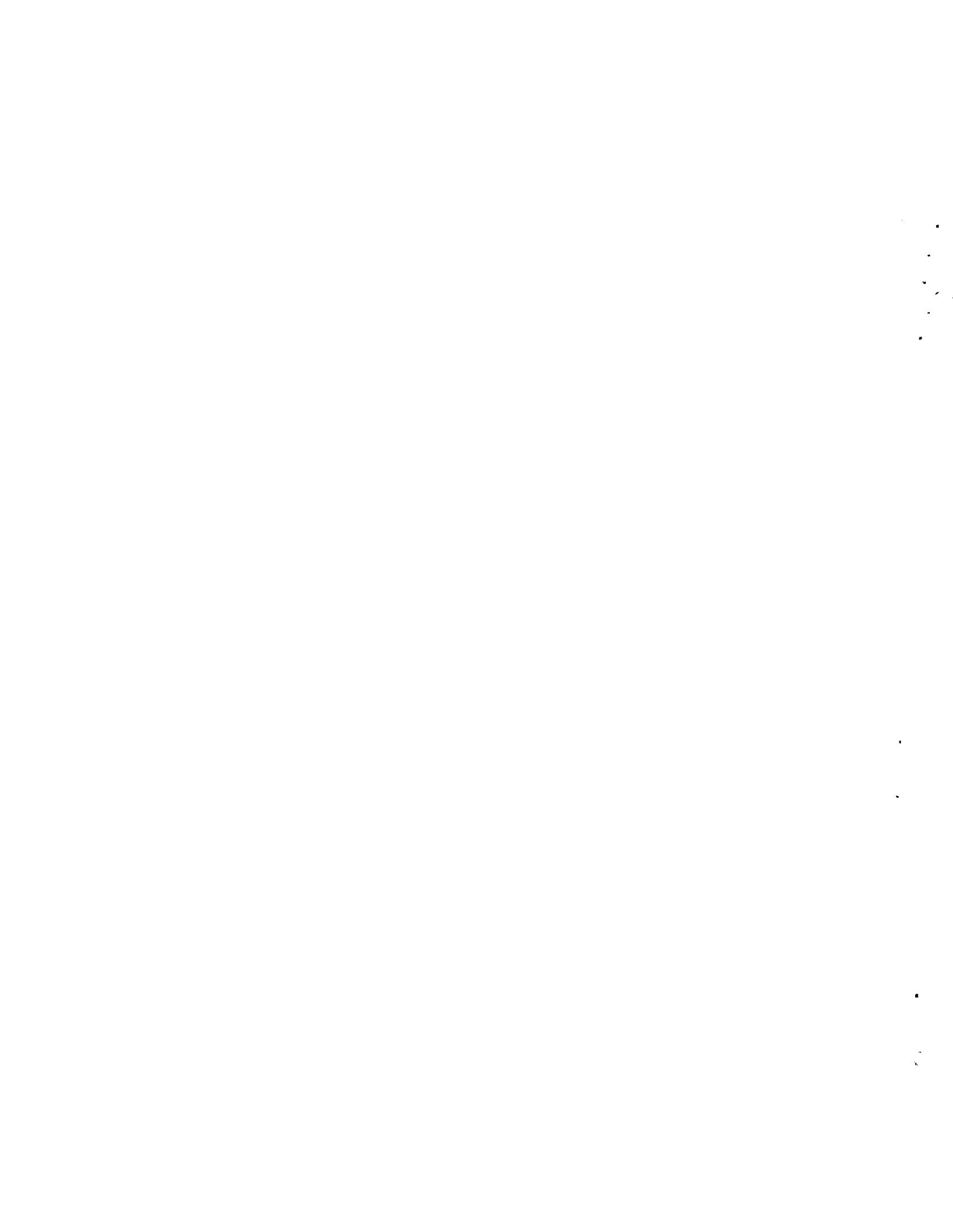
COMPANY	INDUSTRY	MOST SERIOUS	PROBLEM TYPE	FOULIN G FACTOR	OVERSI ZING	SPECIAL MAT'L'S	CLEANING EQUIP.	SPECIA L COSTS	CLEANI NG COSTS	OVERSI ZE COSTS	DESIGN CONSIDERATIONS	COSTS OF DESIGN	TEMA ST'D
HENRY VOGT	CHEM, PETRO-CHEM.	BOTH	PART.BIO.S CALING	VARIABLES	15%	NONE	INVESTIGAT ING			15%	USE SCRAPED SURFACES, REMOVABLE TUBE BUNDLES-ADD 20-25% COST	20%	YES
HUGHES ANDERSON ENG. CO.	90 % OIL REFINING	PLUGGING, HIGH WATER TEMP.	PARTICULAT E	.002	15-25%	SOME	FLOATING HEAD	15-25%			FLOATING HEAD	15-25%	YES-R
JOHNSON BOILER	INCINERATORS	INCINERATO RS	PARTICULAT E	90%	15%	NONE	SOOTBLOWERS				MAKE SPACE FOR ADDING SOOTBLOWERS.		
KEARNEY INDUSTRIES INC.	CHEM PROCESS, PHARMACEUTIC	PHARM.	PARTICULAT E, CORROSIO	?	25-100		NO				PROCESS SIDE-BORE OUT TUBES, NOTHING ON SHELL SIDE		YES
KILLEBREW ENGINEERING	TURBINE	TURBINE	PARTICULAT E	?	15%	CARBON STEEL	SOOTBLOWERS			15%	MAKE SPACE FOR SOOTBLOWERS.		
MARLEY COOLING TOWER CO.	OIL, CHEM, FOOD, COOLING	FOOD INDUSTRY	BIOLOGICAL	NONE	DON'T	WOOD, PVC	HOSE						NO
MARLEY COOLING TOWER CO.	REFINING PETRO-CHEM	REFINING-HI VISCOSITY	PARTICULAT E	.002	VARIABLES	STAINLESS STEEL	SOLVENTS&C HEM	10-150		VARIABLES	PLUG HEADERS OR REMOVABLE HEAD FOR CLEANING		NA
RILEY BRAIRD INC.	GAS TURBINES	GAS TURBINES	PART., CORROSION	.005-01	NONE	ALUMINA ALLOY	SOOT BLOWERS	50-100	20%		ALL EXCHANGER DESIGNED TO BE DISSASSEMBLED		ASME
STRUTHERS WELLS CORP.	REFINERIES, FERTILIZER	REFINING	PARTICULAT E, CORROSIO	.002	10-20%	TITANIUM SS	NONE	50-100	0	25-30%	REMOVABLE TUBE BUNDLES VS. FIXED SHEETS	20%	R&C
THE CARBORUNDUM CO.	CHEM PROCESS	PHOSPHATE	PARTICULAT E CORROSIO	.002	VARIABLES	GRAPHITE	NO				REMOVABLE TUBE BUNDLES.	20%	YES
TRANTER INC.	PETRO, FOOD, CHEM.		CORROSION, PART.	NONE	NONE	STAINLESS TITAN	BACKWASH&C HEM				NO		
UNION CARBIDE CORP.	PHAR. CHEM., PLASTIC, FERT.	FERTILIZER	PARTICULAT E, CORROSIO	.003	40%	GRAPHITE	CHEMICAL CLEAN						YES
VOSS FINNED TUBE	CHEMICAL	CHEMICAL	CORROSION	.005	LITTLE	NONE	SOOTBLOWERS			20%	MAKE SPACE FOR ADDING SOOTBLOWERS.		ASME

SUMMARY OF HEAT EXCHANGER MANUFACTURERS

COMPANY	INDUSTRY	MOST SERIOUS	PROBLEM TYPE	FOULIN G FACTOR	OVERSI ZING	SPECIAL MAT'L'S	CLEANING EQUIP.	SPECIA L COSTS	CLEANI NG COSTS	OVERSI ZE COSTS	DESIGN CONSIDERATIONS	COSTS OF DESIGN	TEMA ST'D
YUBA HEAT TRANSFER CORP.	PETRO CHEMICALS	REFINING	PART. CORROSION	.001	<10%	SS, TITANIUM	NONE	15-75%		10%	REMOVABLE TUBE BUNDLES.	30-40%	YES



APPENDIX H
INDUSTRY SURVEY



APPENDIX H INDUSTRY SURVEY

This section provides a state-of-the-art review of fouling problems encountered in the following industries:

- Food and Kindred Products
- Textiles
- Pulp and Paper
- Chemicals
- Petroleum
- Stone, Clay and Glass
- Primary Metals

These seven industries encompass a broad diversity of heat-transfer operations and fuels. Fouling on the process side of heat-transfer operations varies markedly among the industries due to the wide variation in products. Fouling on the heat-source and heat-sink sides (as defined in the previous section) may be quite similar across industries, depending on the fuel burned, the water quality and/or the operating conditions.

Discussions with industry personnel served as the primary source of information for this section. The type and quantity of information available from each of the industries varied significantly. The quantity of information available for a particular industry reflects the level of resources allocated by that industry to address fouling problems. In general, the petroleum, chemicals, and pulp and paper industries appear to have undertaken the most extensive analyses of fouling in their respective processes. The type of information available from the industries indicates the areas of fouling research to which industry has given priority. Typically, the industries have placed primary emphasis on process-side fouling because this has an immediate impact on product quality and throughput.

Industries often rely on cleaning product and service suppliers and heat exchanger equipment designers and manufacturers to deal with nonprocess fouling problems. In many cases, the companies that supply these services to the manufacturing industries are more familiar with generic fouling problems than are the industries. Thus, the information gathered from industry was supplemented with information from the heat exchanger designers and manufacturers and cleaning product suppliers.

Information on the cost of fouling to industry is fragmented. Few of the industries were able to provide estimates for their entire industry. Thus, the discussions of cost generally present several independent observations that range in scope from estimates of the capital cost of a specific type of cleaning equipment to the annual cost of cleaning for a given plant. The petroleum industry has undertaken the most comprehensive assessment of fouling costs of the industries surveyed. However, their assessment of costs is for process-side rather than generic problems.

The following sections provide a brief description of the manufacturing processes, identify the major heat-transfer operations and the types of fuel burned to generate process heat or steam, and discuss the uses of cooling water. A discussion of the nature of the fouling problems encountered in various processes is provided. The approach taken by each industry in dealing with its fouling problems is discussed and, when information is available, the cost of fouling to that industry is provided.

H.1 FOOD INDUSTRY (SIC 20)

The Food and Kindred Products Industry is a diverse industry consisting of 47 four-digit subgroups. This industry encompasses more than 35,000 manufacturing plants or food-processing establishments representing approximately 22,000 individual companies or firms. Although the industrial subgroups within food processing are relatively non-energy intensive, the industry as a whole is the sixth largest energy consuming industrial group. During 1980, the Food and Kindred Products Industry consumed 948 trillion Btu, or nearly a quad of energy. This represents about 7 percent of the total energy consumed by all U.S. industries. About 51% of the energy used for food processing is supplied by natural gas, followed by electricity at 15%, coal and coke at 13%, and fuel oil at 11 percent.

H.1.1 Processes

Because of the diversity of this industry, there is no single process or flowsheet that is representative of the industry. Combined, the top ten energy consuming industrial subgroups within food processing consume about 517 trillion Btu of energy, or about 55% of all the energy consumed by the industry.

The total energy consumed by each of these ten industrial subgroups in 1980 is given in Table H.1. The largest energy consumer was Wet Corn Milling (SIC 2046), which used about 10 percent of the total energy consumed by the industry.

Flowsheets for these ten industries are shown in Figures H.1 through H.10. The energy consumption patterns for these ten industrial subgroups are shown in Table H.2 by fuel type and in Table H.3 by end use. Although the food industry is quite diversified in terms of the products produced, a number of similarities exist among the processes with respect to the use of energy. Four main process operations consume most of the energy in the food industry:

- Evaporation and drying
- Refrigeration and freezing
- Sterilization and heating
- Machinery operations.

Electricity is used for machinery operation (mechanical power), refrigeration, and freezing. Natural gas, fuel oil, coal, and coke are used as boiler fuels to generate steam. Steam may be used for cooking, heating evaporators, or for space heat. If the steam can come into contact with the product, there

TABLE H.1. Energy Consumption for the Top 10 Food Processing Industries⁽¹⁾

Rank	SIC No.	Industry	Purchased Fuels & Electric Energy (Trillion Btu)
1	2046	Wet Corn Milling	92.1
2	2063	Beet Sugar	71.7
3	2011	Meat Packing Plants	69.6
4	2082	Malt Beverages	52.8
5	2075	Soybean Oil Mills	48.0
6	2033	Canned Fruits and Vegetables	44.7
7	2051	Bread, Cake & Related Products	41.0
8	2026	Fluid Milk	32.9
9	2062	Cane Sugar Refining	32.2
10	2037	Frozen Fruits and Vegetables	32.0

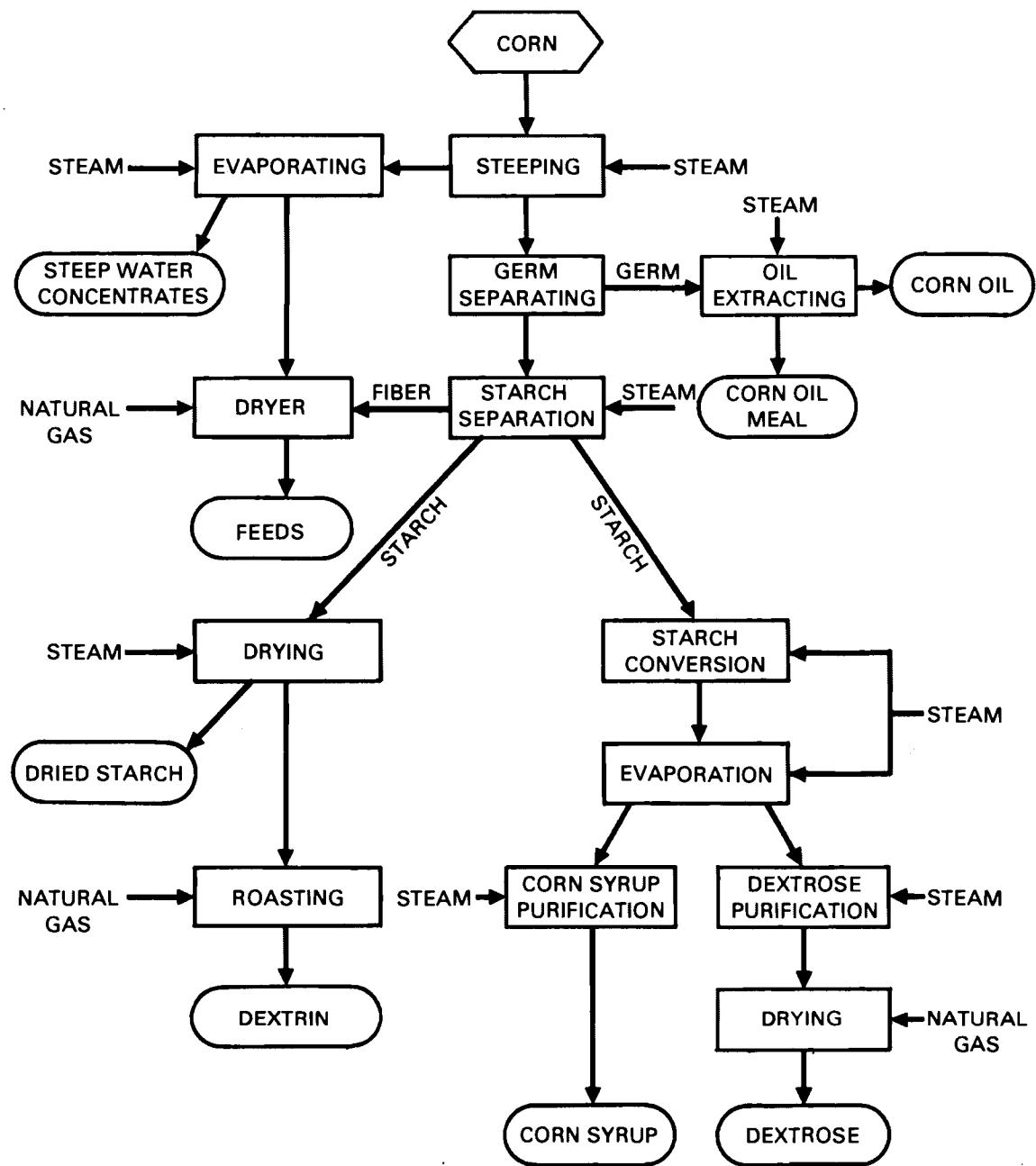


FIGURE H.1 Wet Corn Milling Process Flow Diagram (SIC 2046)

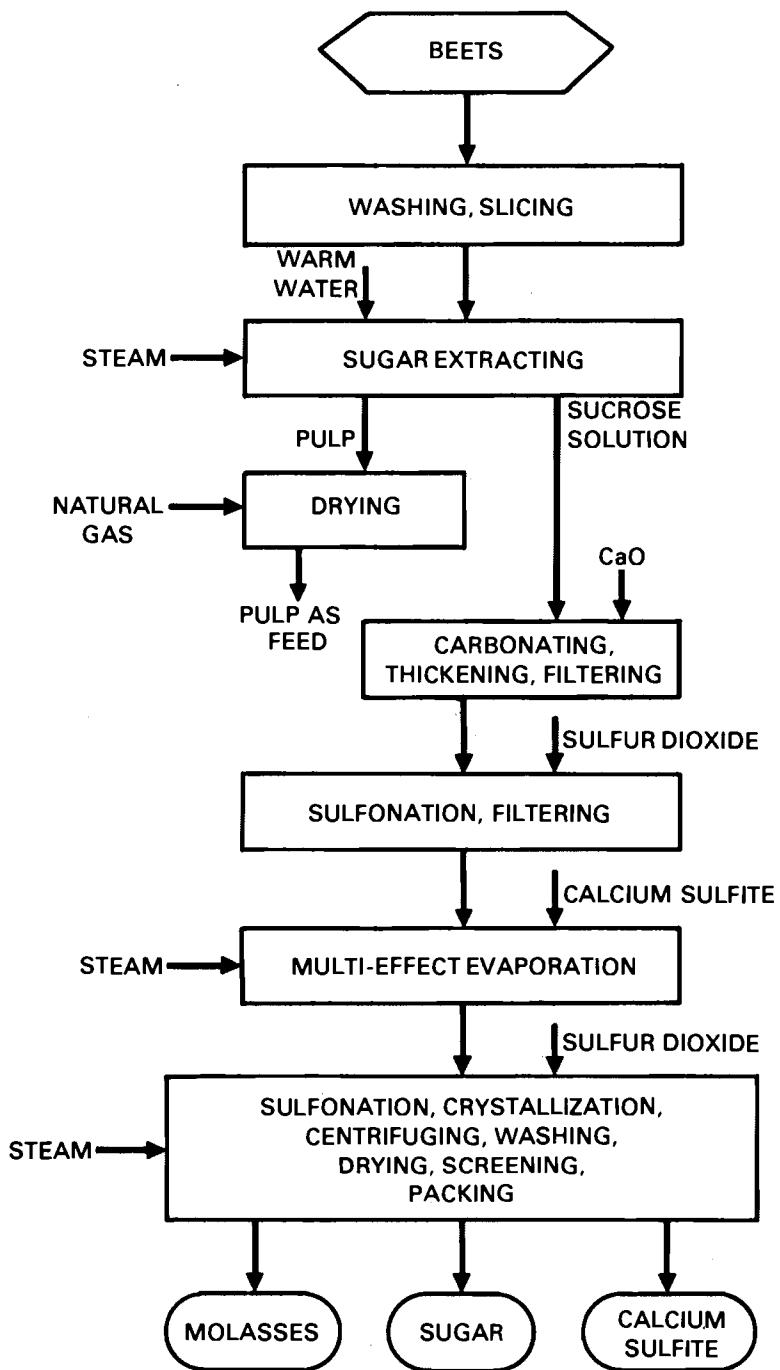


FIGURE H.2 Beet Sugar Process Flow Diagram (SIC 2063)

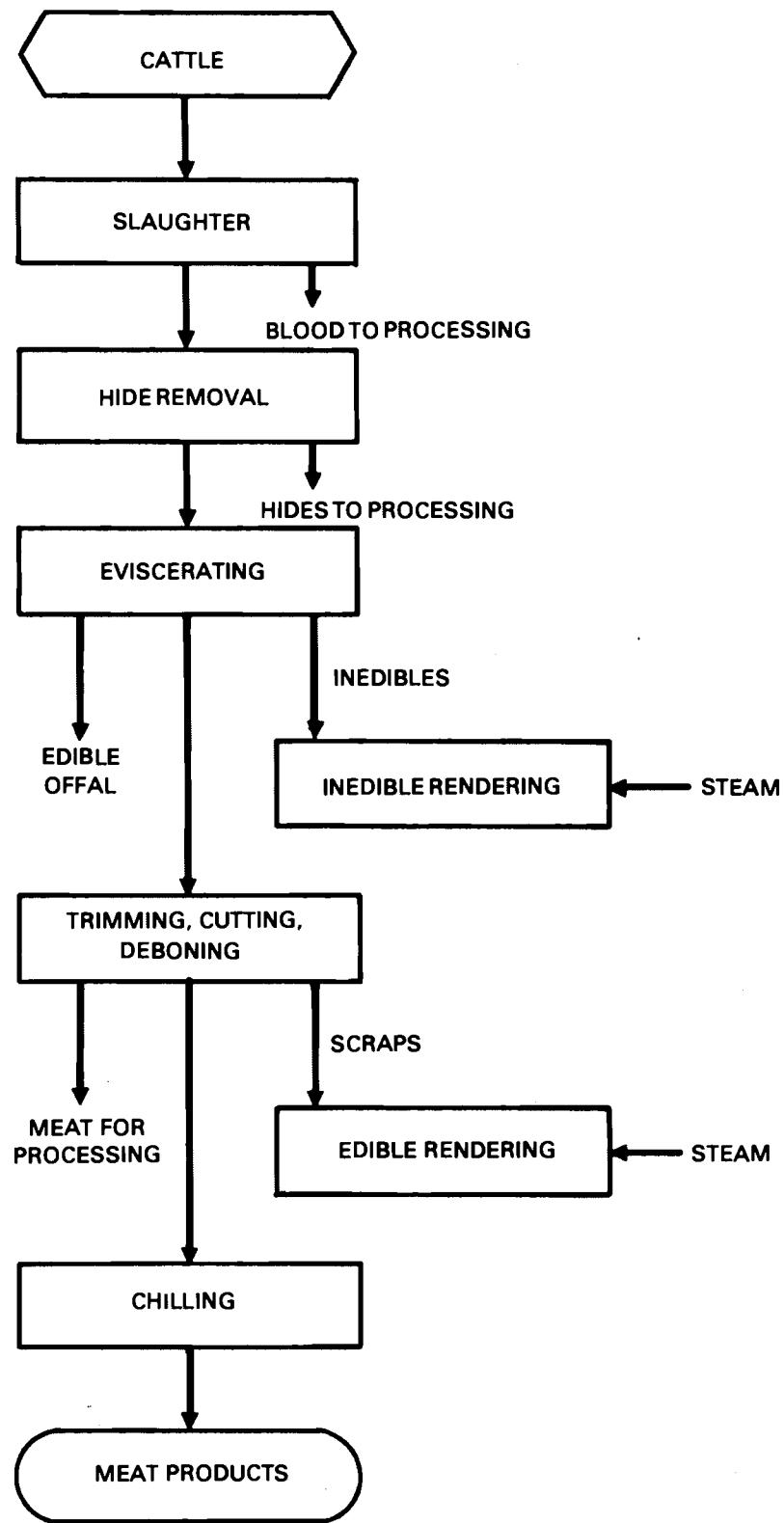


FIGURE H.3 Meat Packing Plants Process Flow Diagram (SIC 2011)

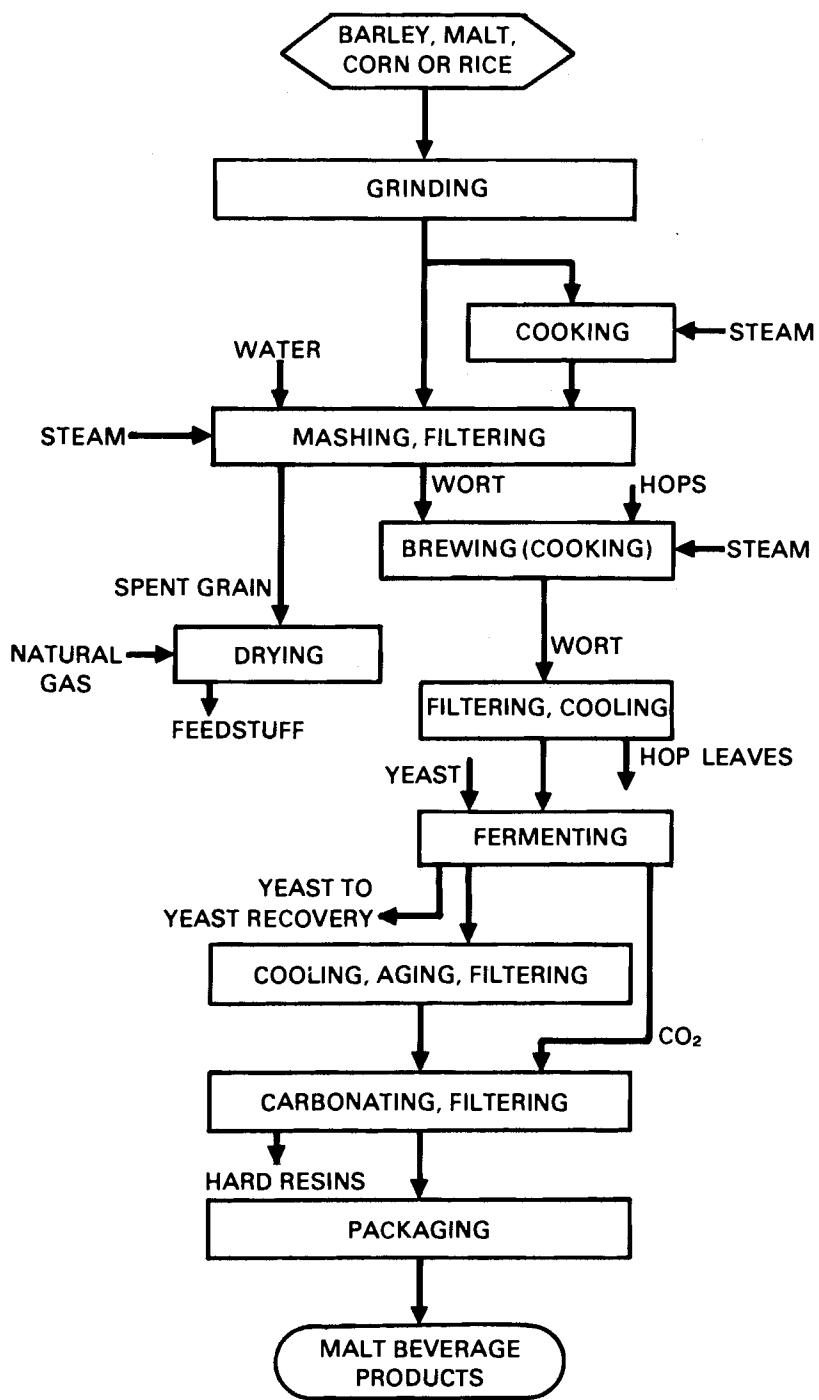


FIGURE H.4 Malt Beverages Process Flow Diagram (SIC 2082)

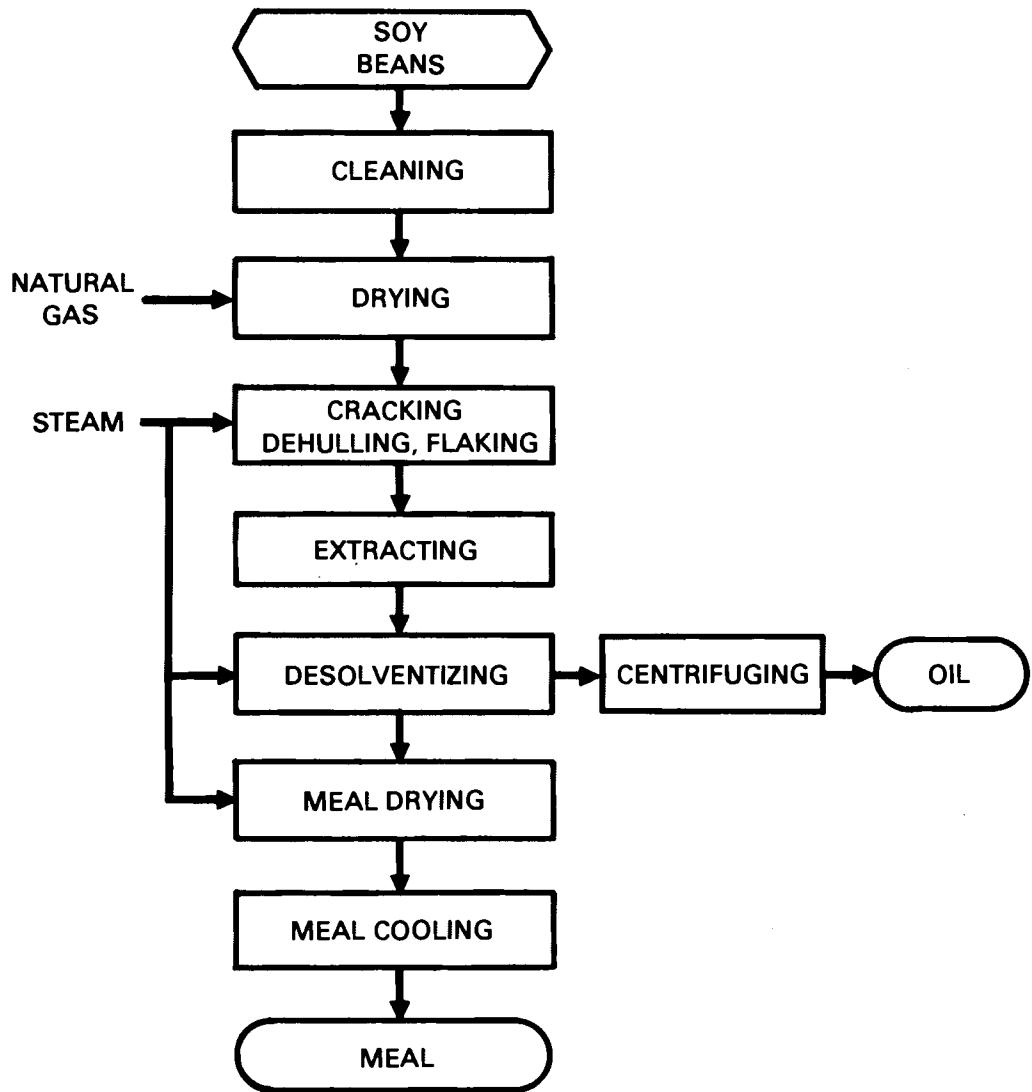


FIGURE H.5 Soybean Oil Mills Process Flow Diagram (SIC 2075)

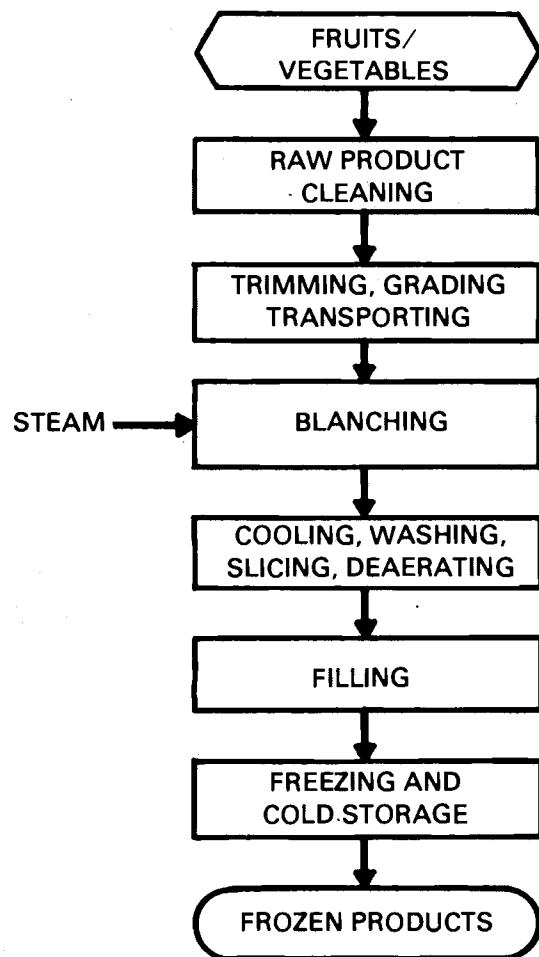


FIGURE H.6 Canned Fruits and Vegetables
Process Flow Diagram
(SIC 2033)

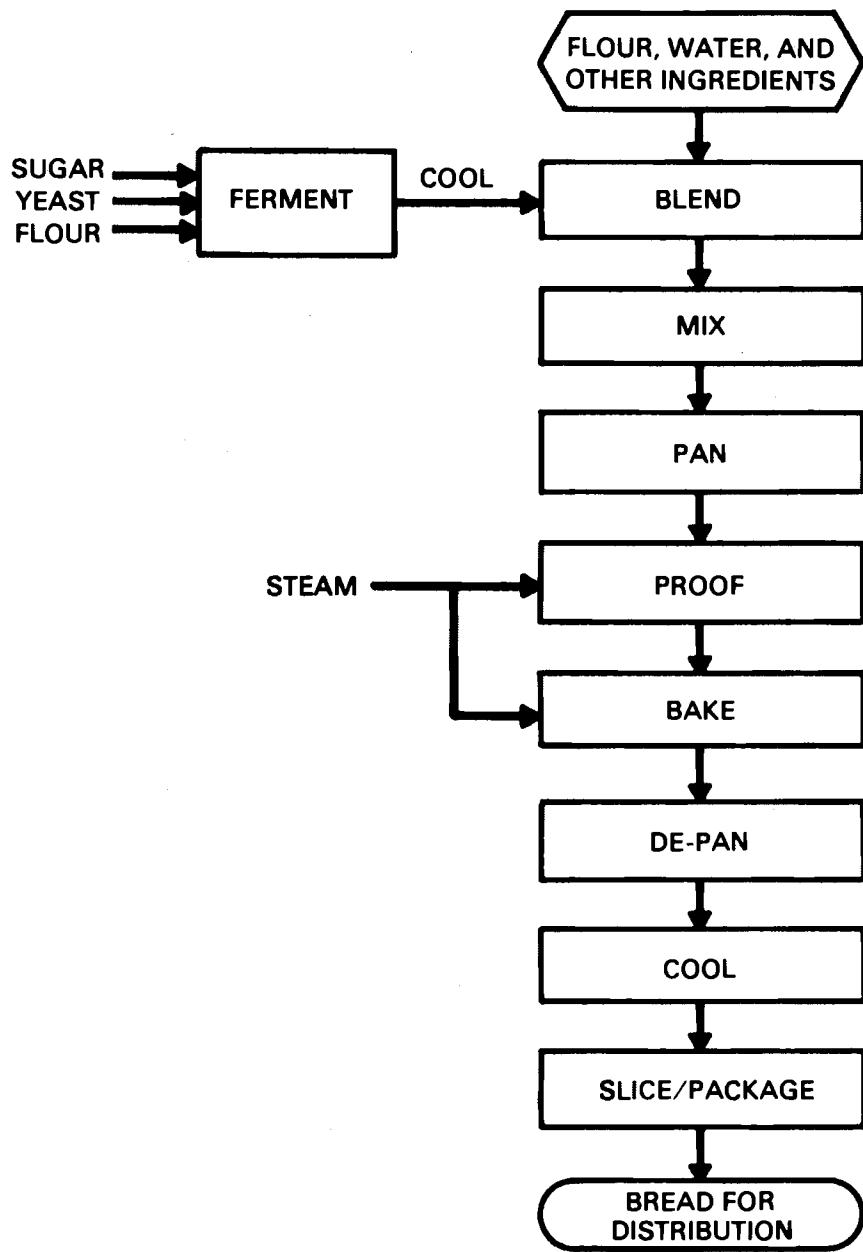


FIGURE H.7 Bread, Cake, Related Products Process Flow Diagram (SIC 2051)

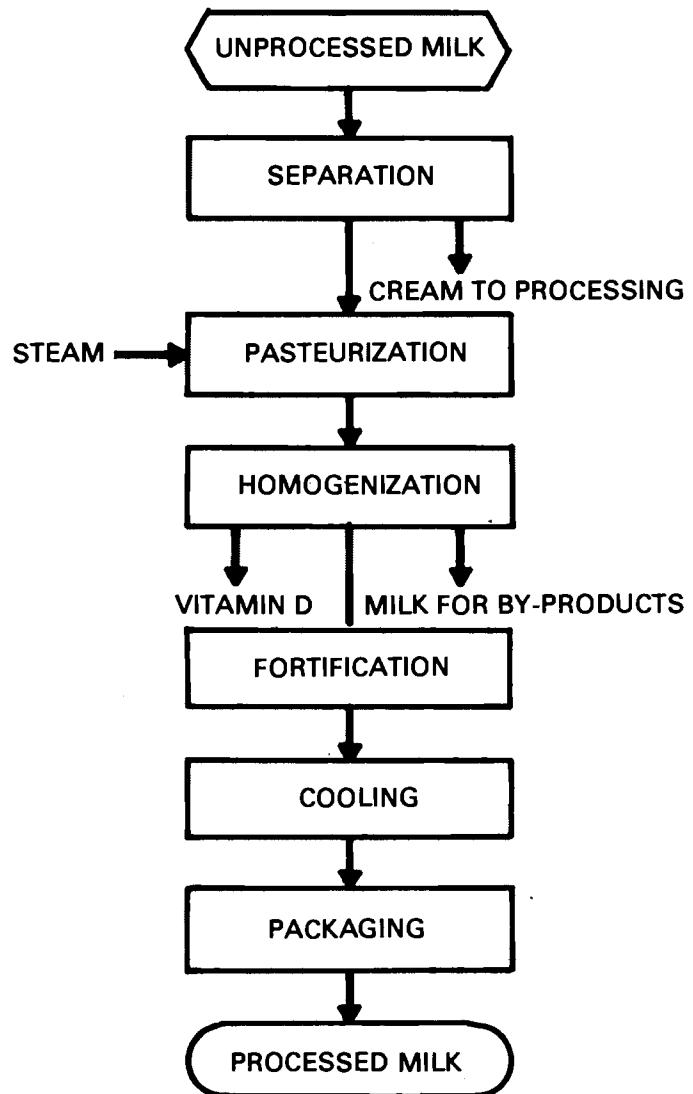


FIGURE H.8 Fluid Milk Process Flow Diagram
(SIC 2026)

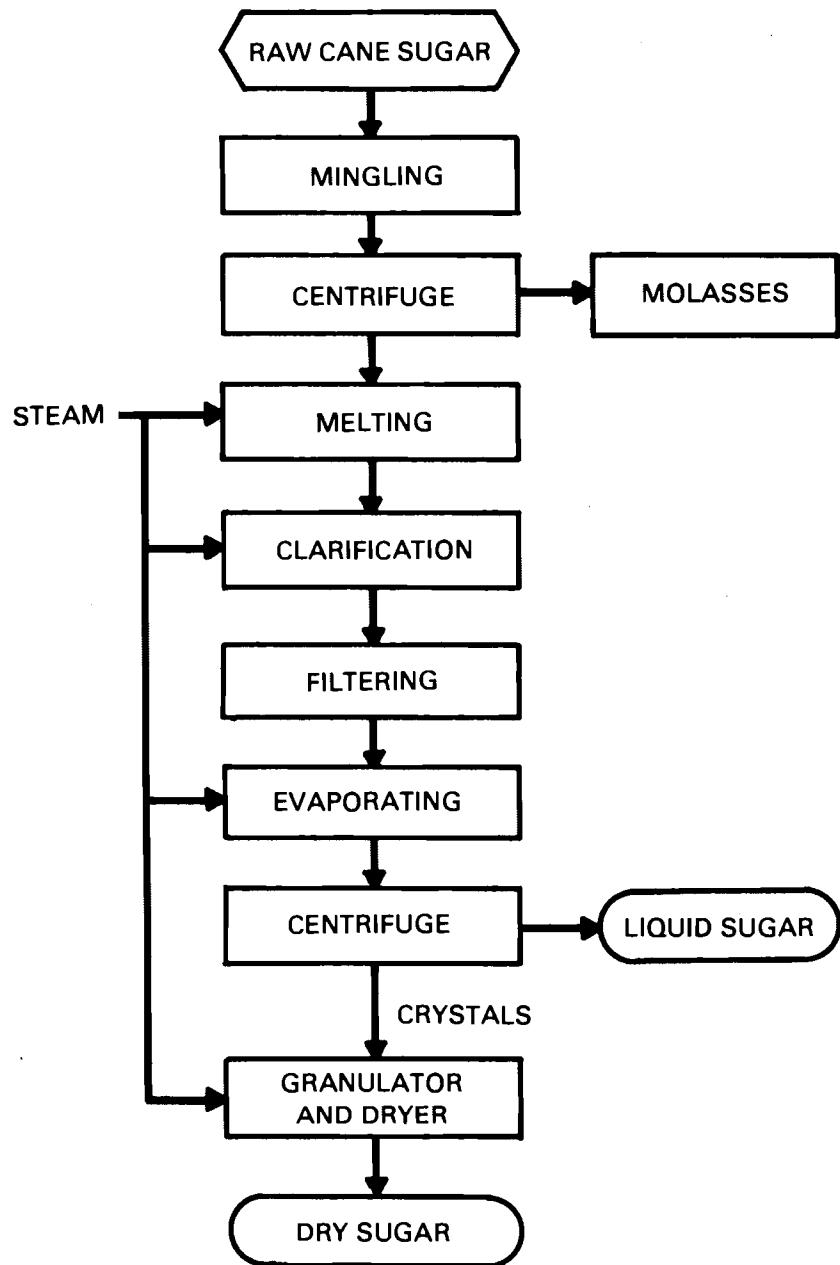


FIGURE H.9 Cane Sugar Refining Process Flow Diagram
(SIC 2062)

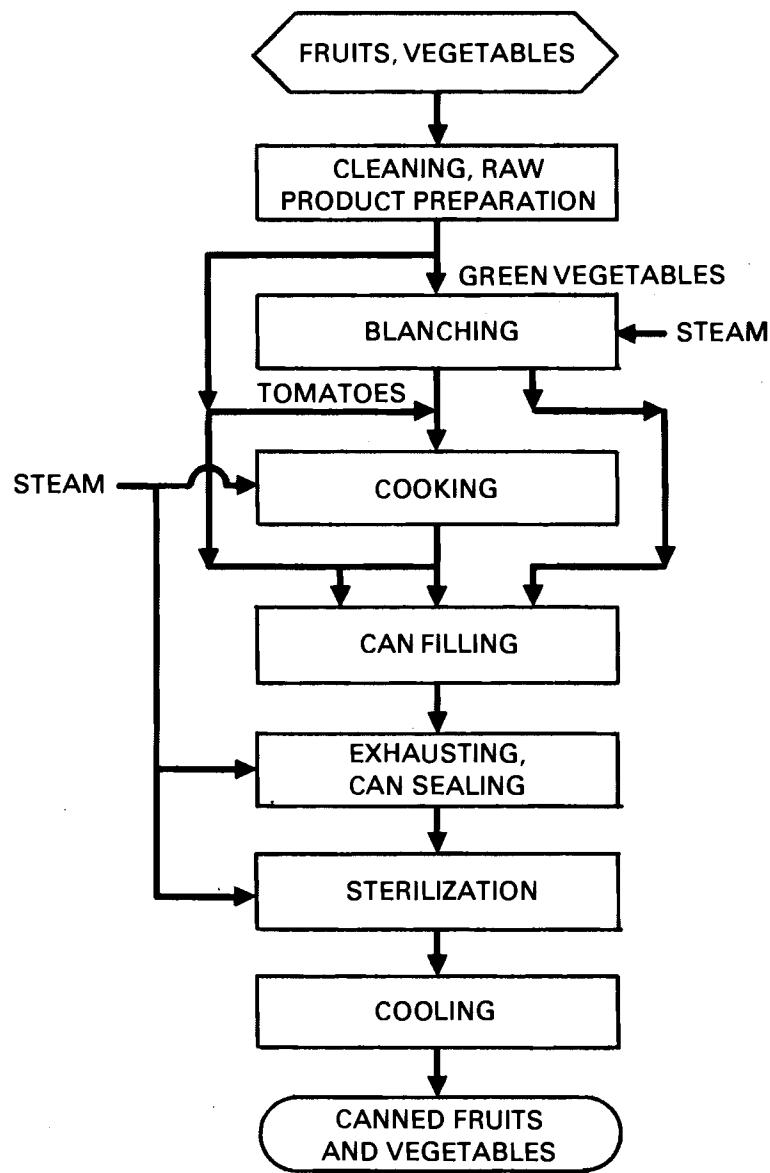


FIGURE H.10 Frozen Fruits and Vegetables Process Flow Diagram (SIC 2037)

TABLE H.2. Purchased Fuels and Electric Energy (% of total by major type)

<u>Industry</u>	<u>Electricity</u>	<u>Distillate Fuel Oil</u>	<u>Residual Fuel Oil</u>	<u>Coal</u>	<u>Natural Gas</u>
Wet Corn Milling	6.5	8.3	9.0	35.7	40.2
Beet Sugar	1.6	4.1	9.9*	47.7*	36.7
Meat Packing Plants	18.0	8.3	6.8	18.2*	48.7
Malt Beverages	13.9	7.9	21.6	12.1*	44.6
Soybean Oil Mills	11.0	2.4	5.0	17.1*	64.4
Canned Fruits and Vegetables	10.0	3.3	12.1	-	70.3
Bread, Cake, Related Products	15.2	3.8	NG	-	55.4
Fluid Milk	26.9	5.9	6.3	<8.7*	43.9
Cane Sugar Refining	1.6	0.6	15.5	<2.5*	79.8
Frozen Fruits and Vegetables	22.5	3.5	12.3	-	56.3

* Estimated

NG-not given

TABLE H.3. End-Use Energy Consumption Patterns

Industry	Direct			Boiler			Electricity		
	Primary End-Use	% of Total	% Direct of Total	Primary End-Use	% of Total	% Boiler of Total	Primary End-Use	% of Total	% Elec. of Total
Wet Corn Milling	Drying	14.3	15	Process steam	31.2	80	Mechanical power	4.8	5
Beet Sugar	Drying	26.1	30	Evaporators, proc. steam	38.6	69	Mechanical power	0.9	1
Meat Packing Plants	Smoke-house, cook ovens	2.4	8	Rendering	19	76	Refrigeration	5.2	14
Malt Beverages	Drying	4.2	8	Steam, hot water	42.9	81	Mechanical power	4.5	11
Soybean Oil Mills	Drying	21.0	21	Desolventizer, toaster	20.7	69	Mechanical power	9.6	10
Canned Fruits & Vegetables	Receiving, Warehousing, etc.	8.0	8	Processing	78.7	82	Processing	2.3	10
Bread, Cake, Related Products	Ovens	33.8	45	Space heating	7.6	38	Lighting	5.1	17
Fluid Milk	Milk Drying	4.0	6	Hot water cleaning	16.6	69	Process equipment	8.0	25
Cane Sugar Refining	Kiln	2.0	2	Vacuum pans	48.5	97	Mechanical power	1.0	1
Frozen Fruits & Vegetables	Receiving & misc.	6.0	6	Processing	71.8	74	Processing	7.4	20

are restrictions on the chemicals that can be used for steam and boiler water treatment, and on their concentration.⁽²⁾ A small portion of the natural gas is used for direct drying of by-products that are used for livestock feed.

In the food industry, cooling water is used to operate refrigeration equipment, to condense steam from evaporators or turbines, and to cool process equipment such as compressors, cookers and engine jackets. The sugar industry has the highest cooling water requirement within the food industry.⁽²⁾ In this process, the water used for condenser cooling is subsequently used as process water. Because the process water comes in contact with the product, there are restrictions on the types of water treatment chemicals that can be used.

H.1.2 Fouling Problems

Food industry representatives indicate that there are two general areas of concern with fouling and corrosion in the food processing industry. These are nonprocess fouling (heat-source and heat-sink) and process-side fouling. Generally, the industry has relied upon heat exchanger manufacturers and cleaning equipment suppliers to deal with the nonprocess fouling problems. Researchers and manufacturers in food processing industries have largely concentrated on problems associated with the process side of heat-transfer equipment.

Fouling and corrosion problems associated with nonprocess heat transfer equipment, such as boilers, boiler preheaters, cooling towers, and evaporative coolers for freezers, are similar to those experienced by other industries. Most of the problems occur on the water side of heat exchangers where potable water is being heated to 140 to 180⁰F, and in evaporative coolers in refrigeration systems.

The primary areas of concern with fouling of process heat exchanger surfaces in the food industry are the adhesion of bacteria and the deposition of components of biological fluids. Laboratory and pilot experiments have been conducted to characterize the fouling rate of proteins as a function of various process parameters. These studies deal with fouling problems that are very specific to the type of biological fluid used in the process.^(3,4,5,6) The literature largely reports these food-specific laboratory studies and, in general, does not provide data on the nature or extent of fouling on an

industry-wide basis. The process heat exchangers are usually stainless steel (for sanitation), and the corrosion problems are therefore limited.

H.1.3 Mitigation Techniques

The sanitation requirements of the food processing industries typically result in frequent cleaning intervals on the process side, thus eliminating any biological fouling buildups that may occur. The primary cleaning techniques are spray washing and chemical cleaning. To facilitate cleaning it is common in the food industry to use plate exchangers. These exchangers can either be cleaned in place or the plates can be easily removed.

Discussions with heat exchanger manufacturers for the food industries indicated that the primary design techniques for lessening the impacts of fouling are to oversize (10 to 20%) and to use specialty materials, such as stainless steel and titanium. Fouling and corrosion do not generally require installation of parallel processing lines. Bypasses on heat recovery devices are used where applicable.

H.1.4 Costs

Costs associated with fouling in the food industry include:

- Additional capital costs (oversizing)
- Specialty materials
- Chemical cleaning
- Water treatment (boiler and cooling water)
- Lost-energy (waste-heat-recovery bypasses).

The additional costs of designing and constructing heat exchangers to help cope with fouling problems depends on the plant and process. It is difficult to distinguish the costs due to sanitation and process requirements from costs incurred to mitigate fouling problems.

One firm reported that the costs associated with downtime for maintenance, repair, or replacement due to fouling and corrosion represented about 1% of its annual energy expenditures.

The amount of oversizing depends on the type of heat exchanger, the material it is made of, and the fluid on each side of the heat-transfer surface. Plate and frame exchangers can easily and inexpensively be oversized by simply

adding more plates. The cost increases less than 5% for oversizing 10 to 20%. Shell and tube heat exchangers with glass tubes require no oversizing because fouling is not a problem, but they do cost about 1/3 more than a comparable exchanger made of carbon steel. Some exchangers in the Food and Kindred Products Industry must be made of titanium because of highly corrosive streams; this can increase costs two- to five-times over comparable exchangers made of less exotic materials.

H.2 TEXTILES (SIC 22)

The textile industry produces a wide variety of products from natural and synthetic fibers. These products include knit and woven fabrics, rugs and carpets, and thread and yarn. In 1977, there were 7202 textile mills in the United States.⁽⁷⁾ Most of these are located in the southeast, particularly in North and South Carolina and Georgia. Textile mills range from highly integrated mills that process fibers into finished products, to smaller, non-integrated mills that perform certain processing steps on a contract basis.

The remainder of this section discusses textile processes and identifies the major heat-transfer processes, fouling problems, current mitigation techniques, and costs of fouling.

H.2.1 Textile Manufacturing Processes

Textile production consists of two basic operations: 1) the production of undyed, unfinished (greige) goods and 2) the production of finished goods from greige goods. Figure H.11 shows typical processing steps for knit and woven greige goods mills. These front-end operations are essentially dry operations, with the exception of slashing and subsequent drying.

Finishing operations (dyeing and finishing) transform the greige goods into finished fabric. Figure H.12 shows the processing steps in a typical finishing plant. Many of the finishing steps are wet operations which use water heated by direct steam injection. Drying operations use direct-fired natural gas or indirect steam heating of teflon-coated drying cylinders.⁽⁷⁾

Two-thirds of the energy consumed in textile manufacture is used in fabric finishing.⁽⁸⁾ Most of the energy is used to raise steam, which is used

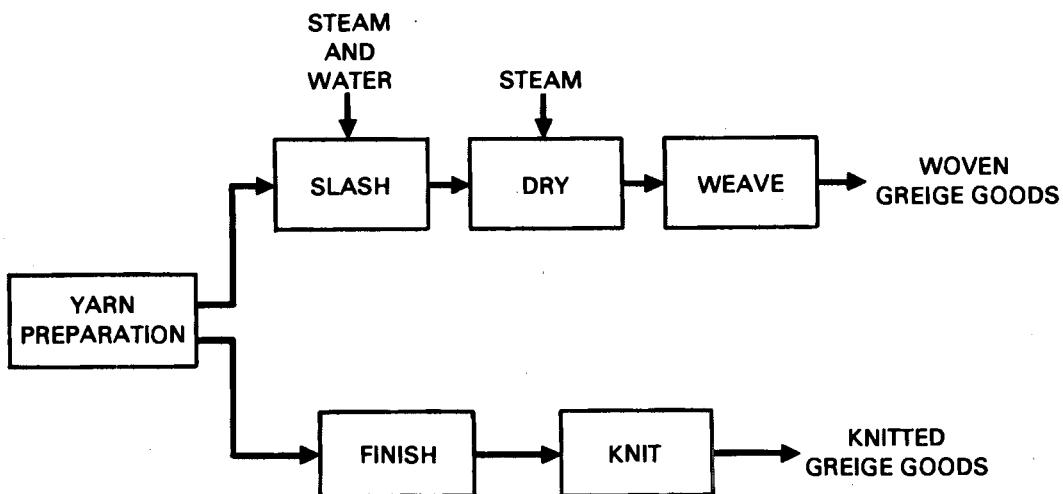


FIGURE H.11 Greige Goods Production

for water heating or drying. Between 50 to 70% of the fossil energy used in the textile industry is for steam production.⁽⁹⁾ Direct firing of natural gas for drying operations is the second largest consumer of energy, accounting for almost 25% of total energy use.

A great deal of water is used in textile mills for both process and non-process operations. Process uses of water include washing operations, boiler makeup, cooling of process equipment, and as a diluent for process chemicals. Nonprocess uses include air-washing and air-conditioning operations.

The major heat-transfer operations in a textile mill are listed in Table H.4. An operation is designated "indirect" if the heat-transfer fluids do not mix and "direct" if they are in contact.

H.2.2 Fouling Problems

Current and potential fouling problems in textile mill operations are discussed in this section. Current problems are those encountered in existing operations. Potential problems refer to those that could occur if the industry adopts new technologies, particularly waste-heat recovery.

The trend in the textile industry has been toward the increased use of coal for steam generation. Fouling problems associated with coal-fired boilers

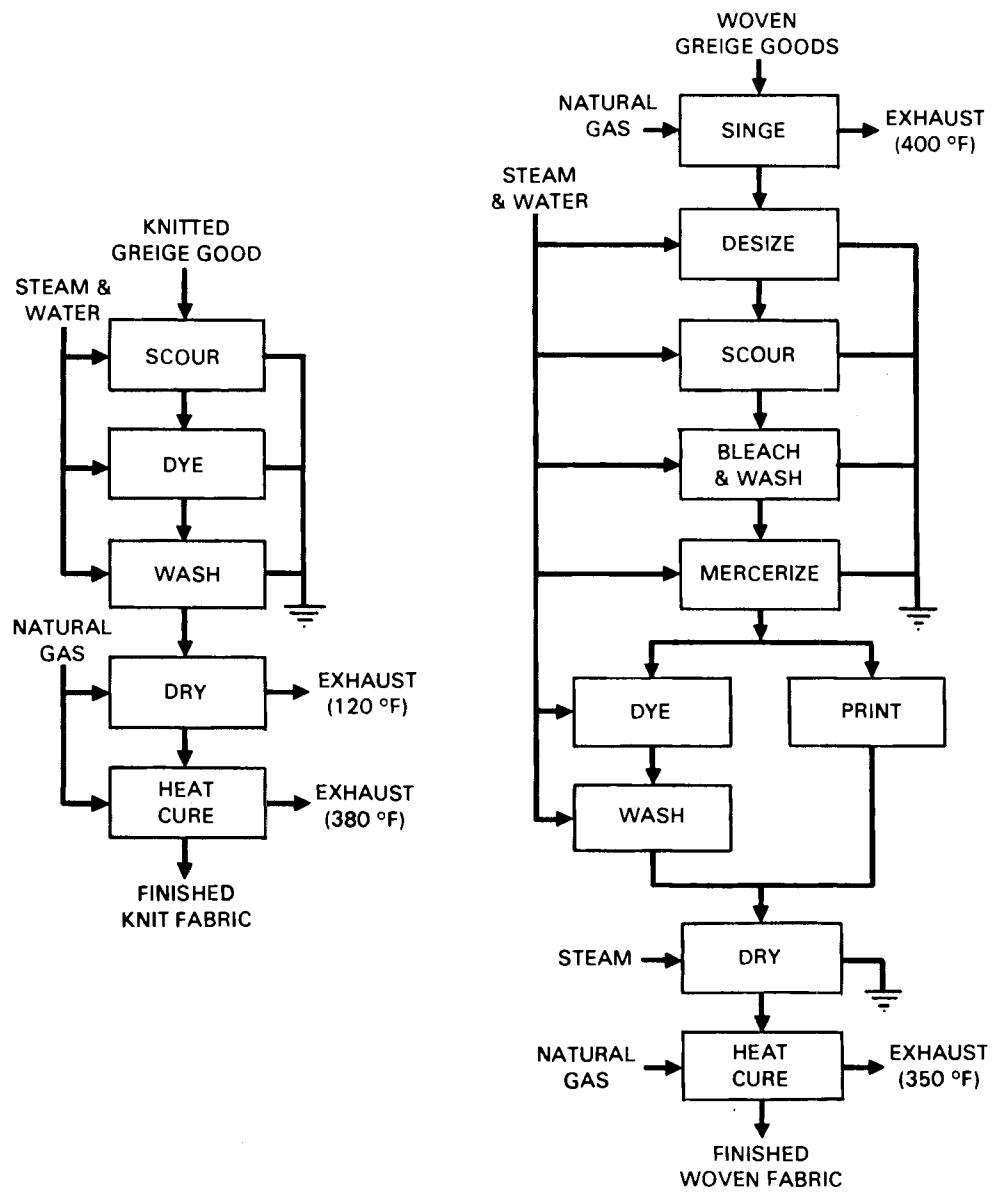


FIGURE H.12 Finishing Operations

TABLE H.4 Textile Mill Heat-Transfer Operations

	<u>Operation</u>	<u>Equipment</u>	<u>Heat-Transfer Media</u>
INDIRECT:	Steam generation	Boiler	Combustion gases: coal, fuel oil or natural gas, water
	Boiler exhaust heat recovery	Economizer	Combustion gases, water
	Drying	Drying cans or cylinders	Steam
	Air conditioning	Cooling coil	Cold water, refrigerant
DIRECT:	Singeing	Ovens	Combustion gases: natural gas
	Drying	Frame dryers	Combustion gases: natural gas
	Air conditioning	Cooling tower	Water to air
	Water heating	Injection nozzle	Steam

include slagging on the gas side and scaling on the water side. In addition, if temperatures drop below the acid dew point on the gas side, corrosion problems may occur. No reference was made in the literature to any fouling or corrosion problems associated with the steam drying cans.

Two major barriers to the adoption of heat-recovery equipment for textile dryers and ovens are the buildup of lint and the condensation of finishing chemicals on heat exchanger surfaces.⁽⁹⁾ Finishing chemicals include anti-statics, fire retardants, softeners, water repellants, or durable-press resins.⁽⁷⁾ These chemicals act as adhesives to hold the lint on the surface.

In the air conditioning system, airborne solids (particularly lint) can buildup on the gas side of the cooling coils, reducing effectiveness. Lint can also enter the cooling water loop via the natural scrubbing effect of the

tower, which may tend to entrain airborne particulates.⁽¹⁰⁾ This could lead to particulate buildup on the liquid side of the cooling coils.

H.2.3 Mitigation Techniques

Table H.5 summarizes mitigation strategies used to deal with the fouling problems presented in the previous section. As shown in the table, mitigation techniques used for fouling and corrosion problems that occur in boilers are typical of those used by other industries. Limited experience with an economizer in No. 6 fuel oil exhaust indicates that no additional fouling problems, beyond those experienced in the boiler, occur in the economizer.⁽⁹⁾

A heat recovery system with glass rather than metal tubes has been developed for use with dryer exhausts. The smooth, nonporous surface is more effective than metal tubes in preventing deposition of finishing chemicals or lint. In addition, the glass tubes are assembled in modules that can be easily removed for cleaning or replacement. The manufacturer recommends cleaning at six-month intervals. Cleaning takes approximately 12 hours in a heated tank with a circulating pump that is part of the system package.^(9,11)

TABLE H.5 Mitigation Techniques for Fouling in Textile Plants

Equipment	Problem	Mitigation Technique
Boiler/Economizer	Gas-side slagging	<ul style="list-style-type: none">• additives• control excess air
	Water-side scaling	<ul style="list-style-type: none">• additives• chemical cleaning• mechanical cleaning
Dryer Heat Recovery System	Lint buildup & condensation of finishing chemicals	<ul style="list-style-type: none">• removable, glass tubes• regenerator design with air blowing to remove lint
Air Conditioning Coils	Lint buildup on gas side	<ul style="list-style-type: none">• air washing• coil cleaning
	Lint buildup on water side	<ul style="list-style-type: none">• air washing• side-stream filtration• antifoulants

Another heat-recovery system that may mitigate the lint and finishing-chemical deposit problems consists of two regenerator units that attach to the dryer. The dryer exit gas passes through one regenerator that stores heat from the exhaust while the cool, makeup air is heated as it passes through the opposite regenerator. Flow direction is alternated through the regenerators at set intervals. Deposition problems are minimized because lint builds up at the hot end of the regenerator and the finishing chemicals do not condense until they reach the cold end. The lint can then be easily removed by blowing with air. Weekly air cleaning is recommended.^(9,11)

The textile industry is one of the largest users of air-washing equipment to clean and temper air.⁽²⁾ Reducing the quantity of airborne particulates reduces the probability of buildups occurring on either side of the air conditioning cooling coil. Other techniques used to eliminate or accommodate fouling problems that may arise if particulates become entrained in the cooling water loop include side-stream filtration and use of antifoulants. Side-stream filtration reduces the particulate content of the cooling water, whereas anti-foulants keep the particles in suspension until they can be filtered off.⁽¹⁰⁾

H.2.4 Costs

The economic penalties associated with fouling and corrosion problems in the textile industry include additional heat exchanger capital costs, the cost of additives used in the boilers and air-conditioning systems to prevent fouling, the capital cost of cleaning equipment and the value of waste heat that is not recovered due to potential fouling problems. These costs vary widely from plant to plant and depend on variables like the size of the operation, operating conditions and water quality among others.

A heat recovery system with glass tubes costs about 1/3 more than a similar heat exchanger made with metal tubes. Additionally, a specially designed and engineered spray washer for glass tubes will increase the cost 5 to 10% and a spare tube bundle will add about 25 to 30% to the equipment capital cost. The increased capital costs of equipment with low fouling tendencies must be

balanced against both the cost of using conventional exchangers with greater fouling and cleaning problems and the cost of unrecovered waste heat.

Lost production resulting from fouling problems is unlikely to occur because the typical mill operates less than seven days per week, allowing for routine maintenance during scheduled shutdowns. Since the textile industry is currently operating below capacity due to the recession and to strong foreign competition, the likelihood of lost production resulting from fouling problems is remote.

No downtime is required to perform regular cleaning of economizers.⁽⁹⁾ Downtime is defined as any period when the boiler is not operating due to anything other than regular maintenance. Cleaning of heat recovery devices on dryers and ovens can most likely occur during scheduled shutdowns. The removable glass tube modules can be replaced with a backup module to allow for cleaning without shutting down. The cleaning process itself takes about 12 hours. With the regenerator design, air blowing to remove lint is recommended on a weekly basis.⁽¹¹⁾

One source indicates that about 1.887×10^{13} Btu/yr are rejected from textile drying operations.⁽¹²⁾ If this heat were to be recovered for air preheating or for heating process water with a ten percent efficiency, approximately \$6 million per year in energy costs could be saved (1982 dollars).^(a) The amortized capital cost of the heat recovery equipment would have to be subtracted from this amount to determine the net savings that could be realized from waste heat recovery. Of course, fouling is only one of the factors that acts as a barrier to waste heat recovery. Thus, the net savings would represent an upper bound on the opportunity cost of fouling in this industry.

H.3 PULP AND PAPER (SIC 26)

This industry produces pulp, paper and paperboard^(b) for conversion into paper and related products. This is accomplished in four types of mills: pulp

(a) $1.887 \times 10^{13} \frac{\text{Btu}}{\text{yr}} \times 10\% \times \$3.49/1000 \text{ ft}^3 \times \frac{1000^3 \text{ ft}}{1024 \times 10^3 \text{ Btu}}$

(b) Paper more than 0.012 in. thick.

mill, paper mill, paperboard mill and integrated mill. An integrated mill combines pulping and papermaking at one site.

There are three major steps in the manufacture of paper:

1. wood or fiber source preparation
2. pulping
3. papermaking

Fouling of heat-transfer equipment creates problems for pulp mills and, to a lesser extent, for paper and paperboard operations.

H.3.1 Pulp and Paper Processes

This section describes the pulping and papermaking processes. Paperboard processes are similar to papermaking processes and encounter the same fouling problems.

H.3.1.1 Pulping Process

Three principal processes are used to make pulp: chemical, chemimechanical, and mechanical pulping.

Mechanical pulping reduces the wood or alternate fiber source (wastepaper, cotton, linen, or grass) to a fibrous condition through grinding or crushing actions, generally using electrical energy to operate the pulping equipment.⁽¹³⁾ The mechanical methods produce high yields of pulp and relatively low wood losses. There is little potential for heat, chemical or waste recovery, and only a few fouling problems are associated with heat transfer operations in these processes.

The two leading chemical processes are the sulfite method and the sulfate or Kraft method. All chemical pulping processes are similar in that each digests the fiber source with a chemical cooking liquor and removes spent pulping liquor from the pulp.⁽¹³⁾ Differences among the various pulp types occur in the preparation, end use, and recovery of spent liquors.

Most of the pulp produced is chemically pulped, with the Kraft process, producing over 70% of all pulp consumed in the United States.⁽¹⁴⁾ Kraft pulping is the dominant process because it: 1) produces a high strength pulp, 2) accepts a variety of woods, and 3) is compatible with heat, waste and chemical recovery.

Neutral sulfite semi-chemical (NSSC) pulping is the leading chemi-mechanical method. The fiber source is chemically treated before a mechanical grinding step and then allowed to cook with pulping liquors. The advantages of this method are that it uses hardwoods^(a) that at one time were considered unsuitable for pulping and produces a pulp with desirable characteristics.

Because of the nature of the chemicals used and the economic aspects of recovery systems, the chemical and chemi-mechanical pulping systems experience problems with gas-side, low-temperature heat exchanger fouling.

H.3.1.2 Papermaking

After the pulp has been bleached and passed through stock preparation steps such as beating, refining, screening and cleaning, it is ready for the paper machine. The paper is made by depositing a layer of fiber on a fine screen of wire or filaments from a dilute water suspension of the pulp. The water is allowed to drain as the wire moves. As it dries, a continuous paper sheet is created that is sent through a series of pressing, drying and calendering machines before the final paper product is formed.

H.3.2 Fouling Problems

Most of the heat-transfer-related fouling problems for the Pulp and Paper Industry occur in the following equipment types:

Pulp Mill

- digesters
- evaporators
- recovery boilers

Paper Mill

- waste-heat-recovery systems

Power Generation Pulp/Paper Mills

- wood, coal, oil and combination boilers

H.3.2.1 Pulp Mill Fouling

The digester contains the fiber source (usually wood chips) and chemicals during the cooking stage of the chemical or chemi-mechanical pulping process. Digesters are classified as follows:

(a) Hardwood - woods of broadleaf trees.

1. Stationary bath: Direct and indirect cooking methods can be used (Figure H.13).
2. Continuous: This digester can be top fed or bottom fed. The Kamyr digester is a type of top-fed digester (Figure H.14).
3. Rotating: Rarely used for Kraft pulping.⁽¹⁵⁾

The digesters can be heated by direct or indirect methods. Steam is added directly to the digester in the direct method. Indirect methods employ pre-heaters to heat the cooking liquors, which are pumped out at the bottom and the top of the digester, sent through the preheater, and then pumped into the digester at the center. This insures complete circulation of cooking chemicals. Fouling occurs in the liquor heaters, particularly in the upper heating regions.⁽¹⁶⁾ The heaters maintain the temperature of the circulating cooking liquor in the pulp digestion process (Figures H.15 and H.16).

Most of the heaters are of a two-pass design.⁽¹⁵⁾ Tube size used in these heaters varies from 1 to 1-1/2 inch O.D. and from 10 to 15 feet in length.⁽¹⁵⁾ The overall heat-transfer coefficient varies from 200 to 700 Btu/hr-ft²-⁰F depending on the amount of scale present, fluid temperature and velocity.⁽¹⁵⁾ Liquor passing through the tubes can be heated by steam or condensate. For Kraft pulping, operating conditions are usually 392⁰F steam on the shell side and 302 to 338⁰F cooking liquor in the tubes.⁽¹⁷⁾

Deposits are combinations of organic and inorganic materials. The inorganic material is primarily calcium carbonate.⁽¹⁶⁾ Fouling in the heater tubes prevents proper heat transfer due to the poor conductivity of the scale and decreased fluid flow. With time, tube pluggage can become a problem.

Patterns of calcium carbonate scale deposition, liquor circulation and chip loading causes certain areas of the digester to become susceptible to corrosion attack.⁽¹⁸⁾ A potential risk when deposits are present is crevice corrosion, which occurs under the deposits, and mainly results from calcium and silicon compounds entering the system.⁽¹⁹⁾

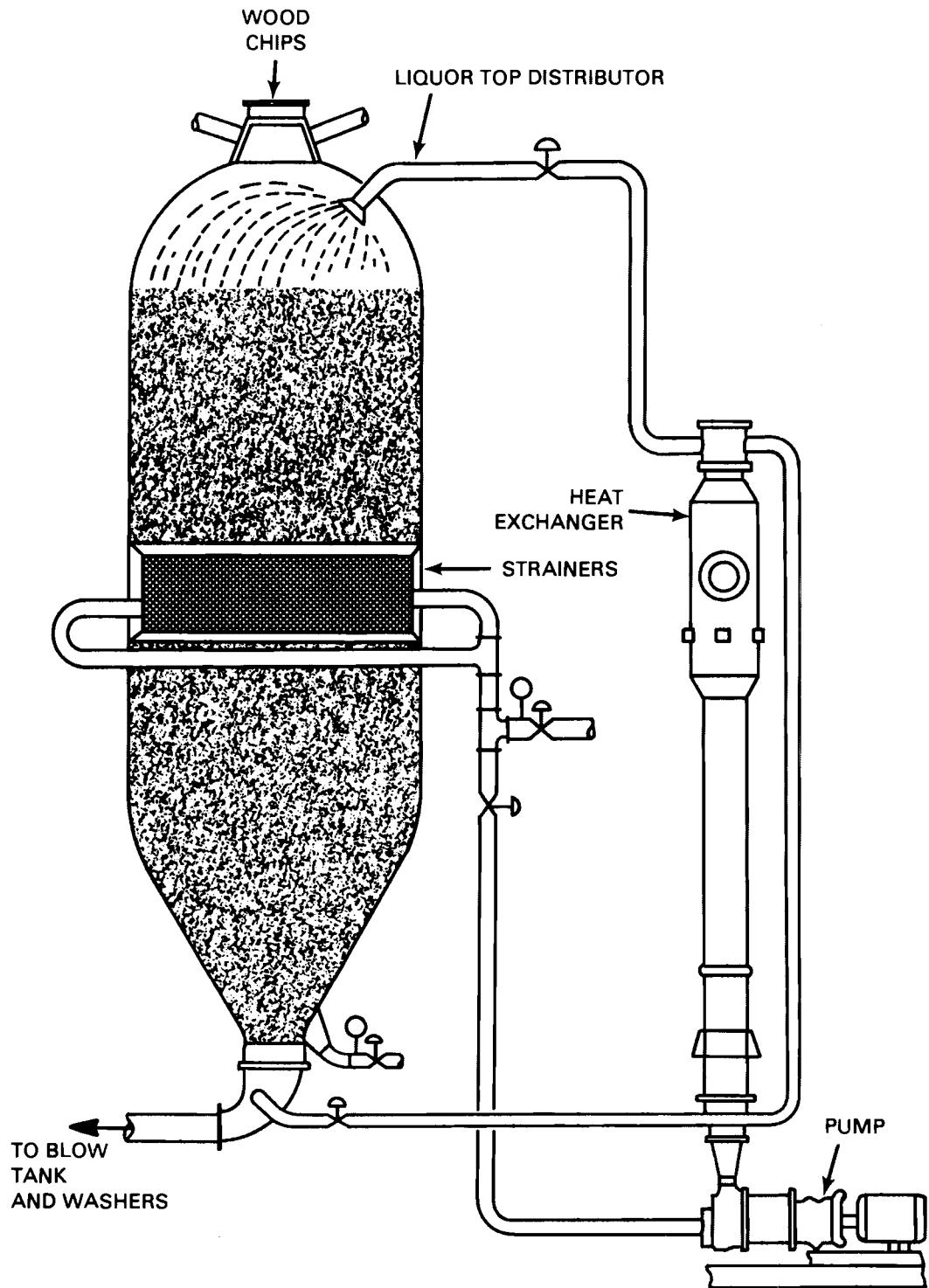


FIGURE H.13 Batch Digester with External Black Liquor Heat Exchanger

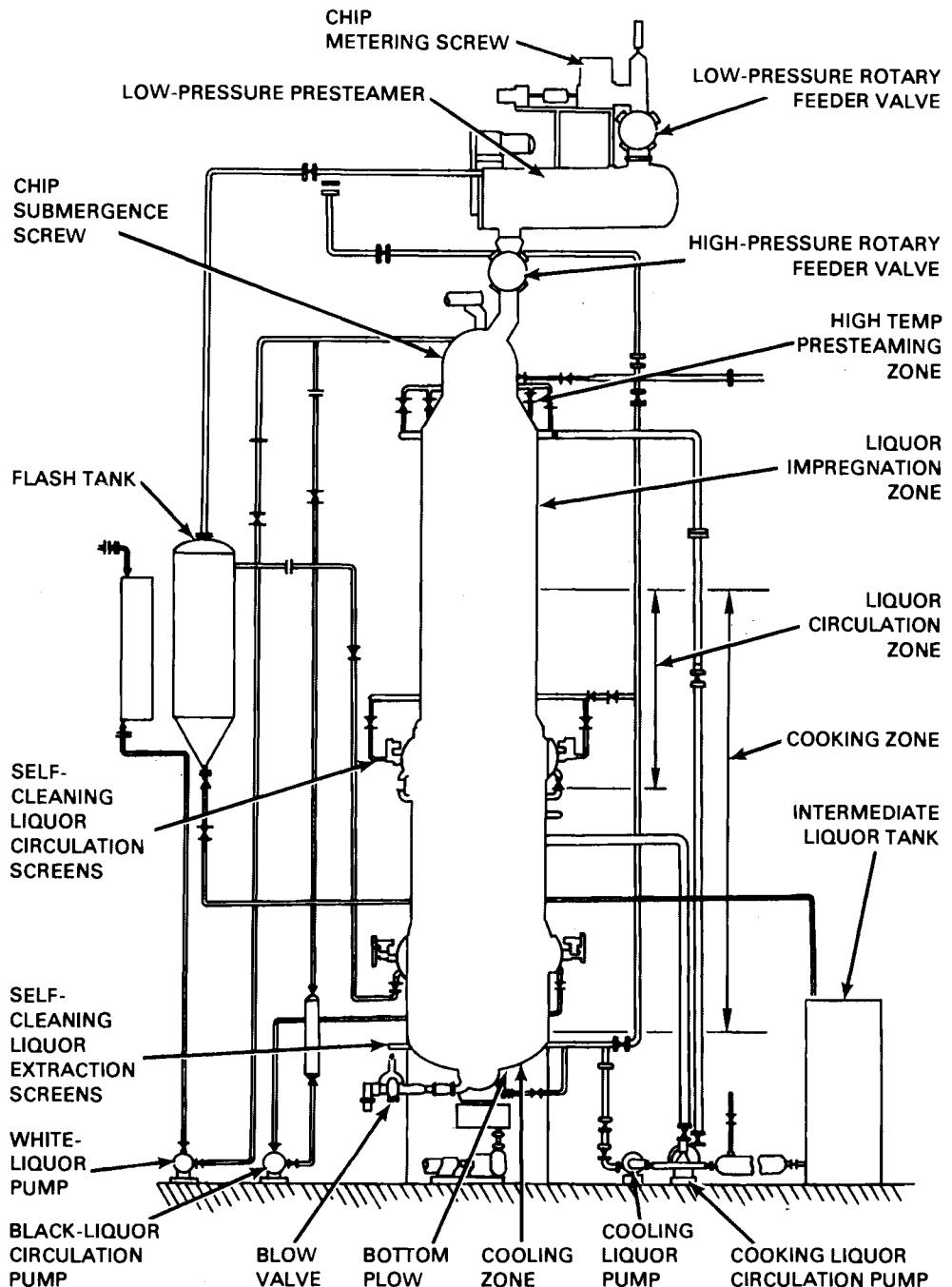


FIGURE H.14 Downflow Continuous Digester

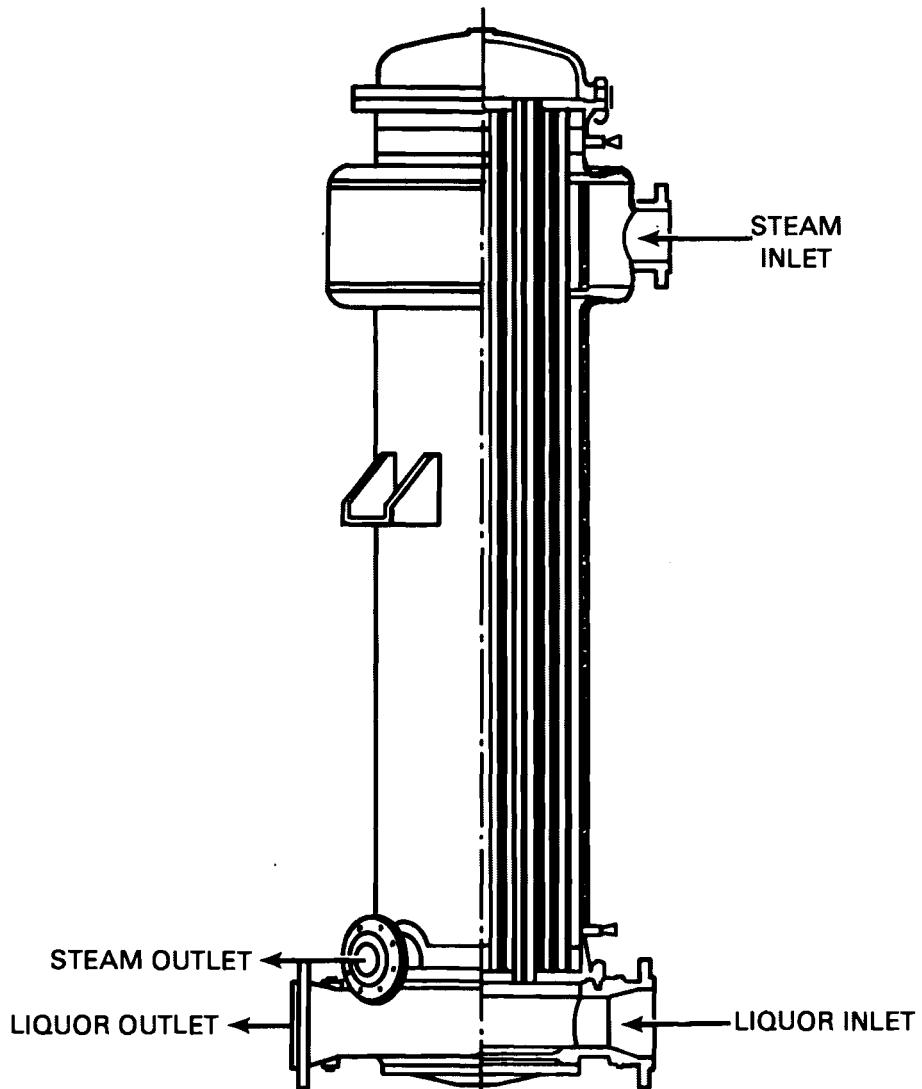
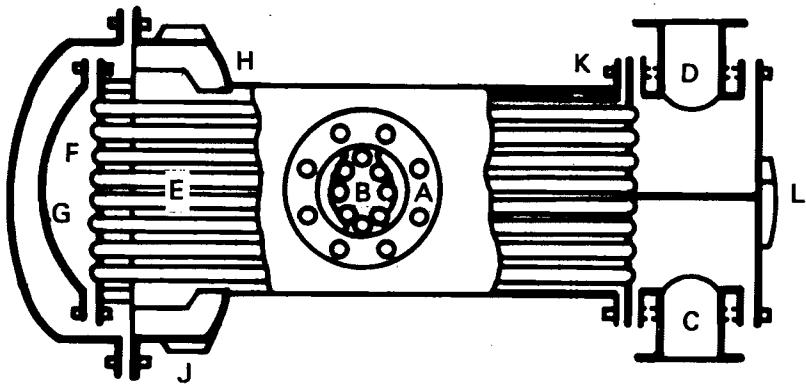


FIGURE H.15 Liquor Heater

Common causes of scale formation in heater tubes are:

1. poor clarification of the white liquor (a)
2. excessive superheat in the steam
3. excessive temperature rise of liquor passing through the heater
4. low liquor velocity passing through tubes
5. insufficient heater surface area. (15)

(a) White liquor - fresh Kraft cooking liquor.



A-STEAM INLET	G-FLOATING HEAD
B-PERFORATED PLATE	H-SHELL
C-LIQUOR INLET	J-DRAIN
D-LIQUOR OUTLET	K-VENT
E-TUBES	L-BLOW OFF
F-TUBE SHEET	

FIGURE H.16 Two-Phase, Floating-Head Heater

The main life-limiting factor presently for 304 and 316SS digester liquor heater tubes is stress corrosion cracking.⁽¹⁷⁾ Conditions necessary for this to occur are:

1. sufficient stress level
2. causative reagent - such as chlorides that can be traced to steam or liquor leakage since corrosion occurs on the outside of the tubes
3. temperature greater than 149⁰F
4. crack-sensitive material.⁽¹⁷⁾

After the pulp has been digested, the spent pulping liquors are concentrated by evaporation to high densities. All Kraft pulp mills process spent pulping liquors to recover valuable chemicals and to provide a source of heat and power.⁽²⁰⁾ Spent liquor from the NSSC method is usually evaporated, combined with Kraft spent liquor and processed. Chemical recovery is more difficult in the sodium-base NSSC process than in the Kraft process. The spent liquor is low in solids, with a relatively high inorganic/organic constituent ratio, and will not burn easily.

Sulfite mills may have recovery boilers to burn the spent cooking liquors. These boilers generate steam that can be used for the evaporation process or for pulping process requirements.

Evaporators for concentrating the liquor can use direct- or indirect-contact heating. Hot gases are used in direct-contact evaporation. Several units or effects are used in series to accomplish indirect-contact evaporation, with steam as the heating medium (Figure H.17).

Spent cooling and pulping liquor from the digester and washing operations contains about 10 to 16% solids. It is concentrated to 45 to 50% solids in multiple-effect evaporators. The liquor is concentrated further to a consistency of 60 to 65% solids in a concentrator or in the recovery furnace direct-contact evaporator. Once concentrated, it is referred to as strong black liquor.

Scaling of evaporators and concentrators is a major problem for this industry.⁽²¹⁾ Evaporator capacity and steam economy can be reduced due to fouling. Frequent downtime is often necessary for cleaning. Types of scales encountered in black liquor evaporators are:

1. calcium compounds - primarily calcium carbonate
2. sodium compounds - Na_2CO_3 and Na_2SO_4
3. silica
4. aluminum silicate
5. organic material.

Calcium carbonate scaling in the black liquor evaporators has been attributed to reverse solubility or excess loading of the liquor.⁽²²⁾ One study indicates that pH may be the controlling variable for this type of scaling.⁽²²⁾ Temperature strongly affects CaCO_3 scaling rates, whereas liquor solids concentration has a lesser effect.⁽²³⁾ Calcium carbonate scales have an average heat-transfer range in spent-pulping liquor evaporators below 200 $\text{Btu}/\text{hr}\cdot\text{ft}^2\cdot{}^{\circ}\text{F}$ and the water soluble scales range from 200 to 280 $\text{Btu}/\text{hr}\cdot\text{ft}^2\cdot{}^{\circ}\text{F}$.⁽²¹⁾

Soluble scales (sodium sulfate and sodium carbonate) deposit rapidly once the solubility limit is reached, which makes it impossible to operate a natural-

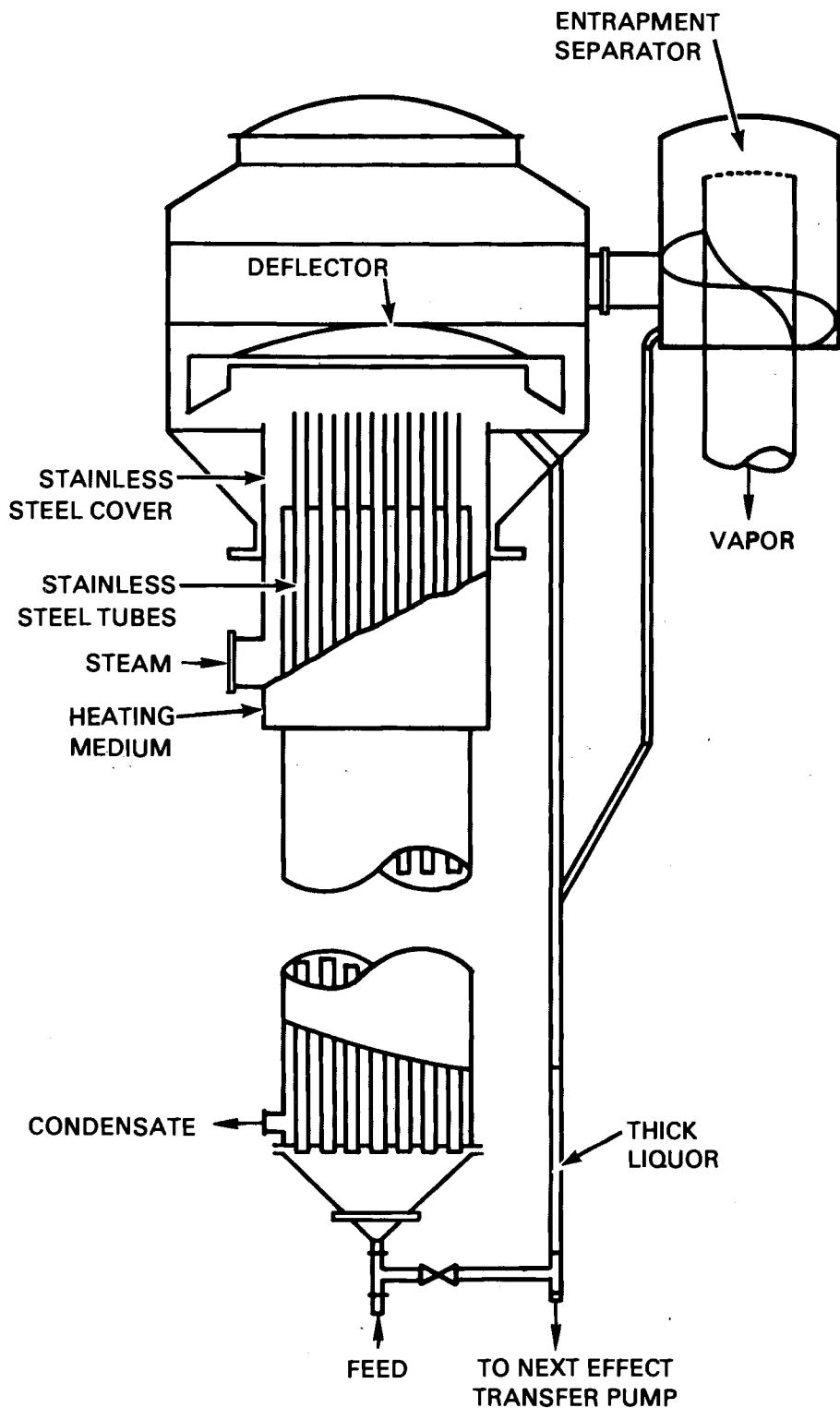


FIGURE H.17 Long-Tube Vertical Evaporator

circulation evaporator above this limit for very long.⁽²³⁾ Concentrators that evaporate to a final solids concentration of 65% are predominately fouled by water-soluble sodium salt scales.

In some cases there is a tendency toward formation of a coating of organic material on the surface of the evaporator tubes. This is generally a result of slow polymerization and carbonization during the destructive distillation reaction that occurs during heating in the presence of caustic soda.⁽¹⁵⁾ This deposit is a black gummy carbonaceous material.

Strong black liquor is burned in specially-designed boilers. Fouling problem areas for the recovery-boiler systems are:

1. air pre-heaters
2. black liquor heaters
3. superheaters
4. boiler tube banks
5. economizers

Slow overheat failure is generally found in the high heat transfer areas of the boiler, such as the furnace water walls. Primary causes are internal deposition due to poor internal chemical treatment, severe feedwater contamination, bad flame pattern or a combination of these.⁽²⁴⁾

Under normal circumstances, boiler fireside tube metal (even in the furnace area) is only 100 to 140⁰F above the saturation temperature at the operating pressure, although the furnace gas temperatures can be 2200 to 2800⁰F. Internal deposition can cause the temperature difference necessary for a given heat-transfer rate to increase well above 900⁰F and weaken the tube metal.⁽²⁴⁾

Hard, dense iron oxide scale can form around superheater tubes and create a thinning of tube metal due to steam-side burning. This is the result of a chemical reaction between the steam and the tube metal. It is caused by insufficient steam flow to cool the tubes.⁽²⁴⁾

Failure of superheater tubes is almost always attributed to overheating, which may be caused by the insulating effect of deposits carried over from the

boiler water or by starvation.⁽²⁵⁾ Starvation of the tubes occurs from poor startup or operating practices.

Two mechanisms are believed to account for the formation of gas-side deposits in superheaters: carryover and vaporization.⁽²⁶⁾ Gas-side deposits in the superheaters can be highly enriched in chloride and/or potassium. The two fouling theories are described as:

1. Carryover - burned black liquor particles entrained in upward flowing combustion gases impact the superheater surface, forming a hard, thick layer.⁽²⁶⁾
2. Vaporization - vaporization occurs in the lower furnace followed by condensation in the cooler upper regions. The vapor diffuses upward through cracks in any deposits already formed and condenses on the cooler surface, creating a white powder.⁽²⁶⁾

Economizers preheat feedwater entering the boiler with flue gases. These gases contain products of combustion and vapor and particle species: carbon dioxide, water, nitrogen, sulfur dioxide, sulfur trioxide, oxygen, sodium sulfate (particles), sodium carbonate (particles) and small amounts of H_2S , $NaCl$, and K_2SO_4 .⁽²⁷⁾

Soot deposits in economizers entrap condensable acid vapors that can lead to acid corrosion. This condensate can combine with soot on the surface of the economizer tubes and inner casing and build up gummy, sticky sulfur-carbon deposits.⁽²⁸⁾

H.3.2.2 Paper Mill Fouling

Fouling can occur in paper machine waste-heat-recovery systems. In this type of system, hot air from the drying section of the paper machine enters exhaust hoods and is routed through a heat exchanger. The exhaust air is filtered and passes through the exchanger to heat cold water. The exchanger can become plugged with dirt and pulp fiber in the air stream.

H.3.2.3 Power Generation Fouling

Many mills provide their own steam and a portion of their electric power through on-site generation. They often burn waste bark or hogged fuel (wood

waste from lumber operations) with other fuels such as oil, coal, and spent liquor. This sometimes leads to fireside deposit problems. The furnace walls and superheaters may collect thick and tough deposits that can lead to a shutdown. The deposits generally consist of inorganic compounds originating from the fuel. The inorganic compounds are liberated in the flame and may react with oxygen from combustion air to form oxides or new compounds. ⁽²⁹⁾

Fouling deposits are discussed below according to fuel type.

1. Wood Waste

Deposits are brittle, consisting mainly of alkaline earth and alkali oxides. ⁽²⁹⁾

2. Wood Waste and Fuel Oil

Sulfur oxides from the oil react with the alkaline oxides from the bark resulting in sulfur formation. Growth rate of the deposit depends on the amount of sulfates in the flue gases, and the heaviest deposits occur in boilers using a weight ratio of dry bark to fuel oil of about one. ⁽²⁹⁾ This ratio gives nearly maximum sulfate formation. Silica can be a problem, depending on the sand content of the wood. ⁽³⁰⁾

3. Wood Waste and Natural Gas

No problems are expected beyond those for wood waste alone.

4. Bark and Coal

High ash content with major components - Al_2O_3 , Fe_2O_3 , and SiO_2 . Aluminum and iron silicate deposits are formed on the hottest parts of the boiler--the furnace walls and tubes of the superheater. ⁽²⁹⁾

5. Bark and Spent Liquor

Deposits from the furnace and the superheater contain as much as 90% $CaSO_4$ and CaO , with minor amounts of MgO . The toughness of the deposits increases with increasing alkali sulfate content, and bark additions decrease the deposit problem. With bark addition, the alkali content increases in the deposit, which has the effect of lowering the melting point of $CaSO_4$. ⁽²⁹⁾

H.3.3 Mitigation Techniques

The strategies currently used to mitigate fouling are listed in Table H.6. Table H.7 presents cleaning options.

Whenever a Kamyr digester cooking heater is fouled such that the maximum flow of cooling liquors has been decreased 20 to 25%, the dirty heater is chemically cleaned. By using deposit-control additives, some mills have reduced the frequency of cleaning these heaters.⁽¹⁶⁾

Calcium carbonate scales are water insoluble and difficult to remove from evaporator tubes. The following methods are often used to handle this kind of scaling:

Preventive Techniques

1. Thermal deactivation - the black liquor is heated to 302°F and held at that temperature for 10 to 15 minutes. In some cases, this reduces or eliminates the calcium-scaling tendencies of the liquor.⁽²¹⁾

2. Chemical additives

Control Methods

1. Control calcium input - Hardwoods contain more calcium than softwoods, especially the bark, and clean separation of bark from pulping wood chips is important in controlling scale formation. The calcium levels in the white liquor and process water are monitored and controlled.
2. Control process operations - The evaporators are run at the lowest operating pressure and in the first evaporator effect, steam temperature is kept below 266°F.⁽²¹⁾ The liquor solids content should be controlled and there should be routine removal of tall oil soap (soap acts as calcium scavenger and removal reduces scaling potential of the liquor).⁽²¹⁾
3. Caustic addition - Adding caustic to the black liquor is thought to offset the impact of increasing temperature on the pH of the liquor, while stabilizing concentrations of complexing organic species and reducing the net calcium ion released.⁽²²⁾

TABLE H.6 Mitigation Techniques

Type of Equipment	Problem	Mitigation Techniques
Digester cooking heaters	<ul style="list-style-type: none"> deposit fouling & tube pluggage 	<ol style="list-style-type: none"> deposit control additives
Multiple-effect evaporators	<ul style="list-style-type: none"> CaCO_3 tube scaling Soluble salts tube scaling Vapor-side scale steel tubes 	<ol style="list-style-type: none"> caustic additon to black liquor control process operations thermal deactivation additives <ol style="list-style-type: none"> re-circulate black liquor monitor saturation limit <ol style="list-style-type: none"> vent later effects to the condenser use stainless steel or chromium-plated steel tubes in later effects
Recovery boilers	<ul style="list-style-type: none"> waterside tube deposits fireside deposits 	<ol style="list-style-type: none"> water treatment continuous monitoring with chordal thermocouples <ol style="list-style-type: none"> sonic soot blowers soot blowers steam lancing vibration
Superheaters (boiler)	<ul style="list-style-type: none"> fouling corrosion tube failure 	<ol style="list-style-type: none"> decrease operation temperature limit NaCl levels fuel additives
Economizers (boiler)	<ul style="list-style-type: none"> tube surface fouling, plug-gage, erosion, & corrosion 	<ol style="list-style-type: none"> sonic horns steam lancing soot blowers control flue gas condensation maintain operating temperature
Air preheaters	<ul style="list-style-type: none"> pluggage 	<ol style="list-style-type: none"> sonic horns, soot blowers
Liquor heaters	<ul style="list-style-type: none"> deposit fouling & tube pluggage 	<ol style="list-style-type: none"> additives
Papermaking heat recovery systems	<ul style="list-style-type: none"> fibrous fouling of heat exchangers biological fouling 	<ol style="list-style-type: none"> pass exhaust air stream through water spray screens

TABLE H.7 Cleaning Methods

Type of Equipment	Chemical	Water/Steam	Mechanical
1. Digester heaters	X		
2. Multiple-effect evaporators	X	X	
3. Liquor concentrators	X	X	
4. Recovery boilers	X	X	X
5. Economizers (boiler)			X
6. Air preheaters	X	X	X
7. Liquor heaters	X		
8. Papermaking heat-recovery systems	X		

Scale Removal

1. Boiling and thermal shocking - Water or weak black liquor is used to boil out the fouled evaporator tubes. Although CaCO_3 is water-insoluble, this method physically weakens the scale structure.
2. Acid wash - usually after several boilout cycles, the tubes will be cleaned with weak sulfonic or nitric acid solutions. (21)
3. Mechanical cleaning - High-pressure water jets are generally used to clean tubes that become completely plugged with scale. (21)

Soluble evaporator scales are easily removed from surfaces by water washing. These scales can be controlled by staying below the saturation limit of the deposit compound, and by recirculating product liquor through the evaporator. The scaling rate drops rapidly with increasing liquor velocity and approaches zero at 12 ft/sec. (21)

Boiler waterside deposits can be minimized by proper water chemical conditioning, increased liquid velocity and controlled steam formation. (25) Waterside deposits are monitored in three ways:

1. Removal of wall section - Annually, a section from the primary air zone, 24 to 36 inches long, is cut out and sent for analysis. (31)

2. Trepanning - A small portion of the tube is removed opposite the fire-side surface of a water-wall tube in the primary air zone to provide visual examination of internal tube surfaces.⁽³¹⁾
3. Chordal thermocouples - Water-wall tube metal temperatures can be monitored with chordal thermocouples. Readings determine an average operating temperature, and when this rises above a pre-determined value, chemical cleaning is necessary.⁽³¹⁾ Industry representatives indicate that the temperature increase usually occurs when the deposits reach approximately 12 to 15 g/ft deposit.

Boilers are usually cleaned chemically, but they can also be cleaned with mechanical and water-flushing methods.

Fouling and corrosion of superheaters and economizers can be controlled through:

1. maintaining optimum operating temperatures
2. using fuel conditioners
3. maintaining proper water chemistry

Soot blowers help remove particulate buildup in air preheaters. Fouled liquor heaters are periodically chemically cleaned.

Fouling of papermaking waste heat recovery systems with pulp fibers and dirt can be controlled by passing the fouling air stream through a water spray. If the fouling stream is liquid, screens can be used to remove the fibers.

H.3.4 Costs

Detailed information on the cost of fouling and corrosion of heat exchangers in the pulp and paper industry was not available. However, an estimate of the 1980 cost of just corrosion is presented in Table H.8.

It has been estimated that 100 to 400 lbs of sulfonic acid is required to clean a fouled continuous digester heater.⁽¹⁶⁾ Acid costs run from \$30 to \$164 (1983 dollars)^(a) per cleaning and 4 to 8 man hours are needed.

(a) April, 1983 Chemical Marketing Reporter.

TABLE H.8 1980 Cost of Corrosion in the Pulp and Paper Industry

<u>Process</u>	<u>Annual Capital Cost</u>	<u>Annual Operating Cost</u>	<u>Total Annual Process Cost</u>
Kraft	69,500,000	189,100,000	258,500,000
Sulfite	3,700,000	3,000,000	6,600,000
Mechanical	8,200,000	5,500,000	13,700,000
Other	8,900,000	16,700,000	<u>25,500,000</u>
Industry Total			304,300,000

Heater cleaning can occur once a month or daily depending on the severity of fouling. (16)

One study of a pulp mill hogged fuel boiler experiencing particulate fouling estimated that steam lance cleaning required 17.5×10^9 Btu/yr at a cost of $\$2.95/10^6$ Btu (1979 dollars). Addition of sonic soot blowers reduced the cleaning energy requirements by 8.75×10^9 Btu/yr. (32)

Discussions with heat exchanger manufacturers for the pulp and paper industry indicated that the primary cleaning technique that they recommended is mechanical vibration, which adds about 10% to the final cost of the exchanger. However, the particular cleaning technique used depends on the application of the exchanger in the pulp and paper mill.

H.4 CHEMICALS (SIC 28)

Combustion product and cooling water fouling and corrosion are major problems in the chemical industry. The areas of most concern are fouling of cooling water systems and combustion product fouling. Little information is available in the literature describing these problems as they apply specifically to the chemical industry. However, an examination of specific chemical processes can provide an estimate of the amount of cooling water and fuel used by these industries. This information together with data from people in the industry and companies associated with mitigation of fouling problems provides an order-of-magnitude estimate of the cost of fouling to the chemical industry.

H.4.1 Process Descriptions

This report covers the following chemical processes:

olefins

chlorine/caustic

ammonia

oxygenated petrochemicals (methanol, ethanol, isopropanol)

phosphorous

sulfuric acid

soda ash

oxygen/nitrogen

synthetic fibers (polyester, nylon 66)

ethylbenzene/styrene

These chemicals are among the major chemicals produced in the United States, and they represent a wide variety of manufacturing processes, and thus a wide variety of fouling problems.

The following sections give a brief description of the processes and discuss the types of fuels used and the amount of fuel and cooling water required. Major fouling problems in each process are discussed.

H.4.1.1 Olefins

Olefins, primarily ethylene, are the precursor to many petrochemicals and thus are some of the major chemicals produced in the United States. Ethylene is used exclusively as a building block and is the primary feedstock for over 40% of petrochemical products.⁽³³⁾ The primary feedstocks for olefin production are ethane, propane, butane, naphtha and gas oil. Figure H.18 is a flow diagram of the ethylene production process.

Feedstock is fed to tubular-coil cracking furnaces along with a flow of steam that helps reduce coking. The hot reaction products are then quenched with oil and cooled. The cooled gas is compressed to a liquid and purified. A series of distillation columns separates the primary product, ethylene, from the stream. Propylene and butadiene may also be separated before recycling the remainder of the stream to the cracking furnace as feed.

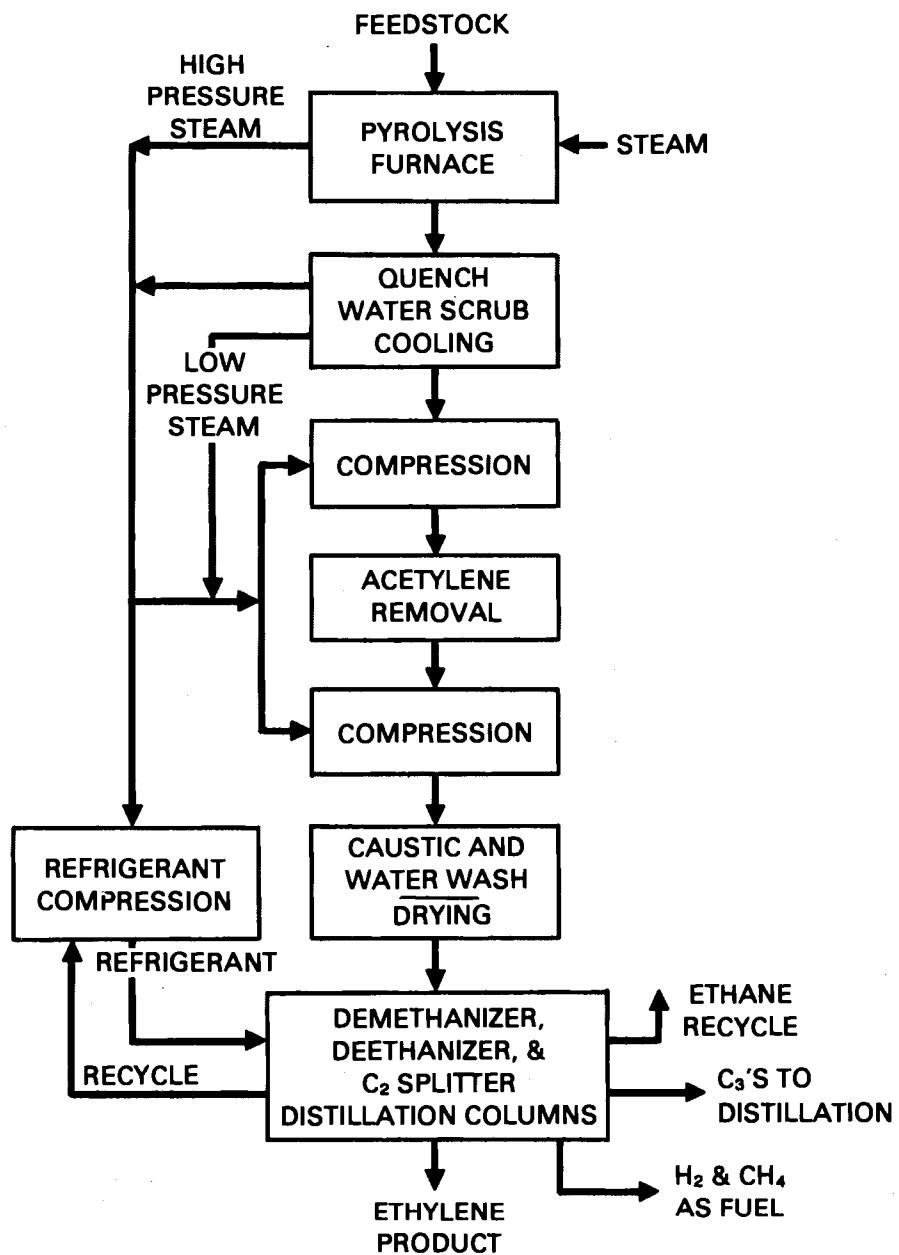


FIGURE H.18 Ethylene Flow Diagram

The cracking reaction is endothermic and takes place at high temperatures (1500°F) with low residence time. The large amount of energy needed for the process is provided by part of the feedstock. In the past, the most common feed material was ethane-propane. However, with an increasing shortage of the lighter forms of fuel, heavier fuels such as butane, naphtha, and gas oil are becoming more common. The change to heavier fuels increases the potential for

fouling problems in the industry, and causes lower ethylene yield and higher yield of byproduct propylene and butadiene per ton of fuel.

Fouling of the cracking furnace by carbon deposits is called coking. The mechanism of coke formation is not well understood and no models have been developed to determine methods of alleviating the problem. Research in this area would be welcomed by the industry. Current mitigation methods include changing operating conditions such as pressure and velocity of feed streams to the furnace, addition of antifoulants to the feed, and periodic cleaning of tubes. These techniques increase heater run length and minimize coking, but do not eliminate it. Periodic shutdowns may be required, ranging from every three days to every three months, depending on the fuel used. The decoking procedure takes about one day. Olefin production is currently at less than full capacity, so shutdowns do not result in lost production. However, a gross estimate of the cost of this problem is that tens of millions of dollars are lost from erosion of equipment, cleaning costs, and other factors.

In addition to fouling of the cracking furnaces, cooling water fouling problems also occur. Large amounts of cooling water are used to cool reaction products between compression stages. Cooling water is also used in the quench tower and to cool final product streams. As much as 38×10^6 lb/hr of cooling water at temperatures of 100 to 120^0F may be expelled from a plant producing 1510 tons ethylene per day.⁽³⁴⁾ Most of the cooling water is used for between-stage compression.

H.4.1.2 Chlorine/Caustic

Chlorine is primarily manufactured by the electrolysis of a salt brine solution. The process flow diagram is shown in Figure H.19. The brine is mixed, then prepared for electrolysis by purification and filtration. Steam is added to preheat the brine to 175 to 200^0F . Two major types of cells are used for the electrolysis step: mercury and diaphragm cells. The mercury cells have the advantage of providing a more-highly-concentrated caustic soda byproduct, but are being phased out due to environmental problems. Diaphragm cells are more common at present. Following the electrolysis step, gaseous

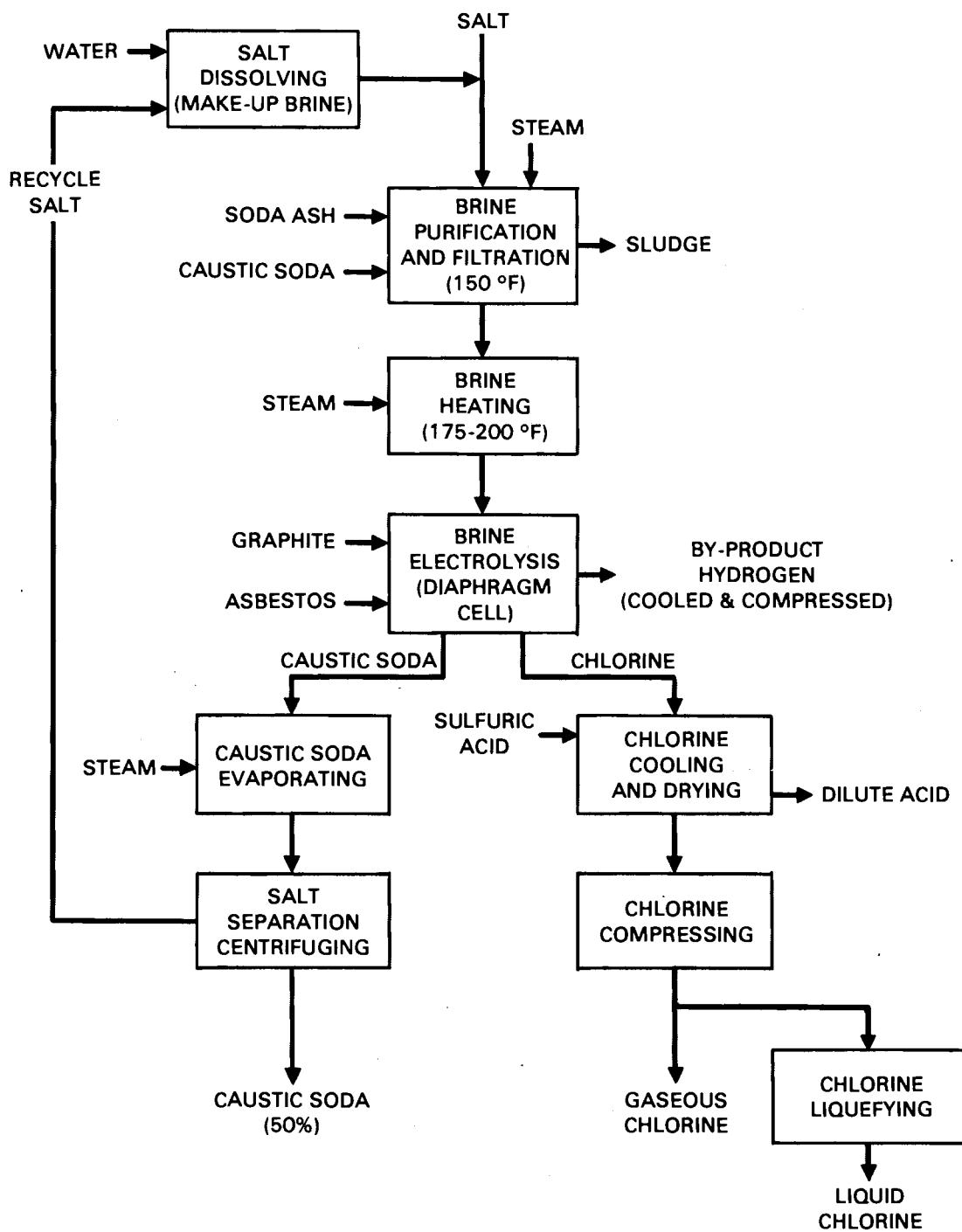


FIGURE H.19 Chlorine and Caustic Soda Flow Diagram
(Adapted from Ref. 36.)

chlorine is cooled, dried, and compressed. Chlorine is liquified in some plants. In the process using diaphragm cells, about 10% caustic soda is evaporated with steam to a concentration of 50%. Higher concentrations of 70 to 75% are sometimes desired or the caustic may be evaporated to the anhydrous form. This drying step is the most energy intensive in the process other than electrolysis. With mercury cells, the caustic is drawn off at a higher concentration and thus does not require as much energy to evaporate to higher concentrations.

Since electricity is the major energy input to the process, any gas-side fouling problems are expected to occur in boilers producing steam for the plant. Many chlorine plants are captive plants and obtain steam from other parts of the complex.

Cooling water is used to cool process liquid and vapor. Table H.9 lists the waste heat streams, their temperature, flow rate, and composition for a 1.5 million lb/day chlorine plant. Palmer⁽³⁴⁾ estimates waste cooling water streams at 5.4×10^6 lb/hr for a 1000 ton/day plant. Estimated temperature of the stream is 100 to 120°F. Cooling water fouling is the major fouling problem on the nonprocess side in chlorine manufacturing.

H.4.1.3 Ammonia

Ammonia is made primarily by steam reforming of natural gas. Figure H.20 shows a simple flow diagram of the process. The feed material (usually natural gas and sometimes naphtha) is desulfurized, then fed to a reforming furnace along with steam. The primary reforming step converts fuel and water to carbon monoxide and hydrogen. Nitrogen is introduced to the mixture in the secondary reformer when stoichiometric quantities of air are added. The next step is a shift conversion that converts carbon monoxide and water to carbon dioxide and hydrogen. The carbon dioxide and other catalyst poisons are then removed in the following two steps. Ammonia synthesis takes place over a nickel catalyst at elevated temperatures and pressures.

Large amounts of high-pressure steam are required for the process. It is estimated that 560,000 lb/hr of 1500 psig steam is required for a 1200 tons/day plant.⁽³⁴⁾ Boilers used to supply this steam experience fouling problems.

TABLE H.9 Sample Plant Waste Heat Stream Summary⁽³⁶⁾

Source	Throughput (1b/day)	Flow (10 ³ lb/hr)	Temperature Input (°F)	Composition	Phase/* Disposition	Heat Content (10 ³ Btu/day)	Specific Energy (Btu/lb)
Chlorine/Caustic Plant	1,534,246					426.8	2,782
o Brine heat exchanger		1,152	180/122	25% salt	L/CW	(262.1)	
o Primary hydrogen coolers		3	230/105	moist H ₂	V/CW	(10.6)	
o Hydrogen compressors		1		moist H ₂	V/CW	(4.3)	
o Primary chlorine coolers		47	175/100	wet Cl ₂	V/CW	(15.6)	
o Chlorine compressor oil coolers			150/	oil	L/CW	(1.7)	
o Dechlorinating flash tank		2	180/125	Cl ₂ ,air,H ₂ O	V/CW	(11.5)	
o Chlorine liquefaction condensers			105/100		L-V/CW	(41.4)	
o Chlorine liquid freon compressors					CW	(1.5)	
o Caustic coolers	90	230/110		50% caustic	L/CW	(19.9)	
o Sodium hypochlorite cooler	40	150/140			L/CW	(5.1)	
o Compressant intercooler	2	220/110		Cl ₂	V/CW	(6.0)	
o Diamond freon compressors	29	235/105		MW 865	CW	(1.2)	
o Diamond snift compressors	16	250/230		dry Cl ₂	V/CW	(1.2)	
o Diamond freon condensers			230/105		L-V/CW	(12.0)	
o Water chillers	960			H ₂ O	L/CW	(33.31)	

*L = Liquid, V = vapor, CW = cooling water.

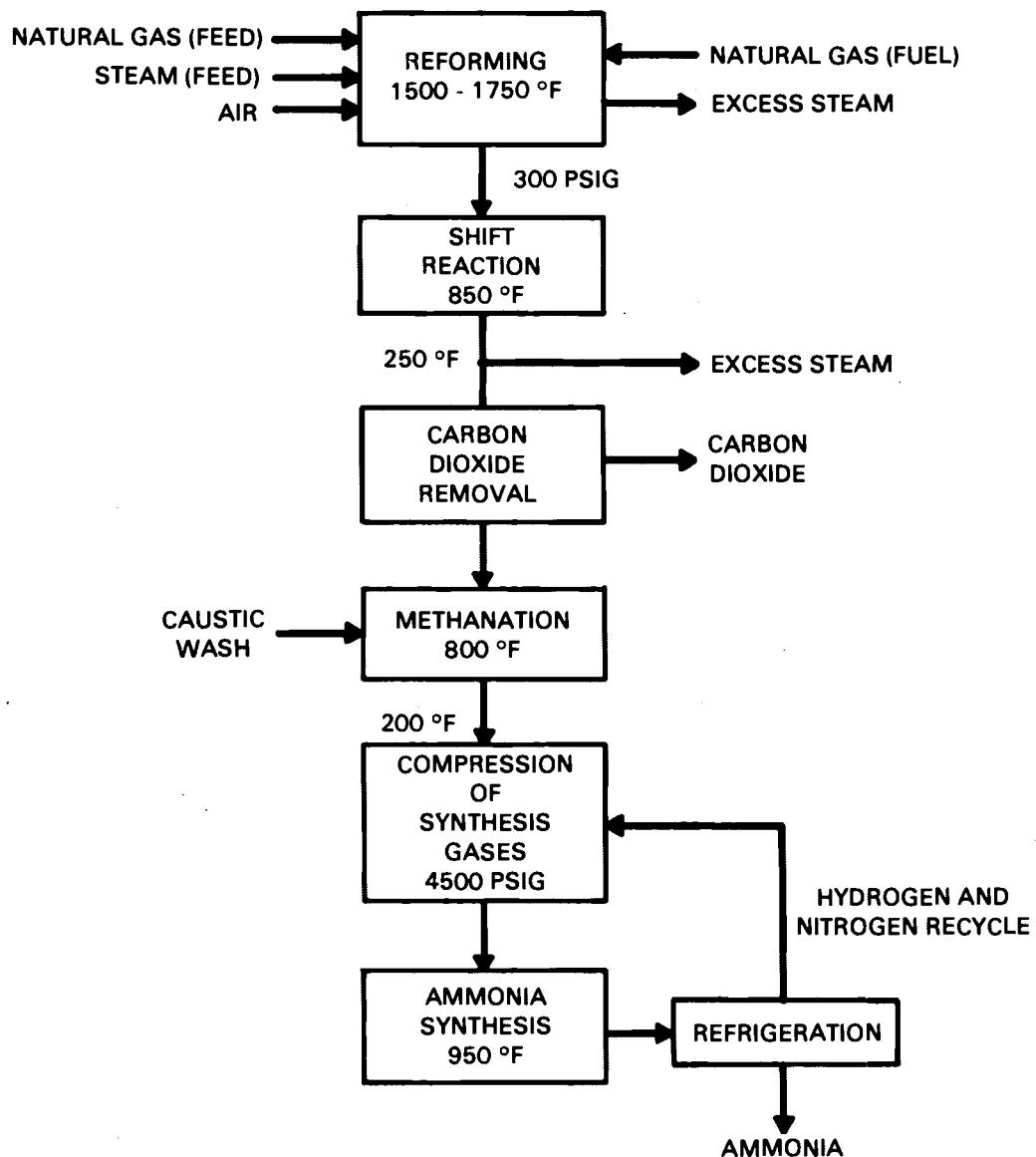


FIGURE H.20 Ammonia Flow Diagram
(Adapted from Ref. 35)

Waste-heat boilers are commonly used in ammonia plants to recover energy from hot process gases. A large ammonia plant may produce up to 300 metric tons per hour of steam at 2200 psi and 985°F from its waste-heat boilers.⁽³⁷⁾ Fouling in the waste-heat boilers may cause failure of the tubes due to buildup of dissolved solids and silica or magnetite corrosion products.⁽³⁸⁾

Cooling water in ammonia plants is used: 1) to cool the product stream after secondary reforming, 2) between high and low-temperature shift conversion, 3) in the CO_2 removal system, 4) following methanation, and 5) in the ammonia synthesis step. About 24×10^6 lb/hr of waste cooling water at 100 to 120°F is discharged from a 1200 ton/day plant.⁽³⁴⁾ Fouling problems in heat exchangers using cooling water are expected.

H.4.1.4 Oxygenated Petrochemicals

Oxygenated petrochemicals include methanol, acetic acid, ethylene oxide, ethylene glycol, and others. Although this category covers a range of processes, the primary fouling problem for each is cooling water fouling in the heat exchangers. Cooling water is used for a range of unit operations. The amount of cooling water in the waste streams of a given size plant is shown in Table H.10.

The amount of fouling depends on water quality, materials of construction of heat exchangers, heat exchanger configuration, type of water-treatment system, water temperature, velocity, and pH as well as other factors. Mitigation methods currently in practice include pretreatment of the water, use of anti-foulants, chlorination, and periodic cleaning both by employees in the plant and by specialty companies depending on the severity of the problem.

The cost of fouling has not been quantified by the plants, but one estimate is at least \$100,000/year for one plant and probably an order of magnitude higher than that. Plant personnel regard process-side fouling as a slightly larger problem than cooling water fouling and would welcome research in both areas.

TABLE H.10 Cooling Water Waste Streams for Oxygenated Petrochemicals⁽³⁴⁾

<u>Plant Type</u>	<u>Plant Size</u>	<u>Temperature ($^{\circ}\text{F}$)</u>	<u>Stream Flow Rate lb/hr</u>
Methanol	1500 tons/day	100 to 120	9.4×10^6
Isopropanol	500 tons/day	100 to 120	17×10^6
Ethanol	800 tons/day	100 to 120	23×10^6

H.4.1.5 Phosphorous

Elemental phosphorous is usually manufactured by the process shown in Figure 6.21. Phosphate rock is nodulized in a rotary kiln or traveling grate at 1400 to 1600⁰F to form spherical agglomerates of 1 to 5 cm in diameter. The particles are fed along with silica and coke to electric furnaces where they are heated to 2700 to 2900⁰F. Phosphorous vapor and carbon monoxide gas are given off in the furnace. Slag is tapped periodically (almost continuously in the larger furnaces) from the furnace floor and put into cars or pots for disposal. Phosphorous vapor is condensed in towers with water sprays maintained at 45 to 55⁰C. The liquid runs into a sump where impurities are precipitated. Carbon monoxide from the phosphorous condenser is usually burned as fuel, along with coal or oil, for the nodulizing kiln.

Fouling problems can occur in the nodulizing stage from phosphorous fines and in the furnace from buildup of ash particles generated from burning coke along with impurities from the other feed materials. Electrostatic precipitators may be used to remove combustion particles from the flue gases. Sonic horns are used in at least one plant to mitigate fouling of the precipitator.

Cooling water is used to cool electrode clamps in the furnace and to prevent corrosion of the slag taphole. A water spray cools the outer shell of the furnace. Another spray condenses phosphorous vapors in towers and thus is slightly contaminated and called "phossy water." The phossy water is recycled until it becomes saturated and is disposed of by evaporation. Soda ash may be added to the phossy water to prevent it from becoming too acidic and causing corrosion.

Characteristics of wastewater streams from a phosphorous plant are given in Table H.11.

The major fouling problem in the phosphorous industry is probably in the nodulizing operation and the furnace. Exit gases from a traveling grate with a feed rate of one million tons of rock feed per year may have a dust loading (before scrubbing) of 450 lbs/hr in 140,000 standard cubic feet per minute of exit gas. The temperature of the gas is 1022⁰F and contains corrosive elements such as HF and SO₃.⁽³⁶⁾

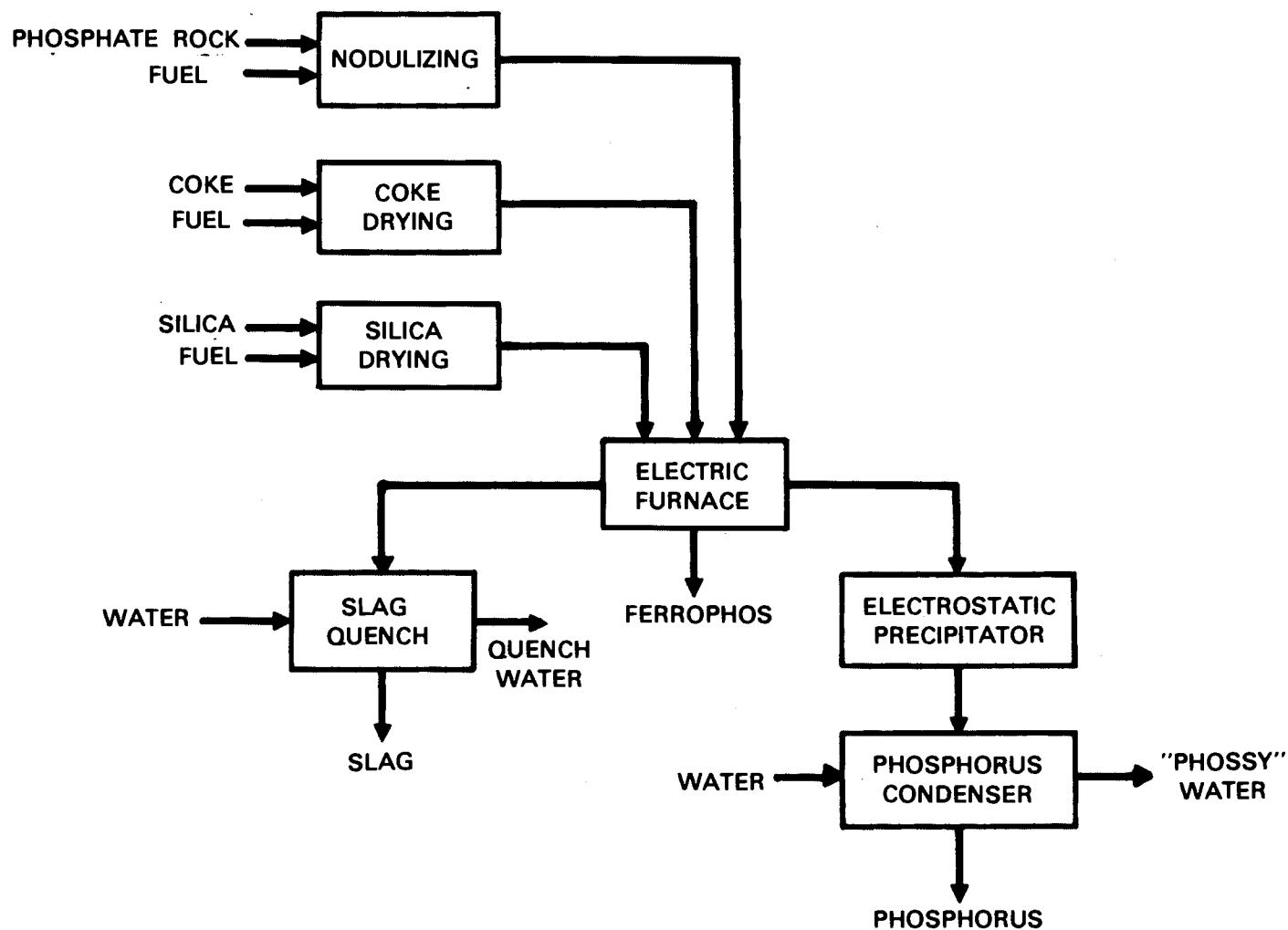


FIGURE H.21 Phosphorus Flow Diagram
(Adapted from Ref. 39)

TABLE H.11. Electric Furnace Production of Phosphorous Wastewater Characteristics⁽³⁹⁾

Basis: 100,000 tpy production (as P₄)
330 operating days/year

H.52

Wastewater Characteristics	Nodulizer Scrubber Liquor* (mg/l)	Phosphorous Condenser Plus Other Phossy Water (mg/l) (lb/day)	Slag Quenching Water (mg/l) (lb/day)	Combined Wastewater (mg/l) (lb/day)
Total suspended solids	280	5,100	135	273
Phosphorus (P ₄)	-	-	8,190	58
Phosphate (PO ₄)	70	1,270	5,460	162
Sulfact (SO ₄)	70	220	13,350	15,230
Sulfate (SO ₄)	1,200	-	40	717
Fluoride (F)	730	21,830	610	344
Total Acidity (as CaCO ₃)	730	13,280	3,000	67,390
Total Alkalinity (as CaCO ₃)	2,000	270	45,560	351
Wastewater Flow Rate	36,380	16,380	2,730	33,040
	2.18 mgd	7.27 mgd	1.82 mgd	11.27 mgd

*Assumes scrubber liquor is recirculated with a 10% blowdown.

H.4.1.6 Sulfuric Acid

The most common method for manufacturing sulfuric acid is the contact process shown in Figure H.22. In this process, atomized molten sulfur is fed with predried air to a sulfur burner. Sulfur dioxide is produced as a hot gas. The

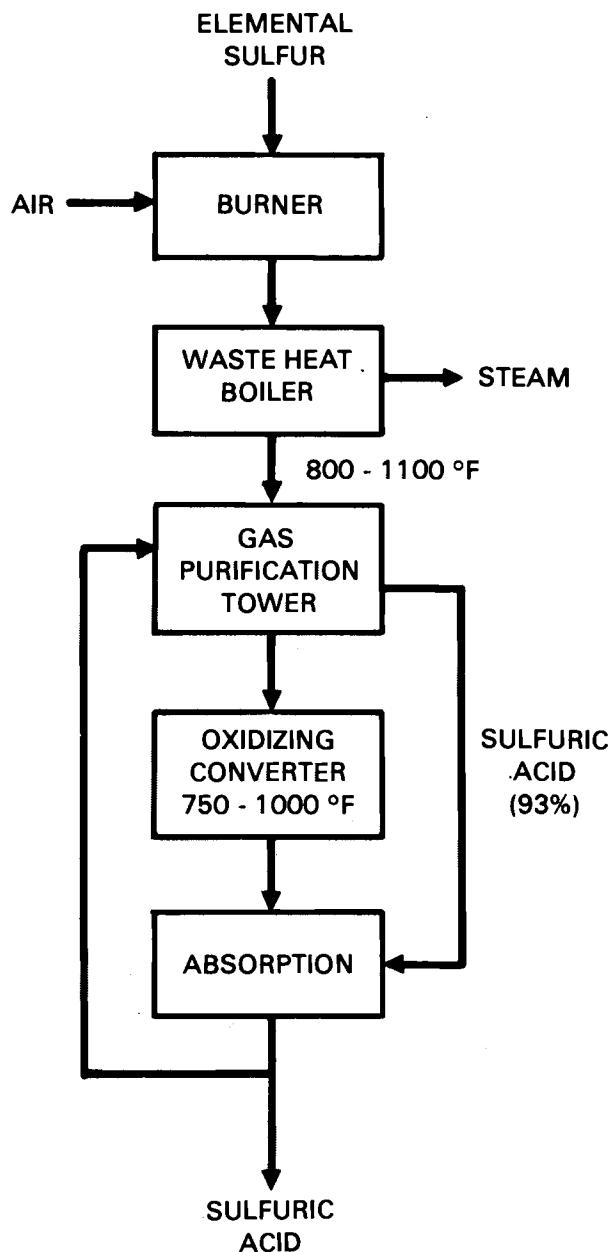


FIGURE H.22 Sulfuric Acid Flow Diagram
(Adapted from Ref. 36.)

exothermic reaction gives off a large quantity of heat that is recovered by waste heat boilers to produce steam for other areas of the plant. Sulfuric acid plants are usually located in a larger plant as a byproduct operation or close to the point of use. The steam generated by the process is a valuable byproduct and is of sufficient quality to provide power.

The SO_2 gas stream is purified to remove water and impurities before passing through a multistage catalytic converter that oxidizes SO_2 to SO_3 . Cooling of the gases between catalyst passes is accomplished by air dilution or heat exchangers. Process gas is cooled further with the heat being recovered by economizers prior to absorption into weak sulfuric acid in packed towers. Hot acid is cooled in heat exchangers before being recirculated or pumped into storage tanks.

Nonprocess fouling problems can be expected in the economizers, waste heat boilers, and heat exchangers. The corrosivity of acid and acid gases necessitates the use of special construction materials in equipment to avoid scaling and corrosion. For example, cast iron acid coolers used prior to 1970 experienced external scaling and corrosion and cost the plants in terms of downtime and maintenance.⁽⁴⁰⁾ Since then, stainless steel shell-and-tube acid coolers have become common.

Scaling on the process side is probably a larger problem than non-process fouling problems. Gas-to-gas heat exchangers are frequently coated with special alloys to avoid corrosion and scaling. Also, dust fouling of the catalyst bed can be a problem and is usually controlled by screening catalyst pellets annually.

H.4.1.7 Soda Ash

Soda ash is manufactured by two common processes: the Solvay or synthetic process and the Trona process. Because of the abundance of natural soda ash in the United States, the Trona process is the most common with few Solvay plants in operation. Therefore, the remainder of this section discusses only the Trona process.

Trona ore is mined, crushed and calcined in a rotary kiln at 160 to 200°C. Figure H.23 is a flow diagram of the process. The calcined ore is

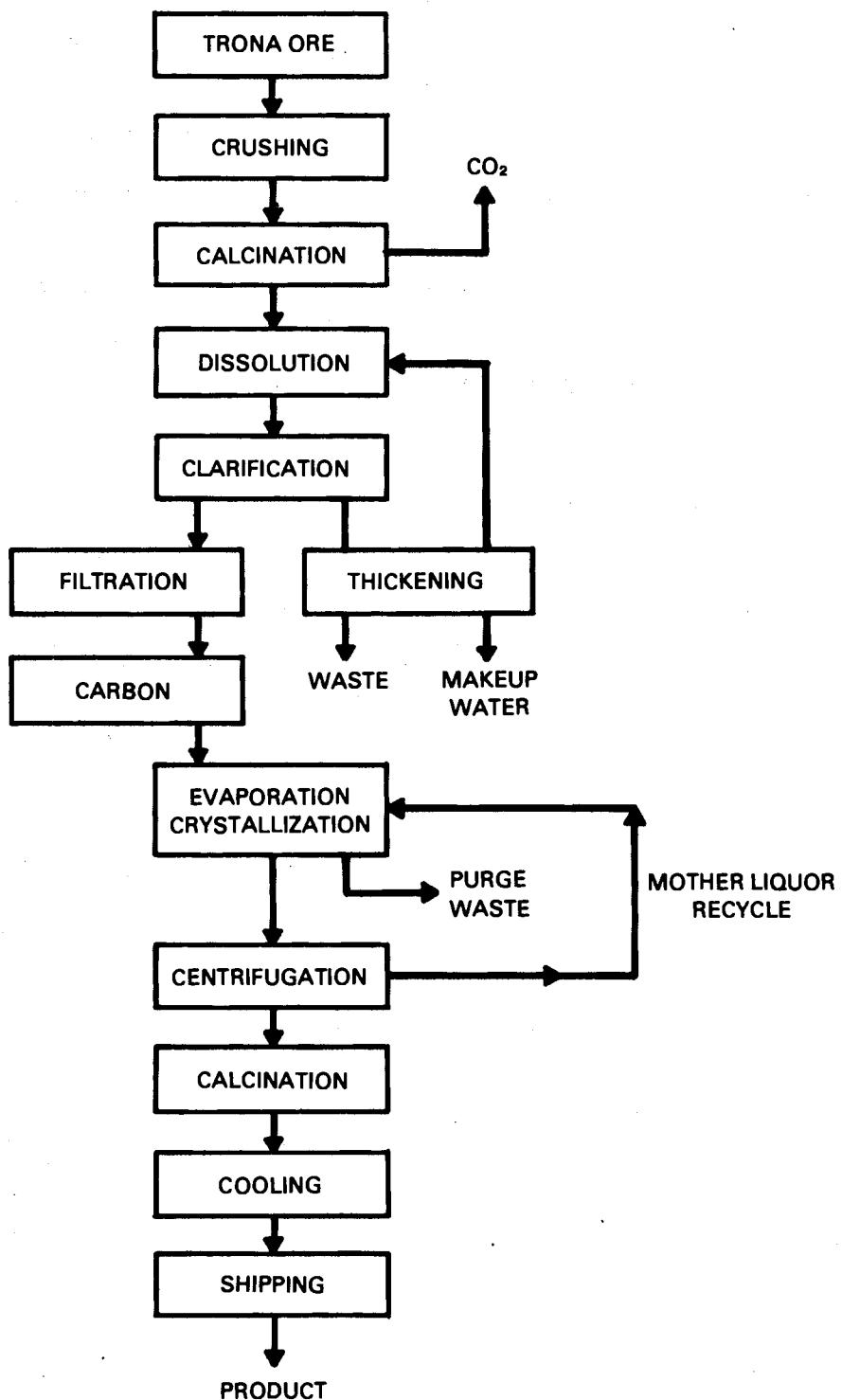


FIGURE 6.23 Soda Ash Flow Diagram
(Adapted from Ref. 40.)

dissolved in hot water, separated from insolubles, filtered, then treated with activated carbon to remove impurities. The soda ash is crystallized in multiple-effect evaporators. Crystals are centrifuged, dried, and cooled.

The major fouling problems probably occur from buildup of dust and fines in the crushing steps. Dry dust separators have been used to lower emissions, although smaller particles escape with these devices. Wet scrubbers have been used. However, they are not common because of the corrosivity of the resulting solution. Boilers providing steam to various parts of the process can be expected to experience fouling problems.

H.4.1.8 Oxygen/Nitrogen

Oxygen and byproduct nitrogen are manufactured by the cryogenic process shown in Figure H.24. Air is cleaned to remove impurities, compressed, dried, and refrigerated until it partially liquifies. It is then distilled into desired components. Compression is the most energy-intensive step requiring large amounts of electricity. Cooling water may be used in some areas of the plant. A waste cooling water stream of 700,000 lb/hr at 100 to 120°F is estimated for a 2000 tons/day plant.⁽³⁴⁾

The waste air stream from the plant may be discharged directly or water cooled. If it is water cooled, fouling in the heat exchanger could be a problem. As much as 2,200 gallons of cooling water per ton of oxygen produced may be required.⁽⁴²⁾

H.4.1.9 Synthetic Fibers

Synthetic fibers such as polyester and nylon are manufactured by the process shown in Figure H.25. A monomer is formed that is then polymerized in a carefully heated, then cooled, reactor. The polymer is usually dried and formed into chips. The chips are then melted, extruded and spun to the desired form. Air drying of fibers under carefully controlled conditions is necessary.

Polymerization reactions are exothermic, but may require high temperatures to initiate. Therefore, both heating and cooling of reactors is necessary. This is usually accomplished with a fluid such as Dowtherm (a trademark of the Dow Chemical Company), which is preheated with fuel. Fouling on the Dowtherm

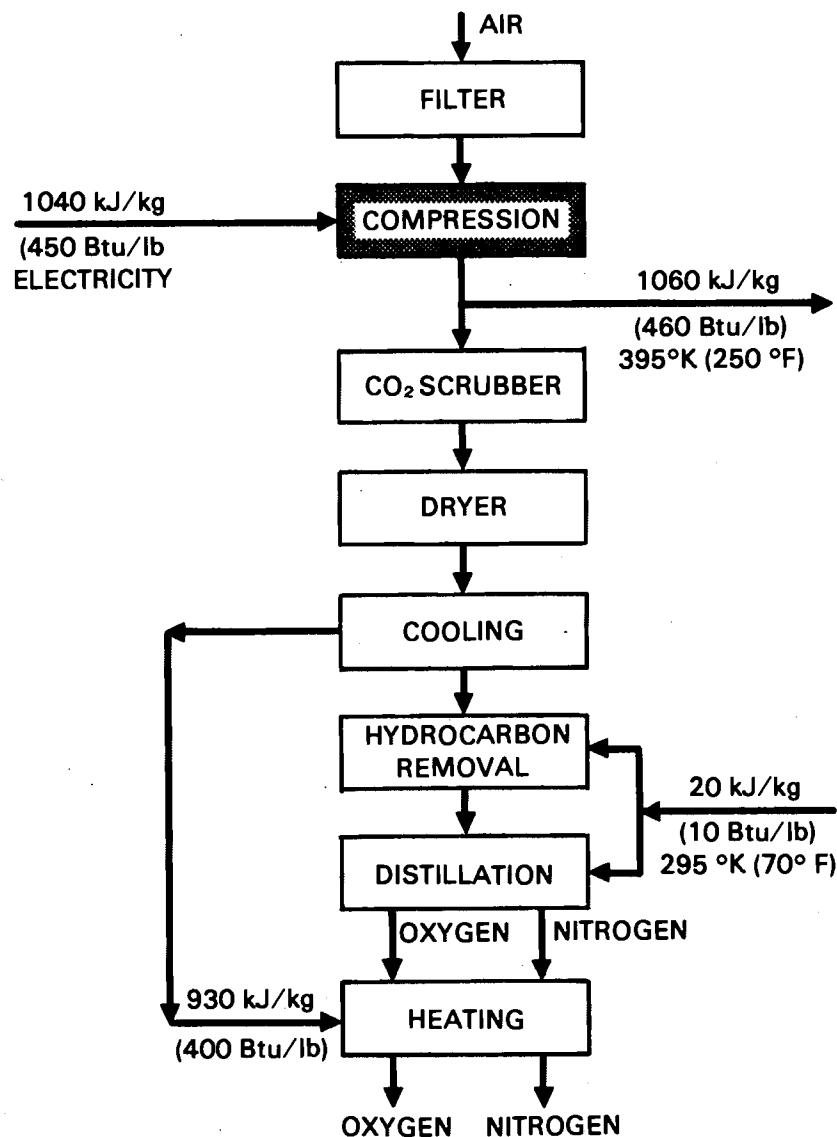


FIGURE H.24 Oxygen and Nitrogen Flow Diagram
(Adapted from Ref. 41.)

side of a heat exchanger or reactor is reportedly not a problem; gas-side fouling in heating the Dowtherm or cooling-water fouling in cooling the Dowtherm may occur.

Cooling water waste streams for two typical synthetic fiber plants are given in Table H.12. Cooling air for fiber-spinning operations is given for polyester. Fouling problems in heat exchangers in cooling service may occur.

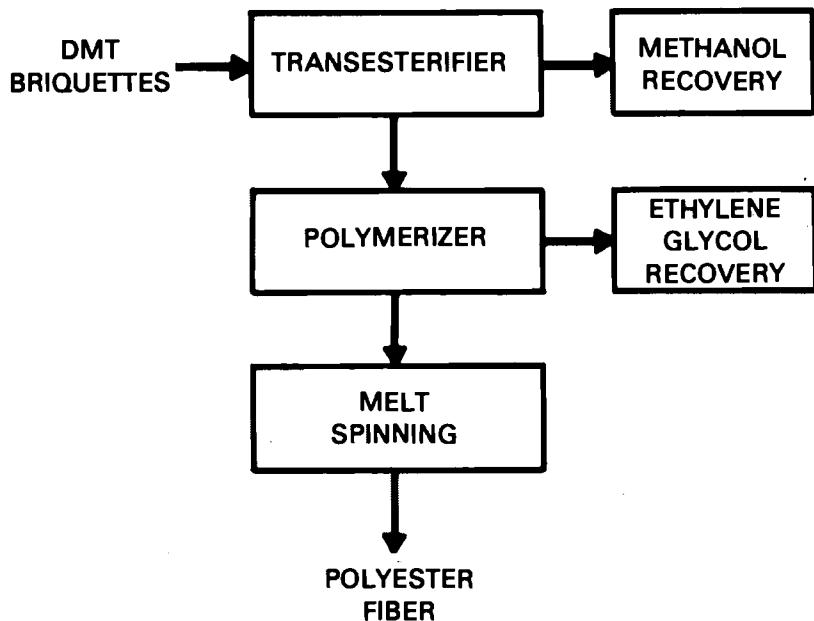


FIGURE H.25 Polyester Fiber Flow Diagram
(Adapted from Ref. 43.)

TABLE H.12 Waste Heat Streams from Synthetic Fiber Plants⁽³⁴⁾

Plant Type	Plant Size tons/day	Waste Stream Type	Temperature F	Flow Rate 1b/hr
Polyester	250	Cooling Water	100 to 120	10×10^6
		Cooling air	90 to 110	750×10^3
Nylon 66	150	Cooling Water	100 to 120	2.5×10^6

Steam is used for evaporation, distillation, and other unit operations that occur with various processes. Since steam is required, boilers provide the steam, and boiler fouling problems may occur.

H.4.1.10 Ethylbenzene/Styrene

Ethylbenzene is the precursor to styrene and is manufactured by a catalytic reaction between ethylene and benzene, followed by product washing and distillation to separate out the product and recycle feed material. Styrene is produced by heating the ethylbenzene in a reactor, cooling and decanting the product, and separating the product in distillation columns.

Large amounts of steam are required to supply heat to the reactors and distillation columns. The steam requirements for a typical ethylbenzene plant and a styrene plant are shown in Table H.13. Gas or oil is used to generate steam in boilers. Fouling in the oil-fired boilers occurs as described in Chapter 3.0. Fouling in gas-fired boilers is negligible. Table H.13 also shows typical fuel requirements for these two types of plants.

Water is used to cool the reactor and the product streams. A majority of the cooling water is used for non-contact cooling of the ethylbenzene dehydrogenation reactor product stream. Table H.14 gives cooling water requirements by stream type for a typical plant. Table H.15 provides estimates of the waste cooling water streams for a 1700 ton/day ethylbenzene plant and for a 1500 ton/day styrene plant.

TABLE H.13 Steam Requirements for Ethylbenzene and Styrene Plants⁽³⁴⁾

<u>Plant-Type</u>	<u>Plant Size Tons/day</u>	<u>Steam Pressure psig</u>	<u>Steam Flow Rate lb/hr</u>	<u>Oil/Gas Rate 10^6 Btu/hr</u>
Ethylbenzene	1700	600	220,000	140
Styrene	1500	75	320,000	16
Styrene	1500	30	190,000	

TABLE H.14 Cooling Water Requirements for Ethylbenzene/Styrene Production
(Adapted from Reference 42)

<u>SOURCE</u>	<u>RATE(Gallons H₂O/Ton Styrene)</u>
Desuperheating and cooling ethylbenzene dehydrogenation reactor stream	79,000
Condensing Styrene distillation column overhead	19,400
Condensing ethylbenzene distillation column reflux	14,400
Cooling and scrubbing gaseous ethylbenzene alkylation reactor product stream	3,600
Cooling and decanting ethylbenzene alkylation reaction products	<u>1,350</u>
TOTAL	117,750

TABLE H.15 Cooling Water Waste Streams from Ethylbenzene and Styrene Plants⁽³⁴⁾

<u>Plant Type</u>	<u>Plant Size ton/day</u>	<u>Temperature F</u>	<u>Flow Rate lb/hr</u>
Ethylbenzene	1700	100-120	245,000
Styrene	1500	100-120	8×10^6

H.4.2 Fouling Problems

The major fouling problems in the chemical industry are cooling water fouling and combustion product fouling. Cooling water systems include heat exchangers, cooling towers, quench towers, steam condensers, boilers, waste-heat boilers, and scrubbers. Combustion product fouling occurs in boilers and fired heaters. Fired heaters include furnaces, kilns, direct-fired heaters, and process heaters. The following sections describe each of these fouling problems and the methods used to treat them.

H.4.2.1 Cooling Water Fouling

The components of cooling water systems that are subject to fouling and corrosion are heat exchangers, cooling tower surfaces, steam condensers, boilers, waste-heat boilers, and scrubbers. In addition, industry contacts also cite engine-jacket cooling systems, quench towers, and refrigeration system coolers as having severe fouling problems, although these are not specifically addressed in the literature. The degree of fouling in each case depends on water quality, type of recirculating system (see Section H.4.3.1 for more details), operating characteristics such as fluid temperatures and flow rates, and other factors.

The chemical industry commonly provides for some degree of fouling in the design of the exchanger. The size, materials of construction, and type of heat exchanger are chosen with consideration of the fouling properties of the cooling water and process liquid. In some cases removable-bundle exchangers may be more economical than less-costly fixed-tubesheet exchangers because of the relative ease of cleaning.

In general, process heat exchangers operating at high temperatures or using process fluids with high heat-transfer coefficients experience more fouling problems than lower temperature exchangers. Also, if the process fluid is on the tubeside of the exchanger, the shellside cooling water is at a lower flow rate, which can result in a higher degree of fouling. Shellside deposits are also generally harder to remove.

To alleviate fouling in heat exchangers, cooling water is usually pre-treated, equipment is oversized to accommodate expected fouling rates and planned cleaning practices, and periodic cleaning of exchangers takes place.

Cooling Towers

Cooling tower surfaces are a prime area for biofouling. Evaporation from the tower causes concentration of dirt, dissolved gases, microorganisms, and biological nutrients in cooling water. This concentration, along with the warm environment, encourages biological growth. Surfaces exposed to sunlight promote algae growth, which in turn provides food for bacteria. Fouling may become so severe that the distribution holes at the top of the cooling tower deck are plugged.⁽⁴⁴⁾ Asiatic clams have also become a problem in the last eight to ten years according to people in the chemical industry.

The most common method of treating biofouling is to add chlorine to the water. Other biocides such as isothiazolins are also commonly used and may become increasingly popular as discharge regulations for chlorine become more stringent. Mechanical cleaning with either brushes or abrasive-surfaced balls is also commonly used.⁽⁴⁴⁾

Steam Condensers

Biofouling of condensers differs from cooling tower biofouling. Macro-invertebrate fouling is associated with cooling towers, whereas microbial fouling or slime is the main concern in condensers.⁽⁴⁵⁾ Many of the factors that influence slime growth are seasonal and tend to enhance fouling more in the spring and summer.⁽⁴⁵⁾

Although condensers for chemical plants are smaller than those used by utilities, the same fouling problems on the cooling water side are expected to occur. In utilities, condenser fouling can cause shutdowns. For this reason, utilities tend to overdesign condensers and incur additional costs for larger or redundant condensers. Oversized condensers can result in a loss of plant efficiency. Some people in the water treatment industry believe that condenser fouling is one of the most costly fouling problems in industry because of overdesign practices. The most common treatments are the addition of chlorine and periodic cleaning of condenser tubes.

Boilers and Waste Heat Boilers

Boilers generate steam from fuel combustion and waste-heat boilers recover heat from process fluids or flue gas. In both cases steam is used for mechanical or thermal energy in the process. Because of the high temperatures and

pressures at which the boilers operate, boiler feedwater requires a more demanding water treatment than other cooling services to avoid fouling. (46)

Waste-heat boilers, which are becoming increasingly common in the chemical industry, have the primary purpose of cooling process gas. Thus boiler application is secondary and is sometimes neglected by plant employees. Inadequate circulation of cooling water and high localized heat fluxes may occur that lead to fouling or corrosion of the boiler tubes. (46)

Boiler feedwater is usually treated by adding antifouling and anti-corrosive agents upstream of the heat-transfer area. Deaeration and addition of chemicals to the water is standard practice.

Scrubbers

Cooling water that directly contacts process liquids or solids as in scrubbers may entrain contaminants such as dissolved gases and suspended solids. These require complex treatment methods to avoid fouling. Treatment will vary depending on the specific application.

H.4.2.2 Combustion Product Fouling

Fouling and corrosion of heat-transfer surfaces by combustion products occurs in boilers and fired heaters. The severity of these problems depends on the type of fuel, the fuel form, and the combustion efficiency. Combustion efficiency is primarily a function of the amount of excess air. With fuel oil, the degree of atomization and the oil viscosity are also factors that affect the combustion efficiency. Inefficient burning increases soot formation, which increases fouling of the tubes in boilers and fired heaters.

Occasionally organic wastes or other byproduct fuels are burned in a boiler or fired heater. If the fuel contains sodium, the low fusion temperature of the combustion product NaO causes it to plate out on boiler tubes and severe fouling can result.

A major problem in fired heaters for olefins manufacturing is coke buildup in the furnace tubes. The coke fouls heat-transfer surfaces and causes localized hot spots in the tube walls, leading to corrosion. The coking problem is one in which industrial representatives believe research is needed to better

understand the coking mechanism and to develop methods of selecting optimum operating parameters.

Current techniques used to minimize coking include adjusting flow velocities and pressures, and periodic tube cleaning. Steam air decoking (described in Section H.4.3.4), mechanical, and chemical cleaning are all commonly used.

H.4.3 Treatment of Fouling Problems

Water treatment is a standard means of preventing fouling and corrosion in cooling water systems in the chemical industry. Fuels are sometimes treated with chemicals, although this is not as common. Mechanical and chemical cleaning of heat-transfer surfaces is employed. Outside cleaning services are used for severe cases; routine cleaning is usually done in-house. Treatment methods are described in more detail in the following sections.

H.4.3.1 Water Treatment

Water treatment includes removal of dissolved gases and salts from water supplies available for plant use. The treatment varies with water quality and depends on factors such as water source, scarcity, type of circulation desired by the plant, and quality required by the process. In a typical plant 80% of the water is used for cooling, 15% for process, and 5% for generation of steam. (46)

Most chemical plants use open recirculating systems in which the water is recirculated through a cooling tower. Makeup water replaces the water evaporated from the tower and the blowdown water, which is removed to control buildup of dissolved solids. Anti-corrosives, antifoulants, and chlorine to control biofouling are usually added.

In once-through systems, chlorination and precipitation to minimize fouling may be used, although extensive treatment is not economical. Closed recirculating systems are used in water scarce areas. The water is fully recycled and very little makeup water is required. Very effective corrosion inhibitors, such as chromate or nitrite, are used in high dosages in these types of systems. (46)

Most industrial representatives believe that although the antifoulants used are adequate, they do not exclude the need for mechanical and chemical

cleaning. Off-line cleaning is normally done during scheduled downtime so that no cost is incurred from lost production.

H.4.3.2 Mechanical Cleaning

Mechanical cleaning of heat exchanger surfaces includes turbining, hydro-blasting, and jet blasting. Soot blowers and sonic horns are used to mechanically clean ash from boiler and furnace tubes.

Turbining involves the use of a rotating cutting head to ream out deposits fouling the surface. Surfaces may be damaged by improper cutting or tube mis-alignment.⁽⁴⁷⁾ Hydroblasting or water jetting uses high-pressure water (2,000 to 10,000 psi) at flow rates of 6 to 40 gal/minute to remove scale and foulants.⁽⁴⁸⁾ Disadvantages of water jetting include generally higher costs in comparison to turbines and use of high volumes of water that must be disposed of or recycled. Tube life may also be shortened from repeated water jetting.⁽⁴⁹⁾ Jet blasting uses solid particle cleaning agents such as sand, clay, or lead shot in a high-velocity gas propellant to dislodge foulants from tube surfaces. An inert gas such as nitrogen is frequently used with gas flows at nearly sonic velocity for more severe cleaning.

Soot blowers and sonic horns are devices that periodically blast tubes with air or sound waves to dislodge soot and other particles from surfaces. Soot blowers and sonic horns are common, but not extensively used.

H.4.3.3 Chemical Cleaning

Acid solutions are used to soften and remove surface deposits. Water washing usually follows to flush deposits from the tubes.⁽⁴⁷⁾ Problems with chemical cleaning include choosing a solution strong enough to be effective without corroding tube surfaces, and disposing of waste chemicals and toxic hydrogen sulfide gas that may be produced in the process.⁽⁴⁷⁾ Surface passivation--applying anticorrosive film to pretreat the surface--may be warranted following chemical cleaning.

H.4.3.4 Other Fouling Treatment Methods

Although additives are available to prevent combustion product fouling, people from the industry have indicated no great success with them and they are not commonly used. Controlling the burning efficiency by controlling excess

air and keeping other parameters at the optimum level is most often done to keep combustion product fouling at a minimum.

Steam-air decoking is most commonly used to clean furnace tubes. The coke buildup is removed by a controlled burn; steam quenches the reaction. This method requires close monitoring of temperatures in the tubes to maintain tube integrity while sustaining the reaction.⁽⁴⁷⁾

H.4.4 Costs

Although detailed fouling costs are not available by chemical process, order-of-magnitude estimates were provided by some of the industry personnel contacted. The greatest cost incurred as a result of fouling in the petro-chemical (primarily olefins) industry is caused by coking of direct-fired furnaces. For example, for an increase in the driving temperature of 50⁰C, the cost in increased fuel alone is estimated at \$500,000 per year for a 100,000-million-barrel-per-day plant.

Wide ranges of costs were provided for the addition of antifoulants, anticorrosives, and biocides to cooling water. These ranges, provided by water treatment industry personnel, are:

- antifoulants \$20 to \$100 per million pounds of blowdown
- anticorrosives \$15 to \$100 per million pounds of blowdown
- biocides \$5 to \$200 per million pounds of blowdown

A plant may use one or all of these chemical treatment methods depending on the water quality, availability, type of circulation or other site-specific factors. Total water treatment costs may range from \$5 to \$400 per million pounds of blowdown.

Water and fuel treatment minimize, but do not eliminate, heat exchanger fouling. To account for this, common industry practice is to size exchangers using TEMA fouling resistances or fouling resistances derived from previous experience with particular fluids. Heat exchanger manufacturers for the chemical industry indicated that they oversize heat exchangers for this industry anywhere in the range from zero to 100%, with about 30% being the average. Additional capital costs due to oversizing are approximately equal to the amount of oversizing.

Special heat exchangers and heat exchangers designed with exotic materials (more expensive) are often used in the chemical industry to avoid fouling and corrosion problems. For example, a shell and tube heat exchanger with Hastelloy®^(a) or titanium tubes and head will cost about twice as much as a comparable exchanger made of carbon steel. Similarly, heat exchangers made of 300 series stainless steel cost 50 to 100% more and exchangers made with graphite or Teflon® tubes cost 100 to 150% more. For some streams with severe fouling, scraped surface heat exchangers are used, which cost 10 to 20 times more than a standard carbon steel shell and tube with the same heat transfer.

Dual exchangers may be installed for more severe fouling problems such that exchangers can be cleaned without disturbing the process. More commonly, cleaning is done during scheduled downtime so no parallel equipment is required.

Fouling and corrosion are major causes of downtime in static equipment such as stills and heat exchangers, but minor causes of downtime for mechanical equipment such as compressors and pumps. Downtime may or may not result in lost production depending on unit capacity, sales volume, alternative means of production, and other variables. Currently, with the chemical industry operating at less than full capacity, this cost is expected to be minimal.

Capital equipment such as sonic horns, soot blowers, high-pressure water rigs, and sand or grit blasting equipment is an added expense for many chemical plants, costing 5 to 50% above the base cost of the exchanger.

Outside cleaning services are commonly used to clean fouled heat-transfer equipment. The cost of the service depends on the severity of the problem, type of equipment cleaned, frequency of cleaning, and other factors.

Two estimates were given by industrial representatives for the total cost of fouling for a petrochemical plant. One believed that a minimum of \$100,000/year was spent up to an order of magnitude higher. Another predicted the cost at \$200,000/year, but believed the cost would be twice as great if none of the current treatment methods were used. This representative indicated that research in the fouling area may reduce the cost by 50%.

(a) Trademark of the Cabot Corporation, Kokomo, Indiana.

H.5 PETROLEUM REFINING (SIC 2911)

This section provides a brief description of the petroleum refining industry. It describes the fouling problems associated with specific pieces of equipment, and identifies current mitigation strategies and costs.

H.5.1 Petroleum Refining Operations

The petroleum refining industry (SIC 2911), as defined by the U.S. Department of Commerce, includes establishments that are primarily engaged in producing gasoline, kerosene, distillate fuel oils, residual fuel oils, lubricants, and other products from crude petroleum and its fractionation products, through straight distillation of crude oil, redistillation of unfinished petroleum derivatives, cracking, or other processes. Although each refinery is characterized by a unique capacity, processing configuration, and product distribution, there are some generic similarities among refineries in a given geographic region, primarily due to the characteristics of the crude oil processed and the products distributed.

In general, petroleum refineries convert crude oil into finished products by employing three fundamental operations: 1) physical separation (distillation, absorption, stripping, and extraction), 2) chemical conversion (changing molecular structure), and 3) treating. Crude oil, as it comes from the ground, is a mixture of thousands of different hydrocarbons. In addition, there may be large amounts of paraffin wax, asphaltic matter, sulfur, salts, and other impurities. It is necessary to separate the complex mixture into various cuts of different boiling ranges before any chemical rearrangements are attempted.

H.5.1.1 Physical Separation

Fractional distillation is based upon the fact that compounds with greater molecular weights have higher boiling points than compounds with lower molecular weights. The crude oil is partially vaporized in the tubes of a furnace and the two-phase mixture then enters the crude unit (distillation column). As the vapors rise, they cool and condense at various levels of the column depending upon their relative volatilities. Light hydrocarbons (C_4-)^(a) rise to

(a) C_4- refers to all compounds that have boiling points less than or equal to the boiling point of normal butane.

the top of the column where they are liquified in a condenser and recovered in a reflux drum. In between the condenser at the top and the reboiler at the bottom of the column, various sidecuts are drawn off, depending upon the particular product slate of the refinery. The heaviest fractions of the crude oil drop to the bottom of the column and are withdrawn.

Hydrocarbons with roughly fourteen or more carbon atoms cannot be boiled at atmospheric pressure without decomposing. Thus the heavier crude fractions must be distilled under a vacuum. Because vacuum distillation equipment is more expensive than atmospheric distillation equipment, most crude units consist of two columns. The bottoms from the atmospheric column are pumped to the vacuum column, where the heavy fractions are split into several boiling ranges. The vacuum column bottoms are used in the manufacture of asphalt.

H.5.1.2 Chemical Conversion

Once the crude oil has been separated, the various fractions are piped to different plants in the refinery. In general, the next step is some type of chemical conversion process, where the hydrocarbon molecules are rearranged to form desired petroleum products such as gasoline. Through chemical conversion, refineries are able to produce an average of 19 gallons of gasoline per barrel^(a) of crude. The major processes that enable refineries to produce gasoline from hydrocarbons that are not in the gasoline boiling range^(b) are thermal cracking, catalytic cracking, hydrocracking, reforming, alkylation, polymerization, and isomerization.

Thermal cracking was the first conversion process introduced in oil refineries. In this process, heavy fractions of the crude are subjected to high temperatures and pressures, resulting in the breaking of molecular bonds. Thus large, complex molecules are cracked into smaller molecules. Cracking produces gasoline that is superior in antiknock characteristics to the gasoline obtained by simple fractionation of the crude. Thermal cracking gives a low rate of conversion and is not used to a great extent anymore.

(a) A barrel, as used in the petroleum industry, is equal to 42 U.S. gallons.

(b) The gasoline boiling range is 100 to 400°F.

The second major conversion process is catalytic cracking. This process accomplishes the same objective as thermal cracking, but the use of a selective catalyst enables cracking to occur at moderate pressures. Also, the gasoline produced has an even higher octane rating than that made in a thermal cracker. Catalysts used in various catalytic cracking processes range from aluminum and platinum to acids and processed clay.

The most modern and most complex of the cracking processes is called hydro-cracking. It is also the most efficient conversion process in terms of extending the usefulness of a barrel of crude oil. The process is described as "a method of cracking in the presence of hydrogen and a catalyst to convert low-value, high-boiling distillates to lower-boiling, higher-value liquid products with essentially no waste gas produced."⁽⁵⁰⁾ In a hydrocracker, hydrocarbons are heated under pressure in the presence of hydrogen and a catalyst. The hydrocracking catalyst has two functions: 1) to crack the molecules, and 2) to hydrogenate the unsaturated products. Most of the products formed are isoparaffins, which make high quality gasoline.

Secondary reactions also occur in the hydrocracking process. The desulfurization reaction produces H_2S and the denitrification reaction produces NH_3 . Water is injected into the reactor effluent stream to force the H_2S and NH_3 into an aqueous phase. The stream then goes to a separator which removes the aqueous phase from the organic phase and sends it to a waste-water-treating plant.

The catalytic reformer's main functions are to produce aromatics and to reform normal paraffins into isoparaffins, which causes an increase in octane number. The reforming reactions occur at elevated temperatures and pressures in the presence of hydrogen and a platinum catalyst. Reforming results in molecular rearrangement; the total number of carbon atoms in the rearranged molecule is not altered, and large quantities of hydrogen are produced as a by-product.

Since large volumes of light hydrocarbon gases are produced in a typical refinery, it is common to see alkylation, polymerization, and/or isomerization units present. The first two of these processes are methods of combining small

molecules to make larger ones. Isomerization is a molecular rearrangement process that produces feedstock for alkylation units or high-octane isoparaffins for gasoline blending. Prior to the 1930's, the light gas streams were burned as fuel. Now alkylation, polymerization, and isomerization have increased the gasoline yield from a barrel of crude and eliminated the wasteful burning of useful refinery by-products.

H.5.1.3 Treating

The main purpose of treating processes is to remove the odorous and corrosive sulfur compounds from refinery products. The crude oil may be desulfurized before conversion, or the products may be desulfurized individually, depending upon the economics of the situation. Due to EPA regulations limiting emission of sulfur compounds into the atmosphere, many refineries are now installing desulfurizers capable of handling all boiling ranges of crude oil. These units are similar to hydrocrackers except that the catalyst performs desulfurization and denitrification without causing cracking to occur.

In addition to sulfur removal, gasoline must also undergo various other blending and treating processes in order to meet strict product specifications. Finished gasoline is a blend of straight-run gasoline, cracked gasoline, reformed gasoline, and polymerized gasoline. To this blend, refiners add a variety of additives to improve the quality of the fuel. Among these additives are anti-knock compounds, anti-rust compounds, anti-icing compounds, and detergents.

H.5.1.4 Energy Use

The petroleum refining industry is extremely energy-intensive. However, as the first supplier of refined fuels to the rest of the country, it has access to by-product fuels not available elsewhere, such as refinery gas and petroleum coke. Only about half of the energy consumed in an oil refinery is supplied by purchased fuels; the other half is supplied by these in-house by-product fuels. Table H.16 shows the petroleum refining industry's 1978 fuel use by energy source.

Within a refinery, energy requirements exist for process heat (both direct and steam) and motive power. In the latter category, considerable flexibility exists regarding the use of electrical, gas-engine-driven, or steam-driven

TABLE H.16 Petroleum Refining Industry Fuel Use - 1978⁽⁵¹⁾

Energy Source	<u>10¹²</u> Btu	<u>%</u>
Refinery gas	1291.7	42.2
Natural gas	820.6	26.8
Petroleum coke	394.8	12.9
Residual fuel oil	314.6	10.3
Purchased electricity	94.8	3.1
Liquid petroleum gas	57.1	1.9
Distillate fuel oil	51.7	1.7
Purchased steam	32.9	1.0
Coal	3.2	0.1
Crude oil	<u>2.6</u>	<u>0.0</u>
	3064.0	100.0

motive power. It is common practice to use engines or steam drivers for major compressors and other heavy equipment, and electrical power for pumps, mixers, air coolers, and miscellaneous services. Even though refineries generate sufficient heat to produce steam to satisfy their total electrical requirements, on the whole, less than 10% of refinery electrical needs are self-generated.⁽⁵²⁾ The balance is supplied as purchased power. Overall, electrical demand is essentially constant throughout the year.

High-temperature thermal energy requirements are met with fired heaters and lower-temperature requirements are met with steam. Although considerable process steam is used throughout the refining process, the ratio of direct heat use to steam use is approximately 4 to 1. Steam pressures range from 200 to 600 psig, with the moderate-to-high-pressure steam being used to supply shaft power, while the lower-pressure steam is used for steam stripping, vacuum condensation, small pumps, and heat exchangers. Steam is generated in both direct-fired boilers and waste-heat boilers. A small amount of high-pressure steam in the 700-to-1400-psig range is also produced for electrical power generation (and shaft power).⁽⁵²⁾ High-pressure steam is usually used in extraction turbines, with exhausts used for process heat. Only a small amount of hot water

is needed for salt stripping of certain crudes. Steam demand is relatively constant throughout the year (except for space heating requirements).

The petroleum refining industry is characterized by year-around, 24-hour-per-day operations, 7 days per week, except for planned and emergency shutdowns. Because of the nature of the processes involved, the needs for steam and direct heat coincide with the need for electrical energy.

H.5.1.5 Cooling Water Use

A petroleum refinery uses large volumes of cooling water. It has been estimated that 80 to 85% of the total water required by a refinery is for cooling if cooling towers are used for water conservation. Most refineries use open circulating cooling systems. Once-through cooling is rare; it is only used at a few coastal refineries that were designed to use seawater.⁽²⁾

The separation and conversion processes described earlier require large amounts of heat. In the interest of energy conservation, the hot product streams are often used to preheat the cold feed streams in feed-effluent exchangers. If additional cooling of the hot product streams is required for either process-related or safety-related reasons, it is provided by cooling water.

Cooling water is used extensively to condense the overhead vapors from distillation columns. Barometric condensers are used on some vacuum distillation columns, resulting in intimate mixing of hydrocarbons, steam, and cooling water. Newer refineries use surface condensers (shell-and-tube exchangers) in which the cooling water and the condensate are not in direct contact.⁽²⁾

H.5.2 Fouling Problems

Nelson⁽⁵³⁾ has classified fouling problems in the petroleum refining industry by the following types of deposits: 1) hard deposits, 2) porous deposits, and 3) loose deposits.

Examples of hard deposits are water scale, corrosion scales, rust, and hard coke. The thickness and resistance of these deposits increase almost proportionally with time. The resistance of a deposit is a function of its composition.⁽⁵³⁾

Porous deposits often have the same composition as hard deposits. Examples of porous deposits are coke or carbon from atmospheric distillation column bottoms, asphalt or tar from vacuum distillation column bottoms, and scale-forming mud and dirt from water or crude oil. These deposits may be more serious than hard deposits because the fluid contained in the porous material usually has a lower conductivity than the hard skeleton of the scale. (53)

Examples of loose deposits are silt, mud, algae, powdered coke, soft carbonaceous material, buttery oxidation products, and leaves or other plant matter. Intermediate refinery products such as gas oils and naphthas readily absorb oxygen during storage and subsequently deposit gums or tarry materials when heated. The resistance of these deposits depends upon the liquid that is trapped within them rather than on the deposit composition. Loose deposits may cause more problems with respect to heat transfer than hard or porous deposits. (53)

H.5.2.1 Boiler Fouling

As shown earlier in Table 6.16, refinery gas and natural gas represented almost 70 percent of the fuels used by the petroleum refining industry in 1978. Petroleum coke represented about 13 percent of the fuel usage, and residual fuel oil represented about 10 percent. Many refinery boilers have dual-fuel capability and can easily switch from refinery gas to fuel oil as fuel prices change. Refinery gas and natural gas are the preferred boiler fuels because they burn much cleaner than fuel oil or coke.

Refinery gas is composed of methane, ethane, propane, butane, ethylene, propylene, and butylene. These low-boiling refinery products serve as petrochemical feedstocks as well as refinery fuels.

Residual fuel oil is the residue from crude oil distillation. It is composed of high-molecular-weight compounds and has more sulfur per pound than other fuels. Typical residual fuel oils include No. 5 and No. 6 heating oils.

Petroleum coke is the product of delayed coking. The ash content of the coke can vary from 0.1 to 2.8 weight percent, and the sulfur content can vary from 0.5 to 7.0 weight percent, depending upon the specific coking process employed. (54)

Even though the ash content of residual fuel oil rarely exceeds 0.2 weight percent, it can still cause significant fireside fouling and corrosion problems in boilers. Compounds of vanadium, sodium, and sulfur have been found in almost every deposit in boilers fired by residual fuel oil. The fouling rates and the thickness of the deposits have been correlated with the sodium-vanadium ratio in the fuel oil, as well as with the velocity and temperature of the flue gases and the tubewall temperatures. (55)

H.5.2.2 Condenser Fouling

Most condensers and coolers used in petroleum refineries are shell-and-tube exchangers. The cooling water is normally on the tube side and the vapor stream is on the shell side. Thus, any scale or other deposits will occur in the tubes, where cleaning is easier. Also, the vapor will pass through the shell without excessive pressure drop. (56)

Water-side deposits in overhead and side-product condensers and coolers may contain dead algae from the cooling tower, iron oxide, oil from contamination, carbonates, silica or silicates, and phosphates from cooling-water-treatment chemicals. Just about any combination of these can be expected on the water side. (56)

H.5.2.3 Process-Side Fouling

Deposits on the process side of condensers may contain oil, partially-carbonized oil, crude salts, sulfides, oxides and residues from specific refinery processes, such as:

1. Hydrofluoric acid sludge (HF alkylation)
2. Antimony trichloride and aluminum chlorides (butane isomerization)
3. Ferro-ferricyanide (vapor-recovery systems)
4. Sulfuric acid sludge (H_2SO_4 alkylation)
5. Catalyst fines (catalytic cracking). (56)

Process-side fouling in a petroleum refinery most often occurs in heat-transfer equipment in the following processes: crude distillation, reforming, cracking, hydrotreating, visbreaking, and coking. The deposits are generally high-molecular-weight polymers which form in various preheat systems. Van

Nostrand, Leach, and Haluska have studied the fouling of heat-transfer equipment in four refining processes: crude distillation, hydrotreating, visbreaking, and reforming.⁽⁵⁷⁾ Fouling problems associated with each of these processes are discussed below.

Fouling in the crude unit is extremely critical for two reasons: 1) more heat is input here than anywhere else in the refinery so potential energy losses are great, and 2) all other refinery streams flow from the crude unit so lowered flow rates due to plugging affect all downstream units. The major crude unit fouling problem occurs in the feed-effluent preheat exchangers. The impact of this fouling is a decline in furnace inlet temperature (preheat exchanger exit temperature), which leads to: 1) an increase in the heat input required in the furnace, or 2) a decrease in the crude unit throughput, or 3) a combination of both.⁽⁵⁷⁾

In a naphtha hydrotreater, naphtha is reacted with hydrogen in the presence of a catalyst at high temperature and pressure to remove sulfur and nitrogen. Fouling in a naphtha hydrotreater can occur in at least three locations: 1) the feed-effluent exchangers, 2) the preheat furnace, and 3) the reactors. Fouling in the feed-effluent exchangers is severe if the naphtha has been stored for a long period or if it has come into contact with oxygen due to inadequate storage facilities.⁽⁵⁷⁾

A visbreaker is a type of thermal cracking unit. There are two types of fouling problems in a visbreaker: 1) formation of coke in the furnace tubes, and 2) plugging of the baffle section of the fractionator.⁽⁵⁷⁾

The major fouling problem in a catalytic reformer occurs in the feed-effluent preheat exchangers. The impact of this type of fouling was assessed at one refinery by plotting the decrease in overall heat-transfer coefficient with time. In three months the heat-transfer coefficient had decreased by 25% and in six months it had decreased by more than 50%.⁽⁵⁷⁾

Catalyst fines suspended in the flue gas from a fluid catalytic cracker foul the tube walls of the CO boiler, hindering heat transfer and necessitating shutdown every five months for cleaning.⁽⁵⁹⁾

Process-side deposits in petroleum refineries usually contain both organic and inorganic compounds, which makes it very difficult to identify the exact cause of fouling. Each constituent in a deposit can act as a binder, a catalyst, or in other ways to influence the formation of the deposit.⁽⁵⁸⁾

H.5.3 Mitigation Techniques

This section describes the mitigation techniques currently used in the petroleum refining industry to control boiler fouling, condenser fouling, and process-side fouling.

H.5.3.1 Boilers

The severity of boiler fouling and corrosion problems depends on the fuel characteristics, the boiler design, and the boiler operation. Table H.17 shows a classification of methods for controlling fire-side fouling and corrosion in oil-fired boilers.

Processes are available for fuel oil desulfurization and de-ashing.⁽⁵⁵⁾ Of course, an even better technique to control the amount of sulfur and ash entering the furnace is to burn refinery gas or natural gas instead of fuel oil.

Alumina, dolomite, and magnesia additives are effective in reducing superheater fouling, high-temperature ash corrosion, and low-temperature sulfuric-acid corrosion. There are several methods of introducing the additives into the furnace; the most common is to meter a controlled amount of an additive oil slurry into the burner supply line.⁽⁵⁵⁾

As mentioned before, fouling problems encountered in the combustion of residual fuel oil are caused by the presence of vanadium and sulfur in their highest oxidation states. These problems can be reduced by lowering the excess air from 7 percent to 1 or 2 percent and, thus, avoiding the formation of fully-oxidized vanadium and sulfur compounds.⁽⁵⁵⁾

The use of soot blowers is standard practice in the petroleum refining industry.⁽⁴¹⁾ To be effective, soot-blowing cycles must be frequent enough so that ash deposits cannot build up to a thickness where their surfaces become

TABLE H.17 Classification of Methods for Controlling Fouling and Corrosion of Oil-Fired Boilers⁽⁵⁵⁾

<u>Fuel Oil Supply</u>	
Reduce amount of fuel ash constituents to the furnace	Selection Blending Purification
<u>Design</u>	
Minimize amounts of fuel ash constituents reaching heat-transfer surfaces	Furnace geometry Tube bank arrangement Metal temperature Gas temperature Soot blower arrangement
<u>Operation</u>	
Minimize effects of bonding and corrosive compounds in ash deposits	Load cycle Soot blowing schedule Combustion-Excess air Additives Water washing

semi-molten. If this point is reached, complete removal of the deposits becomes very difficult.⁽⁵⁵⁾

Chemical cleaning is the quickest, cheapest, and most efficient method for the removal of water-side deposits in boilers. Certain procedures are required prior to the actual cleaning operation, including analysis of the deposit and cleaning tests to determine solvent strength, contact time, and temperature. Babcock and Wilcox cautions that chemical cleaning normally is not necessary more than once a year, and it should not be considered a substitute for proper boiler feedwater treatment.⁽⁵⁵⁾

Boiler feedwater treatment is a very important part of efficient boiler operation. The specific treatment depends on boiler design, steam requirements, heat balance, outside power costs, and further expansion. Many petroleum refineries use hot process softeners, filters, and ion exchange trains.⁽²⁾

Two refineries reported using the following techniques for dealing with fouling of the tube walls of the CO boiler by catalyst fines in the flue gas of the fluid catalytic cracking unit:⁽⁵⁹⁾

- Soot blowers are used and are believed to be the best solution to the problem, cost notwithstanding.
- Use of magnesium-based additives softens the deposits, but does not prevent their accumulation.

H.5.3.2 Condensers

Experience has shown that chemical cleaning is effective in removing water deposits in condensers.⁽⁵⁶⁾ Table H.18 shows two typical chemical cleaning jobs on condensers.

Some refineries are very diligent in monitoring cooling-tower water quality and controlling blowdown volumes to control condenser fouling. As evaporation occurs in the cooling tower, dissolved impurities in the make-up water are concentrated. These impurities include silica, sodium, calcium, magnesium, iron, bicarbonates, chlorides, and sulfates. Cooling-tower blowdown provides a bleed stream to control the concentrations of the impurities.⁽⁶⁰⁾

Most refineries use total hardness, total dissolved solids, or conductivity in their process-control operations. The make-up water is treated to remove calcium, magnesium, silica, or total suspended solids by cold-lime or sodium-zeolite softening, clarification, or filtration. Chemicals are added to the water to: 1) adjust the pH for the prevention of dissolved solids precipitation, 2) control biological growth, and 3) inhibit corrosion or scaling in condensers and coolers.⁽⁶⁰⁾

H.5.3.3 Process-Side

Control of process-side fouling problems involves: 1) prevention of solids formation, 2) prevention of solids agglomeration, and 3) removal of solid deposits. Well-established mitigation techniques used in the petroleum refining industry include: 1) crude desalting to remove most of the solids and salts, 2) corrosion control via the use of selective metallurgy and/or chemicals to prevent the formation of corrosion products, 3) physical or chemical cleaning of fouled process equipment, and 4) use of antifoulants to prevent formation and buildup of solid deposits.⁽⁶¹⁾

TABLE H.18 Typical Cleaning Jobs on Condensers⁽⁵⁶⁾

Type of Unit	Purpose of Cleaning	Method	Results and Remarks	
			Before	After
Catalytic cracker, gasoline condenser	To remove water deposits from tube-side, composed of 22% or- ganic, 50% iron oxide, 10% phos- phates, 12% silicates, 6% cal- cium sulfate	1. Hot alkaline-deter- gent solvent to re- move organic and dis- integrate silicate and sulfate 2. Heated inhibited HCl to dissolve oxides and phosphates	Gasoline temperature to storage, °F.....125	90
H 08	Debutanizer over- head condensers in vapor-recovery plant	1. Alkaline-detergent solvent injected to remove algae and mud 2. Concentrated in- hibited HCl inject- ed into water inlet header	Transfer coefficient.....40.8 Water rate, gpm.....229 Reflux Temp., °F..... 152 Reflux drum pressure, psi 92	Before After 58.5 343 101 70

Antifoulants are widely used in the petroleum refining industry to control process-side fouling. For successful fouling control, two key pieces of information are needed: 1) the most effective antifoulant for the particular fouling problem, and 2) the optimum injection rate of the antifoulant. Haluska and Shaw describe a laboratory fouling test method which provides this information from heat-transfer measurements. Antifoulant treating programs based on this test method have been successfully commercialized in crude-distillation, hydrotreating, reforming, thermal-cracking, catalytic-cracking, coking, and steam-cracking processes.⁽⁶²⁾

Most antifoulants have several functions. Generally, they are dispersants with a variety of corrosion inhibitors, antipolymerants, oxygen scavengers, and/or metal deactivators added to slow down the fouling process. In spite of these additives, insoluble residues still form, but the base dispersant prevents them from agglomerating and depositing on heat-transfer surfaces.⁽⁶³⁾

There are two standard methods of cleaning fouled heat-transfer equipment in the petroleum refining industry--chemical cleaning and hydroblasting. Chemical cleaning is usually more effective, especially on water-side deposits. In some cases, it can be done while the equipment is still in service. The main disadvantage of chemical cleaning is the inability of the chemical solution to penetrate plugged tubes.⁽⁶⁴⁾ Hydroblasting requires that the equipment be taken out of service and dismantled, but this is common practice in the petroleum refining industry, since spare exchangers are commonly included in process designs to provide redundant capacity for continuous operation. The advantage of hydroblasting is that the equipment can easily be inspected after the cleaning operation is completed to verify that the deposits have been removed. The main disadvantage of hydroblasting is the time and the cost of pulling and re-installing the exchanger bundles.⁽⁶⁴⁾

Refineries have been using chemical cleaning for many years. Table H.19 shows some typical deposits found in refinery heat exchangers in which chemical cleaning can be effective. Table H.20 shows some typical chemical cleaning jobs on process-side exchangers. Table H.21 lists the typical refinery processes that use chemical cleaning.

TABLE H.19 Typical Deposits Encountered in Refinery Heat Exchangers
in Which Chemical Cleaning Can Be Effective⁽⁵⁶⁾

Type of Unit	Deposit	Remarks
Crude distillation, bottoms exchangers, shell-side (feed)	1/16-in. black, oily material, composed mainly of iron oxide, ferric oxide, organics, a few phosphates & silicates, & much iron sulfide	This is typical of residual deposit encountered in crude distillation & topping processes or where crude has not yet been subjected to cracking temperatures
Crude distillation, gasoline, naphtha, & kerosene overhead condensers, shell side	Flake deposit, consisting of iron oxide & sulfide, with little organic	Typical fractionating-column overhead products formed in crude distillation, cracking, & vapor-recovery operations. Sometimes cupric sulfide & iron disulfide will be found in these.

Hydroblasting is used in cases where chemical cleaning is unsatisfactory. High-pressure water or a water-sand slurry is often effective. Table H.22 shows the type of deposits found on tube bundles and the results obtained by hydroblasting.

The 1982 NPRA Refinery and Petrochemical Plant Maintenance Conference⁽⁶⁵⁾ investigated the methods that have been used for cleaning badly fouled exchanger bundles where fouling is on the shell-side, including those fouled with heavy residual oils and coke. Mechanical cleaning continues to be the primary method employed in the removal of residual oil deposits from the shell side of exchanger bundles. In general, the bundles are pulled and then immersed in various fluids in an attempt to loosen or soften deposits. They are then subjected to a combination of high-pressure hydroblasting, rodding, sawing, scrapping, scratching, and in some cases an occasional light sandblasting.

Imperial Oil and Petrolite Corporation have developed an off-line, circulation-type cleaning of bundles fouled with straight resid bottoms. The bundle is soaked overnight with an aromatic oil from the cat cracker and then drained

TABLE H.20 Typical Chemical Cleaning Jobs on Process-Side Exchangers (56)

Type of Unit	Purpose of Cleaning	Method	Results and Remarks
Bottoms to crude feed exchangers & pancake coils in crude distillation unit	To remove deposits from tube-side, composed of 48% organic (oil), 35% crude salts, remainder iron oxide & iron sulfide	<ol style="list-style-type: none"> 1. Degrease with hot kerosene emulsion 2. Heated alkaline-oxidation solvent to disintegrate partially carbonized fraction. 3. Heated inhibited HCl to remove iron oxide & sulfide 	Because of design features of pancake coils, no other method possible. Effect of treatment was an increased throughput of 5,000 B/D
Griscom-Russell sections in heavy naphtha cooling service	To remove product deposits from tube side, composed of 10% organic, 20% iron sulfide, heavy cupric sulfide	<ol style="list-style-type: none"> 1. Hot alkaline-oxidizing solvent to dissolve copper compound 2. Heated inhibited HCl with reducing agent to remove oxidized compounds & iron sulfide 	Very satisfactory results. Previous approach has been to pass superheated steam through tubes & then shock with water spray on outside. This was severe on units, causing distortion & warping*

* Loose material also caused operating troubles later. These troubles were avoided by successful chemical cleaning methods.

TABLE H.21 Typical Refinery Process Equipment Subject to Chemical Cleaning⁽⁵⁶⁾

<u>Process or Operation</u>	<u>Equipment</u>
Reforming	Waste-heat boilers, gasoline condensers, compressors
Alkylation	Fractionating towers, refrigeration equipment
Isomerization	HCl stripper, overhead condensers, accumulators, vent-gas scrubbers, catalyst-removal column, deisobutanizer columns, deethanizer columns
Polymerization	Catalyst-warmer banks, product condensers
Catalytic cracking	Surface condensers, gasoline condensers, waste-heat boilers, slurry exchangers, hot-oil pump gland system, gas-oil exchangers
Crude distillation	Naphtha coolers, pancake coils, crude-feed exchangers
Thermal cracking	Gasoline condensers, crude exchangers
Stabilization & vapor recovery	Stabilizers, compressors, absorbers, flare & gas-supply lines to heater burners
Alkymer units	Tanks, lines
Sulfuric acid plant	Acid-contact towers, waste-heat boilers
Toluene unit	Rundown lines, towers, process lines, exchangers
Heavy oils	Wax machines, open-box condensers, ammonia generators, sweating ovens, contact clay filters, jet condensers, caustic scrubbers
Utility department	Economizers, water lines, boilers, boiler feed lines, filters
Gas treating	Caustic tower
Miscellaneous	Propane-dewaxing stripper, propane stripper condensers, jet condensers

the next day. The shell is then refilled with a mixture of 20% of the Petro-lite material and 80% light cat gas oil. The mixture is heated while circulating to 170°F and the flow pattern reversed every hour for about 6 hours. After removal of the cleaning solution, the bundle is steamed for 2 hours. When the bundles are pulled, they are clean to bare metal. The advantage of this procedure is that because the cleaning solution is all hydrocarbon, it can be returned to refinery slop for reprocessing.(65)

TABLE H.22 Results Obtained by Cleaning Tube Bundles with High-Pressure Wet Sandblasting⁽⁵⁶⁾

Type of Deposit	Shell-side Results	Tube-side Results
1. Carbonaceous:		
a. Soft, buttery	Complete removal	Complete removal
b. Oily, granular	Complete removal	Complete removal
c. Tarry	Ineffective ^(a)	Ineffective ^(b)
d. Thin, powdery	Complete removal	
2. Water deposits:		
a. Silt	Complete removal	Complete removal
b. Algae	Complete removal	Complete removal
c. Iron oxide	Complete removal	Ineffective ^(c)

(a) Alternate method: chemical soaking plus wet sandblasting.

(b) Alternate method: chemical soaking plus drilling.

(c) Alternate method: chemical soaking.

The bundle pitch, severity of deposits, and composition of material determine the method used. Although the majority of bundles are successfully cleaned utilizing these techniques, situations periodically arise when retubing is required.

Another method used in cleaning bundles that are in a heavy coking service on the shell-side is baking. Sometimes the bundle is put in an oven and the heavy coke is burned off. Temperature control of the bundle metal in the baking process is a factor that needs to be considered. Temperature excursions can cause deformation of tube bundles. Some method of controlling the rate of oxidation is necessary.⁽⁶⁵⁾

Thermosetting resins or powdered aluminum coatings on either the shell side or tube side of heat exchangers have been used with varying degrees of success to prevent fouling. These are referred to as the Sakaphen process and the Alonizing process.⁽⁶⁵⁾

One company reported using the Alonizing process on its delayed coking unit debutanizer reboiler. This was a gas-oil-driven reboiler which experienced very heavy shell-side fouling and corrosion on the process side with carbon steel exchanger tubes. A bundle with externally-alonized carbon steel tubes and stainless steel baffles and tie-rods was installed. This reportedly substantially reduced the amount of external fouling and corrosion and doubled the run length between retubing.⁽⁶⁵⁾

H.5.4 Costs

Van Nostrand, Leach, and Haluska⁽⁵⁷⁾ discuss some of the economic penalties associated with the thermal fouling of heat-transfer equipment in the petroleum refining industry. The impacts of added energy costs, reduced throughput, and additional cleaning and maintenance costs on the operation of four processes in a hypothetical refinery are presented based on case histories of actual refineries. The offsetting economic effects of the use of antifoulants are described. The authors conclude that use of the right antifoulant at an appropriate concentration in a fouling stream will more than pay for itself through energy savings, increased throughput, and/or lower cleaning and maintenance costs.

Using their hypothetical refinery figures and extrapolating them for both the United States and the non-Communist world petroleum refining industries, Van Nostrand, Leach, and Haluska estimated the order of magnitude of the economic and energy penalties associated with fouling. They calculated a total of \$1.36 billion/year for the fouling-related expenses of all U.S. refineries (Table H.23), and a total of \$4.41 billion/year for the non-Communist world refineries (Table H.24)⁽⁵⁷⁾. These cost include process-side fouling only; cooling water and boiler fouling costs are not included.

Contacts with heat exchanger manufacturers made by PNL indicates that fouling and corrosion result in increased capital costs for heat exchangers.

- Corrosion material on the shell side of an exchanger requires that the tube bundle be removable. A heat exchanger of this type costs about 20% more than a comparable fixed tube exchanger.

TABLE H.23 Fouling-Related Expenses for the United States^{(a)(57)}

	Capacity 10^3 Bbl/SD	Fouling-Related Expenses (millions of dollars)			<u>Total</u>
		<u>Energy</u>	<u>Throughput</u>	<u>Maintenance & Cleaning</u>	
Crude Distillation	18,000	183.6	671.4	6.3	861.3
Hydrotreating	7,500	89.2	85.0	4.2	178.4
Visbreaking	220	37.3	9.2	2.6	49.1
Reforming	3,800	<u>162.6</u>	<u>106.4</u>	<u>2.3</u>	<u>271.3</u>
<u>Total</u>		427.7	872.0	15.4	1,360.1

(a) Including Puerto Rico and the Virgin Islands.

TABLE H.24 Fouling-Related Expenses for the Non-Communist World⁽⁵⁷⁾

	Capacity 10^3 Bbl/SD	Fouling-Related Expenses (millions of dollars)			<u>Total</u>
		<u>Energy</u>	<u>Throughput</u>	<u>Maintenance & Cleaning</u>	
Crude Distillation	62,000	632.4	2,312.6	21.7	2,966.7
Hydrotreating	21,500	255.6	243.7	11.9	511.2
Visbreaking	1,500	254.3	63.0	18.0	335.3
Reforming	8,400	<u>359.5</u>	<u>235.2</u>	<u>5.0</u>	<u>599.7</u>
<u>Total</u>		1,501.8	2,854.5	56.6	4,412.9

- The use of special materials for heat exchanger construction is also prevalent in the industry. The most common varieties are 300 series stainless steel and titanium. These exotic materials result in a heat exchanger cost of 50 to 100% more than a similar carbon steel unit.

H.6 STONE, CLAY AND GLASS (SIC 32)

Industries in this classification are characterized by their predominant use of direct-fired heating. Thus, potential gas-side foulants include constituents in the combusted fuels, volatilized and entrained species from the product, and erosion and corrosion products from the process equipment.

Cement and glass (including flat glass, container glass, pressed and blown glass, and fiberglass) manufacturing consume almost 65% of the energy used by this industry grouping.⁽¹⁾ These industries reject 3.45×10^{14} Btu of waste heat each year in kiln and furnace exhausts.⁽⁴²⁾ Potential fouling problems act as a barrier to the adoption of recuperators or waste-heat boilers for recovering waste heat. Thus, for these industries, the value of the unrecovered waste heat could be considered one of the costs of fouling.

The fouling problems in the cement and glass manufacturing processes are discussed in the following sections.

H.6.1 Cement (SIC 3241)

This section provides a brief description of the cement manufacturing process, describes the fouling problems associated with specific pieces of equipment, and identifies current mitigation strategies and costs.

H.6.1.1 Cement Manufacturing Process

Two types of processes are used to manufacture cement: the wet process and the dry process. The basic processing steps are the same in both cases, with the exception that in the wet process, raw materials are fed to the kiln as a slurry, whereas in the dry process, raw materials are dried prior to being fed to the kiln. The basic steps in cement production are: 1) feed preparation, 2) feed grinding (to a slurry or a powder), 3) calcining, 4) air cooling clinker, and 5) grinding clinker with gypsum. These steps are shown in Figure H.26.

Fossil fuels used to supply direct heat to the kiln account for about 80% of the energy used in cement manufacture.⁽⁶⁶⁾ The remaining 20% is electricity for crushing, grinding, fan power and materials handling. In 1980, 87% of the cement plants in the United States used coal, 10% used natural gas, 2% used waste fuels and one percent used fuel oil.⁽⁶⁷⁾ The trend toward converting to coal is expected to continue, along with an interest in burning waste materials, such as wood chips or waste oils.⁽⁶⁷⁾ Thus, the industry will be increasingly faced with fuels with higher gas-side fouling potential.

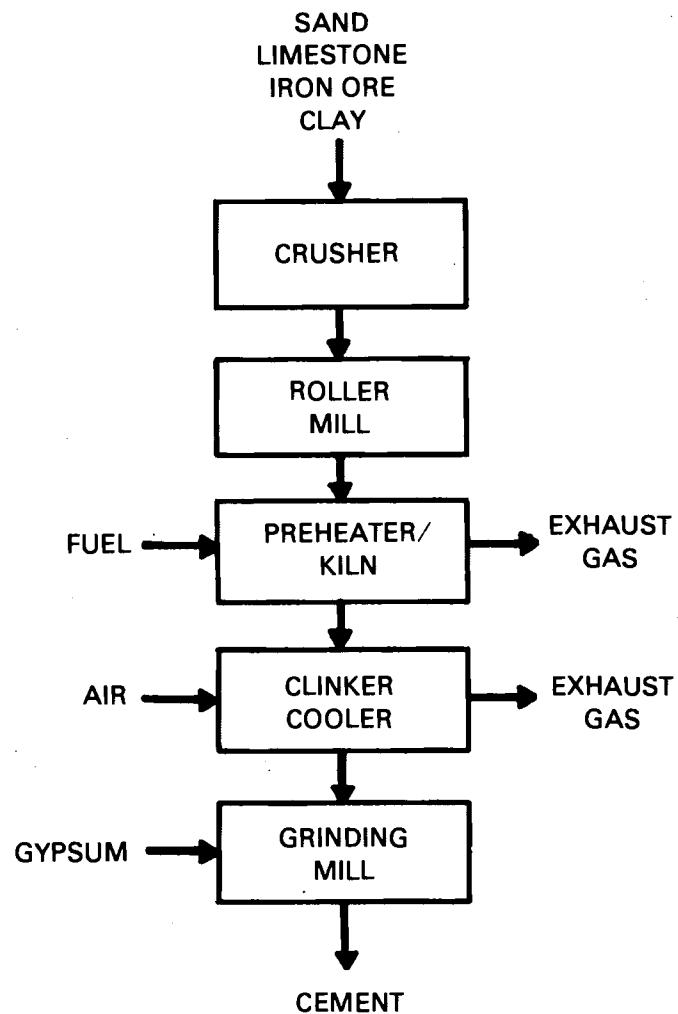


FIGURE H.26 Cement Manufacturing Steps

H.6.1.2 Fouling Problems

In the cement industry, the primary heating and cooling operations are direct contact. Therefore, exhaust gases from heating operations contain constituents from the product stream as well as from the fuel. Cooling air that directly contacts the product also carries entrained particles from the product. Since only small amounts of water are used for cooling equipment, gas-side fouling is of primary interest.

Fouling problems play a significant role in secondary heat recovery from exhaust gases in cement plants. Fouling problems have been reported in gas-to-

air exchangers, waste-heat boilers, and suspension preheaters and precalciners. In many cases, the potential for fouling acts as a barrier in the adoption of more-energy-efficient heat-recovery devices, such as suspension preheaters and precalciners, and waste-heat boilers.

Also of interest from a fouling standpoint is the trend toward conversion from wet to dry process kilns. Although there are currently more wet kilns (175) than dry kilns (152) in the United States, about 50% of total cement production is from dry kilns.⁽⁶⁶⁾ The wet process uses about 5.2×10^6 Btu/ton of clinker compared to 4.2×10^6 in the dry process.⁽⁶⁷⁾ This trend toward dry kilns is significant because the exit gases from dry kilns contain more dust than the exit gases from wet kilns. Wet kiln gases are estimated to contain between 3 and 18% dust, whereas dry kiln gases are estimated to contain between 25 and 35% dust.⁽⁶⁶⁾

Suspension preheaters (see Figure H.27) are used with dry kilns to provide for preheating the incoming kiln feed by direct contact with the kiln exit gases. Between 40 and 50% of the feed is calcined in the preheater, reducing energy requirements to about 3.0×10^6 Btu/ton of clinker.⁽⁶⁸⁾ If auxiliary fuel burning is introduced in the last stage of the preheater, up to 90% of the calcining occurs before the feed enters the kiln.⁽³⁴⁾ The latter configuration is referred to as a precalciner. The fuel efficiency of the precalciner is reportedly 3 to 6% better than a four-stage preheater.⁽⁶⁹⁾

Despite their increased fuel efficiency, adoption of preheaters and precalciners in the United States has been slow. Problems related to fouling have acted as a barrier to their adoption. Currently about 48 of the long-dry kilns in the United States use suspension preheaters, eleven of which are precalciners.⁽⁶⁷⁾

In the preheater, there is a tendency for deposits to form on the preheater surfaces. These deposits cannot be strictly classified as fouling since they do not occur on a heat transfer surface. However, they are of interest because they cause blockages and operational malfunctions that result in downtime, and they may loosen and be deposited on heat-transfer surfaces downstream.

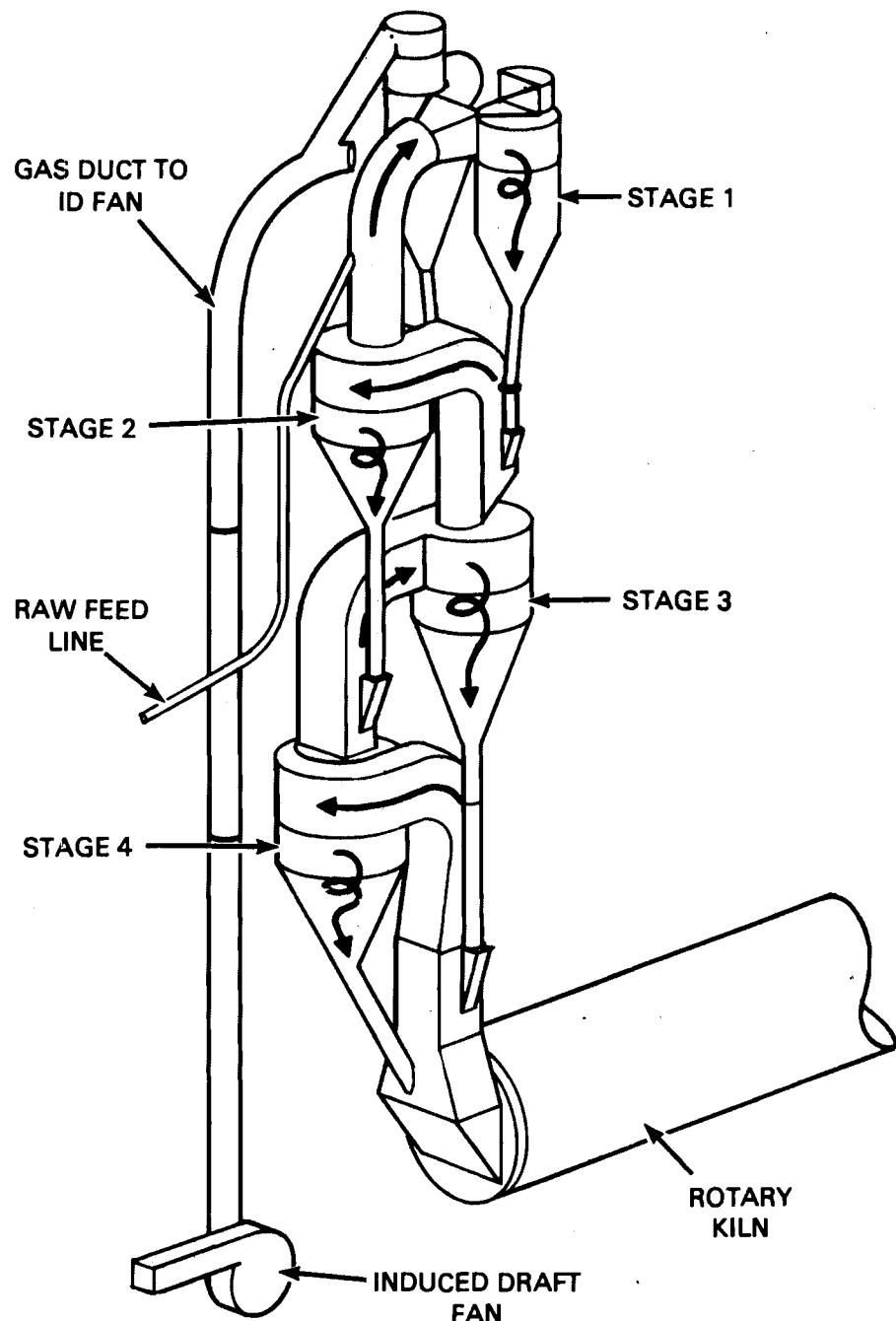


FIGURE H.27 Four-Stage Suspension Preheater

In the preheater, buildups also occur at the heat-transfer interface, which in this case, is the surface of the feed material. Molten salts tend to condense on the cold raw feed and then are revolatilized in the kiln. A molten salt recycle can be set up between the preheater and the kiln, resulting in the concentration of the salts. The direct impact of this phenomenon is on product quality, but the mitigating strategy has heat-transfer implications. Currently to avoid concentrating salts, between 5 and 25 volume percent of the exhaust is routed around the preheater through a bypass loop. The bypass results in a loss of much of the energy-saving potential of the preheater.

Buildups on the preheater walls and on the feed can also lead to problems elsewhere in the system, particularly in the gas-to-air exchangers on the preheater exhaust. Chemical reactions that occur in the buildups in the preheater may form species that have a tendency to deposit in these exchangers.

Chemical analyses of the buildup in the last stage of the preheater showed significant amounts of calcium oxide, calcium carbonate, spurrite and chloride salts.⁽⁷⁰⁾ Calcium oxide particles are deposited on the surface via one of the particulate fouling mechanisms. If the chloride concentration is high due to the recycle mechanism described earlier, the chloride may attack the steel to form iron chloride, $FeCl_3$, on the metal surface. Iron chloride has a melting point of about 500⁰F; as a liquid, it serves to bond the particles (CaO, SiO_2 , and clay) to the surface. At the surface, calcium oxide combines with carbon dioxide to form calcium carbonate, which is a strong, hard deposit.

The other major constituents of the deposits were spurrite ($Ca_5(SiO_4)_2CO_3$) and alkali chlorides.⁽⁷⁰⁾ Spurrite forms at intermediate temperatures (1200⁰F) but decomposes at high temperatures. The temperature range in the last stage of the preheater (1200 to 1800⁰F) spans the range in which alkali vapors condense.

Gas-to-air exchangers are used to cool exhaust gases from the preheater to less than 500⁰F before they enter the baghouse. Gas-to-air exchangers are also used on clinker cooler vent exhaust gases to either cool the gases to about 150⁰F for recirculation to the clinker cooler, or to cool the gases to about 400⁰F prior to being routed to the baghouse.⁽⁶⁷⁾

No fouling problems have been reported in the exchangers used on the clinker cooler vent exhausts. It is thought that since the exhausts contain highly abrasive dust particles they tend to clean the tubes of any buildups that might occur.⁽⁶⁷⁾ Exchangers on the preheater exhausts have experienced problems with moisture condensing on the tube surfaces and attracting dust, which caused the tubes to plug. There has also been some mild corrosion reported in this type of exchanger operating in an environment high in SO₂ and moisture. The sulfur dioxide resulted from the burning of coal. A 0.125-inch deposit was measured in a gas-to-air exchanger installed in the downcomer between the suspension preheater and the induced draft fan in one plant. This deposit reportedly reduced heat transfer by a factor of about two and increased the pressure drop threefold.⁽⁶⁷⁾

Waste heat boilers recover heat from kiln exit gases to generate steam for power production. Currently, only four firms use waste-heat boilers.⁽⁶⁷⁾ Experience with existing waste-heat boilers has indicated that severe fouling can occur in the superheater section of the waste-heat boiler at gas temperatures above 1800°F. In initial operation of one system, gas passages became completely plugged with a hard deposit in a few days of operation. It is believed that condensation or desublimation of potassium sulfate and sodium sulfate was the cause of the problem.⁽⁶⁷⁾

Chemical analyses of waste-heat boiler deposits indicate the presence of the following compounds: calcium carbonate, calcium langbeinite (K₂Ca₂(SO₄)₃), calcium sulfate (CaSO₄), and dicalcium silicate (Ca₂SiO₄).⁽⁷¹⁾ The mechanism of carbonate buildup on the heat-transfer surfaces in the waste heat boiler appears to be in-situ recarbonation of CaO.

Deposits that contain sulfates are probably associated with plants that use coal as a kiln fuel as opposed to oil or gas. The sulphur dioxide in the exhausts may react with either calcium oxide or calcium carbonate to form calcium sulfate. At this point it is unknown whether calcium sulfate is formed in-situ or formed in the kiln gases and subsequently deposited on the waste heat boiler surfaces.⁽⁷¹⁾

Initial laboratory tests indicate that calcium langbeinite may form in-situ by a slow reaction. (71)

In summary, the chemical mechanisms that contribute to buildup formation either on preheater walls or waste-heat boiler heat-transfer surfaces include:

1. in-situ recarbonation of calcium oxide;
2. formation of stable intermediate compounds, such as spurrite, which are often catalyzed by compounds such as alkali chlorides;
3. condensation of molten salts, particularly alkali sulfates and chlorides; (69)
4. in-situ sulfonation of calcium oxide or calcium carbonate; or
5. formation of sulfates in the exhaust gases followed by deposition on the surface. (71)

H.6.1.3 Mitigation Techniques

The strategies currently used to mitigate fouling are listed in Table H.25 along with the type of equipment.

Potential buildups in the preheater are avoided by provision of a bypass to route a certain amount of the exhaust around the preheater. This avoids concentrating compounds that lead to buildup problems. The drawback of the bypass is that it reduces the effectiveness of the preheater.

The Krupp preheater design, which is used extensively in Europe but not in the United States, reportedly experiences no downtime as a result of buildup problems. This is attributed to the large cross-sectional areas of the tubes in which buildups fall off as a result of their own weight before any significant problem can occur. The major drawbacks of this design are: 1) it appears to be less effective from a heat-transfer standpoint, 2) it does not have a bypass, and 3) there is no provision for addition of a precalcining system. (67)

Bhatty (70) has suggested the following additional techniques that could be used to prevent preheater buildups:

- Reduce or avoid using feed materials that contain excessive amounts of chloride or sulfur compounds;

TABLE H.25 Mitigation Techniques for Fouling in Cement Plants

Type of Equipment	Problem	Mitigation Techniques
Preheater/Precalciner	Buildups on walls or feed	<ol style="list-style-type: none"> 1. Bypass loop 2. Large-passage design (Krup) 3. Shutdown to manually clean 4. Use feed low in chlorides or sulfur 5. Use clean coal (low-chloride, low-sulfur, low ash)
Water Heat Boilers	<ul style="list-style-type: none"> • Blockage of superheater section • Particulate fouling 	<ol style="list-style-type: none"> 1. Maintain exhaust temperature below de-sublimation point (evaporation gas-cooling-system) 2. Soot blowers 3. Remove dust from exhaust stream 4. Increase gas velocity with induced draft fans
Gas-to-Air Exchangers	<ul style="list-style-type: none"> • Erosion • Acid dew point 	<ol style="list-style-type: none"> 1. Removeable tube insert 2. Soot blowers 3. Mix inlet air with some exhaust to keep wall temperature above dew point 4. Vibrators 5. Sonic soot blowers

- Use low-chloride and moderate- or low-sulfur coals; avoid using calcium chloride for freeze protection of coal;
- Avoid use of coals with high ash content and low ash fusion temperature.

Various techniques have been used to prevent fouling in the few waste heat boilers that are currently on line. The plant that experienced the blockage of the superheater section with the hard, glass-like deposit has tried several techniques to keep the temperature in the superheater section below the sulfate desublimation temperature. The use of rotary soot blowers and the installation of additional chains in the kiln to lower the exhaust temperature below 1250⁰F proved to be unsatisfactory. Currently, an evaporative gas-cooling system is being installed to maintain gas temperatures in the superheater below the desublimation point. (67)

A plant which uses coal uses plain tube waste heat boilers to generate electricity. This plant uses steam soot blowers on a regular basis and reports no problems with gas-side fouling. (67)

Other mitigation strategies used for waste heat boilers in cement plants identified by Marner include:

- removing some of the dust from the exhaust gas stream before it enters the waste heat boiler;
- increasing gas velocity by using induced draft fans, rather than stacks; and
- using a water spray system to lower exhaust gas temperatures to prevent condensation of sulfates. (67)

In the gas-to-air exchangers, gases are placed on the tubeside to allow for cleaning. In addition, a replaceable sleeve is inserted in the inlet of each tube to reduce the erosion problems caused by the highly-abrasive particles entrained in the gas. A number of techniques have been used to avoid acid and water dew point problems that lead to fouling and corrosion. Two techniques that were successful were using a soot blower activated at 15-minute intervals and mixing some of the exhaust gas with the ambient air before it

enters the exchanger to keep wall temperatures above the dew point temperature. In the exchanger installed in the preheater downcomer to the induced draft fan, vibrators and sonic horns were tried without success.⁽⁶⁷⁾

H.6.1.4 Costs

Marner⁽⁶⁷⁾ has estimated the cost of fouling in U.S. cement plants to be \$238 million per year (in 1982 dollars). This includes capital costs, maintenance costs, lost production costs and energy losses, as shown in Table H.26. The energy loss estimate quantifies the amount of energy that is not recovered from kiln exhausts due to the potential for fouling problems in recovery equipment, then uses Rankine cycle efficiencies to calculate the amount of power that could be produced, and uses the average industrial cost of electricity to calculate an opportunity cost. However, since the energy loss figure does not deduct the cost of the heat recovery or generating equipment, it overstates the actual value of lost energy.

TABLE H.26 Annual Cost of Fouling in Cement Plants
(Adapted from Ref. 67.)

Type of Cost	Components	Estimated Cost (Million \$)
Capital	<ul style="list-style-type: none"> ● oversizing ● larger fans ● cleaning equipment 	5
Maintenance	<ul style="list-style-type: none"> ● manual cleaning ● trouble shooting ● chemical analyses 	4
Loss of Production	<ul style="list-style-type: none"> ● downtime for cleaning 	108
Energy Losses	<ul style="list-style-type: none"> ● increased fan power ● dumping dirty gas streams 	<u>121</u>
		TOTAL 238

H.6.2 Glass (SIC 3211, 3221, 3229, 3296)

Fouling problems, costs and current mitigation practices in the glass industry are discussed in this section. The glass industry refers to the following SIC categories:

3211 Flat Glass
3221 Glass Containers
3229 Pressed and Blown Glass
3296 Fiberglass

H.6.2.1 Glass Production Processes

Although the end products differ, the basic glass manufacturing processes are similar for each SIC category. Glass-making operations are typically grouped into the five basic operations shown in Figure H.28. These are: 1) batch handling, 2) melting and fining, 3) forming, 4) post forming, and 5) product handling.

Batch handling involves preparing and transferring the feed to the melting furnace. The feed is primarily composed of sand, soda ash, limestone and feldspar. In addition, the feed may contain significant amounts of cullet, which is scrap glass from the production process or from recycling centers.

The batch is heated by direct firing in the furnace to about 2800°F.⁽⁷²⁾ Natural gas is the principal fuel used for this purpose because, historically, it has been relatively cheap and because it is a clean fuel. Fining involves holding the glass in the furnace to allow entrapped gas bubbles to escape.

Forming converts the molten glass to an intermediate shape by pressing, blowing, drawing or casting. A major post-forming operation through which most glass products pass is annealing, in which internal stresses are removed. Annealing involves heating the glass to about 1100-1200°F, followed by controlled cooling.

In the glass industry, approximately 90% of all glass is melted in regenerative furnaces.⁽⁷³⁾ The remaining 10% is melted in recuperated glass furnaces. Metallic recuperators are used on smaller-capacity furnaces (generally less than 100 tons/day). The recuperators are an annular type, with the hot gases

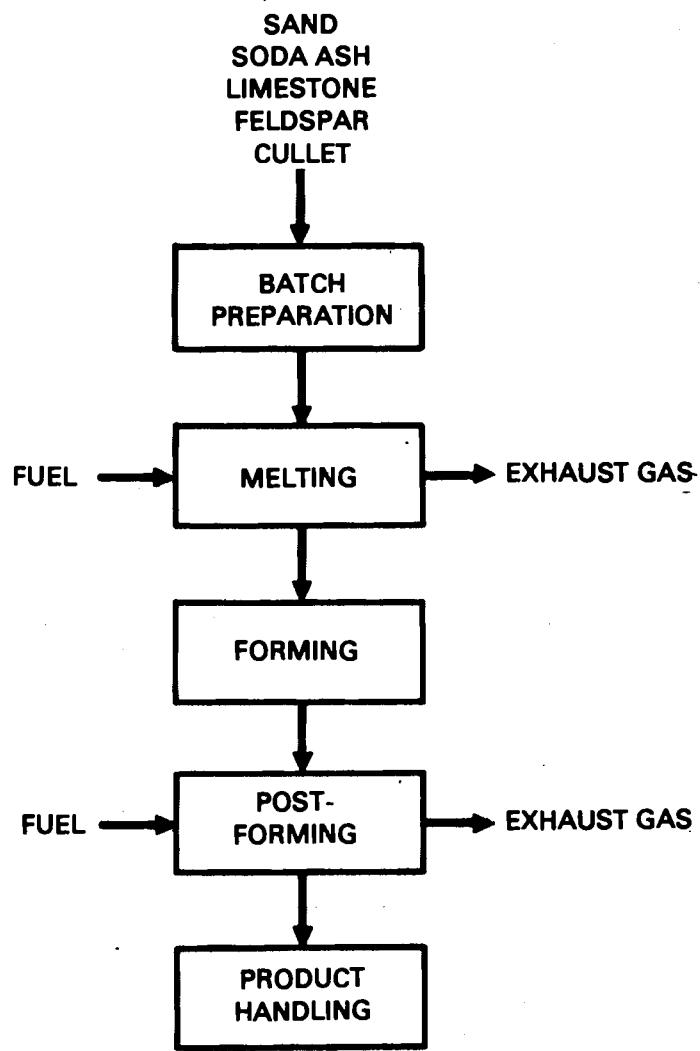


FIGURE H.28 Glass Manufacturing Steps

on the inside. These are typically not used on larger furnaces because of their cost.

The regenerators are constructed of refractory bricks in an open matrix arrangement (see Figure H.29). Combustion gases are directed across the batch surface and are routed downward through one of the checkers, through the reversing valve and finally to the stack. The hot gases transfer a significant amount of heat to the checker bricks. Combustion air is preheated as it is

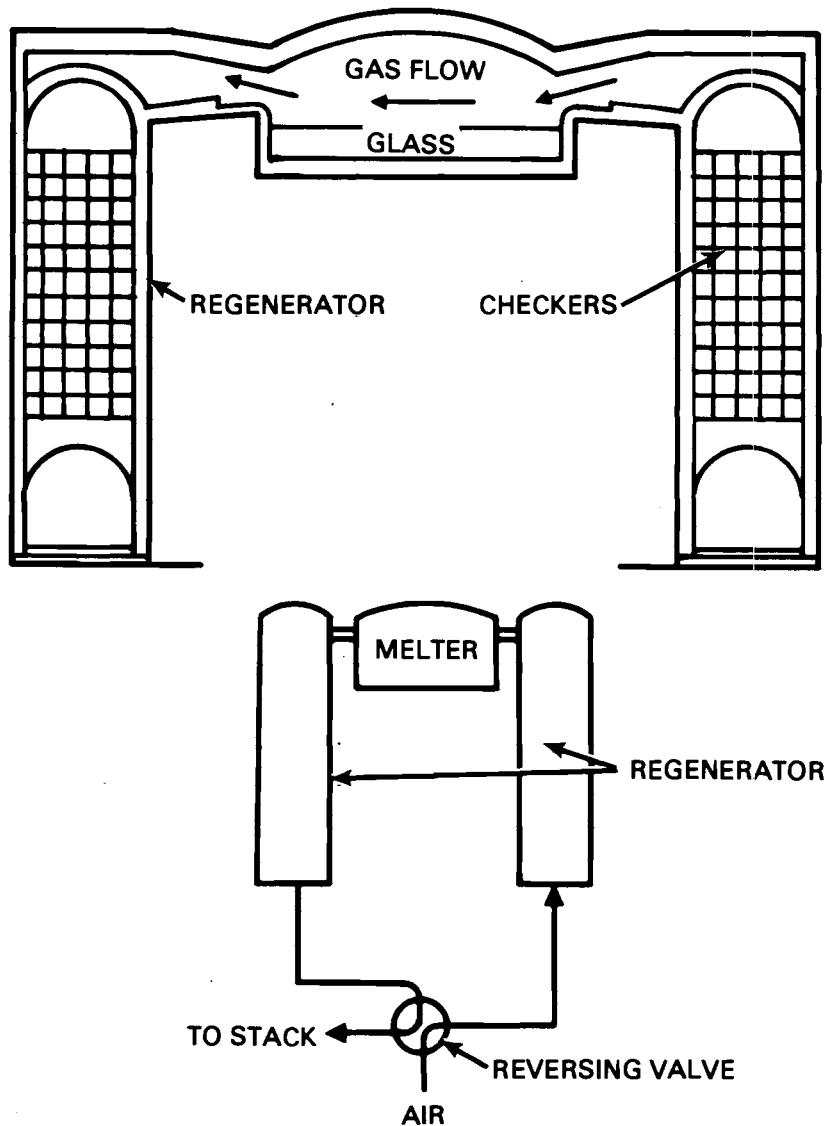


FIGURE H.29 Regenerative Glass Furnace

drawn up through the opposing checker. The reversing valve is alternated at 20-to-30-minute intervals, thus directing the exhaust gas and combustion air to the opposing checkers. (74)

H.6.2.2 Fouling Problems

Potential foulants in glass melter exhausts include constituents from fuel combustion and from the batch, as well as degradation products from the refractory-lined furnaces and from the checkers. Three zones in the melter off-gas

train are of interest from a fouling and corrosion standpoint: 1) the top of the regenerator, 2) the bottom of the regenerator, and 3) downstream of the regenerator.⁽⁷⁵⁾ The first two zones are of interest because fouling here impacts current operations. Fouling downstream of the regenerator is of interest because it is the key barrier that inhibits adoption of secondary heat recovery equipment.⁽⁷⁶⁾

Natural gas is preferred over oil for firing glass melters because of its low sulfur and vanadium content. These contaminants tend to promote fouling and corrosion problems. Natural gas accounts for about 80% of the energy used by the glass industry.⁽⁷⁶⁾ The remaining melters use fuel oil or are electric. For fuel oil to be acceptable, the sulfur content must be less than 2% and the vanadium content (as V_2O_5) must be less than about 200 to 400 ppm.⁽⁷³⁾ Above this point, refractory wear is increased considerably. Oil flame temperatures and velocities are above those of natural gas leading to more SO_x , NO_x and particulates in the exhaust.⁽⁷⁵⁾ There are, of course, no combustion products with electric melting.

Because of the direct contact between the combustion gases and the glass batch in fuel-fired furnaces, the furnace exhausts are laden with particles and volatilized species from the glass. Gases bubble up through the melted glass and propel particles from the batch.⁽⁷⁵⁾ These become entrained in the combustion gases which are flowing across the surface of the batch. The particulate is primarily sodium sulfate (Na_2SO_4) from the salt cake added to the feed.⁽⁷⁷⁾ Particulates also include Na_2O , SiO_2 , CaO and cullet dust.⁽⁷⁵⁾ The primary liquid component is sodium pyrosulfate ($Na_2S_2O_7$) which is formed by the reaction of sodium sulfate and SO_3 .⁽⁷⁷⁾ The gas phase constituents are primarily NO_x and SO_2 .^(75,77)

Particulates collect in the regenerator and in the off-gas passages following the regenerator. The ultimate results of particulate deposition may include: 1) loss of regenerator effectiveness, 2) complete plugging of regenerator passages, or 3) destruction of regenerator brick. Particles collect within the checkers by impingement and settling, with impingement as the dominant mechanism.⁽⁷⁵⁾ Dust and condensate collect on the surface of the bricks in the upper part of the checkers and form a slag that drips down into the lower zones.

Here, because of the lower temperature, the slag solidifies and blocks the passages. Slag may also stay in the upper zones, causing plugging.⁽⁷⁵⁾ The loss of effectiveness occurs as the pressure drop increases across the regenerator through constriction of the flow passages.

In the top zone of the regenerator, the following mechanisms are reported to contribute to erosion and corrosion of the brick:⁽⁷⁸⁾

- The flow of high-temperature gases erodes brick,
- MgO in magnesite brick reacts with SiO₂ in the exhaust to form forsterite (Mg₂SiO₄). This leads to volume expansion and subsequent crumbling of the brick, and
- MgO and CaO combine with SO₃ to form sulfates. The melting temperature of the bricks is lowered, leading to subsequent crumbling. This process is accelerated by vanadium oxide and sodium sulfate.

In the bottom zone of the regenerator, the following mechanisms are reported to lead to fouling and corrosion problems:⁽⁷⁸⁾ Na₂O and SO_x combine to form sodium sulfate, which condenses on the brick surface. The liquid sodium sulfate dissolves SO₃ from the exhaust and it is transferred through the liquid to the refractory surface. The SO₃ attacks the magnesium oxide (MgO) in the magnesite bricks and the calcium oxide (CaO) in the silicate bond to form magnesium sulfate (MgSO₄) and calcium sulfate (CaSO₄), respectively. Both reactions weaken the brick. These compounds form an eutectic mixture with the sodium sulfate, which drips down the bricks. When the gas flow is reversed, the eutectic is thought to form a white slag upon cooling. The sodium sulfate, still in the vapor phase, condenses when the gas flow is reversed to form a light powder.

Currently glass manufacturers do not employ secondary heat-recovery equipment downstream from the checker regenerator. Potential fouling problems are the barrier to the adoption of secondary heat-recovery equipment. Although much of the particulate carried over from the glass furnace collects in the regenerator, the exhausts leaving the regenerator still contain a high concentration of particulate. The composition of the particulates and the vapor contaminants leaving the regenerator are listed below for soda-lime glass.⁽⁷⁶⁾

<u>Particulate Composition</u>	<u>ppm</u>	
Na ₂ SO ₄	90	
K ₂ SO ₄	3	
CaSO ₄	4	
SiO ₂ , Al ₂ O ₃ , others	3	
<u>Vapor Composition</u>	<u>Gas-Fired (ppm)</u>	<u>Oil-Fired (ppm)</u>
SO ₂	10-80	up to 270
SO ₃	0-2	2-10
NO _x	433	433
HCl	13.7	13.7
HF	0.1	0.1

Potential fouling problems in heat exchangers for secondary recovery have been reported for the hot end and the cold end of the exchanger as follows: (76)

HOT END:

- Corrosion may result from the reaction of SO₃ with K₂SO₄ and Na₂SO₄, which form corrosive pyrosulfates, K₂S₂O₇ and Na₂S₂O₇, respectively.
- The liquid pyrosulfates entrap particulates.
- The pyrosulfates dry to a hard scale as the surface temperature is lowered. Scales are not removable by air blowing, but are water-soluble.

COLD END:

- If the surface temperature is below the dewpoint temperature, H₂SO₄ condenses. The condensed acid may react with sodium sulfate to form corrosive Na₂S₂O₇.
- If water condenses with the acid, NaHSO₄ may be formed.
- The Na₂S₂O₇ and NaHSO₄ form a sticky surface which traps particulates, forming a sludge.

H.6.2.3 Mitigation Techniques

Mitigation techniques used in the glass industry are summarized in Table H.27. These techniques are used to reduce the concentration of potential foulants, to

TABLE 6.27. Mitigation Techniques for Fouling in Glass Furnace Regenerators

Technique	Description	Result
Additives	Add MgO to fuel or exhaust	Combines with SO_3 to form $MgSO_4$, which is relatively nonreactive and high melting. Deposit is friable.
	Add small amount of carbon to batch	Decreases particulates
Process Control	Control excess air	Reduces SO_3 and particulates
	Decrease melt tank load	Decreases relative amount of particulates, SO_2 , SO_3 and NO_x
	Maintain constant charge & pull rates	Avoids excessive particulates generation during process upsets
High Quality Fuel or electricity	Main high cullet ratio in batch	Reduces particulates, SO_2 , SO_3 and NO_x
	Low sulfur fuels	Reduces SO_2 but not SO_3
	Electric melting	No combustion products
Batch Pretreatment	Add moisture or fluxing materials	
	Preheating, pelletizing, briquetting, moisturizing, prereacting	Reduces particulates
Equipment design	Enlarged checker area	Reduces fuel consumption and thereby reduces particulates
	Proper selection and application of furnace insulating refractories	
Mechanical Cleaning	Air lancing, steam soot blowers, or water washing	Removes friable deposits
Equipment Repacement	Replacement of checker bricks	

convert the foulants to a relatively benign form, or to remove the fouling layer once it is deposited.

Additives are used to decrease the amount of particulate entrained in the exhaust and to combine with potential fouling and corrosion promoters to reduce their effects. Magnesium oxide is added either to the batch or the exhaust to react with SO_3 to form $MgSO_4$. This deposit is relatively benign and forms an easily-removable deposit.⁽⁷⁸⁾ Carbon can be added to the batch to reduce the particulate concentration in the exhaust. The mechanism by which this occurs is not well understood.⁽⁷⁸⁾

Various process control measures are used to control the amount of particulate and vapor species in the melter exhaust. Reducing excess air reduces the level of SO_3 and particulates in the exhaust, but has the effect of increasing NO_x .⁽⁷⁸⁾ The relative amount of particulates, SO_x and NO_x has been reported to decrease with respect to ton of product if the melter load is decreased.⁽⁷⁸⁾ Adding cullet to the batch results in lower foulant concentrations in the exhaust because less fuel is required to melt the batch.⁽⁷⁵⁾ Cullet is only used in the container glass industry and some segments of the pressed and blown glass industry. Usage of recycled cullet is generally unsuitable for the flat glass and fiberglass industries.⁽⁷⁹⁾

Using natural gas as opposed to fuel oil reduces potential foulants in two ways. First, natural gas contains fewer contaminants that can lead to fouling problems, relative to other fossil fuels. Secondly, the flame temperature and flame velocity of natural gas is lower than oil, leading to fewer SO_x , NO_x and entrained particles in the exhaust.⁽⁷⁵⁾ Electric melting has the advantage of not generating combustion products.

Several batch pretreatment methods are available for reducing particulate carryover from the batch. Some soda-lime glass manufacturers spray water on the charge to keep the dust down.⁽⁷⁵⁾ Fluxing materials appear to be more effective in controlling dust because they promote melting before the batch has traveled very far into the tank.⁽⁷⁵⁾ The remaining techniques listed in Table 6.27 are mostly of an experimental nature.

Equipment design techniques which lead to fuel efficiency in general tend to reduce particulates in the exhaust, since the volume of the combustion air that moves across the batch surface is reduced. Two of these design considerations are enlarging the checker area and proper selection and application of insulation.

Various mechanical cleaning techniques may be used to remove friable deposits. These include lancing with air or steam, or washing with water.^(75,76) Lastly, deposits that can't be removed by these mechanical cleaning methods tend to plug regenerator passages with time. Regenerators are normally rebuilt at the same time the melting furnace is rebuilt, which occurs about every four to eight years.⁽⁵²⁾ Individual sections of the regenerator could be replaced more frequently, without shutting down, by routing the exhaust through the opposing regenerator.

H.6.2.4 Costs

The major cost of fouling to the glass industry is the energy that is rejected in dirty exhaust gas streams. About 5×10^{13} Btu of waste heat are rejected from glass furnaces each year at about 1200°F.^(a)

The savings that could be realized by recovering the waste energy can be estimated in terms of the input energy it would displace. Two alternatives will be considered here: 1) secondary recovery for air preheating, and 2) secondary recovery to generate electricity. The latter provides a higher-valued product.

It has been estimated that secondary heat recovery for the purposes of providing additional combustion air preheat can result in about a 10% improvement in fuel efficiency.⁽⁵²⁾ Thus, about 3×10^{13} Btu/year could be saved^(b). Using an average 1982 cost of natural gas (\$3.49/1000 ft³)⁽⁸⁰⁾,

(a) 3×10^{14} Btu/year fuel input⁽⁷⁶⁾

about 1/3 of fuel input energy is rejected in exhausts⁽⁷³⁾

about 50% is recovered in the regenerator⁽⁵²⁾

$(3 \times 10^{14} \text{ Btu/yr})(.33)(.50) = 5 \times 10^{13} \text{ Btu/year}$

(b) 10% of 3×10^{14} Btu/year fuel input

the savings are estimated to be about \$102 million (1982 \$). The amortized cost of the heat recovery equipment must be subtracted from this value to determine the net savings.

It is estimated that the annual revenue if secondary recovery is used to generate electricity is about \$260 million (1982 \$).^(a) This figure was derived using the methodology used to calculate the savings due to waste heat from cement plants.⁽⁶⁷⁾ Again, the amortized cost of the recovery and generating equipment must be subtracted to determine the net savings.

H.7 PRIMARY METALS (SIC 33)

This section provides an overview of the heat-source and heat-sink fouling problems within integrated steel mills, gray iron foundries, primary copper refineries, and aluminum reduction plants. Brief descriptions of each process are provided along with discussions of fuel usage and heat-source fouling problems, cooling water usage and heat-sink fouling problems, and estimates of fouling and corrosion cost impacts, where available.

H.7.1 Integrated Steel Mills

This section provides a brief description of the unit operations and process flow streams associated with an integrated steel mill. The fouling and corrosion problems associated with combustion fuel usage are assessed and information regarding the cost impact of fouling and corrosion in the steel industry is summarized.

H.7.1.1 Process Description

An integrated steel mill can be a rather complex combination of unit operations that transform iron ore and other raw materials into semi-finished steel products. The major steel mill operations are materials preparation (coking,

(a) $\eta_{\text{Rankine}} = 40\%$ (81)

average electricity cost to industry (1982) = \$.045/kWh⁽⁶⁷⁾
 $(.5 \times 10^{14} \text{ Btu/year})(.40)(\$.045/\text{kWh})(\text{kWh}/3413 \text{ Btu}) = \260
million

sintering, pelletizing), blast (reduction) furnace, steel making furnaces (open hearth, electric, basic oxygen), casting (continuous or ingot casting coupled with a roughing mill), rolling and finishing. These operational steps are shown in Figure H.30.

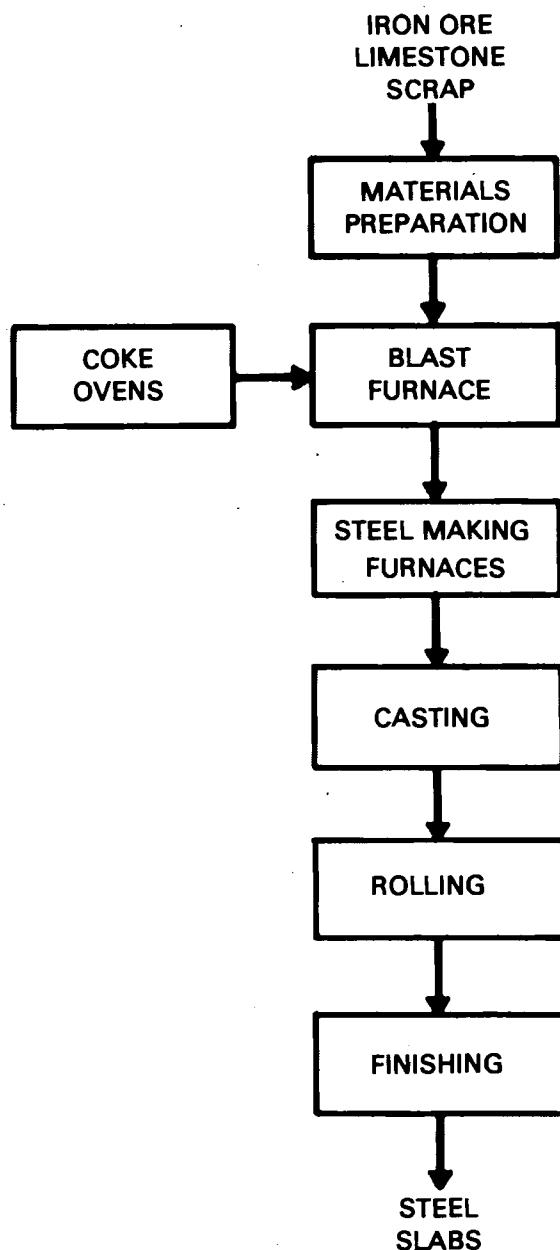


FIGURE H.30 Major Steel Mill Operations

Blast furnaces and steel mills (SIC-3312) consumed 1.282 quads of purchased fuels and electricity in 1980, making it the largest energy consuming industry in the primary metals group.⁽¹⁾ This energy consumption figure more than doubles when energy produced and consumed within the plant (such as blast-furnace gas and coke-oven gas) and fuels converted to other fuel types (such as coal converted to coke) are included.

Electricity accounted for approximately 15% of the purchased energy total for 1980; electricity is used throughout the steel mill, but primarily in the electric steel furnace and in rolling operations. The remainder of the energy consumption within a steel mill is split between coke, natural gas, fuel oil, blast-furnace gas, and coke-oven gas. Coal is not a principal fuel in a steel mill, except, of course, as a feedstock for coke production. Coke consumption in the blast furnace is the single largest energy flow stream in the plant, however. Natural gas is used in substantial quantities throughout the steel mill, as are the energy by-product streams: coke-oven gas and blast-furnace gas. Fuel oil is also consumed by various unit operations around the plant, but generally in smaller amounts.

Estimates of water consumption in integrated steel mills vary from 100 to 300 tons of water/ton of steel.^(2,82,83) The variation in the reported figures is probably due to differences in assumptions regarding water recycle, plant designs, and/or methods of accounting for water use. Nevertheless, enormous quantities of water are required; steel making consumes more water than any other single industry.⁽²⁾

Water consumption at steel mills can be broadly classified as either cooling (generally non-contact) or process (generally contact). Cooling water requirements are about 60 to 70% of the total.^(2,82) Nearly all steel mill unit operations use water for either cooling or process needs; most use water for both. Principal cooling water requirements are for cooling the high temperature components of blast furnaces, steel furnaces, rolling mills, and casting plants. Cooling water or non-contact water is also required for boilers and condensers, quenching, electric motors, and product cooling. Contact water uses are oriented toward environmental control. Scrubbing water is required

for the off-gases from all furnaces. Rolling mills require huge amounts of water for surface cleaning, descaling, cooling, and lubrication. Water is used for dust control in the sintering process and for make-up streams in the finishing (pickling, tinning, galvanizing) lines.

H.7.1.2 Fouling Problems

The majority of the fuel consumed in an integrated steel mill is used for direct heating in which the combustion gases are in direct contact with the product. One exception is the coking operation in which coal is externally heated in an atmosphere of low oxygen content, resulting in destructive distillation. Heat for this process is provided by burning a portion of the coke-oven gas produced during the distillation process. The excess coke-oven gas is recovered for use in other mill operations.

Representatives of both Republic Steel and Bethlehem Steel indicated that fuel oil impurities were the cause of fouling and corrosion problems for many operations. Although blast-furnace gas, coke-oven gas, and natural gas supply the majority of plant energy needs, oil is used as either a primary or auxiliary fuel in reheat furnaces, soaking pits, boilers, and electric generating facilities. Additives are used with fuel oil to inhibit fouling and corrosion, but the sources of fuel oil vary from month to month, requiring constant monitoring for quality changes. Sodium and vanadium are two impurities that were cited as being especially corrosive to recuperator tubing.

Recovery of thermal energy from blast-furnace gas (BFG) and coke-oven gas (COG) is inhibited by the sulfur content that must be removed before these off-gases can be used as a fuel source. Additives are also used in conjunction with both BFG and COG as they are combusted at other operations. Bethlehem Steel reports corrosion problems with their waste heat boilers and fouling problems in their process steam boilers.

A significant problem within the steel mill furnaces is the degradation of furnace refractory lining. Furnace linings are attacked by chemical, thermal, and mechanical forces. Even under "normal" operating conditions, furnace walls subjected to the corrosive and abrasive attack of molten slag may last less than two years. Fuel impurities can additionally hasten refractory degradation.

Fouling and corrosion of cooling water can have a deleterious affect on cooling towers, heat exchangers, clarifiers, pumps, and pipes. However, the proper application of corrosion inhibitors and descaling compounds should keep the operation running smoothly. In general, no major problems of scaling or corrosion are occurring that cannot be controlled by applying the available technology. Representatives from Republic Steel and Bethlehem Steel relate that several kinds of additives must be used to keep ahead of potential problems. Some chemicals are added on a regular basis and others when periodic analysis shows a need.

Although process waters are not the focus of this study, it should be noted that the most severe water-related fouling and corrosion problems occur in this area. Scrubber wastes from gas stacks, mill scale from rolling operations, and spent liquors from finishing lines are just three sources that present a multitude of fouling and corrosion problems.

H.7.1.3 Costs

A study completed by Battelle Columbus Laboratories estimated that the direct cost of corrosion to manufacturers engaged in the production of basic steel products was 1.05 billion dollars annually.⁽⁸⁴⁾ Direct costs included all incremental raw materials, capital inputs for expanded capacity and replacement, and maintenance charges attributable to corrosion. This estimate includes the corrosion cost impacts of all steel production operations and not just those associated with combustion products and cooling water.

As was previously noted, large quantities of chemicals are required to keep fouling and corrosion problems under control. Both Republic Steel and Bethlehem Steel have indicated that although technology is available for controlling cooling water fouling and corrosion, it is quite expensive, and can cost "thousands of dollars a day." Further remarks by industry representatives noted that prudent engineering requires an allowance for overdesign to compensate for fouling and corrosion and that critical equipment must be generously overdesigned.

H.7.2 Gray Iron Foundries

This section provides a brief description of the unit operations and process streams associated with a gray iron foundry. The fouling and corrosion problems associated with combustion fuel usage and cooling water usage in gray iron foundries is assessed and the cost impact of fouling and corrosion in the foundry industry is summarized.

H.7.2.1 Process Description

The central piece of equipment in a gray iron foundry is the furnace, which can either be a cupola, electric induction, or electric arc type. The furnace charge consists of iron scrap, pig iron, flux, and other metallic scrap. Other major operations include casting, mold making, and cleaning and finishing. Some products are heat treated as a final processing step. These steps are shown in Figure H.31.

Gray iron foundries (SIC-3321) consumed 0.111 quads of purchased fuels and electricity in 1980, making it the third largest energy consuming industry

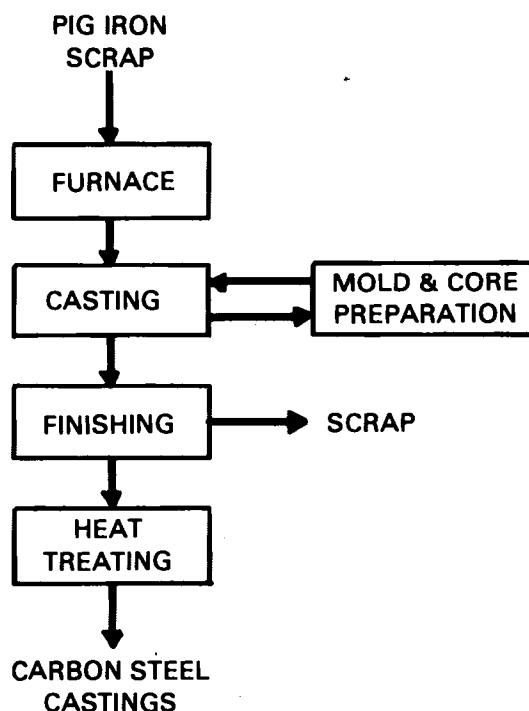


FIGURE H.31 Major Iron Foundry Operations

within the primary metals group.⁽¹⁾ No figures were available for fuels converted to other fuel types (such as coal converted to coke).

Electricity accounted for approximately 25% of the purchased energy total for 1980.⁽¹⁾ The electric furnace is the single largest user, but electricity is also consumed in most of the other unit operations. Coke is the usual energy source for the cupola furnace and natural gas is the principal fuel for core baking, mold drying, and heat treatment operations. Fuel oils are a minor energy source for a few unit operations.

Very little cooling water is required in a gray iron foundry as compared to an integrated steel mill. Only the furnaces and electric generating facility require a significant amount of water. Cooling water protects various parts of the furnaces from their elevated operating temperatures. Cooling water is used for the heat sink in the electric generating facilities.

Again, representatives of the American Foundryman's Society indicated that cooling water fouling and corrosion was not a major problem for their industry. Currently-available chemicals are adequately serving water treatment needs.

H.7.2.2 Fouling Problems

The majority of the fuel consumed in a gray iron foundry is used for direct heating in which combustion gases are in direct contact with the product. The major fuel-consuming operations are the cupola furnace, core baking, mold drying, and heat treatment. Electric generating facilities also consume various grades of fossil fuels.

Data on fouling and corrosion problems in foundries is sparse. A representative of the American Foundryman's Society indicated that there were no severe recurring problems, with the possible exception of cupola shell degradation.

H.7.2.3 Costs

Fouling and corrosion cost impact data was not available for the gray iron foundry industry. Any difficulties that the foundry industry may have

would probably be similar to problems in integrated steel mills, since many of the unit operations are closely related.

H.7.3 Primary Copper Smelting and Refining

This subsection provides a brief description of the unit operations and process streams associated with a primary copper mill. The fouling and corrosion problems associated with combustion fuel usage and water usage are assessed and information regarding the cost impact of fouling and corrosion in the primary copper industry is summarized.

H.7.3.1 Process Description

Copper smelting and refining consists of several consecutive unit operations that remove the non-copper impurities from the feedstock as it moves through the plant. Concentrated ore, either wet and/or partially dried in a roaster, is fed to a reverberatory smelting furnace. Copper and ferrous sulfides collect at the bottom of the furnace; slag is removed from the top. Flue gases from the smelting furnace are passed through a waste-heat boiler prior to cleaning. The matte (copper and ferrous sulfides) is transferred next to the converter. Iron and sulfur are oxidized in the converter with a high silica flux and forced air. Slag from this operation is recycled to the smelter. The product from the converter is called blister copper, which is about 98% pure. Flue gases from the converter are cleaned and sent to a sulfuric acid plant. The final processing steps involve fire refining and/or electrolytic refining to achieve the desired copper purity. These steps are shown in Figure H.32.

The primary copper industry (SIC-3331) consumed 0.053 quads of purchased fuels and electricity in 1980, making it the fifth largest energy-consuming industry in the primary metals group.⁽¹⁾ Electricity accounted for approximately 10% of the purchased energy total for 1980.⁽¹⁾ Electricity is used throughout the plant, but principally in electrolytic refining, casting, and converting operations. Over half of the energy consumed was in the form of natural gas, with fuel oil, coal, and coke contributing smaller portions. The smelting operation is by far the largest energy consumer within the primary copper process, requiring approximately an order of magnitude more fuel than

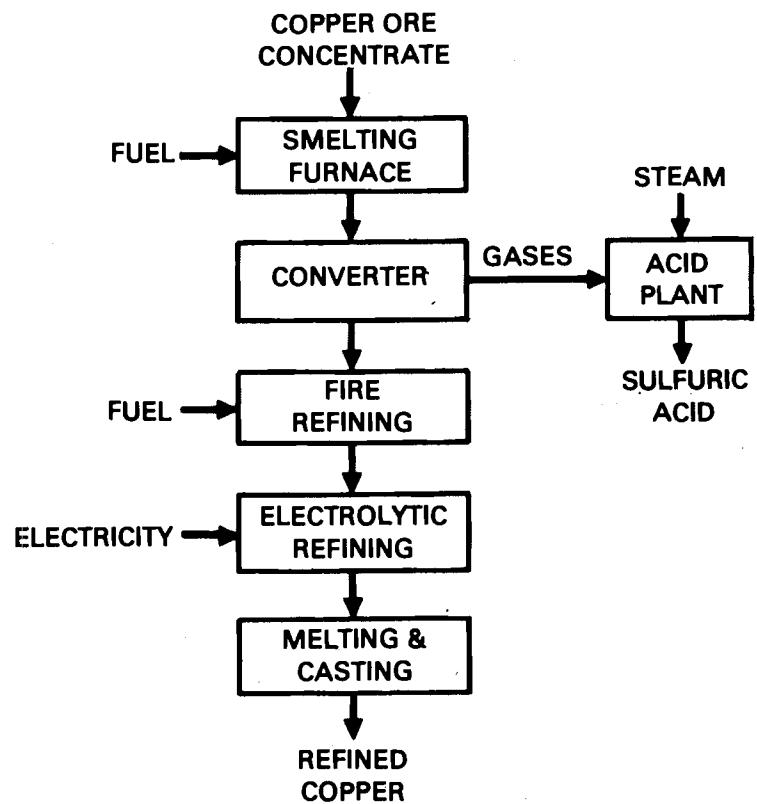


FIGURE H.32 Major Copper Smelting and Refining Operations

any other single operation. Other significant fossil fuel consumers are the anode furnace and cathode melting operations.

Cooling water requirements in copper smelting and refining operations are limited to equipment cooling of various furnace parts and as a heat sink for electric power generation. Fouling is not reported to be a major problem in either case. Presumably, currently available chemicals are adequately conditioning the water.

H.7.3.2 Fouling Problems

The majority of the fuel consumed in a copper smelting and refining plant is used for direct heating in which the combustion gases are in direct contact with the product. Steam requirements are met by recovering the energy from the

smelting furnace flue gases with a waste heat boiler. Part of the steam is used to generate electricity and some is used in the electrolytic refining operation.

Due to the chemical nature of copper ores, an inevitable fouling and corrosion problem results from the sulfur and sulfur compounds that are separated from the copper during smelting and refining. Roasting and converting operations produce SO_2 gas in high enough concentrations to justify sulfuric acid byproduct plants. The hot, abrasive flue gases can lead to erosion, corrosion and precipitation problems. As previously noted, the flue gases from the smelting furnace are routed through a waste-heat boiler for the generation of process steam. Although these gases have a lower SO_2 concentration, they can still create problems for the waste-heat-recovery equipment. Finally, the smelting furnace linings suffer from severe degradation due to chemical, thermal, and mechanical factors.

H.7.3.3 Costs

Data on the cost impact of fouling and corrosion in the primary copper industry was extremely limited. A report by Battelle Columbus Laboratories estimated the direct costs of corrosion to the primary copper industry as being \$191 million per year.⁽⁸⁴⁾ Direct costs were defined as the incremental requirements for capital expansion and replacement, raw materials, maintenance, and operations. The cost estimate would apply to process as well as gas-side and cooling water corrosion.

H.7.4 Aluminum Reduction Plants

This section provides a brief description of the unit operations and process streams associated with an aluminum reduction facility. The fouling and corrosion problems associated with combustion fuel usage and cooling water usage are assessed and information regarding the cost impact of fouling and corrosion in the primary aluminum industry is summarized.

H.7.4.1 Process Description

Activity at an aluminum reduction plant centers on the potlines where alumina (Al_2O_3) is electrolytically-reduced to aluminum. Alumina is charged

to the reduction cell, where it is first dissolved in a solution of molten cryolite. The cryolite solution serves as an electrolyte. A high current passes through the solution from the carbon anode to the cathode, where aluminum is deposited. Oxygen liberated in the process collects at the anode and combines with the carbon surface to form CO_2 .

The carbon anodes are prepared for reduction cells onsite, either by the pre-baked or Soderberg process. High-grade petroleum coke and pitch is ground, calcined, and blended into a paste-like mixture that is sent directly to the reduction cell in Soderberg operations. The molding and baking of the paste occurs in the reduction cell for the Soderberg systems and external to the cell for pre-baked systems.

The casting and cooling of ingots are the final operations at a reduction plant. Some integrated facilities allow for transportation of molten aluminum directly to rolling facilities. The steps described above are shown in Figure H.33.

Aluminum reduction plants (SIC-3334) consumed 0.360 quads of purchased fuels and electricity in 1980, making it the second largest energy-consuming industry within the primary metals group.⁽¹⁾ Electricity, of course, is the predominate form of energy consumed at a reduction plant, accounting for approximately 70% of the total energy used. In addition to the reduction cell, electricity is used for the crushing, mixing, and molding of coke and pitch into carbon electrodes, as well as in the casting and cooling operations. Fossil fuels, principally natural gas, are consumed to generate electricity and steam and for the baking of anodes. The above figures do not include the consumption of coke and pitch in the anode-making process. Due to the nature of the process, coke and pitch are classified as raw material feedstock.

Although aluminum reduction plants are not large consumers of cooling water as compared to steel plants, they do have some significant cooling needs, most notably in the casting and cooling of ingots and at electric generating facilities. Transformers, compressors, and the hydraulic oil system also require some cooling capacity.

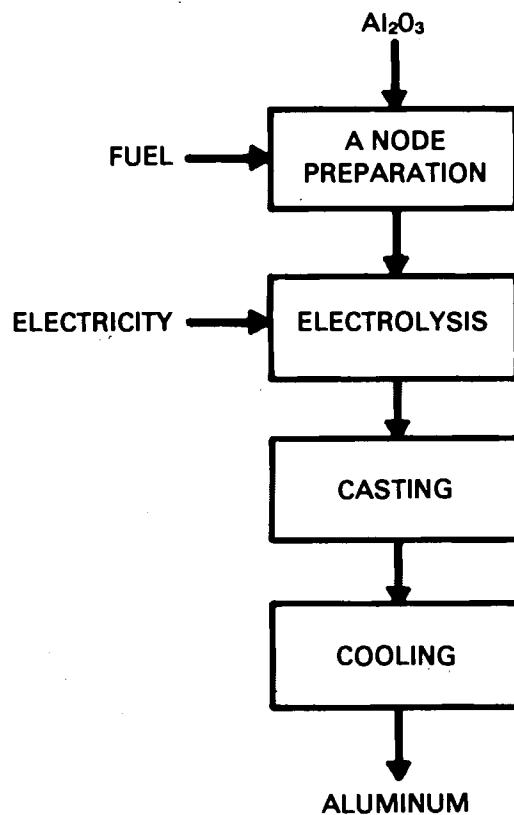


FIGURE H.33 Major Aluminum Reduction Plant Operations

Water is used for mold cooling in continuous casting operations. Both air and water are used for additional cooling after the casting operation, the water most often being applied in the form of spray. Plant cooling water is circulated through open air cooling towers; blowdown is used to control scaling and various chemicals are used to control biological growth. Both Kaiser and ALCOA reported no major fouling and corrosion problems associated with cooling water.

H.7.4.2 Fouling Problems

Fossil fuels are consumed at aluminum plants for the production of electricity, anode baking, and to generate relatively minor quantities of steam. Anode baking is the only operation where combustion gases directly contact the products. A representative of Kaiser Aluminum indicated that anode baking

combustion products presented no fouling and corrosion problems, even though fuel additives were not used. (Since natural gas is the principal fuel employed, the lack of fouling and corrosion problems is expected.) ALCOA personnel indicated that fouling and corrosion problems were more prevalent in the power plant than in the anode furnace, but the problems were not particularly troublesome in either place. Both sources noted that the reduction cells suffer fouling and corrosion problems due to fluoride fumes, sulfur, and high temperature oxidation. Degradation of both the pots and the anodes was another problem.

H.7.4.3 Costs

A report from Battelle Columbus Laboratories provides the only estimate of corrosion costs for the primary aluminum industry. ⁽⁸⁴⁾ They estimated the direct cost of corrosion to be \$101 million per year. This estimate includes the incremental charges for capacity and replacement capital, raw materials, and operations attributable to corrosion. ALCOA and Kaiser personnel indicated that fouling was not perceived to be a significant enough problem in the reduction plant to warrant a detailed economic impact study. However, the plants that extract alumina from bauxite ore were mentioned as having much more serious fouling and corrosion problems and subsequent economic impacts.

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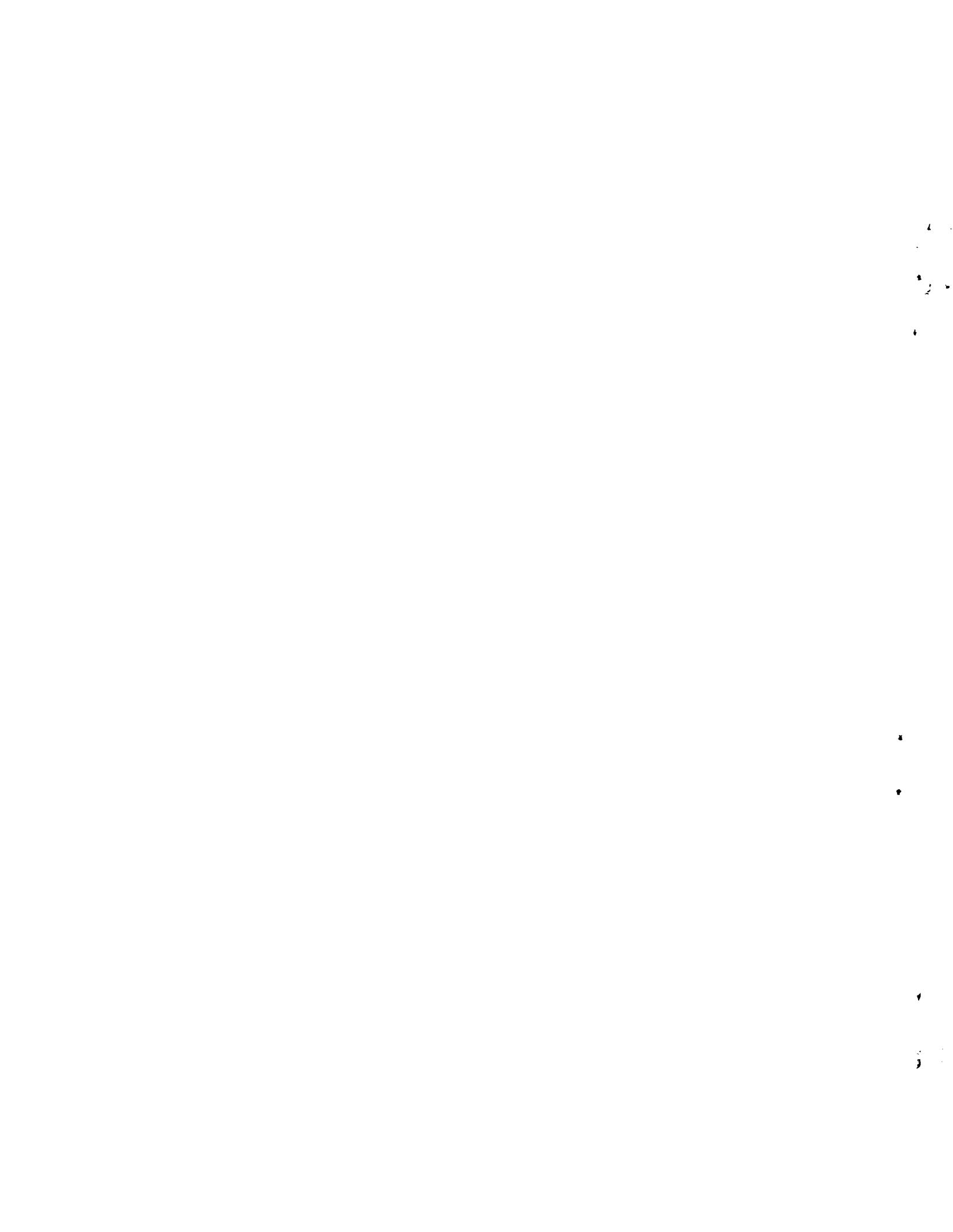
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