3.17 FOULING IN HEAT EXCHANGERS

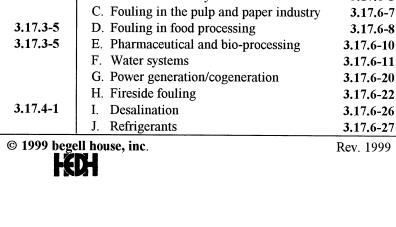
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Fouling in heat exchangers

(Edited by J. G. Knudsen, G. F. Hays and T. R. Bott)

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3.17.1

Overview and summary

G. F. Hays and J. G. Knudsen

The term fouling refers to the deposition of material on a heat transfer surface, usually resulting in an increase in the resistance to heat transfer and a subsequent loss of thermal exchange capacity of the heat transfer equipment. Furthermore, the deposits restrict flow to a greater or lesser extent which results in increased pumping energy requirements. In practice, some fouling usually occurs in most heat exchangers, and in some it becomes the predominant resistance. It is therefore necessary for the designer to estimate the probable magnitude of the fouling resistance as well as means by which it may be reduced.

Once fouling is accepted as unavoidable, steps must be taken to provide for periodic shutdown and cleaning of the equipment or proper treatment of the streams involved so that fouling is mitigated. In some cases, provisions for cleaning may be the dominating factors in heat exchanger design. Since 1960 considerable progress has been made in understanding the fouling process; however, this has not resulted in significant improvement in the ability of the designer to predict fouling resistances. Evidence of increased interest is noted in the rapidly expanding literature on fouling and the number of conferences and reviews on the subject.

Sizing of heat exchangers is based on the heat duty and the temperatures, properties, and flow rates of the hot and cold streams. This information is used to determine the individual heat transfer coefficients in the equation for the overall heat transfer coefficient

$$\frac{1}{U_1} = \frac{1}{\alpha_1} + R_{fI} + \frac{x}{\lambda_w} \frac{A_w}{A_2} + \left(\frac{1}{\alpha_2} + R_{f2}\right) \frac{A_1}{A_2}$$

Where U_1 is the overall heat transfer coefficient based on the area A_1

 A_1 , A_2 , A_w are the inside, outside and average wall areas of the heat exchanger

 R_{fl} is the fouling resistance associated with area A_1

 R_{f2} is the fouling resistance associated with area A_2

x is the thickness of the wall separating the hot fluid from the cold fluid

 α_1 is the heat transfer coefficient associated with area A_1

 α_2 is the heat transfer coefficient associated with area A_2

 $\lambda_{\rm w}$ is the thermal conductivity of the wall

This equation contains the fouling resistances. The quantities R_{f1} and R_{f2} are thermal resistances, which are included in series along with all the other thermal resistances encountered as heat flows through a heat exchanger tube wall from a hot fluid to a cold fluid. Fouling may occur on either or both sides of the heat transfer surface. It is usually not possible to determine the individual values of R_{f1} and R_{f2} , even under conditions of known local heat flux, wall temperature, and known values of α_1 and α_2 . Therefore, fouling resistances for operating heat exchangers are usually reported as a single value $R_f = (R_f + R_f)$. Usually, the fouling characteristics of the fluids are known and often only one fluid is the major contributor to the fouling resistance. The fouling resistance, R_f is frequently called the *fouling factor*. However, this is misleading since R_f is not a factor by which something is multiplied

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but is a *resistance* to heat transfer with appropriate units of m² K/W (h ft² F/Btu).

What follows is a comprehensive discussion of fouling of heat exchangers by a group of contributors who are experts in various aspects of fouling. Sections 3.17.2 through 3.17.5 are a generic discussion of fouling including types of fouling, analysis of the fouling process, measurement of fouling and its

environmental impact. Section 3.17.6 emphasizes the design of heat exchangers for fouling conditions. Section 3.17.7 describes various types of heat exchangers and the potential for fouling in them. Section 3.17.8 is concerned with fouling mitigation and cleaning of heat exchangers. No complete reference list is included at the end but a list of references is included at the end of each section.



3.17.2

Types of fouling

N. Epstein

A. Methods of classifying types of fouling

There is more than one way to classify the types of fouling which occur on heat transfer surfaces. One can classify, according to the type of heat transfer service, which is being provided, (e.g. change-of-phase (boiling, condensation) vs. sensible (heating, cooling) vs. chemical reaction (endothermic, exothermic) heat transfer); according to the type of fluid, which is causing the fouling, e.g. aqueous solutions, petroleum fractions, flue gases, etc.; according to the type of equipment undergoing fouling, e.g. plain vs. extended vs. enhanced heat transfer surfaces, tubular vs. plate vs. spiral heat exchangers, etc.; according to the type of phase interface involved, e.g. liquid-solid, gas-solid, gas-liquid-solid; according to the type of industry in which the fouling occurs; and according to the key chemical/physical mechanism giving rise to the fouling. Here the focus is primarily on the last mentioned method of classification, on the grounds that a mechanistic approach gives rise to greater insight and generalization. Differences involved with different phase interfaces and with different industry groups will also be briefly discussed.

B. Types of fouling according to key mechanism

(a) Crystallization fouling

This broad category, which connotes nucleation and crystal growth on the heat transfer surface, is conveniently subdivided into precipitation fouling and solidification fouling:

I. Precipitation fouling

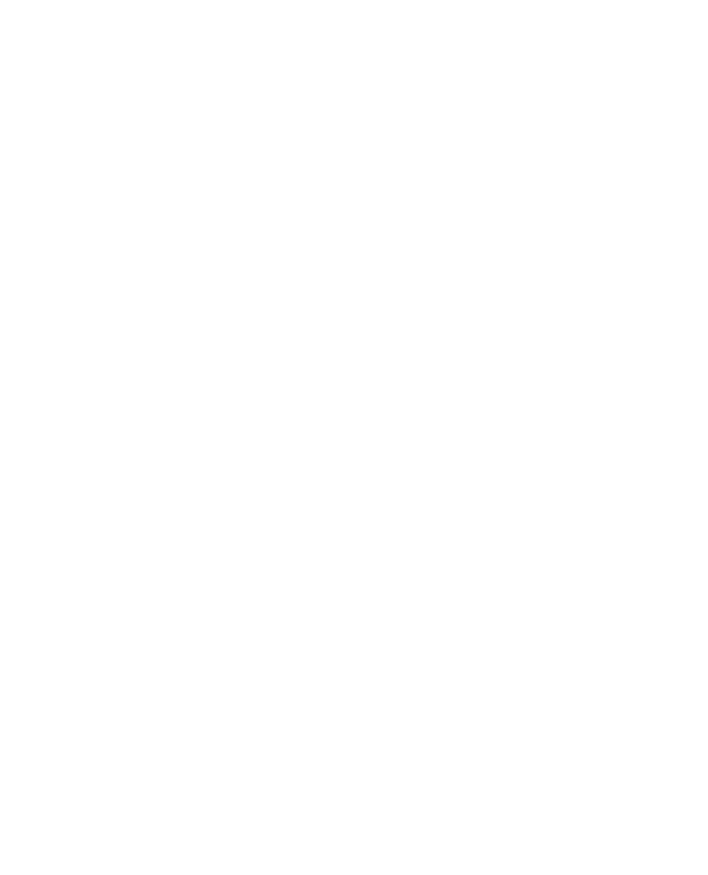
Precipitation fouling involves crystallization from solution of dissolved substances onto the heat transfer surface, the temperature of which renders the adjacent fluid supersaturated with respect to the depositing material [1]. When the solvent is water and the depositing solute is an inorganic salt, the fouling process is sometimes called scaling. Inorganic salts can show normal solubility (solubility increasing with increasing temperature) or inverse solubility (solubility decreasing with increasing temperature). Figure 3.17.2 -1 shows the solubility of calcium sulfate in water with both normal and inverse behavior. Normal-solubility salts precipitate on subcooled surfaces, while the more troublesome inverse-solubility salts precipitate on superheated surfaces. Examples of the latter include calcium carbonate (the most common cooling water scale), calcium sulfate, calcium and magnesium silicate. calcium and magnesium hydroxide, sodium sulfate and various forms of calcium phosphate. Fouling by a normal-solubility solute is exemplified by the precipitation of silica from geothermal brines on a cold surface [2].

Precipitation fouling can occur in cooling water systems, desalination processes, steam power generators, geothermal systems, food processing plants and black liquor evaporators.

II. Solidification fouling

Solidification fouling involves crystallization from the melt onto a subcooled surface of a solid substance,

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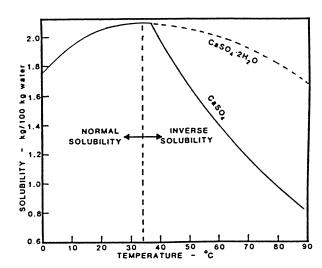


Figure 1 Solubility of calcium sulfate in water as a function of temperature

which is identical chemically, or closely related chemically, to the fouling fluid [3]. This type of fouling is sometimes called freezing fouling, the most common example of which is ice formation from stagnant or flowing water, or from condensed water vapor. Other examples, involving two or more components, include the deposition onto cold surfaces of molten naphthalene -- o-naphthol mixtures [4], of eutectic salts formed by the oxidation of liquid metals [3] and, arguably, of paraffin wax from hydrocarbons [5]. The last example actually falls somewhere between solidification fouling and precipitation fouling, depending on whether (solidification) or not (precipitation) the molecular weight range of the wax crystals significantly overlaps that of the hydrocarbon solvent. Solidification fouling is a complex process, particularly in complicated geometries. In simple geometries it can be subjected to mathematical analysis and the extent of fouling with time can be predicted. Deposits can be removed by increasing the temperature of the heat transfer surface to a value above the melting temperature of the deposit, although it is not always convenient or practical to do

(b) Particulate fouling

This type of fouling is the accumulation of solid particles suspended in the process fluid onto the heat transfer surface [6]. In a minority of instances settling by gravity occurs and the process may then be referred to as sedimentation fouling. More common and more troublesome, is the deposition by other mechanisms of colloidal particles, which are difficult to pre-filter.

Particulate fouling occurs in a variety of processes. Boiler waters and reactor coolants contain corrosion products. Cooling tower waters contain particles carried into them by air and corrosion products (iron oxides and hydroxides). Gaseous streams are often heavily laden with dust particles, which deposit out on heat transfer surfaces. Particles in the form of inorganic salts can be present due to supersaturation of a solution somewhere in the circulation system.

(c) Chemical reaction fouling

This category of fouling occurs when chemical reactions take place at a heat transfer surface and the solid products of reaction are deposited on the surface. The surface, however, is not involved in the reactions except possibly as a catalyst. A recent review [7] of chemical reaction fouling of organic fluids, mainly hydrocarbons, attributes such fouling to three general classes of reactions: auto-oxidation for aerated systems, polymerization and thermal decomposition for deoxygenated systems.

Chemical reaction fouling has been most studied for, but is certainly not limited to, the petroleum and petrochemical and food processing industries [8]. In the latter domain, milk processing especially has received much attention [9].

(d) Corrosion fouling

In this type of fouling the heat transfer surface itself reacts to produce corrosion products which foul the surface and may promote the attachment of other foulants. The category, corrosion fouling, has been used by some authors to include deposition of corrosion products that originate from a source other than the heat transfer surface [10]. Such fouling due to ex situ corrosion should be exluded from this category, which refer only to in situ corrosion fouling. It is more correctly categorized as either precipitation or particulate fouling, depending on whether the corrosion products are soluble or insoluble at bulk conditions.

The literature on corrosion, particularly in aqueous systems, is voluminous, but little of it deals with the effect of corrosion in promoting fouling as opposed to metal loss. The important case of corrosion fouling on heat transfer surfaces exposed to flowing oxygenated water has recently been reviewed [11].

(e) Biofouling

Biological fouling refers to the attachment of macro-organisms (macro-biofouling) and/or microorganisms (micro-biofouling or microbial fouling) to a heat transfer surface, along with the adherent



3.17 FOULING IN HEAT EXCHANGERS / 3.17.2 Types of Fouling

slimes generated by the latter. Macro-organisms such as mussels in their early life stages can pass through the strainers in the intake to industrial plants and grow on warm heat exchanger surfaces, subsequently impairing their performance. The organic biofilms or slimes produced by micro-organisms such as bacteria, not only add thermal resistance and pressure drop in their own right, but can also entrap silt or other suspended solids. Additionally, they can give rise to various types of corrosion.

There is always a tendency for biofouling to occur, since bacteria are ubiquitous in cooling tower systems and in oceans, lakes and rivers. Biofouling can usually be controlled with proper treatment in recirculating cooling systems. Its control in once-through seawater or river systems is much more difficult, especially with regulations that increasingly limit the allowable concentrations of residual chlorine or other noxious chemicals. Reviews of biofouling have been mainly limited to micro-biofouling (12, 13, 14).

(f) Combined fouling modes

Some ambiguities exist in applying the above fouling categories. For example, in the case of crystallization fouling from solution, if the flowing solution is supersaturated with respect to the heat transfer surface but not with respect to bulk conditions, pure precipitation fouling occurs. If it is also supersaturated with respect to the bulk then precipitation may occur both at the surface and in the bulk of the solution. In the latter instance, precipitation fouling at the surface will likely be supplemented by particulate fouling of the precipitated particles from the bulk. Similarly, chemical reaction fouling at a heat transfer surface, may sometimes be supplemented by and difficult to distinguish from chemical precipitation of a solid product in the bulk of the fluid which gives rise to particulate fouling. The co-existence of several fouling modes giving rise to a mixture of foulants is a frequent occurrence especially in cooling water systems, where deposits can be the result of crystallization, particulate, corrosion and biological fouling. Synergistic (i.e. mutually reinforcing) effects exist among many pairs of the above fouling modes, e.g. particulate fouling deposits can create velocity shelters for bacteria which produce slimes assisting even more particles to stick to the surface. One reported exception is the case where particle deposition in conjunction with precipitation fouling tends to weaken an otherwise tenacious inverse-solubility scale [15]. While progress has been made in understanding individual types of fouling, only recently has a start been made in studying the synergy, which exists among the various fouling modes [16].

(g) Afterword

It should be noted that the above fouling categories do not denote the rate-governing process for the fouling (e.g. transport control, attachment control, etc.). These can be discovered only by a detailed analysis of the effect on fouling rate of process variables such as fluid velocity and surface temperature. The sequential events that commonly occur in many fouling situations --- initiation, transport, attachment, removal, aging [17] --- are more relevant to this purpose.

3.17.2-3

C. Types of fouling by phase interface involved

Heat transfer and fouling can conceivably occur at the following six types of interface:

liquid-solid liquid-liquid gas-solid gas-liquid gas-liquid-solid gas-liquid-liquid

(The distinction between a vapor and a gas is neglected in this terminology). The first three involve direct contact heat transfer between a fluid and a liquid phase, where the crud, which develops at the interface is mobile and relatively easy to remove. For this reason, therefore, focus will be on the last three only.

(a) Liquid-solid

The majority of the literature on heat exchanger fouling deals with this type of interface, more often in the (sensible) heating than in the cooling mode. The classification of fouling above according to key mechanism is based primarily on this kind of interface, i.e. on liquid- side fouling.

(b) Gas-solid

This is the principal interface encountered in gas-side fouling, which has been less studied than the liquid-side counterpart. While all five categories of fouling according to the key mechanism can manifest themselves in gas-side fouling, particulate fouling is the most common and both chemical reaction and corrosion fouling can be important [18]; biofouling is far less common, particularly at the elevated temperatures which often occur on the gas side. As for crystallization fouling, it is unlikely in most instances to occur by direct desublimation rather than by condensation and subsequent precipitation or solidification.



(c) Gas-liquid-solid

The vapor-liquid-solid or triple interface comes into play during boiling and condensation.

When liquids are boiled or evaporated, saturated and supersaturated solutions may be produced from which salts will precipitate and deposit on heat transfer surfaces. The local concentration effect due to the evaporation process may be very high and the deposited salts may be very corrosive. The crystal deposition rate during boiling, is proportional to the difference in concentration between the bulk liquid and the liquid at the heat transfer surface, raised to a power between one and two [19].

In the absence of polymerization or other chemical reactions, most condensing liquids are clean and relatively pure, so that fouling is commonly not a problem during condensation. However, condensation

in the presence of acidic gases such as SO_2 and SO_3 can cause corrosion problems, while traces of high-boiling constituents such as compressor oil in refrigerants have a potential for fouling. Vapor condensation may assist in depositing any particles that are present.

D. Types of fouling by industry

In virtually every industry in which heat transfer is a major operation, and heat exchange equipment is a major capital investment, it is important to be cognizant of fouling and of how it affects the processes involved and their design and maintenance. Table 1 is a list of major industry groups, the types of fouling that occur frequently in heat transfer equipment, and a qualitative assessment of the severity of the fouling problems involved.

Table 1 Fouling of heat transfer surfaces in industry groups

| | Type of fouling that occurs in | Usual extent |
|--|---|--------------|
| Industry group | heat exchange equipment | of problem |
| Food and kindred products | Chemical reaction | Major |
| | Crystallization (milk processing) | Major |
| | biofouling | Medium |
| | Particulate (gas side) (spray drying) | Minor/major |
| | Corrosion | Minor |
| Textile mill products | Particulate (cooling water) | Minor |
| | Biofouling (cooling water) | Medium |
| Lumber and wood products | Crystallization (liquor, cooling water) | Major |
| including paper and allied | Particulate (process side, cooling water) | Minor |
| products | Biofouling (cooling water) | Minor |
| | Chemical reaction (process side) | Minor |
| | Corrosion | Medium |
| Chemical and allied | Crystallization (process side, cooling water) | Medium |
| products | Particulate (cooling water) (gas side) | Minor/medium |
| | Biofouling (cooling water) | Medium |
| | Chemical reaction (process side) | Minor/major |
| | Corrosion | Medium |
| Petroleum refining and | Chemical reaction (process side) | Major |
| related industries | Crystallization (cooling water) | Medium |
| | Particulate (cooling water, gas side) | Minor/medium |
| | Biofouling (cooling water) | Medium |
| | Corrosion (process side) | Medium |
| Stone, clay, glass and concrete products | Particulate (gas side) (heat recovery) | Minor/major |
| Electric power production | Biofouling (cooling water) | Major |
| | Crystallization (cooling water, boiler water) | Medium |
| | Particulate (furnace side) | Major |
| | Freezing (furnace-side stag formation) | Major |
| | Corrosion (air-cooled condensers) | Minor |

Sources: Fassbender (20) and Garrett-Price et al (21).



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3.17.3

Analysis of the fouling process

J. G. Knudsen

A. Processes involved in fouling

Fouling of heat transfer surfaces is made up of at least five distinct processes, each of which may be subjected to analysis [1]. These are:

- 1. Processes in the body of the fluid.
- 2. Transport to the heat transfer surface.
- 3. Attachment or formation of the deposit at the heat transfer surface.
- 4. Removal of material from the heat transfer surface by dissolution (material leaves in ionic form), erosion or re-entrainment (material leaves in particulate form), or spalling or sloughing (material leaves as a large mass).
- 5. Transport of removed material into the body of the flowing fluid.

Epstein [2] classified the processes in five main categories---initiation, transport, attachment, removal, and aging---and combined these in a 5 X 5 matrix that includes the five main types of fouling. Figure 1 shows the matrix and the areas that have received the most and the least attention from the standpoint of research. A research goal should be to fill in our knowledge in all 25 spaces of the matrix.

Clearly, a fundamental knowledge of the processes described above would permit the development of models with which fouling could be predicted. However, such complete fundamental knowledge is not available at present.

| | TYPES OF FOULING | | | | |
|------------|------------------|-------------|-------------------|-----------|------------|
| PROCESSES | PREC-P-TAT-ON | PARTICULATE | CHEMICAL REACTION | CORROW-OZ | B-OFOJJ-zG |
| INITIATION | М | | | L | |
| TRANSPORT | М | М | М | M | М |
| ATTACHMENT | М | | | L | |
| REMOVAL | М | | | L | |
| AGING | L | L | L | L | L |

M - HAVE RECEIVED THE MOST ATTENTION

L - HAVE RECEIVED THE LEAST ATTENTION

Figure 1 The 5 x 5 fouling matrix. From Epstein [2]

The outcome of the processes listed above is net deposition of material on the heat transfer surface. The results can be represented as a fouling resistance-time curve that shows how the fouling resistance varies with time.

B. Mechanism of deposition and removal

In the formulation of mathematical models to describe the fouling resistance-time curve the usual starting point is the rate equation

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$$\frac{dR_f}{dt} = \phi_d - \phi_r \tag{1}$$

where dR_f/dt = rate of change of fouling resistance with time, ϕ_d = the deposition rate and ϕ_r = the removal

It should be noted that, while this fundamental model applies to many types of fouling, there are examples in which the rate of fouling decreases and ultimately becomes zero even though there is no removal.

Integration of Eq. (1) at constant heat flux and constant surface temperature to give R_f as a function of time requires knowledge of ϕ_d and ϕ_r . A classical model was developed by Kern and Seaton [3,4] who assumed ϕ_d to be constant and ϕ_r to be proportional to shear stress on the surface of the deposit. The result is an exponential relation between fouling resistance and time. A significant improvement in the Kern-Seaton model was made by Taborek et al. [5,6] who expressed the deposition and removal functions more generally in terms of the basic quantities that control fouling. Developed specifically for water, the deposition rate is expressed as

$$\phi_d = C_1 P_d \Omega \exp\left(-\frac{E}{RT_s}\right)$$
 (2)

where

 C_1 = constant

 P_d = deposition probability factor related to velocity and the "stickiness" or adhesion characteristics of the deposit

 Ω = water quality factor

 $\exp(-E/RT_s)$ = Arrhenius reaction rate function

= activation energy

= gas constant

= absolute temperature at the surface of the deposit

The removal function is

$$\phi_r = C_2 \ \tau \left(\frac{x}{\psi}\right) \tag{3}$$

where

 $C_2 = \text{constant}$

 τ = shear stress exerted on the surface of the deposit

x =thickness of the deposit

 ψ = strength or "removal resistance of the deposit

Substitution of Eqs. (2) and (3) results, upon integration, in the relation

$$R_{f} = \frac{C_{1} P_{d} \Omega^{n}}{C_{2} \tau \lambda_{f} / \psi} \exp\left(-\frac{E}{RT_{s}}\right) \left(1 - \exp\left(\frac{-C_{2} \tau \lambda_{f} t}{\psi}\right)\right)$$
(4)

where λ_f = thermal conductivity of the scale.

Equation (4) is a conceptual representation of factors that influence fouling but numerical values of C_1 , C_2 , P_d , Ω , and ψ are not known.

As t, the time, becomes large the expression for the asymptotic fouling resistance, R_f^* , is

$$R_f^* = \frac{C_1 P_d \Omega}{C_2 \tau \lambda_f / \psi} \exp\left(-\frac{E}{RT_s}\right)$$
 (5)

The integration assumes that T_s , P_d , Ω , τ , and ψ are constant and therefore applies to one deposit, one water quality, and one set of flow conditions. Equation (4) may be used to show the effect of the variables above as they are changed. Equation (4) is exponential in time, and the time constant t_c---that is, the time required for the fouling resistance to reach 63% of the asymptotic value---is given by

$$t_c = \frac{\psi}{C_2 \lambda_f \tau} \tag{6}$$

In three time constants, the fouling resistance has attained 95 % of the asymptotic value. Morse and Knudsen [7] obtained preliminary data relating to to scale composition. The time constant decreased significantly as the concentration of non-calcium carbonate components in the deposit increased with all other variables held constant. The results indicated that as the scale composition approached that of pure calcium carbonate (higher scale strength), the time constant became infinite, suggesting a type of fouling resistance-time relationship in which the fouling resistance increased indefinitely.

Other models have been formulated to describe the fouling resistance-time relationship. Pinheiro [8,9] developed a generalized model that incorporates the major features of several previous models for particulate deposition, precipitation fouling, and chemical reaction fouling. It is based on fundamental processes that occur during fouling, but it cannot be applied until more knowledge of the processes involved becomes available. Epstein [10] gave an excellent summary of deposition and removal models for various types of fouling. These models may be included in Eq. (1), which can then be integrated to obtain a relationship between fouling resistance and time.

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From a practical standpoint, Eqs. (4) and (5) provide a suitable basis for determining the effect of the several fundamental variables on fouling. Based on experience or known fouling resistances, the model may be adjusted as variables are changed.

C. Variables influencing fouling

On the basis of Eqs. (4) and (5), the effects of several variables on fouling resistance are described below. The qualitative effects of these variables are shown in Table 1. These qualitative effects are generally applicable to cooling water fouling and may not be completely applicable to all types of fouling.

(a) Deposition probability P_d (effect of velocity and stickiness)

Deposition probability increases as velocity decreases, since a particle or crystal will have a longer residence time at the surface at a lower velocity. Deposition probability is also related to the stickiness or adhesion of the deposit. As stickiness increases, the deposition probability and the fouling resistance increase. The deposition probability is a complex quantity. Mass transport to the surface increases with increasing velocity. Stickiness may or may not be a function of

velocity, depending on the properties of the surface and how they are affected by shear stress. This complexity indicates the need for basic studies of the fundamental variables that affect fouling.

(b) Water quality Ω

Water quality is related to the scaling characteristics, mainly of treated cooling water. It is generally based on some index related to the calcium hardness of the water. Indices commonly used are the Langelier index [11] and the Ryznar index [12]. Water is considered to have a scaling tendency if the Langelier index is greater than 0 or the Ryznar index is less than 6.

Bodnar [13] developed a criterion for estimating the scaling tendency of cooling water which is also based on the solubility of calcium carbonate. He defined a "crystallization head" as a function of the amounts of dissolved calcium carbonate, carbonic acid, and free carbon dioxide and the pH of the water. A plot is used to determine the crystallization head from the values of these parameters. When the crystallization head is unity the water is saturated; when it is negative the water is unsaturated.

It is important to note that all the criteria above are based only on calcium carbonate-bicarbonate equilibria, interaction with other ions in solution is not considered.

Table 1 Effect of various parameters on fouling resistance

| | | | |
|-----------------------------------|---------------------------|---------------------------------|-------------------------------|
| Parameter (increasing) | Rate of deposition | Rate of Removal | Asymptotic fouling resistance |
| Stickiness and adherence | Increases | Decreases | Increases |
| Heat transfer surface temperature | Increases | Depends on character of deposit | Increases |
| Strength and "removal resistance | Probably slight | Decreases | Increases |
| Surface roughness | Possibly increases | Possibly increases | Possibly no effect |
| Ex situ corrosion | Increases | Probably no effect | Increases |
| In situ corrosion | Increases | Depends on product formed | Increases |
| Velocity | Decreases (almost always) | Increases (always) | Decreases |

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Computer programs have been developed for predicting which species will precipitate from a solution that contains a large number of dissolved mineral salts. These programs consider the interactions between various ions as well as the solubility products of sparingly soluble constituents. They should provide a more reliable means of predicting scaling tendencies of cooling water. It is doubtful, however, that any criterion will predict the amount or rate of scaling (and hence the fouling resistance) for any cooling water. Such predictions will, no doubt, be based on experimental fouling data obtained on a real-time basis.

(c) Surface temperature, T_s

Equation (4) indicates that as the temperature at a heat transfer surface increases, fouling resistance due to crystalization fouling by inverse solubility salts increases. However, under boiling conditions the increase in fouling with surface temperature may hold for all salts. The same is true of biofouling up to a certain surface temperature limit, usually about 35 °C (95 °F). For crystallization fouling by calcium carbonate, magnesium silicate, and their mixtures, Knudsen and Lahm [14] reported values of the activation energy E in the range 4.65 X 10⁷ to 9.3 X 10⁷ J/kmol (20,000 to 40,000 Btu/lb mol). This gives some basis for calculating the effect of surface temperature on crystallization fouling.

Temperature affects particulate deposition through thermophoresis, which acts in the direction of the temperature gradient and is enhanced by cooling rather than heating surfaces [10]. Chemical reaction fouling is enhanced by increasing temperature according to the temperature function shown in Eqs. (4) and (5).

(d) Shear stress (velocity), τ

According to Eq. (4), fouling resistance decreases with increasing shear stress. The mechanism of deposit removal by the action of shear stress is described by two theories. According to one theory, the shear stress exerted by the adjacent laminar sublayer is sufficient to fracture the upper layers of the deposit and remove material. The other theory is based on the fine structure of the Iaminar sublayer in which sudden random eruptions of fluid normal to the wall occur. These socalled turbulent bursts are thought to influence both deposition and removal of material from the surface; a model of this process is described by Wright [15]. With either theory, increasing velocity means increasing shear stress (or turbulent bursts) and removal of the deposit is enhanced, particularly if the deposit consists of mixed crystals or has weak fault lines.

(e) Deposit strength or "removal resistance" of deposit, ψ

The effects of velocity and associated shear stress are closely linked to the strength or "removal resistance" of the deposit. According to Equations.(4) and (5), fouling resistance is proportional to a strength factor P. A hard, adherent deposit such as pure calcium carbonate follows a linear fouling resistance-time relationship. As the strength factor is reduced by the presence of other types of crystals or by weakening crystalline structure, the fouling resistance is reduced and an asymptotic fouling resistance is approached

(f) Surface material

The effect of the material of the heat transfer surface is not included in Eqs. (4) and (5). There are several ways in which materials may influence fouling. Biofouling is generally retarded by copper-containing materials. Ritter et al. [16] compared copper alloys and titanium for biofouling in seawater. Biofouling occurred on both surfaces, and it appeared that the toxicity of copper had a significant effect at lower velocities. At higher velocities the difference between the two materials was much less significant. Copper and copper alloys can be effective in reducing biofouling only if they slowly corrode so that copper ions are released.

Baier [17] studied the effect of surface free energy on biofouling and showed that through appropriate surface treatment biofouling can be reduced. Minimum biofouling was found at a surface free energy of about 0.02 N/m (20 dyne/cm).

Surface charges can also effect fouling rate. Bowen and Epstein [18] showed that asymptotic behavior of the fouling resistance-time curve could be obtained without appreciable removal but by changing surface forces and geometry as deposition proceeded. For crystalline and particulate fouling, the material of the surface may have an effect on the induction period during which the surface is being covered with nuclei. This is a stochastic process and not easily predictable. As soon as enough nucleation sites have formed on the surface, the fouling resistance will increase with time. In this period of deposition, the surface material appears to have no effect on the fouling resistance, except for the case in which corrosion is enhanced at the deposit-metal interface when the surface is completely covered by deposit.

(g) Surface roughness

Rough surfaces are thought to enhance deposition of materials, especially in the incipient stages. Grocki and Westergren [19] indicate that scaling can be minimized

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3.17.3-5

in alkaline evaporator service by using tubes of high surface finish made by a special process. Enhanced heat transfer surfaces have not been used extensively in services where fouling liquids are used. It is possible that turbulence created by the geometry of enhanced heat transfer surfaces could contribute to the removal of any fouling deposit that is formed. Watkinson, et al. [20] studied the scaling of plain, internally longitudinally finned, and spirally indented tubes. The finned tubes showed fouling resistances 15-35% greater than those of plain tubes. At 1 m/s, the fouling resistances of the spirally indented tubes were 25-50% below those of the plain tubes. Knudsen and Roy [21] reported identical fouling resistances for a spirally corrugated tube and a plain tube. Moore [22] described several applications in which radial finned tubes had distinct advantages over plain tubes under fouling conditions. He contended that irregular thermal expansion on the fins tends to produce a looser scale which is easier to remove.

Plate exchangers have very complicated flow geometries and develop high levels of turbulence and shear. Plant experiences indicate that plate heat exchangers have lower fouling rates than tubular exchangers because of the turbulence induced by the

corrugations on the plate. Cooper et al. [23] studied the fouling of plate heat exchangers and confirmed that they showed considerably lower fouling resistances than a circular tube under similar operating conditions with cooling tower water.

Fouling of enhanced surfaces is discussed in more detail in Section 3.17.7.L and compact heat exchangers are discussed in Section 3.17.7.C

(h) Corrosion

In situ corrosion has been discussed as one type of fouling. Corrosion occurs quite frequently with other types of fouling when the heat transfer surface reacts with the flowing process fluid. In these cases, corrosion does not appear to affect other types of fouling that occur simultaneously [21]. However, corrosion can also occur under a deposit of crystals, particles, or biological material even when it would not normally occur with the material directly in contact with the flowing fluid. In any case, corrosion results in additional thermal resistance to heat transfer.

NOMENCLATURE

- C_1 factor in Equation (2), m^2K/J
- C_2 constant in Equation (3)
- E activation energy, J/kg
- P_d deposition probability factor
- R gas constant, J/kgK
- R_f fouling resistance, m²K/W
- t time, s
- t_c time constant for fouling (Equation (6)), s
- T_s absolute temperature at the surface of the deposit, K
- x thickness of deposit, m
- λ_f thermal conductivity of deposit, W/mK
- τ shear stress, N/m²
- ϕ_d deposition rate factor, m²K/J
- ϕ_r removal rate factor, m²K/J
- Ω water quality factor
- ψ strength or removal resistance of deposit, kg²s⁴K

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3.17.4

Measurement and modeling of fouling

G. F. Hays

A. On-line monitoring of operating heat exchangers

The ability to monitor fouling of operating heat exchangers is especially critical in the heat exchangers that are currently process bottlenecks or have the potential of becoming such, possibly as a result of fouling. However, a significant amount of instrumentation is required. Thus the benefits must be measured against the cost. For complete monitoring of fouling in operating heat exchangers to be achieved, the inlet and outlet temperatures of each fluid must be measured, preferably with Resistance Temperature Device (RTD) technology, and so must the flow rates and pressure drops. Finally, all of the data must be collected and processed in real-time. Data storage and processing may be done on a Distributed Control System (DCS) or on a stand-alone computer. There are a number of very good software programs available for that purpose. One critical aspect of such monitoring is that it must include data trending over a prolonged

In some instances, with certain types of processes, there are shortcuts, which may be sufficient. For example, for compressor intercoolers and aftercoolers, one may plot the approach temperature, that is, the temperature of the compressed gas leaving the heat exchanger to the temperature of the entering cooling water. For turbine condensers, a plot of actual vs. ideal vacuum, in mm Hg, may suffice. Ideal vacuum would be, for instance, a plot of mm Hg versus inlet cooling water temperature with zero fouling. In refrigeration machines it may be inlet cooling water temperature versus head pressure.

B. On-line modeling of operating heat exchangers

There are two generally accepted means for modeling process heat exchangers, heat transfer models and pressure drop models. Heat transfer is a more universal technique because it can be used to model either side of a heat exchanger and can be applied to a wider range of heat exchanger designs. On the other hand, pressure drop models can be applied to non-heat transfer applications such as deposition in circulating lines. Online monitoring usually involves a side stream. The major advantage and disadvantage of on-line modeling is that it must utilize the same circulating fluid as the operating heat exchanger. That is an advantage, because it is the same, including the amount of any anti-foulant/dispersant, which may be in use. If the purpose of modeling is to evaluate another antifoulant/dispersant technology, that can only be done in addition to what is already in the stream. In order to evaluate an alternate anti-foulant or dispersant as a full substitution, the evaluation must be done either by terminating one treatment and initiating the substitute or use an off-line method such as in the laboratory.

On-line monitors are available from several sources. Typically, such monitors utilize steady-state heat transfer models. Both annular and internal tubular heat transfer designs are used. Those, which use annular designs, incorporate algorithms to permit them to emulate internal tubular flow conditions. In all cases, the parameters most critical for modeling are the temperature of the heat exchange surface adjacent to the fluid and the shear stress generated by the fluid velocity. Materials of construction are important as long as they

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remain exposed to the fluid. Once a foulant covers the heat exchange surface, the materials of construction are no longer a factor. In addition to measuring the change in heat transfer coefficient and fouling factor, a comprehensive monitor should monitor other parameters such as pH, conductivity, corrosion and oxidation-reduction potential (ORP).

On-line monitors, which utilize pressure drop technology, are particularly applicable to heat exchangers operating with small temperature drops, or where the fluid film characteristics do not vary linearly with changes in fluid and surface temperatures. Two such applications are in chilled water and in heat exchangers operating with once-through river water or seawater

Devices, which utilize these techniques, are available from a variety of sources [1].

C. Laboratory modeling

Off-line modeling of fouling conditions may be done in the laboratory using technologies similar to those used for on-line modeling. Such techniques are a good first cut at understanding fouling; however, they rarely provide a complete picture of fouling conditions in operating heat exchangers. For example, cooling water systems are subject to a variety of contaminants, such as the microflora, agglomerated biomass, process contamination and suspended solids, which are difficult, if not impossible to duplicate in the laboratory. No method has yet been developed to duplicate microbiologically active foulants in the laboratory except as pure cultures, which do not behave similarly to the microflora and biomasses in operating systems.

Laboratory models for fouling of hydrocarbon process streams generally utilize recirculating batch processes, which make it impossible to maintain a constant level of foulants and precursors in the modeling system. Thus, the results may not be directly equitable to the actual process. In order to utilize experimental results from laboratory models, those models must emulate the actual process as close as practical.

D. Laboratory measurement of fouling

A variety of fouling test sections have been developed in order to measure fouling in the laboratory. Knudsen [2] describes a variety of apparatus for measuring fouling and indicates the various advantages and disadvantages of each method. Often the test sections are heated

electrically and fouling tests are operated at constant heat flux. Thus, as fouling occurs at constant flow rate and constant bulk temperature the wall temperature increases. Hence, most test sections that involve flow in a duct include temperature sensors in the duct wall so that the local fouling resistance may be determined. Under these conditions, the local fouling resistance is determined by the following equation:

$$R_f = \frac{T_{wf} - T_{wc}}{q} \tag{1}$$

Where

 R_f = Fouling resistance, m² K/w

 T_{wc} = Tube wall temperature of the clean tube, K

 T_{wf} = Tube wall temperature under fouled

conditions, K

 $Q = \text{Heat flux, W/m}^2$

Since fouling often occurs inside circular tubes, a tubular fouling test section is the most desirable geometry to use. However, the tube does have some disadvantages. The test section usually must be destroyed in order to examine the deposit. Many researchers have used an annular fouling test section that was first used by Heat Transfer Research Incorporated in its fouling studies [2, 3, 4]. At moderate pressures a transparent outer tube may be used so that the progress of fouling may be observed. At the conclusion of a test, the inner tube may be removed in order to examine the nature of the deposit. It is possible to set the thermal hydraulic conditions in the annulus so that they are identical with those in the circular tube in an operating heat exchanger [5]. A variety of other types of test sections have been used and the reader is referred to Reference [2] for a description of these.

E. Computer simulations

There are several different approaches to computer simulation of heat exchange processes. They vary from the very complex to the very simple. The most complex of which is capable of modeling all process heat exchangers on a plant DCS, as long as they have the instrumentation to do so. The very simple programs such as HEX-EVAL and HEX-FOUL utilize the design and operating data for each heat exchanger and calculate both the fouling resistance and hydrothermal stress coefficient.

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3.17 FOULING IN HEAT EXCHANGERS

3.17.5-1

<u>3.17.5</u>

Environmental impact of heat exchanger fouling

T. R. Bott

It is not well appreciated that the problem of heat exchanger fouling has wide environmental repercussions. The effect may sometimes be very apparent but much of the impact is less obvious, and is hidden in general industrial activity.

The essential purpose of a heat exchanger as the name implies, is to transfer heat as effectively as possible. In essence in general terms, heat used in industrial processes is derived from a primary fuel source e.g. fossil fuels, biomass or waste combustion. The heat may be recovered directly for use in the process such as in a pipe still on a petroleum refinery. It is perhaps more common for the combustion heat to be used to raise steam for direct use as a heating medium, or in conjunction with a turbine to produce electricity. Inefficiencies principally due to heat transfer surface fouling, occur in the heat transfer processes, that result in the consumption of additional fuel to make up for the shortfall between what is theoretically possible and what is actually achieved in practice.

In order to reduce energy costs, particularly in large scale processing operations, such as a chemical complex or petroleum refinery, it is essential to recover as much heat as possible. The technology involves the transfer of heat contained in hot product streams, which require cooling, to cold streams that need to be heated to satisfy process requirements. In large-scale operations there is likely to be a complex arrangement of heat exchangers that may be optimized by the application of the concept of process integration or pinch technology [1]. The effectiveness of the whole heat recovery process

however, is dependent on the sum of efficiencies of each individual heat exchanger in the network.

In broad general terms, it ought to be possible to reuse much of the heat involved in processing, except where the heat is used in endothermic reactions, or where the heat becomes degraded to relatively low temperatures. The opportunity to utilize low grade heat is affected by the overall thermal efficiency. The sum of these individual inefficiencies gives rise again, to a short fall in heat recovery that has to be made up from the energy source, ultimately from the combustion of primary fuel.

The efficiency of an individual heat exchanger for a given set of operating conditions of temperature and flow rate, is largely governed by the extent of the fouling experienced on both sides of the exchanger, as described elsewhere in this chapter. In addition to the resistance to heat transfer, the presence of the fouling deposits restricts flow and, for a given throughput will increase the pressure drop through the exchanger. In order to maintain the flow to satisfy process requirements, this will represent an increase in pumping energy. Many industrial systems will use electrically driven pumps, so that the increased energy requirement will ultimately be manifest in increased combustion of fuel.

In summary, the inefficiencies in heat recovery and the associated increase in pumping energy, as a result of heat exchanger fouling, will have an environmental impact, through the increased fuel combustion and the associated increase in emissions i.e. particulate solids and greenhouse gases.

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3.17.5-2 3.17 FOULING IN HEAT EXCHANGERS / 3.17.5 Environmental Impact of Heat Exchanger Fouling

Many industrial operations e.g. power stations, require the use of large quantities of cooling water. Often the effectiveness of cooling is impaired by the presence of deposits on the heat transfer surfaces. Depending on the source of the water, the deposits may be biological, particulate or inorganic scale. Inefficiencies in cooling in a power station, can reduce the conversion of energy contained in the primary fuel into electrical energy [2]. As a result, for a given electrical output, more fuel has to be burnt with the associated production of additional emissions. Furthermore, just as with heat recovery, the presence of the deposit on the surface of the heat exchangers increases pressure drop through the cooling water system, with a consequent increase in energy needed for a given power output, and a further contribution to the emissions from the combustor.

Many cooling water systems use water from natural sources e.g. a river, lake or canal. After use the water is often returned to the source. In order to control the formation of deposits in cooling water systems, and since these deposits are often biological in character, it is usual to apply a biocide. The discharge of the water to the original source, constitutes a risk to the environment not only from thermal pollution, but pollution from the biocidal residues. Chlorine has been the preferred biocide for many years but this element persists in the environment and some chloro-organic compounds are toxic and carcinogenic. So called environmentally friendly biocides are being developed which do not have an environmental impact in their use, but may do so in the process by which they are manufactured.

The presence of fouling deposits on heat exchangers gives rise to other costs. In addition to reduced heat recovery and increased pressure drop, in particular, there is the need to clean the heat exchanger. Cleaning often involves the use of large quantities of high-

pressure water. The resulting effluent may represent an environmental risk if not treated before discharge.

Where it is not possible to use high-pressure water, it may be necessary to use chemical cleaning involving perhaps, more than one chemical. By the very nature of the chemical cleaning process the chemicals employed are aggressive in character. As such, they represent an environmental risk. Treatment will most likely, be required before disposal of the spent cleaning liquor, and may be mandatory with additional costs.

The presence of deposits on heat transfer surfaces and the mitigation of heat exchanger fouling, represents a serious environmental hazard. In the first instance the increased use of energy derived from the combustion of primary fuels, contributes to the problem of emissions, not least the discharge of greenhouse gases. It is probably true to say that a substantial reduction in heat exchanger fouling throughout world industry, would be sufficient to meet the reduction targets for the year 2010 for CO₂ emissions agreed at the international meeting in Kyoto in 1997.

Furthermore, the use of physical techniques such as electric fields, inserts and ultrasound as opposed to chemical antifoulants, in water systems (as described in section 3.17.8.A) may reduce the ecological impact of discharge to the environment.

The concept of zero discharge is being actively pursued in some industries. As the name implies the water is reused after suitable treatment. Although this may reduce the environmental impact, the cost may be high.

The techniques used to return water to a suitable condition for reuse may involve chemical treatment, with further implications for environmental protection. The imposition of additional costs will be the penalty.

There is a considerable need for research into viable technologies that would mitigate fouling in heat exchangers, but at the same time reduce the environmental impact of tackling the problem.

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3.17.6

Designing heat exchangers for fouling conditions

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A. Refinery processes

(by A. P. Watkinson)

(a) Introduction

Fouling of heat exchangers in petroleum processing may be due to a number of mechanisms acting alone or together. Causes of fouling include both phase separation and chemical reaction of constituents of the petroleum, and deposition of impurities such as corrosion products, sediments and aqueous emulsions. The cost of fouling in refineries which process conventional crude oils is dominated by the crude unit. followed by reforming, hydrotreating and visbreaking units. TEMA Standards for wet crudes indicate high fouling resistances of 0.35 to 1.23 m²K/kW depending on temperature and flow velocity, 0.35-0.9 m²K/kW for dry crudes, 0.9 m²K/kW for heavy gas oils, and 1.8 for asphalts. For catalytic reforming, hydrotreating and light ends processing, fouling resistances are lower, generally falling in the range 0.18 to 0.35 m²K/kW. In oil refinery applications, the TEMA fouling resistances may be exceeded in periods as little as four months. With increased use of low quality crudes and heavy oils. understanding the fouling process in hydrocarbon streams is of great importance to the design of heat exchangers.

Petroleum streams may form deposits through chemical reactions such as autoxidation (gum formation), polymerization, and thermal decomposition (coking and cracking). Fouling precursors are formed, and deposit on the surface either from the dissolved or suspended state [1]. With crude oils, physical processes such as asphaltene precipitation can be the major cause of fouling. Impurities such as dissolved inorganic salts, water, and suspended corrosion products can cause deposits on their own, or through interactions with asphaltenes, gums and polymers. The complex nature of petroleum systems, which may contain thousands of chemical species, has made identification of fouling precursors difficult. Deposit analysis reflects the different causes of fouling and extent of aging reactions, in the various units, where wide variations of organic and inorganic fractions have been reported [2-4].

Autoxidation and polymerization provide major mechanisms for petroleum fouling at moderate temperatures (<300°C). For the former, the required oxygen is provided by ingress of air through storage tanks, pumps etc. Conjugated or cyclic olefins are particularly susceptible to reaction with oxygen, although other species will also react in the free radical process to produce insoluble gums. In the absence of oxygen, vinyl type polymerization may occur with reactive species. Asphaltenes and polar species are also susceptible to autoxidation, and readily produce fouling precursors. Asphaltene precipitation is reported to be the primary cause of fouling in crude oil streams [5]. Asphaltenes are said to be present in a colloidal suspension, and are peptized by resins. Incompatibility which leads to asphaltene precipitation may be produced by temperature or pressure changes, or by blending of less compatible oils. Asphaltenes can then agglomerate into high molecular weight micelles or flocs. The solubility of asphaltenes in the surrounding

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maltenes and resins is of key importance, as it is not a high asphaltene concentration itself, but the precipitation of asphaltenic substances into the surrounding oil which results in fouling. For some crude oils the ability to retain asphaltenes in the peptized state, first increases with temperature to about 100°C, and then decreases as temperature is raised further. Rheological measurements have suggested that the ability of resins to protect asphaltenes from agglomeration ceases at about 200°C [6]. temperatures are raised to the 350°C range, formation of coke precursors by thermal decomposition reactions begins. Polar species are the primary reactants [7]. Although progress is being made in thermal reaction pathways of complex hydrocarbons, for fouling, models based on solvent fractions rather than individual species are more tractable. Coke formation in heavy oils can be described by the kinetic models of Wiehe [8,9]. Although the chemistry of fouling is very complex in hydrocarbon systems, and hence the a priori prediction of fouling rate for a given feedstock is virtually impossible, the effects of process variables on fouling shows some consistency of behavior which can be exploited to advantage in the design process.

(b) Crude oil fouling

It is the polar and asphaltene fractions of crude oils which contribute to fouling during heating of crude oils. Impurities such as water from the desalter, and suspended corrosion products or other sediments will contribute, as is discussed below. Dickakian [7] showed that increased asphaltene contents in distillates gave rise to higher fouling rates. Other workers [10,11] have studied the effects of asphaltene concentration. Although fouling data from the latter study could be correlated with a colloidal instability index, no universally accepted characteristic of crude oil has been developed which will predict its fouling rate under given circumstances. Care is clearly needed in blending of oils, in order to avoid precipitation of colloidal asphaltenes.

For a given crude oil, the effect of the process variables on the fouling rate can be predicted through the Ebert and Panchal [12] model:

$$dR_f / dt = a Re^b \exp(-\Delta E/RT_f) - c \tau$$
 (1)

where τ is the shear stress at the wall, and the film temperature $T_{\rm f}$ is used in the Arrhenius term. The exponent b has been found to be roughly equal to -0. 88; constants a and c are specific to the oil. Figure 1 shows the raw data from an earlier study in which the model was tested. As the film temperature is raised at a given velocity, fouling increases. The activation energy

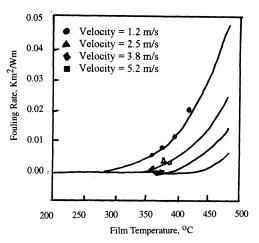


Figure 1 Comparison of experimental and predicted fouling rates

for fouling, ΔE , was equal to 68 kJ/mol, which corresponds to a doubling of fouling rate as the film temperature is raised by 32 °C, from 328 to 360 °C. As velocity increases at a given film temperature, fouling is reduced. Equation (1) implies that at sufficiently high shear stress, the fouling rate will go to zero. Hence a map of fouling and non-fouling regions can be constructed, as shown in Figure 2. Designers could therefore specify conditions where little or no fouling would occur, according to this model. Figures 3 and 4 show data for different crude oils reported in two other studies [13,14], which suggests some degree of generality of these results. Additional supporting evidence for the velocity effect being described by the first term of the above equation arises from gas oil tests, which will be discussed below. Table 1, [15], supports the use of the film temperature to correlate fouling rates of crude oils. Results on fouling of asphaltenes [11] in heavy oil/fuel oil blends at lower temperatures also showed fouling to be inversely proportional to velocity.

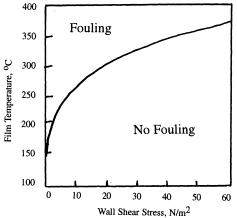


Figure 2 Threshold-film temperature as a function of wall

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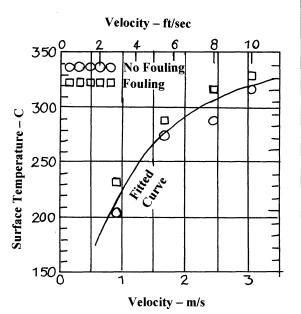


Figure 3 Effect of velocity on fouling threshold surface temperature

However, the surface rather than the film temperature was used in the fouling rate expression, and an activation energy of 89 kJ/mol was reported.

Lambourn and Durrieu [4] suggested that crude oil preheat train fouling was caused by deposition of stable emulsions which form from water, particulate corrosion products and asphaltenes. Coking reactions then occur. By doping clean crudes with emulsions of asphaltenes, iron sulfides and water, fouling rate increases of 100-fold were measured (Figure 5). Sludges, and tank

bottom slops can also contaminate oils, leading to higher fouling rates than expected from the base oil. Fouling in a blend of light crude oil and waxy residue from a crude oil storage tank was reported in [16]. Particulate additions of 2800 ppmw iron oxide to a crude oil were also shown to increase fouling by a factor of about ten [17]. These results show the importance of good desalter operation, corrosion control, and avoidance of particulates and sediments which, taken together, will go a long way toward mitigating fouling in crude oil pre-heat trains.

3.17.6-3

(c) Gas oils and other feedstocks

Early work on gas oil fouling [18] at T_b 100 °C, and $T_s < 175$ °C, carried out at tubeside velocities to 7.8 m/s showed that fouling rate could be described by

$$dR_f/dt = a \exp\left(-\Delta E/RT_s\right) / U_b^{1.07}$$
 [2]

The inverse velocity dependence suggests attachment rather than transport was governing the deposition process. The activation energy was high at 140 kJ/mol. Fouling deposits were of similar ash and sulfur levels as gum particulates found in the oil at 15 ppm concentration. Another study using a fuel oil cut at bulk temperature of 85 °C, and surface temperatures from 187–320 °C, showed an activation energy in equation (2) of 51 kJ/mol. As in Equation (1), designing for increased velocities will have positive effects through reduction of adhesion, and through wall cooling. Dissolved iron and sulfur species were found

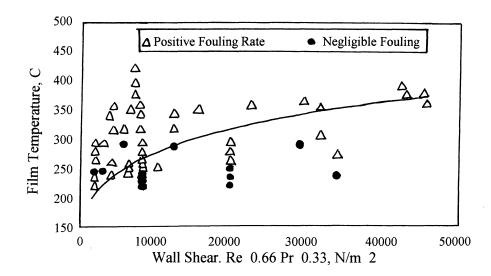


Figure 4 Threshold-film temperature as a function of wall shear

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Table 1 Fouling resistance behavior in a preheat train [PA - pumparound, SS – sidestream]

| Hot Stream (in order from crude inlet) | Mean Film Temperature ° C | dR/dt (x10 ¹¹) m ² K/J |
|--|---------------------------------|---|
| Atmospheric PA | 105 | 6.2-8.7 |
| Atmospheric PA | 115 | 6.1-7.9 |
| Atmospheric SS | 150 | - |
| Atmospheric SS | 170 | - |
| Vacuum Residue | 190 | 8.0 |
| Vacuum PA | 215 | 12.7 |
| Atmospheric PA | 255 | 11.1 |
| Vacuum SS | 310 | heavily fouled |
| Vacuum Residue | 250 | 22-40 |
| Atmospheric PA | 300 | heavily fouled |
| Vacuum PA | 310 | 4-19 |
| Vacuum Residue | 315 | 20, heavily fouled |

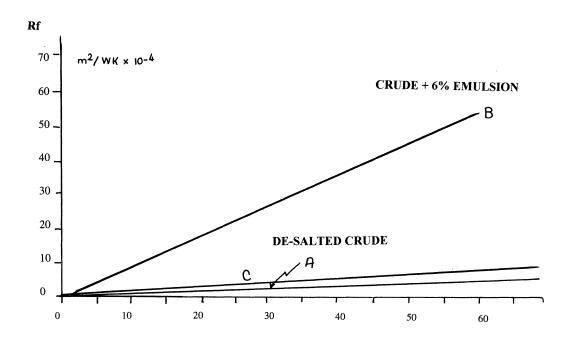
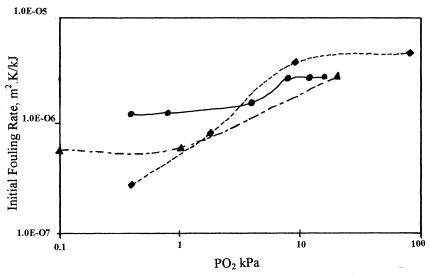


Figure 5 Fouling resistance build-up measured on a pilot plant [4]

to increase fouling of heavy gas oils [19]. Data for fouling of a number of petroleum cuts, including hydrotreater feeds, in both a laboratory unit and in a refinery, are reported in [20]. The role of hydrogen in suppressing coke formation at temperatures above 400 °C is evident in [21].

Dissolved metals were also a factor in the fouling of visbreaking and delayed coker feeds [22]. Here compositions of feedstocks and of deposits are compared to show the important relation between feedstock impurities and the deposit chemistry.

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| Symbol | System | Temperature °C | | Total Pressure kPa | Reference |
|----------|---------------------|----------------|------------|--------------------------|-----------------------------------|
| | | Bulk | Wall (t=0) | | |
| • | Indene- Kerosene | 85 | 188 | 410 | Asomaning, et al (1997) |
| • | Crude Oil | 75 | 260 | 410 | Navaneetha- Sundaram (1998) |
| A | Petroleum Cut | 25 | 260 | 1480 | Braun and Hausler(1976) |

Figure 6 Effect of oxygen partial pressure on fouling of hydrocarbons

The presence of oxygen promotes autoxidation, which forms gums that deposit and can subsequently degrade into coke-like material. This type of fouling has been the subject of much research [1]. Figure 6 shows how the fouling rate in three different systems depends on the oxygen partial pressure. At low dissolved oxygen contents, the fouling rate depends on the dissolved oxygen level, but becomes independent of that variable at about 10 kPa O_2 in the systems shown. Hence for refinery fluids, rigorous exclusion of oxygen, or the use of antioxidants will mitigate fouling by this mechanism.

B. Chemical industry

(by T. R. Bott)

The major difficulty in presenting a general assessment of fouling in the chemical industry, is the wide variety of processes, involving liquids or gases. Moreover,

most heat exchangers are unique not only in terms of operating conditions e.g. particularly velocity and temperature, and fluids being handled, but also in terms of geometry.

Where inorganic solutions are being processed the problem of fouling is likely to be associated with crystallization or particle deposition, although chemical reaction fouling may be a problem in some examples. The processing of organic fluids on the other hand, will probably lead to fouling problems associated with chemical reactions. Such reactions may be cracking processes, or polymerization depending on the prevailing temperature and flow conditions. Where aggressive chemicals are being handled, it would be anticipated that corrosion could be the basis of fouling problems. However, the material of construction is an important factor. High quality corrosion resistant materials carefully chosen, may eliminate the problem of corrosion fouling altogether. Fouling due to micro or

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macro organisms is not likely to be a problem in the chemical industry, except in special circumstances or in cooling water used for temperature control.

In an assessment of a particular problem, either at the design stage or when the heat exchanger has been in operation for some time, it is vital to determine the fouling mechanism (or mechanisms) that are likely to be present in the system. This will give an indication of the opportunities available to overcome the problem.

If the foulant for instance, is not part of the process stream itself, but some sort of impurity perhaps dependent on the origin of the feedstock, its removal may be a way of combating the potential fouling problem. Removal may involve filtration or flocculation followed by sedimentation or filtration, but these techniques may be expensive in terms of capital and operating costs. Under such circumstances it might be more economical to allow the fouling to occur and concentrate the resources on cleaning, that might be on line or off line depending on the problem.

Where the problem of fouling involves the actual fluid being processed, a different approach is required, but it is still necessary to have a full understanding of the mechanisms involved. The process variables that will have the greatest influence on the fouling process are velocity and temperature. In very general terms, the higher the velocity that can be tolerated the lower the potential fouling is likely to be.

Of course it is necessary, under such circumstances, to keep in mind two important aspects mainly pumping costs (energy use) and potential erosion of heat exchanger surfaces. It is also necessary to assess the likely effect of changing velocity on the temperature profile across the heat transfer surface.

An example of the improvements that may be made by raising the velocity of an inorganic slurry has been reported [23]. The process required that the temperature of an aqueous solution containing a suspension of particulate material be raised from 80 to 95°C, before entry into a precipitator. Steam on the shell side of a shell and tube heat exchanger was used to heat the solution flowing through the tubes at 1.1m/s. Considerable backpressure was experienced, attributed to particulate deposition and associated hydrolysis reactions. Mitigation of the problem was achieved by increasing the tube side velocity to 1.3m/s and reducing the outlet temperature slightly to 91°C to reduce the extent of the hydrolysis reaction. As a result of these changes the time between cleans was extended from 22 to 40 days

Temperature (as already indicated in this chapter) can have a profound effect on the rate of fouling where the mechanism is temperature dependent such as chemical reaction, corrosion, or precipitation fouling mechanisms.

Bott [23] gives an example of a fouling problem in a chemical process that is affected by temperature rather than velocity. A pregnant liquor involving a slurry of inorganic particles, passes through a complex system of shell and tube heat exchangers, after leaving a high pressure digester at 240°C, countercurrent to spent liquor returning to the digester. Two groups of heat exchangers are involved (1) high-temperature and (2) low-temperature. The spent liquor leaves the low temperature group at around 130°C and the high temperature set, prior to discharge into the digester at about 205°C. The liquor pH is high necessitating the use of special materials of construction. An inorganic scale forms on the heat exchanger tubes.

Data on the operation of the heat exchangers at different velocities (2.8 and 3.8 m/s for the low temperature exchangers and 1.9 and 2.5 m/s for the high temperature) demonstrate that the decay in heat transfer coefficient over time, is not a strong function of velocity. Whereas additionally, there is little fouling on the low temperature surfaces, there is a marked drop in heat transfer coefficient over a relatively short period of time at the higher temperatures. In general terms under these conditions the fall in heat transfer coefficient is about 50% over a week's operation. Thereafter the heat transfer coefficient appears to remain stable at about 50% of the clean coefficient, attributable to the changed temperature distribution due to the presence of the fouling.

An example of the effect of temperature on the fouling in a C_4/C_3 hydrocarbon stream passed through the tubes of a shell and tube heat exchanger has been reported [23]. High-pressure steam on the shell side of the exchangers raises the hydrocarbon stream from 15 to 130° C. The velocity in the tubes is relatively low. Fouling occurs on the hydrocarbon (tube) side of the exchangers. As fouling develops the steam pressure is raised in compensation, to maintain the desired heat flux.

Analysis of the performance of the exchangers shows that the mean fouling resistance rises from zero to 0.011 m²K/W in 28 days and, furthermore, that the mean fouling resistance versus average wall temperature shows a virtual straight line relationship i.e. rising from 144-190°C. Maximum fouling in the tubes occurred near to the high-pressure stream inlet, presumably where the wall temperature was high.

It is suggested [23] that some improvement in performance might be obtained by increasing the tube side velocity in an attempt to reduce the wall temperature. No data is provided to substantiate this suggestion.

The three examples taken from the chemical industry illustrate how the effects of velocity and temperature can affect heat exchanger fouling, suggesting how an intelligent approach can result in some relief of the problem.



C. Fouling in the pulp and paper industry

(by H Müller-Steinhagen)

Pulp mills have always been confronted with organic and inorganic deposition and with corrosion. Evaporator fouling is caused by materials which are insoluble (such as fibres, sand, scale flakes, etc.), only moderately soluble (CaCO₃, silica, aluminium silicates) or highly soluble (2Na₂SO₄-Na₂CO₃) in the liquor [24-27]. Modern operation conditions have severely aggravated these problems. Increasing energy costs, stronger environmental control combined with the trend towards higher yields has led to much higher levels of organic and inorganic solids circulating in the water system. Most, but certainly not all, fouling problems occur in the multiple effect evaporator set, in which the black liquor is concentrated from 15% to up to 70% solids content. Traditional designs use long vertical tube evaporators with forced circulation combined with a flash stage. A modern design option is falling film evaporators with continuous switching of high concentration effects to achieve some level of cleaning [28]. Figure 7 shows fouling resistances measured in the CHH Kinleith Mill in March 1988. A, B, C indicate the three high concentration effects which can be operated in various sequences to concentrate the liquor from 45% to 70%. When effect C is in contact with the 46% liquor, some removal of previously formed deposit is achieved. After switching, higher concentrations are processed in effect C, and a corresponding increase in fouling resistance is observed.

Systematic experiments of black liquor fouling are described in [29]. Hardly any deposition was found for concentrations below 55%. A sharp increase in fouling rate was observed if the surface temperature was increased from 132°C to 136°C, see Figure 8. The effect of flow velocity on the observed fouling rates was only small.

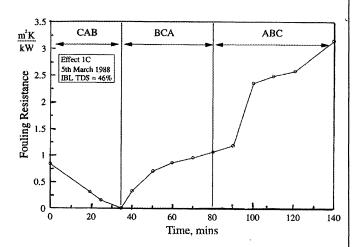


Figure 7 Effect C black liquor fouling resistances

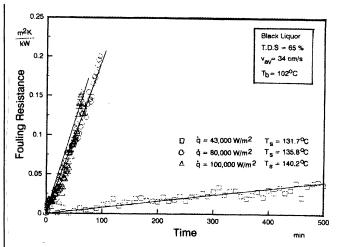


Figure 8 Effect of heat transfer surface temperature on black liquor fouling

Experiments with electropolished and PTFE coated surfaces produced significant reductions in deposit formation. This is shown in Figure 9. Chemical additives have produced mixed results, and should be evaluated with care [29]. Experiments with 65% solids liquor in a plate and frame heat exchanger did not show any reduction over 20 hours of operation, whereas the parallel double pipe heat exchanger fouled excessively after about 90 minutes [31].

Experiments have been performed on the removal of black liquor deposits by water washing. Fig. 10 shows that the cleaning rate increases strongly with Reynolds number. No effect of surface temperature could be detected [27].

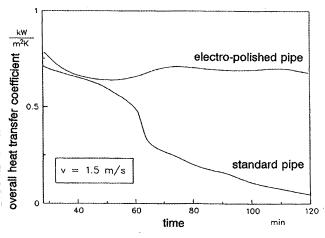


Figure 9 Heat transfer to black liquor on standard and electropolished steel surfaces [30]



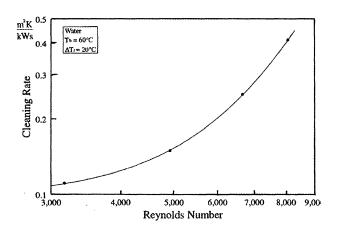


Figure 10 Cleaning rate as a function of Reynolds number [27]

D. Fouling in food processing

(by D. I. Wilson)

Fouling in the food industry principally involves deposition from liquids and suspensions of liquids in liquids (i.e. emulsions, such as milk), solids in liquids and occasionally gases in liquids. Fouling also arises due to corrosion, particulate deposition and scaling of utility side transfer surfaces, but this section will focus primarily on the challenges posed by heating of the process streams. This section will focus on fluid-type systems. The processing of solid and semi-solid materials in the food industry is discussed by Holdsworth [32] and by Hallström *et al* [33].

(a) Non-biological fouling

This section will focus on non-biological fouling in food processing operations. The prevalence of aqueous fluids containing suitable nutrients for biofilm growth in food processing operations means that bio-fouling is likely to occur unless appropriate cleaning and disinfection operations are performed on a regular basis. Biofouling is unlikely where process temperatures exceed 90°C, but lower temperatures may occur during cleaning periods or between production runs. Biofilm formation is almost always undesirable in food processing on hygienic grounds. Biofouling and biofilm formation are discussed in Section 3.17.6.E.

Heating and cooling is used in the food industry to reduce the viscosity of process streams so that they can be pumped, bring streams to process temperatures, remove induce changes in microstructure and/or chemistry, or to inactivate bacteria (sterilisation or pasteurisation). Evaporation is also used to concentrate streams by driving off water. The diversity of stream

compositions involved, and the range of responses to thermal treatment, means that fouling can involve any of the types in Section 3.17.2 – most frequently crystallisation, particulate or chemical reaction fouling or by a combination of these. Successful mitigation of fouling has been achieved by careful investigation of the fouling mechanism, identification of the key factors and incorporation of this knowledge into design and operation. The monograph by Visser *et al* [34] on fouling caused by heating milk fluids is an example of this approach.

The following factors apply in most cases of non-biological fouling

I. Complex composition

The fluids being processed usually contain a large number of different components. The composition may vary on a seasonal basis, causing fluctuations in fouling rate and deposit nature. Many fluids feature aqueous solutions or suspensions, but non-aqueous systems are also common (e.g. in processing oils and fats). Suspensions and emulsions frequently exhibit non-Newtonian rheology, and many food suspensions involve very large particles or micelles. Basic heat exchanger design is not straightforward, particularly in cases where the microstructure of the product is determined by the shear-temperature-time history of the fluid. The principal species or precursors responsible for fouling may be present in small or large concentrations. The latter case can result in very rapid fouling, as experienced in dairy plant (Changani et al.

II. Variation in feedstocks

Heat exchangers are often part of multi-product plants, which change feedstock on a regular basis. The fouling behaviour of each feedstock can vary widely, so that a heat exchanger designed to mitigate fouling caused by one fluid is less effective with other fluids. The exchanger design will therefore often be a compromise, based on possible worst cases, and careful attention must be paid to operating conditions for each fluid. Care should therefore be exercised in using exchangers on other processes. Heat exchangers, along with the rest of the plant, must be designed to be cleaned completely between batches in order to avoid product cross-contamination.

III. Cleaning and cleaning-in-place (CIP)

All exchangers processing fluids destined for human consumption must be designed for hygienic operation. Potential sites for microbial growth, and thus contamination, must be eliminated at the design stage

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and during installation. Guidelines on hygienic design are available from the EHEDG [36]. Fouling deposits present attractive sites for microbial growth so must be removed on a regular basis. Opening units to be cleaned is expensive and can introduce other contaminants, so CIP is often practised where the deposits can be removed by circulation of appropriate cleaning reagents.

The large fouling rates in many food applications mean that regular cleaning is essential and must be considered at the design stage. The maximum operating period between cleaning actions may be fixed by hygiene considerations, or the ability of the CIP system to remove aged deposits, rather than thermal or pressure drop considerations. The cleaning reagents and rinsing fluids (often water) are usually circulated at high velocities, which must be considered in the exchanger design. The choice of cleaning fluids is limited to those chemicals that are compatible with the food(s) being processed. This also applies to boiler make-up water where steam is used as a cleaning fluid (e.g. in sterilisation). CIP is discussed in more detail in Section 3.17.7.B.a.

IV. Mitigation options

The sensitivity of food materials to their environment means that the options available to mitigate fouling by manipulation of process parameters or conditions are very limited. Controlling fouling by chemical dosing is usually infeasible. Temperature, ion concentration and ionic strength, oxygen content and pH are frequently subject to narrow quality limits.

The temperature targets set by the process can mean that fouling is unavoidable. A prime example is milk pasteurisation, where the temperature required for inactivation of bacteria causes denaturation of proteins in solution, generating high concentrations of foulant precursors in the bulk liquid. Mitigation in such cases, therefore, involves selection of process parameters and exchanger type to minimise the amount of deposition of these precursors.

Knowledge of the fouling mechanism(s) involved will determine the best combination of operating conditions for a particular unit and should be incorporated at the design stage. Small temperature differences, and thus low heat fluxes, are frequently used in order to reduce the rate of fouling and subsequent ageing (e.g. 'cooking on) of deposits. The use of vacuum in evaporation units gives lower process temperatures (and associated fouling) and reduces the loss of volatile flavour components.

Process and hygiene requirements can also place limitations on the choice of exchanger material. The material of construction must be able to withstand the conditions used in processing and subsequent cleaning and disinfection. Food processing equipment is generally constructed from stainless steel with highly polished surfaces to restrict the opportunity for deposits to accumulate.

3.17.6-9

Aqueous process streams often contain a range of hydrophobic and hydrophilic species, which rapidly adsorb to form microlayers on heat exchanger surfaces. These microlayers pose little resistance to heat transfer but present a foundation for subsequent deposition and fouling. It may not be possible to find a fouling-resistant surface material that can both prevent adsorption and withstand the demands of the cleaning process [34]. Similarly, it should be noted that a surface which may be considered 'clean' from a heat transfer perspective can be significantly soiled from a microbiological or microlayer perspective.

The complex composition of food fluids means that more than one type of fouling can occur in a heat exchanger. These may occur in parallel, where interaction between the mechanisms can increase the fouling rate; or in sequence, where the temperature/concentration profile in the bulk fluid and the heat transfer surface determine the dominant fouling mechanism. One mechanism can generate an initial layer of foulant, which then provides sites for subsequent deposition by other mechanisms. Examples of reported cases of fouling are given in Table 2.

Much important information about the dominant fouling mechanism(s) can be obtained by inspection of the deposit nature and composition. For instance, minor components responsible for foulant generation will be present at enhanced concentration in the deposit. Comparison of deposit distribution with temperature and velocity profiles will indicate the importance of bulk and surface temperatures, and surface shear stresses. Particular care must, however, be exercised in interpreting the information provided by such assays. The fouling deposits generated are often heterogeneous, and can entrap components of the fluid which are not actually involved in the principal fouling mechanism(s). Alternately, crystalline scales can be generated where porous deposits hold solutions of hardness salts near hot surfaces for extended periods. Moreover, the organic food and bio-materials involved in chemical reaction, and chemical reaction/particulate deposits, may undergo ageing reactions under the conditions at the heat transfer surface so that the inspected sample differs significantly from the freshly generated deposit.

Many instances of fouling in food applications involve chemical reaction fouling in association with other types (e.g. denaturation of proteins in milk fouling). It is therefore important to establish which reactions are likely occur and by considering the exchanger as a chemical reactor establish whether these are likely to generate fouling precursors in the unit.

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Table 2 Examples of food fouling

| Process fluid | Components responsible for fouling | Fouling mechanisms |
|---------------|------------------------------------|---|
| Milk | Calcium phosphate | Crystallisation |
| | | (dominant at high temperatures) |
| | | Chemical reaction |
| | Proteins (notably whey) | (denaturation forms aggregates in bulk) |
| Carbohydrates | Sugar | Chemical reaction |
| - | | (caramelization or Maillard reactions) |
| | Starch | Particulate/chemical reaction |
| | | (starch breakdown/degradation) |
| Oils and fats | Unsaturated fats | Chemical reaction |
| | | (polymerisation/oxidation) |
| · | High melting point fractions | Crystallisation in coolers |
| Fruit juices | Proteins | Chemical reaction |

Fouling can also occur in sections where there is no driving force for heat transfer, such as holding sections, distributors and headers. Deposition in these cases can be caused by the laydown of sticky species generated by heat treatment, or by particulate or crystallisation fouling from oil and fat fractions with high/low melting points.

The most commonly used heat exchanger types in the food industry are plate heat exchangers, shell and tube, spiral, concentric tube and scraped-surface units; all are readily easy to clean on- or off-line. Scraped surface units are used for very viscous fluids, streams which undergo crystallisation (e.g. ice cream manufacture), or thermally sensitive materials which foul rapidly and require mechanical cleaning in situ. Plate heat exchangers are frequently used, particularly where the fluids being processed do not contain particles that would cause blockage. These units often feature larger heat transfer coefficients than other designs, allowing the use of smaller approach temperatures and surface temperatures. The flow patterns in these units give larger surface shear stresses, which also mitigate fouling. The complex flow distribution gives uneven fouling and can make complete cleaning difficult, but in many cases disassembly for jet or brush cleaning is much easier than with shell and tube units. Monitoring fouling in such units by reconciliation of process data is complicated by the tendency of deposition to occur in stagnant zones and at plate-plate contacts. Both pressure drop and thermal performance data should be collected in order to monitor the extent of fouling. Fouling in dairy units is discussed at length by Visser [34] and guidelines for dairy CIP system design have been published by the IDF [37].

E. Pharmaceutical and bio-processing

(by T. R. Bott)

In the manufacture of pharmaceutical products and bioprocessing, the overriding consideration is cleanliness and sterility. Contamination of the products cannot be tolerated. Thus, it is very unlikely that any form of chemical additive to prevent or reduce fouling would be allowed. Maintenance of clean surfaces must be accomplished by physical means without any risk to the quality of the products or intermediates. Fortunately, the products of these processes have a relatively high sales value, which provides the opportunity for a higher initial capital investment in the process plant, than might otherwise be possible. As a consequence, the equipment is of a high quality, particularly with respect to surface finish. Moreover, 316 stainless steel is the preferred material of construction, since it is corrosion resistant thereby eliminating a potential source of equipment fouling.

Published data [38,39] on the effects of surface finish on biofouling demonstrate that smooth surfaces are less hospitable to biofilm accumulation, than "as received" material. Both electrochemical and traditional polishing techniques are used to eliminate discontinuities on the equipment surfaces.

Bio-processing and pharmaceutical industries use jacketed vessels as reactors and mixing vessels. Furthermore, this type of equipment is multifunctional. As with food processing, reducing the number of crevices helps to reduce the risk of contamination from residues of previous operations. Batch operation is common in these industries, which necessitates frequent cleaning with the removal of any surface contamination that could be regarded as fouling.

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The risk of deposit formation may be reduced considerably or eliminated altogether by attention to hygienic design and operation, with frequent cleaning.

F. Water systems

(a) Cooling water*

(by G. F. Hays and R. K. Fuller)

I. Sources of foulants:

(i) Natural waters

Three sources of natural waters, surface waters, well waters and seawater are used as makeup water to cooling systems. Surface waters are taken from rivers and lakes and frequently in the form of potable water from a city water supply. Well water may either be sourced from an on-site well or from a potable water supply, while seawater is normally drawn directly from the sea. Each of these natural waters is a source for inorganic and organic impurities, which are potential foulants in a cooling water system.

(ii) Other sources of makeup water

Other sources of makeup water are reclaimed process wastewater, such as reverse osmosis reject water, boiler blowdown, condensate, treated process waste and treated sanitary waste. The constituent impurities in each of these sources are source and site specific. As such, each must be thoroughly understood to determine the effect it may have on fouling of heat exchange surfaces. In some instances, multiple sources of water are used as make-up to a single cooling water system. The design of a chemical treatment program should take into account the impurities in each makeup stream.

(iii) Airborne contamination

Airborne contamination may include dust, exhaust gasses from nearby processes, atmospheric contamination, such as acid rain, all of which may be scrubbed from the air, as well as wind-blown dust and dirt and microorganisms and spores. The type and level of each contaminant may vary with the wind direction and velocity.

(iv) Process leaks

Generally, cooling water systems are designed to be at a lower pressure than the processes, which they are cooling in order to prevent inleakage of cooling water into the processes. Thus, if a leak does occur, the process material will flow into the cooling water. Unless there is a history of process leaks, it is very difficult to predict when and where such leaks will occur.

II. Typical foulants:

(i) Scale formation

Scale is defined as a deposit formed from the precipitation of mineral salts in the cooling water. While there are many factors that influence the formation of scale in cooling water systems, the three major factors are: temperature, pH and water composition. Many mineral salts found in cooling water systems, have inverse solubilities with respect to temperature and pH. Specifically, as the temperature and/or pH of the water increase, the solubility of many scales decreases, resulting in an increased tendency for system deposition. Accordingly, the composition of impurities is an extremely important variable in determining the scaling potential of a water. In general, the higher the concentration of scale forming ions, the greater the potential for scale formation. The following is a brief discussion on various scales encountered in cooling water systems.

(ii) Calcium carbonate

Calcium carbonate is probably the most common scale found in cooling water systems; it forms an extremely tenacious heat insulating deposit.

Calcium ions and bicarbonate alkalinity are found in almost all cooling waters. The addition of heat, or a sharp rise in pH, will cause calcium bicarbonate to decompose and form carbon dioxide and calcium carbonate according to the equation.

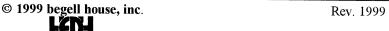
$$Ca(HCO_3)_2 \rightarrow CaCO_3 + CO_2 + H_2O$$
 (3)

Although the bicarbonate salt is moderately soluble, the carbonate salt has very low solubility. The Figure 11 shows a plot of the solubility of calcium carbonate as a function of temperature.

Calcium carbonate solubility is extremely in at any temperature. It is logical that the deposition of calcium carbonate is found on heat transfer surfaces where cooling water is subjected to the highest temperatures.

Due to problems associated with calcium carbonate scale formation, it is important that the cooling water control parameters be such that the potential for CaCO₃ formation is minimized.

^{*} Section 3.17.6F(a) is reprinted with permission from Ashland Inc.





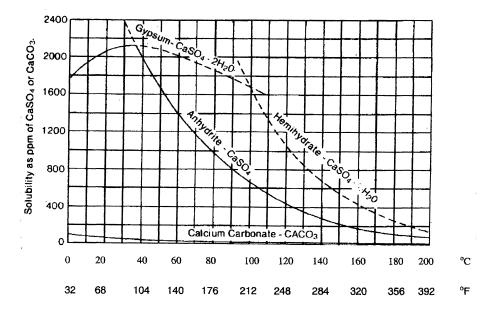


Figure 11 Comparison of solubilities of calcium sulfate and calcium carbonate. The calcium carbonate solution is in equilibrium with the normal carbon dioxide content of the atmosphere

(iii) Calcium sulfate

Various forms of calcium sulfate scale are found in cooling water systems. The most important is gypsum, which contains two waters of hydration. The hemihydrate and anhydrite forms are found to a much lesser extent. Figure 11, which shows the solubility of various hydrated forms of CaSO₄,

The solubility of gypsum increases until the temperature reaches approximately 38°C (100°F) and then gradually decreases. This scale, however, has more than one hundred times the solubility of calcium carbonate at normal cooling water temperatures. Traditionally, this fact has provided the basis for scale control. Specifically, sulfate ions replace alkalinity when sulfuric acid is fed to cooling water systems to control system pH. The result is that the system can be run at higher cycles of concentration without exceeding carbonate solubility limits. However, it is important to be reasonably sure that the addition of sulfuric acid does not cause the solubility of calcium sulfate to be exceeded. If it does, there are various other alternative acids that can be used, the benefits and drawbacks of which are discussed in more detail later in this section. The sulfate contribution from sulfuric acid must be included when determining the total sulfate concentration of the recirculating water.

(iv) Silicate scales

Calcium and magnesium silicate scales are very difficult to remove by chemical means. In some instances hydrofluoric acid or ammonium bifluoride has

been used with some success. However, the handling of these materials is extremely dangerous. First alkaline cleaning and then acid cleaning have also been used to combat this problem. Usually, limiting silica levels to approximately 150 ppm in the circulating water can prevent the formation of silicate scales, although the precise limits are determined by other system and makeup water parameters. For example, if magnesium is present with sufficiently high concentrations of silica, magnesium silicate can form.

To prevent magnesium silicate deposition, the magnesium and silica concentrations are controlled so that the following solubility product is not exceeded:

Raw SiO_2 (ppm) x Raw Mg (ppm as $CaCO_3$) x (cycles)²

- = 36,000 (ppm) if circulating water pH is 7.5 or below
- = 25,000 (ppm) when pH exceeds 7.5

It is important to note that many silica deposits are due to adsorption on other precipitates. In general, silica should not be a problem if deposition is controlled and the above guidelines are followed.

(v) Calcium orthophosphate

The solubility product of calcium and orthophosphate is very low. As a result, if orthophosphate is present in the water phase, it can react with calcium to form monohydrogen, dihydrogen and tricalcium phosphate. Phosphate sludge can bake onto heat exchange surfaces

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and, like other deposits, can both decrease heat transfer efficiency and yield underdeposit corrosion.

Unfortunately, it is more difficult to predict the formation of tricalcium phosphate than it is to predict the formation of calcium carbonate. However, there are some general guidelines to be followed. First, whenever controlling an inorganic or organic phosphate program, the orthophosphate concentration in the recirculating water should be determined. Second, if the orthophosphate concentration is greater than 2 ppm, tests should cover for both filtered and unfiltered orthophosphate.

Within reasonable testing error, these two concentrations should be the same. If the filtered orthophosphate is lower than the unfiltered result, it is a good indication that there is a potential phosphate precipitation problem in the water. Note that the

makeup water sometimes contains a detectable concentration of phosphate. Once cycled in the cooling tower, this phosphate, if not properly controlled, can create fouling problems.

The formation of tricalcium phosphate is largely dependent upon 4 parameters: system pH, calcium concentration, phosphate concentration and temperature. As any or all of these increase in value, the potential for phosphate sludging also increases.

In order to determine the theoretical pH_s, the pH of saturation of Tricalcium Phosphate, of a water of known quality, the following three tables are provided. Obtain the calcium factor from Table 3. Obtain the phosphate factor from Table 4. The sum of these two factors is used in Table 5. Enter Table 5 using this sum at the correct temperature range. Read pH_s from the left column.

Table 3 Calcium factor for calculation of pH_s of tricalcium phosphate

| Calcium ppm as | | Calcium ppm as | Calciun |
|-------------------|----------------|----------------|---------|
| CaCO ₃ | Calcium Factor | $CaCO_3$ | Factor |
| 1 | 15.00 | 80 | 9.28 |
| 2 | 14.10 | 100 | 8.99 |
| 4 | 13.19 | 120 | 8.75 |
| 6 | 12.66 | 140 | 8.55 |
| 8 | 12.28 | 160 | 8.38 |
| 10 | 11.99 | 180 | 8.22 |
| 12 | 11.76 | 200 | 8.08 |
| 14 | 11.55 | 250 | 7.79 |
| 16 | 11.37 | 300 | 7.56 |
| 18 | 11.22 | 350 | 7.38 |
| 20 | 11.08 | 400 | 7.18 |
| 30 | 10.55 | 500 | 6.89 |
| 40 | 10.18 | 600 | 6.66 |
| 50 | 9.89 | 800 | 6.28 |
| 60 | 9.65 | 1000 | 5.99 |

Table 4 Phosphate factor for calculation of pH_s of tricalcium phosphate

| Orthophos-phate ppm | | Orthophos-phate ppm | Phosphate |
|---------------------|------------------|---------------------|-----------|
| as PO ₄ | Phosphate Factor | as PO ₄ | Factor |
| 1 | 9.96 | 12 | 7.79 |
| 2 | 9.35 | 15 | 7.60 |
| 3 | 9.00 | 20 | 7.35 |
| 4 | 8.75 | 25 | 7.16 |
| 5 | 8.56 | 30 | 7.00 |
| 6 | 8.40 | 35 | 6.87 |
| 7 | 8.27 | 40 | 6.75 |
| 8 | 8.15 | 45 | 6.65 |
| 9 | 8.05 | 50 | 6.56 |
| 10 | 7.96 | 55 | 6.48 |

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- If the actual pH is less than pH_s, Ca₃(PO₄)₂ will tend to go into solution.
- If the actual pH equals pH_s, the water is balanced.
- If the actual pH exceeds the pH_s Ca₃(PO₄)₂ will tend to precipitate.

(vi) Iron phosphate

The solubility product of iron and orthophosphate is very low. Unfortunately, there are no solubility curves available to predict the formation of ferric phosphate.

Therefore, it is suggested the filtered and unfiltered orthophosphate levels in the system be monitored. This will at least help you to determine if phosphate is precipitating in the system.

(vii) Zinc phosphate

Zinc phosphate, like iron phosphate and tricalcium phosphate, is extremely insoluble and its formation is often preventable through the use of a phosphate deposit control agent.

Table 5 Determination of the pH_s for Tricalcium Phosphate using the factors obtained from Tables 3 and 4

| | 20°C | 30°C | 40°C | 50°C | 60°C | 70°C | 80°C |
|-----------------|-------|-------|-------|-------|-------|-------|-------|
| pH _s | 68°F | 86°F | 104°F | 122°F | 140°F | 158°F | 176°F |
| 6.0 | 14.00 | 14.32 | 14.64 | 14.86 | 15.04 | 15.30 | 15.42 |
| 6.1 | 14.38 | 14.69 | 15.02 | 15.44 | 15.56 | 15.69 | 15.83 |
| 6.2 | 14.76 | 15.07 | 15.38 | 15.90 | 16.04 | 16.05 | 16.20 |
| 6.3 | 15.13 | 15.45 | 15.74 | 16.30 | 16.46 | 16.44 | 16.57 |
| 6.4 | 15.51 | 15.82 | 16.14 | 16.68 | 16.84 | 16.81 | 16.94 |
| 6.5 | 15.87 | 16.19 | 16.50 | 17.04 | 17.20 | 17.18 | 17.32 |
| 6.6 | 16.24 | 16.53 | 16.88 | 17.38 | 17.56 | 17.54 | 17.70 |
| 6.7 | 16.61 | 16.88 | 17.24 | 17.70 | 17.68 | 17.91 | 18.06 |
| 6.8 | 16.95 | 17.22 | 17.60 | 18.00 | 18.18 | 18.25 | 18.40 |
| 6.9 | 17.29 | 17.57 | 17.92 | 18.31 | 18.49 | 18.60 | 18.73 |
| 7.0 | 17.61 | 17.92 | 18.24 | 18.59 | 18.78 | 18.92 | 19.06 |
| 7.1 | 17.92 | 18.25 | 18.56 | 18.88 | 19.08 | 19.25 | 19.40 |
| 7.2 | 18.23 | 18.57 | 18.86 | 19.18 | 19.36 | 19.57 | 19.70 |
| 7.3 | 18.53 | 18.86 | 19.14 | 19.44 | 19.66 | 19.87 | 20.00 |
| 7.4 | 18.81 | 19.13 | 19.42 | 19.72 | 19.94 | 20.16 | 20.30 |
| 7.5 | 19.08 | 19.40 | 19.70 | 19.96 | 20.20 | 20.44 | 20.56 |
| 7.6 | 19.35 | 19.66 | 19.96 | 20.22 | 20.46 | 20.71 | 20.84 |
| 7.7 | 19.60 | 19.92 | 20.20 | 20.46 | 20.70 | 20.96 | 21.10 |
| 7.8 | 19.84 | 20.17 | 20.44 | 20.69 | 20.94 | 21.20 | 21.34 |
| 7.9 | 20.08 | 20.40 | 20.68 | 20.92 | 21.18 | 21.43 | 21.58 |
| 8.0 | 20.32 | 20.64 | 20.92 | 21.16 | 21.40 | 21.67 | 21.80 |
| 8.1 | 20.54 | 20.86 | 21.14 | 21.37 | 21.64 | 21.89 | 22.03 |
| 8.2 | 20.76 | 21.08 | 21.36 | 21.58 | 21.86 | 22.12 | 22.24 |
| 8.3 | 20.98 | 21.29 | 21.58 | 21.81 | 22.06 | 22.33 | 22.46 |
| 8.4 | 21.19 | 21.50 | 21.78 | 22.02 | 22.28 | 22.54 | 22.68 |
| 8.5 | 21.41 | 21.72 | 22.00 | 22.23 | 22.50 | 22.75 | 22.90 |
| 8.6 | 21.62 | 21.94 | 22.22 | 22.44 | 22.70 | 22.96 | 23.10 |
| 8.7 | 21.83 | 22.15 | 22.42 | 22.66 | 22.90 | 23.17 | 23.31 |
| 8.8 | 22.04 | 22.36 | 22.62 | 22.86 | 23.10 | 23.36 | 23.51 |
| 8.9 | 22.25 | 22.56 | 22.83 | 22.08 | 23.30 | 23.57 | 23.72 |
| 9.0 | 22.46 | 22.76 | 23.02 | 23.28 | 23.52 | 23.76 | 23.93 |
| 9.1 | 22.66 | 22.96 | 23.26 | 23.48 | 23.71 | 23.97 | 24.12 |
| 9.2 | 22.86 | 23.17 | 23.46 | 23.69 | 23.92 | 24.17 | 24.32 |
| 9.3 | 23.06 | 23.37 | 23.66 | 23.90 | 24.12 | 24.36 | 24.53 |
| 9.4 | 23.27 | 23.57 | 23.86 | 24.10 | 24.32 | 24.56 | 24.74 |
| 9.5 | 23.47 | 23.77 | 24.06 | 24.30 | 24.54 | 24.75 | 24.93 |

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(viii) Magnesium salts

The concentration of magnesium salts in a system is usually considerably lower than that of the calcium. In addition, magnesium salts are usually more soluble than those of calcium, with the result that calcium will precipitate first. This combination of factors results in reduced scaling potential for magnesium salts.

(ix) Manganese

Often found in well water, the behavior of manganese is similar to that of iron but more difficult to control. Manganese can exist in either the +2 or +4 oxidation states and forms a tenacious, black deposit in cooling water systems. Manganese is controlled by oxidizing with chlorine, chlorine dioxide, permanganate, aerating tower or oxidizing filters.

(x) Zinc hydroxide

Zinc forms zinc hydroxide precipitates at system pH of 8.0 and above. However, there are specific zinc stabilizers available that can maintain zinc in solution at a system pH as high as 8.5 and above.

(xi) Iron hydroxides and hydrated oxides

Iron is probably second only to microbiological growth as the primary cause of fouling in open recirculating cooling systems. Soluble iron is often present in recirculating water as either a corrosion product or a contaminant in the makeup water supply. Once in the cooling system, it quickly oxidizes and deposits as a ferric hydroxide or ferric oxide floc. The rate of oxidation is even greater in systems that use oxidizing agents for microbiological control. Ferric hydroxide and ferric oxide cause other suspended matter, including biomasses, to agglomerate and precipitate.

(xii) Aluminum

While not as common as some of the other foulants discussed in this section, aluminum contamination in a cooling water stream can pose a serious fouling potential. Like iron, calcium, and zinc, aluminum in the presence of orthophosphate is extremely insoluble and can form aluminum phosphate sludge. Typically, though, the foulant formed when aluminum is present is a combination of various other foulants such as suspended mud or silt.

A typical source of aluminum contamination is alum carryover from a raw water clarifier. This can be avoided by installing filters after the clarifier. There is no deposit control agent specific for preventing aluminum precipitation. Thus, it is important to ensure

proper clarifier operation. However, when this is not possible, a surfactant may help reduce the severity of the deposition. If phosphate is present, a deposit control agent specific for preventing phosphate fouling may be warranted.

(xiii) Other waterborne foulants

A variety of materials such as mud, sand, clay, biological matter or even oil may enter a cooling water system through its makeup supply. They usually accumulate in low flow areas, or in locations at which an abrupt decrease in flow velocity occurs. Therefore, the most sedimentation is found in such places as cooling tower basins and heat exchangers. Most commonly, the deposition occurs in the waterbox, shell-side and plate and frame heat exchangers. The particle size, density and certain water characteristics will affect the probability that a suspended solid will settle and foul a system. The larger and more dense the suspended material, the greater the chance of settling.

The extent of fouling is largely a result of the time afforded for the particle to settle. Cooling tower basins, waterboxes and shellside flow areas involve appreciable holding times and dead areas, which result in extensive settling of sediment. Once the particles have settled, the nature of the resultant deposition depends upon the strength of the attractive forces between the particles and the surfaces they contact. If the attractive forces between the particles are strong, the deposit will be dense and well structured; if the forces are weak, the deposit will be soft, or even fluid in nature. Similarly, if the forces between particles and the surfaces they contact are high, the deposit is adhesive and difficult to remove

Certain foulants, such as river water silt, enter the system in colloidal form in particle sizes ranging from 1.0 to 100 millimicrons. These particles are too small to be seen by the naked eye and are usually negatively charged which cause a tendency towards continued dispersion rather than precipitation. Introducing ions of opposite charge can cause these colloidal particles to agglomerate and settle in the cooling system.

Therefore, nonionic surfactants are often used to control the deposition of suspended solids in cooling water systems.

(xiv) Microbiological growth

Microbiological growth may be a particularly troublesome foulant in a cooling water system. The microbiological population in a cooling tower often approaches, or exceeds, the upper control limit for proper tower operation. This condition seriously strains both microbiological and deposit control programs. Slime (biomass) in a cooling water system is also a

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deposit. It entraps materials, which normally would not have deposited, and leads to greater problems that would otherwise have not occurred.

Hydrocarbons often adhere to metal surfaces and act as deposit binders. Oil films serve as insulators and can seriously retard heat transfer. In addition, Hydrocarbons are nutrients for microbes, increasing microbiological activity, fouling and slime binding. Finally, hydrocarbon films prevent corrosion inhibitors from reaching and passivating metal surfaces.

Control of suspended matter by clarification of makeup water is a good example of a method that has successfully minimized fouling by these causes. There may be small but continuous carryover of suspended aluminum and iron floc from the clarifier. Post-precipitation of aluminum and iron hydroxides, which can foul heat exchange surfaces. This floc carryover may cause a greater deposit problem than the turbidity that was originally in the water supply.

(xv) Airborne foulants

The air in contact with open cooling water systems often contains many of the same suspended materials found in surface water makeup sources such as rivers and lakes. Because the cooling tower may use fans or natural draft to draw in air to maximize the efficiency of evaporative cooling, the tower, in effect, scrubs the air of any particles of sand, silt, clay, dirt, bacteria or oil that it may contain. These contaminants add to the overall suspended solids loading in the cooling system and, for reasons discussed in the previous section, will increase the potential for fouling in the system.

Airborne contamination by gases can also increase deposition. Oxygen and carbon dioxide accelerate corrosion, leading to deposition and further corrosion by the underdeposit mechanism. Since pickup of both gases occurs continuously, near saturation levels of these dissolved gases are present in the water. Gaseous contaminants such as sulfur dioxide, hydrogen sulfide and ammonia may also be scrubbed from the air. Hydrogen sulfide is very corrosive and quickly forms iron sulfide deposits, which lead to further corrosion. Ammonia selectively corrodes copper and its alloys, leading to the deposition of copper corrosion products.

(xvi) Process leaks and contamination

Process fluids and gases often enter cooling water through leaking heat exchangers. These contaminants include hydrophobic organic matter such as lubricating oils, hydraulic fluids and chemical processing industry (CPI) process streams. They are usually reducing agents that deplete oxidizing biocides (chlorine, bromine, chlorine dioxide, etc). These organic fluids also form films on heat exchanger tube surfaces that

interfere with heat transfer and promote under-deposit corrosion. In addition, they may represent bionutrients, which greatly accelerate microbiological growth.

Other reducing bionutrient contaminants include glycols, reclaimed waters such as municipal wastewaters, fermentation broths and food products. These all have adverse effects on cooling water systems similar to those described above.

In addition, ammonia (NH₃) can enter cooling water in ammonia and fertilizer plants through leaking heat exchangers and/or from leaks into the atmosphere. Gaseous ammonia dissolves in water to form ionized ammonium hydroxide (NH₄OH), which is alkaline, and has five detrimental effects:

- 1. It reduces and depletes oxidizing microbiocides.
- 2. It increases the corrosion rate of copper and copper alloys.
- 3. It is a bionutrient and increases, microbiological growth rates.
- 4. It initially raises pH.
- 5. Microbiological activity can oxidize it to nitrous and/or nitric acids, which will depress pH.

Another reducing gas that enters cooling water in refineries and petrochemical plants is hydrogen sulfide (H_2S) . It is one of the most harmful gases that can enter a cooling water system. It adverse effects include:

- 1. It reduces oxidizing microbiocides
- 2. It forms a weak acid that will depress pH.
- 3. It is almost always ionized to bisulfide and sulfide ions which tend to depolarize anodic areas, thus accelerating anodic corrosion.
- It generates iron sulfide, which results in iron sulfide deposits. These deposits are cathodic to base metal, causing severe galvanic corrosion under the deposits.

(b) Geothermal brines

(by S. H. Chan)

I. Introduction

The major contributors to geothermal fouling are scaling due to silica and calcium carbonate. This is a result of the fact that silica is one of the primary components of the earth's crust and so are calcium compounds in some areas. Calcium scaling in geothermal plants is primarily attributed to pressure reductions, such as scaling found in a wellbore, where flashing starts, and in valves, constrictions, or flow

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measuring instruments. When the pressure of the bulk brine is decreased rapidly, the excess dissolved carbon dioxide gas is liberated from the brine due to its decrease in solubility, resulting in a higher pH of the brine. Consequently, carbonate ion concentration increases, which causes the deposition and crystal growth of calcium carbonate. The kinetics of this reaction are very fast, causing scale formation immediately downstream of such pressure reductions. In some cases, this has caused plugging of the pipes, valves, pressure taps, and flow instruments. Since calcium carbonate solubility decreases with increasing temperature, calcium carbonate scale is also found on heated surfaces. Silica scaling is quite different. Silica solubility increases with increasing brine temperature. Silica, being saturated in geothermal brines in the downhole environment in the monomeric state, can become supersaturated as the brine is cooled through the heat exchanger or when part of the brine is flashed into steam. The supersaturation causes precipitation of silica in an amorphous form on heat exchanger surfaces separators, well lines, and discharge lines.

II. Calcium scaling

For calcium relating scaling, reference should be made to section 3.17.6.F(a) on cooling water. Most of data on CaCO₃ showed that, once past the induction period, the scaling curves were linear. Analytical model is available to predict the deposition rate (Chan and Chassemi, [40]. It considered the diffusion of calcium, carbonate and bicarbonate ions to a heated surface to react and form a CaCO₃ scale and dissolved CO₂. It also considered the diffusion of the excess CO₂, produced at the liquid-scale interface, away from the interface to maintain an equilibrium condition at the interface. The result showed that an increased in flow velocity augmented the scaling rate. Figure 12 [41] illustrates the fouling rate and a comparison between the analytical prediction and experimental data of Sheikholeslami and Watkinson [41].

III. Silica scaling

(i) Silica solubility

Silica exists in both the crystalline and amorphous states. Because many ordered arrangements of tetrahedra joined by corners are possible, silica forms various crystal structures or polymorphs. The solubilities of different polymorphs of silica in saturated water at various saturation temperatures are given in Figure 13 [42]. The solubility of the polymorphs increases with increasing temperature up to 300°C; above this temperature the solubility decreases. It can be seen that amorphous silica is more soluble than quartz at all temperatures, but they exhibit similar temperature dependencies. The concentration of silica in

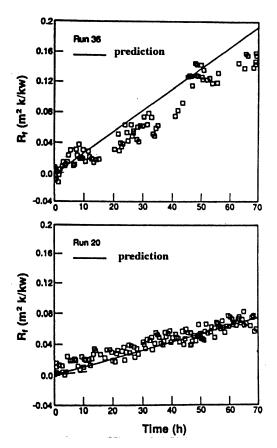


Figure 12 Comparison between the prediction [40] and calcium carbonate fouling data [41]

underground geothermal brines is usually controlled by the solubility of quartz and downhole temperature so that silica is generally present as quartz. However, under most conditions, it appears that silica precipitates out as relatively pure amorphous silica whatever the original silica source may be. The reason is that the kinetics of quartz crystallization below 300°C is much slower than that of amorphous silica. Amorphous silica solubility is a weak function of pressure and therefore the pressure effect can be neglected for most practical applications.

In addition to temperature, pH and salinity can also have significant effects on the solubility of silica. Figure 14 [43] shows that at low pH the solubility remains constant, but, beyond a limit, the solubility increases drastically with pH values. When the salinity of brine is changed due to the addition of salts in the pure water, the magnitude of the activity of water decreases and so does the solubility of silica. Figure 15 [44] illustrates how the solubility of amorphous silica decreases as the amount of additional NaCl increases at various temperatures.

The solubility of amorphous silica in aqueous sodium nitrate up to 300°C (Marshall, [45]), and in sodium chloride, sodium sulfate, or magnesium sulfate



solutions (Chen and Marshall, [44]) up to 350 C has been measured. Other investigators have also studied the solbulity in ten (Marshall et al., [46] and eleven (Chan et al., [47]) different salt solutions (NaCl, NaBr, Nal, LiCl, KCl, NaNO₃, NaAc, Na₂SO₄, MgCl₂, CaCl₂, and SrCl₂) at 25 C. For a given temperature and salt concentration, the effect of different salts on solubility can be correlated by the hydration number of salt

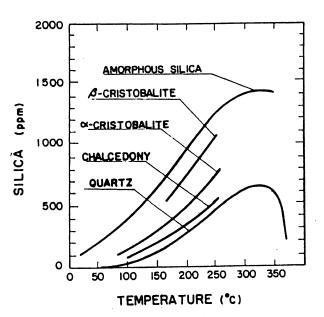


Figure 13 Solubilities of various silica phases at various saturation temperatures with pH = 7 [42]

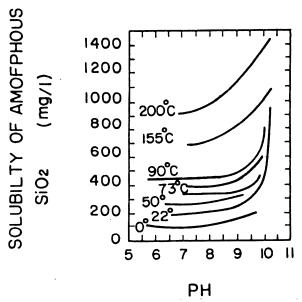


Figure 14 Solubility of amorphous silica as a function of pH at various temperatures [43]

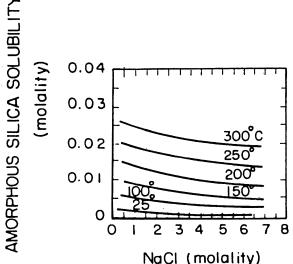


Figure 15 Molal solubility of amorphous silica in aqueous NaCl solutions at varkious temperature [44]

cations. The order of decreasing effect of cation on the amorphous silica solubility is found to be (Chan et al.,

$$Mg^{2+} > Ca^{2+} > Sr^{2+} > Li^{+} > Na^{+} > K^{+}$$

Similarly, the effects of the presence of sodium halide salts (NaCl, Nal, and NaBr) in brine solutions were studied. It was found tht the gradients of silica concentration with respect to the salt concentration for sodium halide salts can be correlated in terms of the molecular weight of the anionic ions, such that the order of anionic effect can be stated as (Chan et al., [48]):

$$> Br^{-} > Cl^{-}$$

and that the solubility of silica C_{SiO2} (in ppm) in the sodium halide salt solutions can be correlated as a function of salt concentration C_i (in molality), temperature T °C and the atomic weight of halide ions M_i as follows:

$$C_{SiO_2} = C_{op} - \frac{11.75 \left[M_j + (3.78 - T) \right]}{281 - T} C_j$$
 (4)

where C_{on} is the silica solubility (in ppm) in pure water; $\log C_{op} = 4.52 - 731/T$.

(ii) Silica deposition model

Prediction of silica deposition rate is difficult. For silica deposition governed by surface reaction rate, an approximate model can be used (Chan et al. [48]). The

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| = | <u> </u> |
| 2 | 0.03 |
| | |
| - | 0.02 300°C |
| | 250° |
| | 0.01 |
| | 150 |
| | 25 |
| | 0 |
| | 0 1 2 3 4 5 6 7 8 |
| | NaCl (molality) |
| | raci (molatily) |

model is based on a kinetic study by Bohlman et al. [49] on simulated geothermal brines in an isothermal system and extends it to non-isothermal systems. The supersaturation effects, pH effects, salinity effects due to presence of impurities and thermal-hydraulic effects

supersaturation effects, pH effects, salinity effects due to presence of impurities, and thermal-hydraulic effects due to heat transfer and fluid flow, are all accounted for in the model.

IV. Control of deposition

Since increased carbonate concentration caused by a pH increase associated with removal of CO₂ causes deposition, controlling pH can control calcium carbonate deposition. However, due to the large quantity of brine being processed and its relatively low unit value, the use of chemicals to control pH may not be economically practical. Generally, it is known that maintaining pressure on a geothermal brine solution prevents precipitation not only of calcite or calcium carbonate, but also of other hydroxide salts and certain silicates. Another known scheme involves the design of a process such that deposition will occur in the bulk liquid phase rather than on the walls so that the settled solids can be collected in a special vessel. An example is to flash a sufficient amount of brine so that the solution is greatly supersaturated with respect to calcium carbonate to form calcite crystals in the bulk. This will decrease deposition downstream of a flash separator tank for high degrees of flashing.

Similarly, silica deposition may be controlled by use of a holding tank in which the geothermal brine is maintained for a sufficiently long time due to the relatively slow kinetics so that the silica will deposit in the bulk of the solution. This colloidal precipitate is carried through the process equipment in the solution to reduce pipeline deposition. Other approaches have been to maintain the brine above the temperature at which deposition would occur, to dilute the brine such tha the concentration of the salts is maintained below their solubility limit, or simply to avoid the problem by not using wells that show severe scaling problems. In all these cases, significant energy is not utilized. There is a lack of anti-scalants for the control of silica scales. A better approach to scale deposition is to alter process conditions, based on an understanding of the mechanism and kinetics of the deposition, to control the formation of the deposit in a desired location where mechanical removal can be easily achieved.

(c) Waste and reuse water

(by L. F. Melo and G. F. Hays)

Fouling problems caused by wastewater have been neglected so far in the heat exchanger literature. Although there are practically no internationally known publications on the subject, the problem is real and it is

expected to increase in the next decades due to the reuse of treated wastewater.

Most wastewaters contain the main types of agents that are usually involved, directly or as precursors, in the build up of unwanted deposits: inorganic salts, microorganisms, organic compounds, etc. Untreated municipal wastewater is reported to contain 200 mg/L of organic carbon [50], a basic condition for the growth of many microorganisms. Microbial and (bio-) corrosion and precipitation fouling are the more common types of fouling occurring in wastewater treatment plants. Heat exchangers are used upstream or downstream of these plants and are, therefore, subject to intensive fouling problems. The fact that such problems are rarely mentioned in the literature is probably related to the relatively minor costs of heat exchanger fouling when compared to the costs of the wastewater treatment itself. For example, if the price of US\$0.50-1.00 is paid per cubic meter of wastewater (as it happens frequently), the treatment of 10 m³ per hour will correspond, after one year, to the cost of buying two heat exchangers to heat/cool this stream.

However, environmental concerns, cost of fresh make-up waters and governmental regulations have substantially increased the reuse of municipal and process wastewaters. The tendency to reduce the use of antifouling chemicals, such as biocides, dispersants, pH stabilizers, etc., and to stimulate "zero-discharge" industrial plants will inevitably result in an increase in the fouling potential within industrial processes and power plants.

In anaerobic wastewater treatment plants, the temperature must be kept around 35-37°C (optimum for the metabolism of methanogenic bacteria), which often demands a heat exchanger to be installed before the anaerobic reactor. As an illustration, an animal rendering wastewater treated in an anaerobic reactor may contain 5,000-10,000 mg/L of BOD₅ (Biological Oxygen Demand measured during 5 days), 50-10,000 mg/L of grease, 2-20 mg/L of orthophosphates, 500-1,700 mg/L of ammonia nitrogen and 10-25 mg/L of sulfides [51]. This certainly points to potentially severe fouling problems in the heat exchanger upstream of the reactor. In some cases, plate heat exchangers have been used, since they offer high heat transfer coefficients even when the flow Reynolds number is low (as in many wastewater systems), and they can be easily cleaned.

In another example [52], a heat exchanger is used to cool the already treated wastewater coming from an anaerobic system at 40°C in a potato-starch factory before discharge (to avoid thermal pollution problems). This treated water still contains 1,200 mg/L of BOD5 and microbial fouling should be expected to occur, stimulated also by the presence of suspended microorganisms in the treated effluent.

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One of the few published cases of fouling caused by wastewaters is the precipitation of struvite (MgNH4PO4), which occurs in : a) anaerobic treatment of wine distillery and of pork packing plant wastewaters; b) systems containing sludge waste resulting from biological phosphate removal plants [52]. All these wastes contain high concentrations of orthophosphates, ammonia and magnesium ions that lead to the formation of struvite. A recently published study (53) is focused on the struvite precipitation fouling in pipes and in the secondary settler, but not in heat exchangers. The authors conclude that the partial pressure of CO₂ in the gas space above the anaerobic digester should be maintained at a certain level, in order to avoid an increase in pH in the liquid (due to the release of CO₂) which would favor struvite precipitation.

Wastewater may be produced in heat exchangers that remove toxic vapors from air streams [54] by condensation. As a consequence, corrosion and/or chemical reaction fouling may occur. Surface condensers, where the gas-vapor mixture flows in the shell or direct contact condensers, are used. Contact condensers lead to higher pollution of wastewaters (the outlet liquid stream contains not only the condensate but also substantial amounts of water); this may cause environmental engineers to use contact condensers which will, in turn, suffer greater fouling problems than the contact heat exchangers.

Some of the cases reported above refer to heat exchangers where the wastewater must be heated or cooled as a pre-requisite for biological treatment or for final discharge. However, recycled wastewater is more and more often used as the cooling medium. Normally, wastewater is treated prior to recycling. Treatment may be as simple as settling and filtration, as complex as a tertiary waste treatment process or any process in between. The quality of the wastewater stream and the requirements of the process in which it will be used will determine the type of treatment process.

One common use of recycled wastewater is in open recirculating process cooling systems. The recycled water serves as the cooling medium, while in the process, the water and its impurities are concentrated due to evaporation in the cooling tower. This increases the concentration of both organic and inorganic foulants and promotes biofouling. Frequently, the recycled wastewater is used in existing cooling water systems, which were designed for use with fresh make-up waters. In such cases, changes may be required in both chemical and mechanical treatment to inhibit sufficiently fouling and corrosion of heat exchangers and cooling tower fill.

Use of recycle water on the shell-side of shell and tube heat exchangers should be avoided because of inherently low velocities and undetermined flow path, which will substantially increase the potential and severity of fouling. Where such conditions exist, alternate heat exchanger designs should be considered.

Although the build up of deposits is mentioned in the literature on wastewater treatment, it is seldom analyzed in terms of heat transfer losses. Heat transfer has been so far considered just a secondary problem in the wastewater treatment field. There is a need to undertake laboratory and plant monitoring studies where wastewater streams are used as heating or cooling fluids in heat exchangers, in order to be able to prevent severe fouling problems in the future. A desirable first step would be to assess the actual extent of the problem in industry, by collecting data from plants where waste and reuse water are used in heat exchange processes.

G. Power generation/cogeneration

(by K. W. Herman)

In the production of electrical power, the chemical energy of fuels is converted to heat, which generates steam in a boiler. This steam is then converted to mechanical energy in a turbine that drives an electrical generator.

The exhaust steam from the turbine is condensed in a heat exchanger, which uses either recirculating cooling water or once through cooling water. The fouling associated with these condensers has been described in the previous section and is dependent upon the characteristics of the cooling water used.

However, the boiler itself is a heat exchanger in which water is converted into steam in the process of cooling the heat source. Burning fossil fuels or nuclear energy provide the heat source needed in typical electrical utility suppliers. In addition to burning fossil fuels, the heat for generating steam in industrial boilers that generate electricity can be from various sources such as process hot gases or waste products. An industrial plant may condense the steam used to drive the turbine or it may use a non-condensing turbine in which steam exhausts under pressure into a process steam header.

Boilers in utility power plants can be either drum type or once through design with pressures up to 218.3 bar the critical pressure of water. Above the critical pressure, a supercritical fluid exists and all boilers are of the once-through design. Boilers in industrial plants that generate electricity are normally of the drum design and operate in the pressure range 40 to 136 bar.

The suggested water chemistry limits for industrial drum type boilers that includes superheater, turbine drives, or process restriction on steam purity and fired with primary fuels such as oil, gas, or coal are shown in Table 6 [55]. Depending on the percent of the feedwater that is makeup, pretreatment of the makeup to meet these limits may be required. Table 7 shows a list of

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Table 6 Suggested Water Quality in Modern Water Tube Boilers Drum

| Pressure, bar | 0-20.4 | 20.5-30.6 | 30.7-40.8 | 40.9 - 51.0 | 51.1-61.2 | 61.3-68.0 | 68.1-102.1 | 102.2-136.1 |
|---------------------------------|-----------|-----------|-----------|-------------|-----------|-----------|------------|-------------|
| Feedwater | | | | | | , | | |
| Dissolved O ₂ , mg/l | <0.007 | <0.007 | <0.007 | <0.007 | <0.007 | <0.007 | <0.007 | <0.007 |
| Total iron, mg/l Fe | ≤0.1 | ≥0.05 | ≥0.03 | ≤0.025 | ≤0.02 | ≤0.05 | ≥0.01 | ≤0.01 |
| Total Copper, mg/l Cu | <0.05 | ≤0.025 | ≤0.02 | ≤0.02 | ≤0.015 | ≤0.01 | ≤0.01 | ≤0.01 |
| Total Hardness, mg/l | ≤.3 | €.0≥ | ≥0.2 | ≤0.2 | ≤0.1 | 50.0≥ | ΠN | ND |
| рн @ 25 °С | 8.3-10.0 | 8.3-10.0 | 8.3-10.0 | 8.3-10.0 | 8.3-10.0 | 9.6-8.8 | 9.6-8.8 | 8.8-9.6 |
| | | | | | | | | |
| Boiler Water | | | | | | | | |
| Silica, mg/l | 150 | 06 | 40 | 30 | 20 | 8 | 1 | - |
| Total Alkalinity, mg/l | <350 | <300 | <250 | <200 | <150 | <100 | NS | NS |
| Free Hydrate Alkalinity, mg/l | SN | SN | NS | NS | NS | NS | ND | ND |
| Specific Conductivity, | 5400-1100 | 4600-900 | 3800-800 | 1500-300 | 1200-200 | 1000-200 | 150 | 80 |
| :Siemens/cm @25 °C | | | | | | | | |
| (un-neutralized) | | | | | | | | |
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3.17.6-22 3.17 FOULING IN HEAT EXCHANGERS / 3.17.6 Designing Heat Exchangers for Fouling Conditions

various pretreatment processes that was presented by Herman [56].

In boilers, deposits on the waterside of tubes can reduce the rate of heat transfer causing high metal temperatures, softening of the metal and possible rupturing. Reducing the source of these deposits by appropriate pretreatment of makeup water combined with a chemical treatment program is the technique used to minimize fouling of tubes on the water side. The major cause of deposits in power generating units is metal oxides present from corrosion in the preboiler and/or the condensate systems.

Utility power plants use demineralized makeup water to minimize any fouling of the boiler heat transfer surfaces, use chemical treatment programs that control corrosion and may have condensate ion exchange polishers to insure that only high quality feed water enters the boiler. Drum type units operating at pressures from 68 to 218 bar control corrosion using additives that may consist of a combination of a sodium to phosphate ratio of 2.6 to 0.2, a volatile oxygen scavenger and an amine for condensate pH control. For any once-through unit only an all-volatile treatment program can be used.

H. Fireside fouling

(by E. R. Miller)

(a) Introduction

Fireside fouling refers to fouling that occurs on the hot stream surfaces of equipment heated by combustion sources. Fuels may be either gaseous, liquid or solid. Such equipment includes primary process heaters and boilers plus heat recovery systems that are auxiliary to power generators, incinerators, kilns or other process related operations. The surfaces may be predominately radiant, convective or combinations thereof. Radiant zone surfaces are generally prime surfaces, while convective surfaces may be prime and/or extended. As a rule, the process (cold) stream is located tube-side, although fire-tube boilers still have application, usually for heat recovery from process gases.

(b) Effects of fouling

I. Impact on performance

The detrimental economic effects of fouling that apply to unfired equipment also apply to fired equipment. These include:

 Table 7 External Treatment Systems for Makeup Water for Boilers

Treatment

| 1. Aeration | Reduce iron, manganese, hydrogen sulfide, carbon dioxide. |
|---|---|
| 2. Prechlorination | Reduce organic matter and microorganisms. |
| 3. Clarification | Reduce color and suspended matter. |
| 4. Cold process softening | Reduce suspended matter, iron, calcium, magnesium, bicarbonate and maybe some silica. |
| 5. Cation exchange, sodium cycle | Reduce calcium and magnesium. |
| 6. Split stream cation exchangers, sodium and 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 | Reduce all cations, anions, and silica to very low concentrations. |
| <u>.</u> | |

Effect

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3.17 FOULING IN HEAT EXCHANGERS / 3.17.6 Designing Heat Exchangers for Fouling Conditions

- Reduced heat transfer
- Reduced capacity
- ❖ Poor energy utilization
- ❖ Increased pressure drop (draft loss)

Also, in equipment where radiation plays a dominant (or even contributory) heat transfer role, performance should theoretically be impacted by the effect of fouling deposits on both surface and refractory emissivity. Unfortunately, the present state of the art does not help confident prediction of either the degree or direction of the expected net result.

Although becoming increasingly rare as fuel quality improves, I can personally attest to multiple examples of fouling performance loss in fired heaters relative to the clean condition, e.g.:

- ❖ Convection section heat transfer overall coefficient times area declines of 50-60%
- ❖ Stack temperature elevations (increases) of 190-220 °C (350-400 °F)
- ❖ Efficiency losses of 8-11%

These all translate to significantly higher fuel costs and provide ample incentive to address the fouling issue.

If anticipated in design, the negative consequences of fouling may be offset by providing extra surface, increasing tube clearances, oversizing ducts, stacks and fans and/or including on-stream cleaning facilities. All of these features have their price. Should the fouling be unexpected, the ultimate impact would be reduced capacity, over-firing, reduced run length or (for auxiliary equipment) acceptance of underperformance with respect to heat recovery.

II. Mechanical considerations

In addition to performance loss, several special considerations are unique to combustion systems that affect the mechanical design, safety and integrity of the equipment.

Tube bundles for unfired exchangers are usually designed on an overall basis with respect to temperature, pressure (or differential pressure) and corrosion resistance. Fouling that would completely insulate one section of tube from the cold stream would seldom cause that tube to fail by exceeding its temperature limit. Thus, although the distribution of fouling resistance between hot and cold streams contributes to fixing the tube metal temperature, that fact is of little consequence; it is the overall fouling resistance that matters. Also, in many instances (unless

the streams are incompatible), failure of one or even several tubes can often be tolerated without resulting in shutdown of the unit.

This cannot be said for fired equipment, where tube material and thickness are selected to operate much closer to the metallurgical pressure and temperature limits. In fact, it is standard practice in the design of a furnace tube coil to evaluate the coil limits and life expectancy for both the elastic and creep rupture failure modes, since either might control the design.

Thus, the distribution of fouling resistance assumes a much greater significance in fired equipment because of its impact on tube coil integrity. Process side fouling directly increases the tube metal temperature by insulating the wall from the cold stream. And it might be thought that fireside fouling would protect the tubes by shielding them from the heat source. Given constant average flux or overall duty (the normal control mode for most fired equipment) and absolutely uniform fouling, tube metal temperature should theoretically be fouling independent. In reality, fireside fouling is far from uniform. Localized fouling would, indeed, insulate that section of the coil. But the resulting flux loss would need to be redistributed over the remainder of the surface, thus raising the average and peak wall temperatures elsewhere.

(c) Fouling sources and mechanisms

Sources and mechanisms of combustion side fouling may be categorized as follows:

I. Scaling/oxidation

The term "scaling" has an entirely different connotation in reference to combustion equipment than it does for unfired equipment. In combustion equipment, it refers specifically to the metal oxide scale that is formed by high temperature oxidation of the tube surface. It is a manifestation of corrosion fouling. As might be expected, it is usually a localized phenomenon, occurring at points of highest metal temperature. Depending upon the degree of cleanliness, such points may or may not coincide with points of highest heat flux. Vulnerable locations are at the tube hot face (point in most direct view of the flame) in a furnace radiant section, or at the upstream stagnation point in the shock tubes of a convection bank. Causes of overheating include general over-firing, poor flame patterns, process side fouling and inadequate process stream flow or flow regime. Since tube metal is lost in the process, scaling directly impacts the integrity and life of the tube coil, as well as affecting performance. The approximate relationship between scale thickness and metal loss is about 7:1.

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Tube scaling is an evolutionary process that might be described in successive stages. Initially, the oxide forms as a hard, brittle, dense layer, firmly attached to the tube. Although low in thermal conductivity, there is little or no bond resistance. As the scale thickens, thermal stresses cause it to separate from the tube and, at some point, it begins to fracture and "orange-peel." Exfoliation then occurs, exposing fresh metal for the process to start anew.

In some applications, development never progresses past the first stage. The intact scale may then protect the tube from further damage by lowering its temperature (locally) and by excluding flue gas oxygen from the surface. In the orange-peeling stage, the scale interferes with radiant heat transfer by partially shading the adjacent surface. Scale thickness may reach 6 mm (0.25 in.), although the shedding process more typically limits it to about half of that value.

In extended surface convection banks and economizers, the tips of the fins or studs will be at higher temperature than the tube wall and, depending on metallurgy, may actually burn off. This loss of surface serves to protect the tube from local overheating, but does so at the expense of performance loss

II. Fuel deposits

Fuel deposits may generally be classified as entrained or dissolved particulate matter, or as substances formed as a result of combustion. As might be expected, the type and source of fuel has a lot to do with the nature and extent of the foulants. And, as with non-combustion sources, the combined effect of multiple foulants is usually synergistic.

Gaseous fuels are normally the cleanest of the three types. If incinerated or off-gases are included in this category, particulates may be present that are essentially inert, at least while in the dry state. Examples of these are the alumina catalyst fines in the regenerator gas from a catalytic cracker and fines from cement kilns and glass plants. Dust that may be present in the combustion air would be similarly classified.

Particulates find their way to, and become attached to heat transfer surfaces by gravity, impingement, thermophoresis and random electrostatic attraction. At surface temperatures above the dew point, the deposits usually remain relatively loose and friable.

Fuel borne sulfur, usually in the form of hydrogen sulfide or mercaptans, is another major source of gas side fouling. These components burn to form sulfur dioxide, a portion of which further oxidizes to sulfur trioxide. These gases (most especially SO₃) are extremely water-soluble and, at surface temperatures below the dew point, condense to form their respective acids. If metal oxides are present as particulates, these

may be converted to acid salts. The liquid phase is quite sticky, and entraps other particulates into the fouling layer. Since the liquid is very corrosive, products of corrosion also become part of the fouling, and the corrosion may cause premature failure of the equipment.

At firebox temperatures, these gases are quite innocuous, reacting but very slowly with tube surfaces to form sulfate scale. As might be expected, dew point corrosion mainly occurs at the cold end of convection sections, economizers and air preheaters. Because of environmental regulation, emissions of sulfur from combustion sources in the United States and other developed nations have been significantly abated in the last 25 years. Sulfur removal may be accomplished either upstream or downstream from the heat transfer equipment. With gas fuels, it is easier to clean up the fuel than the resulting flue gas. For this reason, sulfur related fouling from gas fuel sources is no longer the concern that it once was. Natural gas from public utilities rarely has a problem with sulfur. Industrial by-product gas fuels are processed to limit sulfur to 10-15 ppm, normally operating well under that.

With the trend in fuel economics driving cold end approach temperatures to lower values, it is now common in residential and commercial heating plants for combustion products to leave below their dew point. Since carbon dioxide and water are present in all hydrocarbon fuel combustion products, this means that the liquid phase will contain carbonic acid. Although corrosive, it is nowhere close to sulfuric acid in that respect, and is no more sticky than water. Potential fouling problems due to carbonic acid corrosion in this type of equipment have been successfully avoided by material selection and the application of coatings.

Although rare in gas fired systems, given reducing conditions and cold surfaces, it is possible for soot formation to occur. Soot deposits on surfaces according to the particulate model, and may eventually form hard coke deposits. In radiant zones, the deposits are often locallized, resulting from poor flame patterns, while in convection banks, they are more general.

Liquid fuels typically are more fouling than fuel gas. However, there can be a wide range in expected fouling depending on the fuel source and treatment, and this statement cannot be made a priori. Residual oils generally contain both particulates and sulfur. Cations include aluminum, calcium, iron, magnesium, sodium and vanadium. Silica is also a major contaminant. Sulfur is present as hydrogen sulfide, metal sulfides and as any number of organosulfur compounds.

In the combustion process the metals are converted to their respective oxides, hydroxides, sulfites and sulfates, with the resulting distribution determined by equilibria and rate. Sodium and vanadium are particularly insidious because their oxides, and the

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resulting sodium vanadate, have especially low melting points above, which their fouling tendency dramatically increases

The sulfur salts of the metals tend to be acidic and hygroscopic, becoming sticky and corrosive as the flue gas temperature drops. In the cold end of convection sections, this can result in severe fouling and flow restriction, with deposits filling the fin or stud gaps and bridging the tube-to-tube clearances. In radiant sections, where the surface temperatures are higher, deliquescence is less of a problem.

Fuel oil quality can be greatly improved by a number of treatments (directly) or to its crude oil source. Desalting of the crude will significantly reduce both the solid content and the sulfur in the residual oil. Further improvement can be accomplished by replacing the residual oil with a distillate oil. Hydrotreated oils are essentially contaminate-free as is the residue from ethane cracking in petrochemical plants which, although very viscous, is pure hydrocarbon.

Regardless of purity, fuel oil flames are much more susceptible to soot formation than are gas flames. This is because incandescent carbon is a necessary intermediate in the combustion of fuel oil, while fuel gas combustion is predominately a vapor phase reaction throughout. Soot formation in a fuel oil system generally indicates inadequate air supply or poor fuel/air mixing.

The factors and mechanisms that apply to residual fuel oil firing also apply to an even greater degree to solid fuels.

III. Dew point corrosion

Fuel oil sulfur is a major fouling contributor not only with respect to formation of the above acid salts, but as a corrosive agent in its own right below the acid dew point. At flame temperatures, fuel sulfur compounds quickly burn to SO_2 Although both rate and equilibrium dependent, the shift to SO_3 largely takes place outside of the flame envelope since it is thermodynamically favored by lower temperatures. The reaction is catalyzed by a number of things including V_2O_5 and NO_x [57]. Low excess air, of course, minimizes the conversion. The general range of SO_2 to SO_3 conversion in furnaces and boilers is thought to be 1-5%, with 2% being a reasonable default value.

A small amount of SO_3 will substantially elevate the dew point of the flue gas. Values of 150-180 °C (300-350 °F) are quite typical with untreated fuels. The $SO_3(v)$ will partially associate with flue gas water to form $H_2SO_4(v)$. Both species are very water-soluble and independently exhibit their own equilibrium vapor pressure over an $H_2SO_4(l)$ solution condensed on a cold surface.

Prediction of the flue gas dew point thus hinges on two largely system dependent parameters: (1) the extent of conversion of SO_2 to SO_3 and (2) the degree of vapor phase association between SO_3 and H_2O . For estimation, the following correlation [58] is both easy to use and generally reliable:

$$1/(T+273) = 2.276 \times 10^{-3} - (29.43 \times 10^{-6})(\ln p(H_2O))$$
 $- (85.80 \times 10^{-6})(\ln p(SO_3))$
 $+ (6.200 \times 10^{-6})(\ln p(H_2O))(\ln p(SO_3))$
where:
$$T = \text{dew point, °C}$$

$$p(H_2O) = \text{partial pressure of water, mm Hg}$$

$$p(SO_3) = \text{partial pressure of SO}_3, \text{ mm Hg}$$

For ease of application, the partial pressure of sulfuric acid in the literature version is replaced by $p(SO_3)$, representing the total SO_3 converted from SO_2 . In fact, the two species coexist, with the actual composition probably favoring $H_2SO_4(v)$. In developing the above correlation, the authors used laboratory dew point measurements with the results tested against thermodynamic data [59]. Because of discontinuity with the steam tables, it should not be used below $p(SO_3) = 1 \times 10^{-6}$ mm Hg. Other dew point correlations are, of course, available.

The equilibrium $H_2SO_4(1)$ condensed liquid phase composition depends on the gas composition and the surface temperature. Acid concentrations in the range of 10-14% [59] are typical where sub-dew point conditions exist. As might be expected, this creates a very aggressive corrosive environment that impacts both fouling performance and service life.

IV. Refractory debris

Over time, furnace refractory linings break down by spalling, chemical attack and/or erosion. In convection banks, much of the resulting rubble and sand falls and lodges between the fins or studs of the extended surface tubes impairing both thermal and hydraulic performance.

In recent years, ceramic fiber, in either blanket or modular form, has become increasingly popular as a furnace lining. When fiber linings break down, the component fibers often become "plastered" against the upstream face of the extended surface tubes. This, in turn, becomes a filter for particulates. Ceramic fiber is particularly vulnerable to on-line erosion and to exposure to steam or water, usually during turnarounds. It is often following such occasions that loss of performance is observed. In this respect, modular construction is superior to blanket construction.

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I. Desalination (by D. I. Wilson)

Thermal desalination plants obtain potable water from seawater or brackish water by evaporation or multistaged flash distillation. Good energy efficiencies are obtained by using the product streams to preheat the feed water. The temperatures involved range from ambient to boiling; this range, coupled with the variety of species present in the feed, can give rise to different types of fouling in different sections of the plant. The technology used in thermal desalination has moved away from multi-effect evaporation to vapor recompression systems, and multi-stage flash (MSF) systems for large-scale applications. The latter do not feature evaporators, thereby avoiding the fouling problems encountered in multiple effect units, and are often combined with power generation systems for maximum energy efficiency. Nevertheless, Alahmad and Aleem [60] reported that 40% of the heat transfer area in typical MSF plants is added because of fouling, at approximately 10% of the capital cost.

Careful consideration must be given to materials of construction throughout the plant in order to avoid corrosion fouling. Materials selection for MSF units is discussed by Hodgkeiss [61]. Other types of fouling occur principally on the feed waterside in the preheaters and evaporators, and promote sub-deposit corrosion. Pre-treatment of the feed water, involving disinfection, particulate removal and chemical dosing is essential. If feed water pre-treatment is inadequate, the initial preheat exchangers will be subject to particulate fouling caused by deposition of silt, sand and biological matter. Marine and aquatic organisms will promote biofouling, particularly where heat transfer surface-temperatures lie in the range 10-40°C. Filtration is unlikely to remove all such organisms and their food, so consideration should be given to (1) using materials of construction which mitigate biofilm growth, and (2) incorporating equipment for regular application of biocides or cleaning chemicals. Copper alloys are used extensively owing to their resistance to chloride attack and inhibition of biofouling. Ritter et al. [62] compared the performance of a titanium exchanger and a 90/10 Cu/Ni unit at 27° C and flow velocities of 0.6 - 2.4 m/s. At high velocities, the Cu/Ni unit exhibited similar initial fouling rates to the titanium unit, but the deposit later spalled off as the organisms died. At lower velocities, the titanium exchanger exhibited fouling rates up to three times that of the Cu/Ni unit, owing to the formation of biofilms, which entrapped silt. Fouling resistances on the 90/10 Cu/Ni surface ranged from $1.76-3.52\times10^{-4}$ m²K/W. The fouling mitigation performance of the Cu/Ni surface was offset by its greater susceptibility to corrosion fouling.

All thermal desalination processes involve process conditions, which promote crystallization fouling from inverse solubility salts. Severe scaling problems are encountered in evaporators, brine heaters and preheat condensers. The scales consist of the carbonates and hydroxides of magnesium, calcium and barium (alkaline scales), and their sulfates (non-alkaline scales), particularly calcium sulfate [63]. The scale composition depends on the feed water composition, temperature and concentration of CO₂ in solution. Calcium carbonate (aragonite) is the principal scale component at temperatures up to 82°C, whereas magnesium hydroxide is the principal component at temperatures above 93°C. Fouling considerations thus place design limits on the bulk concentrations in desalination plant; Bakish [64] stated that MSF units should not exceed 70 000 ppm total dissolved solids at 122°C in order to avoid CaSO₄ hemihydrate formation. Horizontal tube units are rarely used, while plate heat exchangers are becoming more common [65].

Different mitigation methods are used for the different types of desalination process. The use of vacuum conditions is widespread, as it reduces process temperatures and thus the rate of fouling across the system. Seeding techniques are also used to reduce deposition on heat transfer surfaces; the 'seeds' are added to the bulk liquid and act as preferential nucleation sites for the scaling species. Seeding is most appropriate to systems featuring brine recirculation, as found in vapor recompression units, where the extended residence time of the water promotes growth on the seeds. Care must then be taken to remove large seeded particles in order to avoid corrosion or particulate

The use of anti-fouling chemicals is widespread [60, 66-68]. The choice of dopant is affected by the need to dose large quantities of water at reasonable cost and minimal environmental impact. Polyphosphate- and phosphonate-based formulations are effective at retarding the formation of hard alkaline scales at temperatures below 90°C. Flow velocities must be maintained above 1.5-1.8 m/s and careful control exercised in order to avoid the formation of calcium orthophosphate. Fouling resistances of $1.0-1.5\times10^{-4}$ m²K/W are typically observed before cleaning [60]. Dispersants are added to prevent sludge formation, which would otherwise have to be removed periodically by acid cleaning, or by installation of a sludge drum. Acid dosing, where carbonate species are converted to carbon dioxide and removed from solution, is practiced but requires careful management of pH (in the range 7.7 - 8.0) to avoid corrosion. Acid dosing is effective at higher temperatures than polyphosphate treatment, but has been replaced in many cases by polymer and polyelectrolyte-based formulations containing

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polyacrylic and polymethacrylic acids, or copolymers of maleic anhydride with styrene, vinyl acetate or hydrolyzed polyacrylamide. These high temperature additives promote the formation of non-adherent alkaline and non-alkaline scales, and avoid the corrosion problems associated with acid dosing. The selection of appropriate compounds for different modes of MSF operation is discussed by Alzahrani *et al.* [68]. The level of doping addition ranges from 3 ppm to 10 ppm, depending on the water quality and maximum operating temperature.

Fouling is an inherent feature of desalination units so cleaning must be considered at the design stage. The provision of standby units, or continuous cleaning (e.g. the Taprogge system) should be considered for those units, which foul most severely and require regular cleaning. Temperature upsets and thermal shock can cause the scale to fall off in sizeable pieces, which can accumulate in equipment, promoting corrosion. Similarly, where biocides are used, filters should be installed after exchangers in order to prevent spalled material causing blockages downstream.

J. Refrigerants

(by G. F. Hays)

Unless contaminated, commercially available refrigerants are not susceptible to fouling. Contamination may be caused by inleakage of process fluids or lubricants. Lubricants may enter the system due to seal failure. Process fluids may enter due to corrosion related failure. Absorption systems may be susceptible to fouling if the steam is contaminated.

K. Chilled media

(by G. F. Hays)

Chilled media are subject to contamination from the processes that they chill as well as the ingression of certain refrigerants such as ammonia. While most chilled systems are closed, with minimum makeup requirements, some are open or partially open. Examples of partially open systems are chilled water systems used in the tobacco and textile industries, most of which are associated with air washers. Another example is the winter "free cooling" operation of certain comfort refrigeration systems in colder areas, where the water from the open recirculating system is cold enough to be used directly in the chilled system, bypassing the refrigeration machine.

Makeup to chilled water systems generally are saturated with oxygen and may contain small amounts of microflora, which, in the presence of nutrients such as organic materials, rapidly reproduce to form biomass which, over time, foul the system. Deposition of

biomass and other materials in low velocity areas of such systems also result in under deposit corrosion.

Some chilled water systems are oxygen free and may be subject to fouling by anaerobic bacteria. Sulfate reducing bacteria are known to both foul such systems and to cause corrosion of metallic components of such systems.

Brines are used where chilled water temperatures below 0 °C are required. Brines are usually composed of calcium chloride solutions and are susceptible to the same types of fouling problems.

Treatment techniques: Generally chilled water systems are treated with non-oxidizing microbiocides to kill the bacteria and corrosion inhibitors such as sodium molybdate or nitrite-borate when there is relatively low proportion of makeup-water.

L. Waste heat and energy recovery

(by T. R. Bott)

Most industrial processes require energy to achieve the desired production. The efficient utilization of this energy is essential in order to maintain profitability and competitiveness. The opportunities to recover energy that might otherwise be lost to the environment, are generally appreciated, but one of the principal barriers to cost effective recovery is the problem of heat exchanger fouling. Unless the difficulties due to the likely fouling are recognized and adequate steps taken to cope with the problem, the cost of recovery may be greater than the value of the recovered energy!

In a general discussion it is difficult to give precise guidelines on how to approach a particular problem since each opportunity for energy recovery will be unique. Illustrations that on the face of it, are ideal energy recovery opportunities but have produced operating problems and other difficulties are perhaps the best way of emphasizing the need to examine carefully, the details of the process involved. The following examples may be helpful:

In a cracking process the flue gases left the catalyst furnace at a relatively high temperature. It was decided to utilize some of this waste heat to evaporate a low molecular weight organic liquid in a suitably designed shell and tube evaporator. After installation considerable operating problems due to fouling on the liquid side, were experienced, which necessitated frequent shut downs, with attendant loss of output. The fouling problem arose due to the high wall temperature, bought about by the high gas temperature, causing decomposition of the organic liquid and the accumulation of carbonaceous deposits. The use of the evaporator was finally abandoned due to the excessive costs of cleaning and maintenance.

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In a process for the production of laminated sheets, paper or fabric, is impregnated with resin dissolved in a suitable solvent. The wet impregnated sheet is dried in a continuous dryer through which hot air from steam heaters is passed. The solvent laden hot air from the dryer passes to water scrubbers for solvent recovery where the hot air is quenched. Recovery of the heat from the hot air would seem an ideal opportunity to save energy. Shell and tube heat exchangers were installed for this purpose to preheat the incoming air to the steam heaters. It was not long before the heat recovery units were not performing as required. The problem was traced to the accumulation of polymerized resins on the heat transfer surfaces. During the drying process small droplets of solvent containing resin were ejected from the impregnated sheet. As the droplets evaporated, soft resin particles were produced and carried forward to the heat exchangers, where they formed a tenacious deposit of polymerizing resin. The deposits were so difficult to remove that eventually the heat recovery system was by passed, and the hot air fed directly into the scrubbers.

A distillation column was used to recover the solvent from the dilute solution produced in the scrubbers discussed in the previous example. The bottoms from the column at about 100°C, essentially water, was discharged directly to the effluent treatment plant since it contained the resin particles produced in the dryer and removed from the air in the scrubber. Attempts were made to recover the heat contained in the bottoms, by preheating the feed to the distillation column. A plate heat exchanger was chosen for this purpose since the potential fouling problem was recognized and it was considered that a plate heat exchanger would facilitate cleaning. The fouling problem proved to be far worse than expected. The exchanger required cleaning every five days. Furthermore the sticky character of the resin tended to make disassembly difficult, with the need for frequent replacement of the gaskets. The cost of the cleaning operations and maintenance were far in excess of the cost of the energy saved. Needless to state the heat exchanger was finally abandoned.

In a particular food process meat is washed with large volumes of chilled city water at a temperature near freezing. After use the water containing meat particles, fat and microorganisms is passed straight to the factory effluent plant. Considerable energy is used to bring the city water temperature down to the required level. It is considered that if the effluent water could be used to cool the incoming city water in a suitable heat exchanger, substantial energy savings could be made. Regulations demand the use of potable water in any food process. In the proposed heat exchanger the presence of nutrients, oxygen and micro organisms in the water after the washing process, would most

certainly lead to the formation of biofilms, and although mitigation might be successful, the risk to hygiene from cross contamination in the heat exchanger, could not be taken. The idea of energy conservation by utilizing the cold in the wastewater, was not adopted.

The four examples presented above illustrate that however laudable a particular energy saving concept may be, it could be frustrated by an intractable fouling problem. In some of the examples considerable sums of money were wasted because the full fouling propensity was not recognized at the time the project was conceived. If an energy recovery system is considered, the ramifications of fouling must be one of the important aspects taken into account together with prevailing factors that have an influence on the deposit formation. The temperature of operation is a parameter that needs very careful scrutiny.

M. Recommended good practices

(by J. G. Knudsen)

Ultimately, the designer must decide how much additional surface must be included in the heat exchanger to account for the fouling that occurs during operation. Despite extensive research there has emerged no clear-cut correlation by which accurate fouling resistance may be predicted. The ultimate fouling that occurs in a heat exchanger is highly dependent on the operation of the equipment. Various conditions can contribute to excessive fouling over which the designer has no control.

In specifying the additional surface necessary to account for fouling, the following items should be considered:

- 1. Nature of the fluids and any past operating experience
- 2. Treatments available to mitigate fouling
- 3. Nature of any potential deposit
- 4. Possible geometries that will reduce the potential for deposition
- 5. Effects on operation of specifying more heat transfer surface than is needed

The result of specifying a fouling resistance in design is to provide excess surface over that required for the clean heat exchanger. Figure 16 shows the relation between fouling resistance and overall heat transfer coefficient for the clean exchanger for various percentages of excess surface. For example, 100% excess surface means that the heat exchanger has twice as much surface area as needed when it is clean. Therefore, modifications must be made in the operating

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conditions to achieve the heat duty for which the exchanger was designed.

With many cooling waters, for instance, an increase in velocity and reduction in surface temperature cause a reduction in the asymptotic fouling resistance. This behavior is shown schematically in Figure 17. Such a plot cannot yet be expressed quanitatively for any type of fouling, but Figure. 17 serves to illustrate the problem. Point A represents the design velocity and surface temperature and the corresponding fouling

asymptotic fouling resistance, which was used for one fluid assuming that the other fluid is non-fouling. At start-up, there is too much surface area in the exchanger for the required heat duty. Operating conditions must then be adjusted to point B corresponding to a 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 exist for this higher fouling resistance to develop.

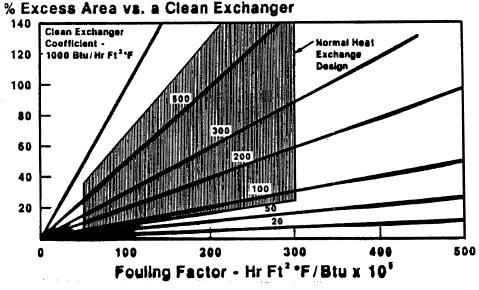


Figure 16 Percent Excess Area as a Function of the Overall Heat Transfer Coefficient and the Fouling Resistance

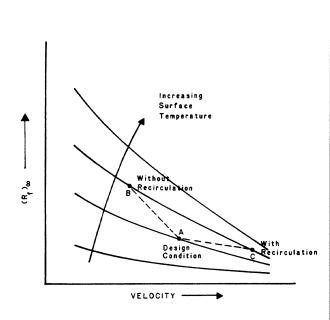


Figure 17 Effect of velocity and surface temperature on the asymptotic fouling resistance.

As fouling proceeds at constant heat duty, the velocity of the fluid must be increased and its outlet temperature decreased. If fouling proceeds beyond the design value of the fouling resistance, the velocity of the fouling fluid must continue to increase, resulting in a significant friction loss penalty.

It would be desirable if, during the initial operating period, the velocity could be maintained at a value equal to or greater than the design value. This can be accomplished by recirculation of the fouling fluid around the heat exchanger so that initial start-up conditions correspond to point C in Fig. 17. With recirculation the exchanger can be operated at or above the design velocity, with the result that the average bulk temperature of the fouling fluid is increased. At high recirculation rates there is a cost penalty for additional friction loss.

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

Good design practice requires that the fouling allowance be such that the exchanger is does not have too much excess area so that there are operational problems but sufficient to take care of the fouling

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characteristics of the fluids to be used. The shaded areain Figure 16 indicates the region of normal heat exchanger design. Using the fouling criterion only may result in abnormally excessive area. When the excess area is too great, the normal methods of balancing the process on start-up may actually cause fouling to occur. Throttling the cooling water flow thereby reducing the velocity and increasing the surface temperature often increases the fouling potential.

In the absence of fouling on the shell-side, it is recommended that the amount of excess area be capped at a maximum of 25 to 30 percent of that needed for the clean heat exchanger. In instances, in which cooling water or other process fluids may have significant fouling tendency, It is recommended that such fluids be placed on the tube side of shell and tube heat exchangers. Design velocity and a well-controlled treatment program should be maintained from the outset for cooling water

The designer should be familiar with the composition and fouling properties of each fluid to be processed in the heat exchanger. For process fluids, which are subject to crystallization, polymerization or chemical reaction, steps should be taken to maintain surface temperatures to avoid fouling of the heat transfer surface especially in the startup phase of a new or recently cleaned heat exchanger.

The mechanical configuration of heat exchangers must also be considered from the standpoint of potential fouling. Stagnant areas on the shell side are to be avoided as these are usually low velocity, high surface temperature locations where fouling is enhanced. Piping and pumping arrangements should avoid the possibility for bypassing and channeling of the heat exchanger fluids. This is particularly a concern with trains of heat exchangers either in series or parallel. Good accessibility for cleaning should be provided particularly if disassembly of the equipment is anticipated. Tube patterns should be such that ease of cleaning of the shell side of the tubes is possible. Backwashing is often a very satisfactory means of cleaning both the shell side and tube side of an exchanger. Provision should be made to accomplish this without undue requirement of time and modification of the facilities. Nitrogen- or air-bumping facilites, if considered effective, should be provided.

N. Fouling resulting from changing the service of a heat exchanger

(by T. R. Bott)

On occasions it is expedient to utilize a redundant heat exchanger for a different service than the one for which it was designed. In other situations, changes in the specifications of products or intermediates may require changes to the operating conditions under which a particular heat exchanger functions. Unless the effects of the changed variables are assessed in a meaningful manner, there may be significant and deleterious effects on the fouling propensity. The problem may be exasperated in heat exchanger networks, where changes are made to improve thermal efficiency by heat exchanger integration (pinch technology), without considering the wider implications for heat exchanger fouling.

Running through the discussion in this chapter, is the effect of the principal process variables, temperature and velocity, given that the quality of the process streams may not generally be changed. However, if the new fluid to be processed has very different physical properties to the fluid for which the exchanger was designed, fouling propensity could be quite different in the two cases! A critical review of the likely effect of changes to these variables is required. For instance, reducing velocity, i.e. passing a lower volumetric flow through the exchanger is likely to increase fouling if the fluid is being heated and is subject to chemical fouling, since the wall temperature will be higher. On the other hand reducing the velocity of a hot fluid being used to heat a heat sensitive liquid, will reduce the wall temperature. The effect is likely to be a reduction in the decomposition of the cold fluid, which might otherwise produce a fouling problem on the cold fluid side. Increasing velocity in these two examples as opposed to a velocity reduction is likely to have the opposite effect on deposit formation.

Where changed velocity is perceived to be a likely problem, adjustments to velocity may be made by say the use of a bypass or changing the pass arrangement in the existing shell and tube heat exchanger. If the new use of the exchanger involves a particulate laden fluid, dead spaces may assume a larger significance than in the original design, to the detriment of performance. The quality of the material of construction must be carefully assessed where the proposed change envisages the processing of aggressive fluids.

NOMENCLATURE

a factor in Equation (1), m²K/J factor in Equation (2), (m²K/J) (s/m)^{1.07}

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- b exponent in Equation (1)
- factor in Equation (1), ms⁴K/kg²
- C_i salt concentration, moles/litre (molality)
- C_{SiO2} concentration of silica, ppm
- C_{op} silica solubility, ppm
- E activation energy, J/kg
- m_i atomic weight of halide ions, kg/kmol
- gas constant, J/kgK
- R_f fouling resistance, m²K/W
- Re Reynolds number
- t time, s
- T temperature, °C
- T_f absolute temperature at surface of deposits, K
- U_b bulk velocity, m/s

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3.17.7

Type of heat exchanger and fouling potential

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A. Shell and Tube (by G. F. Hays)

(a) Tube-side Flow

Fluids on the tube-side of a shell and tube heat exchanger have well defined flow paths and uniform velocity, neglecting the end effects at the entrance and exit of the tubes. The tube-side is the easier side of the heat exchanger bundle to clean. Thus, fluids, which are more susceptible to fouling, should preferentially be placed on the tube-side. Traditionally, the fluid, which is at a substantially higher pressure, has been placed on the tube-side regardless of fouling considerations. This is particularly true for gas-liquid coolers, such as compressor intercoolers and aftercoolers. That practice minimizes the initial cost of a new heat exchanger, but may significantly increase the operating cost due to fouling. Compressor intercoolers and aftercoolers are prime examples of this cost differential. Thus, the total cost of ownership is significantly higher when the higher fouling fluid is on the shell-side.

Cooling water is particularly susceptible to fouling from sources, many of which the designer normally cannot predict. Foulant sources may include water chemistry, airborne contamination, process leaks, biomass and suspended matter. Once-through cooling waters are susceptible to macro fouling; such as zebra muscles and debris from the water source. Open recirculating cooling water is most susceptible to micro fouling. Thus, from a fouling standpoint, cooling water should be placed on the tube-side.

(b) Shell-side Flow

Average shell-side flow velocities are generally significantly lower than are those on the tube-side. Because of the ill-defined flow path on the shell-side, the actual velocities vary from stagnation, in areas adjacent to baffles, to a maximum in the path of minimal flow resistance. Shell-side fluids are particularly susceptible to fouling resulting from suspended matter, polymerization and crystallization. In addition, entrance effects, such as excessive localized heating or cooling may aggravate such fouling problems.

With the exception of fluids which are susceptible to polymerization and crystallization, those, which change phase in the heat exchanger, are generally more suitable for the shell-side. Shell-side deposits are much harder to remove, particularly on-line, than are tube-side deposits. Shell-side deposits tend to accumulate faster and be more disruptive to heat transfer than on the tube-side.

In cases where the process side fluid has a tendency to foul the heat exchanger when it is being cooled, then the use of a small closed cooling water loop would allow the cooling water to be safely placed on the shell-side of such a heat exchanger. The water in the closed loop would benefit from the use of additives to prevent fouling. The use of de-ionized water would also be useful. The closed loop would be cooled by the normal plant cooling water system via an intermediate heat exchanger.

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3.17.7-2 3.17 FOULING IN HEAT EXCHANGERS / 3.17.7 Types of Heat Exchanger and Fouling Potential

Vertical heat exchangers, which have cooling water or another highly fouling fluid on the shell-side, are subject to two types of fouling problems. Typically, the shell-side fluid enters at the bottom of the heat exchanger and exits at the top. Gravity tends to settle suspended solids, particularly those, which have agglomerated with heavier particles. Due to the physical construction of vertical heat exchangers, the shell-side inlet is not located exactly on the bottom of the heat exchanger, right against the tube sheet. There is, in fact, some volume below that connection which is stagnant. Any suspended solids, which settle out of the shell-side stream, will accumulate in that stagnant area. The area covered by those deposits is subject to under deposit corrosion. There is no easy way to remove such deposits without taking the heat exchanger out of service although, in some exchangers a suitably located blowdown connector can facilitate on-line cleaning.

If shell-side cooling water were required on vertical heat exchangers, then the use of a small closed cooling water loop would allow the cooling water to be safely placed on the shell-side of such a heat exchanger. The closed loop would be cooled from the normal plant cooling water system via an intermediate heat exchanger such as a plate and frame heat exchanger.

While process-side conditions may warrant the use of vertical heat exchangers, or having a highly fouling fluid on the shell-side, care should be taken to ensure that the fouling issues are appropriately addressed in the design.

B. Fouling in spiral heat exchangers

(by A. E. Jones)

(a) Introduction

Spiral heat exchangers (also known as spiral plate exchangers or SHEs) have earned a well-deserved place in industrial heat transfer technology. In this section, the fouling characteristics of spiral exchangers is discussed.

Spiral plate exchangers have several design features that are specifically related to their performance in fouling services. First, there is a single flow channel for the hot fluid and a single channel for the cold fluid. This means that SHEs avoid the risk of flow maldistribution or bypassing common to exchangers with multiple tubes or flow passages in parallel. Also, fouling or plugging of a channel tends to be self-limiting. If a deposit blocks a portion of the channel cross-sectional area, the velocity will increase in the remaining open area, and the higher shear stress will tend to remove the deposit or limit further growth. Secondly, adjacent plates are welded at the edges to form the flow channels. With wide plates and a narrow

plate spacing, access to the closed ends of the channels for cleaning is restricted. In many cases, spacer studs welded to the plates determine the channel width, or plate spacing. The presence of these studs increases the heat transfer rate by increasing the turbulence of the channel flow and by providing a fin effect. However, the studs further limit the accessibility of the channels. While the use of high-pressure water or steam for cleaning is common, the use of mechanical devices or brushes is usually not possible.

Spiral heat exchangers are also used widely in boiling and condensing services. In these applications, the process fluid usually flows in crossflow with respect to the heating or cooling medium. The crossflow channels are open at both ends, and are easily accessible for cleaning. However, the service fluid channels are welded closed, and cleaning of these channels must be done chemically.

(b) Types of Fouling

Fouling mechanisms in single-phase flow through SHEs are similar to those in shell and tube exchangers. However, fouling is usually not as severe as in shell and tube exchangers for similar applications. In addition to eliminating maldistribution as mentioned above, the single spiral flow channel induces a secondary velocity that increases the wall shear stress at a given mass flow rate. The spacer studs also generate additional turbulence. As a result, sedimentation of suspended solids usually is not a problem. In fact, a SHE is often the preferred solution for heating or cooling solid-liquid slurries. Even fibrous or stringy solids can be handled, if the spacer studs in the channel can be eliminated. Mean velocities of 2 ft/sec or greater will keep the solids in suspension [1].

The causes of crystallization or cooling water fouling in SHEs are the same as in tubular exchangers. However, the higher heat transfer coefficients at a given mass flow rate for a SHE will reduce the wall temperature and the higher turbulence will increase the wall shear stress. Both effects are beneficial in reducing the rate and extent of fouling relative to a tubular exchanger.

Corrosion can be a problem in SHEs as in any other type of heat transfer equipment. The blind channel adjacent to the welds, however, may be particularly susceptible to stress-corrosion cracking. This can be a particular problem in stainless steel exchangers where cooling water is chlorinated to prevent biofouling. Attempts have been made to combat corrosion problems by applying a phenolic coating to the heat transfer surfaces. However, coatings have had a mixed acceptance. In addition to the costs and associated increase in heat transfer resistance, it is difficult to

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guarantee the absence of pinholes. Anodic protection has also been employed [1].

Process-side fouling in vaporizers or condensers seldom is a problem, and when it does occur the fouling layer is usually easier to remove than in a shell and tube exchanger. Due to the short two-phase flow path, a SHE used as a thermosiphon reboiler will normally have a low pressure drop and an associated high circulation rate relative to a shell and tube reboiler. The resulting low concentration of dissolved solids will reduce their precipitation on the hot channel wall. Similarly, the short flow path in a spiral condenser makes a spray of recirculated condensate more effective for washing solids, polymers, etc. from the cold surface than if condensation were occurring inside tubes.

(c) Spiral heat exchanger applications in fouling services

Listed below are several examples where SHEs are used in fouling services in applications where shell and tube exchangers would be either completely unsuitable, or would result in much more expensive installations.

Spiral exchangers have had wide acceptance in the pulp and paper industry. In recent years, recovery of low-grade heat from paper mill effluent has become an economic necessity. Heat recovery applications are typically associated with large flow rates and large temperature crosses. Because the mill effluent contained solids, SHEs were the preferred solution [2].

From a fouling standpoint, SHEs are well suited for some refinery applications where solids handling is important. Examples are the feed/bottoms interchanger or main bottoms cooler in fluid catalytic cracking units, or desalter exchangers, which must handle bottom sediment, waxes or asphalt [3].

Spiral exchangers have been used successfully as crystallizer coolers. They can achieve the close temperature control required for homogeneous nucleation and crystal growth while avoiding fouling of the cooling surface.

(d) Conclusions

Spiral heat exchangers are the preferred type for heating or cooling slurries, particularly in cases with a large temperature cross. Even in non-slurry applications, provided that SHEs are properly designed for high velocities and low wall temperatures, they will typically perform better from the standpoint of fouling than well-designed shell and tube exchangers in the same service. One vendor suggests that fouling resistances for SHEs be specified in the range of 5×10^{-5} to 2×10^{-4} m² K/W (0.0003 to 0.001 hr ft² °F/Btu [4]. Thus, the user is cautioned against using

the same fouling resistance for SHEs as for shell and tube exchangers. For the SHEs to be effective, velocities must be high, and oversizing the exchanger to allow for nonexistent fouling defeats this condition. In fact, the resultant low velocities resulting from oversizing actually encourage fouling, and the user unfortunately may get the poor performance originally anticipated.

C. Compact heat exchangers

(by H. Müller-Steinhagen)

The widespread installation of compact heat exchangers has been hindered by the perception that the small passages are strongly affected by the formation of deposits. Obviously, compact heat exchangers are unsuitable for fluids containing large particulate material or debris. However, several investigations have demonstrated that the high shear forces, low wall superheat and homogeneous flow distribution typical for compact heat exchangers reduce the formation and adhesion of deposits on the heat transfer surfaces. The use of more corrosion resistant materials with smoother heat transfer surfaces further reduces the formation of deposits. Most compact heat exchangers have to be cleaned chemically. However, gasketed plate heat exchangers are easier to clean than shell and tube heat exchanges. Recommended methods for reducing fouling in compact heat exchangers include [5,6]:

- the use of self-cleaning strainers, biocides, scale inhibitors, etc.
- the use of self-cleaning filters
- chemical cleaning
- employing pulsating flows, reversal of flow direction, or temporary stoppage of cold fluid
- removing and baking the unit in an oven. Residues are removed by rinsing.

(a) Plate and Frame Heat Exchanger

I. Design Fouling Resistances

Plate and frame heat exchangers were originally developed for the dairy industry. However, their application in the chemical process industry is increasing rapidly, where they begin to replace tubular heat exchangers in several traditional applications. While there is much information about the governing equations for clean operation, information for fouling conditions is scarce. As shown by the following equation, the percent excess surface area increases with increasing clean heat transfer coefficient for a given heat duty.

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$$\frac{A_f}{A_c} = 1 + U_c R_f \tag{1}$$

This puts a heavy penalty on compact heat exchanger types such as plate and frame heat exchangers if, because of ignorance or because of caution, the TEMA fouling resistances for shell and tube heat exchangers are used. Typical clean overall heat transfer coefficients for plate and frame heat exchangers are about 3000 W/m²K, for shell and tube heat exchangers about 1000 W/m²K. A design fouling resistances of 0.3 m²K/kW corresponds to 30% over-design for a shell and tube heat exchanger and to 90% over-design for a plate and frame heat exchanger. Most manufacturers of plate and frame heat exchangers recommend that the excess surface should not exceed 25% of the heat transfer surface area calculated for the clean duty.

The fouling resistances listed in Table 1 have been recommended by Marriott [6] for plate and frame heat exchangers. Due to the non-uniformity of flow distribution and deposit formation, measured pressure drop increases are significantly higher than values predicted using an average deposit thickness calculated from the fouling resistance.

II. Effect of Process Parameters on Fouling

Cooper et al. [7] investigated cooling water fouling using an APV model R405 plate heat exchanger. The water was chemically treated before entering the heat exchangers. Some of the important results of this investigation are given in Figure 1.

The fouling resistance in the plate and frame heat exchanger is significantly lower than in the shell and tube heat exchanger, despite the typically lower flow velocities. If the flow velocity is increased, the fouling resistance decreases similarly as is found for shell and tube heat exchangers. This is also demonstrated in Figure 2 which shows the asymptotic fouling resistance as a function of the surface temperature halfway up the plates.

Novak [8] studied the fouling behaviour of Rhine River water near Mannheim (Germany), and of Öresund sea water in Sweden. For both waters, mainly biological fouling was observed. The fouling resistances increased almost linearly over the observed period of time. Table 2 summarises the measured effect of flow velocity.

For constant flow velocity, Novak [8] found that maximum fouling occurred at a surface temperature of about 35°C, due to the preferred living conditions of biological matter.

Bansal and Müller-Steinhagen [9-11] investigated pure crystallisation fouling from $CaSO_4$ in various plate heat exchangers. The rate of deposition increases with increasing wall temperature and bulk concentration and decreasing velocity. With increasing flow velocity, both the initial fouling rate as well as the absolute value of the fouling resistance decreases. Due to blockage of the outlet flow distribution area the increase in pressure drop may be significantly higher than the increase in thermal fouling resistance.

Chemical reaction fouling is strongly affected by the surface temperature which determines the reaction rate. Several fouling experiments have been performed with an α -Laval P01 plate and frame heat exchanger using 68% solids black liquor [12]. Each experiment lasted 24 hours and produced absolutely no fouling, whereas the parallel annular test section (with same flow velocity and surface temperature) fouled rapidly within only 90 minutes.

Table 1 Fouling resistances for plate and frame heat exchangers [6]

| Fluid | Fouling (m ² K/kW) | Resistance, |
|-----------------------------|-------------------------------|-------------|
| Water | | |
| demineralized or distilled | 0.009 | |
| soft | 0.017 | |
| hard | 0.043 | |
| treated cooling tower water | 0.034 | |
| coastal sea water | 0.043 | |
| ocean sea water | 0.026 | |
| river water | 0.043 | |
| engine jacket | 0.052 | |
| Lube oil | 0.017 - 0.043 | |
| Vegetable oil | 0.017 - 0.052 | |
| Organic solvents | 0.009 - 0.026 | |
| Steam | 0.009 | |
| General process fluids | 0.009 - 0.052 | |

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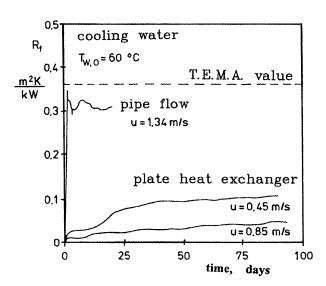


Figure 1 Comparison of fouling in plate and frame, and in shell and tube heat exchangers [7]

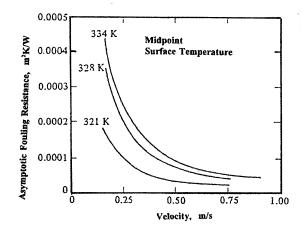


Figure 2 Fouling resistance in a plate and frame heat exchanger as a function of flow velocity and temperature [7]

III. Effect of plate design

Two low velocity zones exist in the plate channels, opposite to the inlet and outlet ports. In these areas shear forces are at a minimum and the wall temperature is close to the temperature of the heating medium. Both conditions promote the formation of deposits. The extent of the stagnant zones depends on the design of the flow

distribution section. It decreases with increasing flow velocity [13,14].

A sensitivity study on the various possibilities of providing excess heat transfer surface area for fouling is given in [14]. Figure 3 shows that minimum fouling occurs if the 20% excess surface area is provided by a two-pass arrangement of the original plates, followed by the use of larger plates with the same width, followed by larger plates with standard width/height ratio. The poorest performance is obtained when the excess surface is simply added as parallel plates.

The actual plate geometry (angle, amplitude and wave length of corrugations) affects the formation of deposits. Delplace et al. found that deposition from whey protein solutions on herringbone plates is only half of that of straight corrugations, for otherwise identical conditions [15].

Plate heat exchanger designs with extra-wide plate gap are available for applications with significant particulate content or severe fouling.

For all types of fouling, the delay time, before deposits appear, decreases with an increase in surface roughness. Heat exchanger plates usually have smoother surfaces than pipes, because of the manufacturing process itself and because the lower area requirement allows more expensive surface preparation. Electropolished plates with a surface roughness below $0.5~\mu m$ are commercially available, and are commonly used in food processing industries. Investigations with plate surfaces modified by Magnetron Sputtering, Physical Vapour Deposition and other technologies which can provide low surface energies are presently underway [16].

(b) Plate-Fin Heat Exchanger

Plate-fin heat exchangers are brazed/welded compact heat exchangers with a heat transfer surface density of about 10 times that of tubular heat exchangers. Typical applications are cryogenic, chemical/petrochemical and hydrocarbon off-shore installations. Molecular sieves and 100 µm filters are used in cryogenic installations to remove particulate matter or components that may freeze-out on the heat transfer surfaces. Systematic investigations have been performed on particulate fouling [17] and on river water fouling [18].

Table 2 Fouling Rates of Rhine River Water for a Surface Temperature of 25°C [8]

| Туре | v, m/s | p, Pa | dR _e /dt x10 ⁴ m ² K/kWh |
|------------------------|--------|-------|---|
| Plate heat exchanger | 0.13 | 6.7 | 7.4 |
| Plate heat exchanger | 0.19 | 14.5 | 4.3 |
| Plate heat exchanger | 0.77 | 190.0 | 0.6 |
| Spiral plate exchanger | 0.43 | 7.5 | 5.0 |

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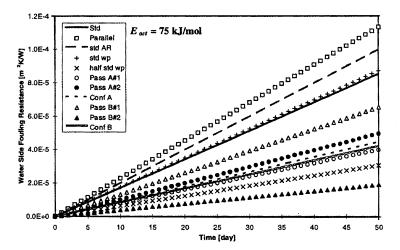


Figure 3 Effect of plate arrangement of fouling [14]

For 3 μm ferric oxide particles suspended in water, no blockage of plain fin or wavy fin channels was observed. Wavy fin channels fouled more than plain fin channels. All experiments showed asymptotic behaviour. Higher deposition rates were obtained for non isothermal conditions and at higher bulk temperatures. Maximum deposition occurred at a Reynolds number of about 1500.

Fibrous and biological material partially blocked the inlet of the aluminium plate-fin test sections when used with river water which was filtered through a 1 mm mesh. Some deposition was found at locations where corrosion of the aluminium had occurred. In the wavy fin test section, a thin, uniform deposit of fine mud was observed. Pressure drop for the plain finning increased linearly with time, whereas asymptotic behaviour was found for the wavy finning. The initial slope of the relative pressure drop vs, time curves was $5.8 \times 10^{-8} \text{ s}^{-1}$ for the plain fins and $1.71 \times 10^{-7} \text{ s}^{-1}$ for the wavy fins. For the latter, an initial deposition rate of 4.8×10^{-12} and an asymptotic fouling resistance of 6×10^{-6} m²K/W was measured.

(c) Printed Circuit Heat Exchanger

The passages in Printed Circuit Heat Exchangers (PCHEs) are typically between 0.3 mm and 1.5 mm deep. The specific design leads to volumetric heat transfer areas of 500-2,500 m²/m³, which is an order of magnitude higher than shell and tube heat exchangers. Two sets of experiments are described in [19] to compare the fouling related drop in performance of a PCHE and of a double pipe heat exchanger (DPHE):

1. Cooling water was used that was treated against corrosion, scale formation and biofouling, and with 0.5/1.0 mm strainers to reduce particulate fouling.

For operating times of 500-660 hours, no change in thermal effectiveness was observed for the PCHE, but the pressure drop increased by up to 55% due to the deposition of particulate material. The addition of a stainless steel mesh insert for the removal of fibrous material significantly reduced the increase in pressure drop. No deposition was observed in the parallel DPHE.

2. Cooling water was used that was treated against corrosion, biofouling and particulate fouling, but supersaturated to induce scaling. In tests of 100-290 hours duration, the thermal effectiveness again remained constant. The pressure drop increased by up to 30% due to the formation of calcium carbonate and calcium phosphate. Pressure drop and thermal effectiveness in the DPHE remained constant.

PCHEs have been used for gas cooling using sea water [20] in which 200 µm strainers have been installed upstream of the heat exchanger and chlorine was added to control biofouling. No operational problems have been reported. Another application involved the heating of tail gas in a nitric acid plant using condensing steam [21]. After 18 months of operation, no indication of channel blockage could be detected.

(d) Polymer Compact Heat Exchangers

Polymer heat exchangers are used for low pressure operations involving corrosive gases or liquids. The low surface energy and the smooth surface of their construction materials (polypropylene, fluoropolymer etc.) reduces the stickability of most deposits. Since clean heat transfer coefficients are already low (150-250 W/m²K), these heat exchangers react less sensitively to

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an additional fouling resistance than metallic heat exchangers.

D. Air cooled heat exchangers

(by T. R. Bott)

Air-cooled heat exchangers consist essentially of a bank of tubes over which the cooling air is made to pass. The design may rely on natural convection to achieve the required cooling, but in general, in order to improve heat transfer, the air is forced across the tube banks with a suitable fan. The air may be induced with the fan mounted down stream of the bundle but in the majority of designs the fan is usually located ahead of the bundle. Because of the relatively low heat transfer coefficient on the airside of the exchanger, it is necessary to employ an extended surface on the outside of the tubes, usually in the form of fins across which the air passes. The process fluid being cooled flows through the inside of the tubes. It will be appreciated that the pattern of airflow across the bundle is complex due to the presence of the fins, the bundle arrangement and the swirling flow pattern imparted to the air stream by the fan. Almost all air-cooled heat exchangers are located outside, in the open.

Air cooled heat exchangers are controlled, in general, by adjustment of the airflow, thereby increasing or reducing, the heat transfer as may be required by the desired outlet temperature of the process fluid. Variable pitch fan blades or suitably placed louvers, are often included in the design for control purposes. In temperate locations there may be considerable changes in air velocity between winter and summer operation, with consequent implications for fouling potential. Low velocities are likely to encourage deposition.

Fouling on the airside can usually be attributed to particulate deposition or corrosion (see Section 3.17.2). Leaks of process fluid can also be responsible for some fouling conditions. The presence of process liquid, on the outside of the exchanger may enhance an existing fouling problem by cementing particles of foulant to the extended surfaces, inducing corrosion, or the presence of the process fluid itself may act as a resistance to heat transfer.

The fouling potential for the outside of a tube bundle depends very much on the location of the heat exchanger i.e. the environment in which it exists, as it affects the quality of the air in the vicinity of the heat exchanger. For example engine coolers on agricultural machinery are likely to experience fouling from dusty conditions associated with soil, dry vegetative material and insects.

Fouling of an air-cooled heat exchanger may be due to the proximity of a dusty operation e.g. a grinding

plant, powder handling or the fall out of particulate matter from an incinerator. It has been reported [22] that fouling has even been due to the storage of insulating fiberglass below the fan of an air-cooled heat exchanger! Cleaning and building work in close proximity to the exchanger, may also give rise to fouling conditions. In process industry facilities these heat exchangers are generally located well above ground level to minimize problems from dust and debris accumulation.

Pollution of the air due to acid gases, possibly from combustion operations, may cause corrosion in the heat exchanger given that in rainy weather the heat transfer surfaces are likely to be wet. Aluminum finning on exchanger tubes is particularly vulnerable to corrosion. In some extreme examples, fins have been almost completely corroded away.

Bemrose [23] demonstrated that the accumulation of particulate matter in a finned tube bundle followed a consistent pattern. The deposit appears to be concentrated at the leading edge, and in the wake at the rear of the tube. The presence of these deposits complicates further, the airflow regime around the bundle. In many respects the finned tube bundle acts as a filter, and as might be expected, it is the first row of tubes facing the incoming air, that sustains the greatest degree of particulate fouling. Zhang et al [24] proposed the use of spoilers or dummy tubes ahead of the first row of tubes, as a means of reducing fouling on the active tubes of the exchanger.

Although the presence of deposits adversely affects the heat transfer efficiency, probably the greater operating penalty, is the restriction to airflow and the effect this has on the energy demand of the fan to maintain airflow. Based on comprehensive experimental work, it has been shown [25] that the energy requirement for an air-cooled heat exchanger fouled with particulate material, was doubled at the same time as the heat transfer was reduced by only 10-20%.

On line mitigation of fouling on the outside of air-cooled heat exchangers is virtually impossible to achieve in a practical way. Filtration of the incoming air for instance, would be economically unsound. The location of the air cooler, particularly in the light of the prevailing wind direction, is a primary consideration, but often the designer does not have the option to choose the location; much depends on the process site requirements. Where potentially corrosive environments are likely to be present, it may be prudent to consider the use of a corrosion resistant material of construction.

In general, operational efficiency of air cooled heat exchangers subject to particulate fouling, may be restored by water washing. Products of corrosion and tenacious deposits are likely to be more difficult, and may even be impossible to remove. Good housekeeping

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in respect of air-cooled heat exchangers is also necessary in order to reduce fouling potential. It is not uncommon to discover debris, e.g. planks of timber, rope and other rigger's equipment left on top of horizontally mounted air blown exchangers; such material affects the air flow distribution adversely affecting deposition.

E. Agitated vessels

(by T. R. Bott)

In some specialized industries such as food processing, fermentation, fine chemical manufacture or polymer production it is necessary to heat or cool chemicals in agitated tanks. Often the units are operated batchwise and often they are multifunctional depending on the prevailing spectrum of production. The physical properties of the vessel contents may undergo considerable change during the batch process. At the beginning of the process the liquid may have a low viscosity but at the completion of the batch process, the viscosity may have increased 100 fold.

Agitated vessels used, to transfer heat either into or out of the liquid may be fitted with a jacket on the outside. For heating, the jacket may be charged with steam or if higher temperatures are required some sort of organic heat transfer medium may be employed. Cooling water, as might be required by the process, can also be passed through the jacket. Additional heat transfer can be accomplished by the use of a submerged coil inside the vessel. In some instances where absolute cleanliness is required, such as in the pharmaceutical industry, the vessel is lined with an inert material, like glass. The glass lining serves to eliminate corrosion and to reduce the incidence of fouling. It has to be remembered however that the glass thickness represents "fouling" itself, since it will impose a resistance to heat flow.

Agitation of the liquid contents of the vessel is generally achieved by a rotating system of blades mounted on a central shaft, that may be classified according to the closeness of the blades to the inner surface of the vessel [26]. The whole assembly is generally referred to as the impeller. Non proximity impellers, such as propellers and turbines generate flow patterns in the fluid. In low viscosity liquids the fluid movement may be quite rapid and the impingement of the liquid on the vessel wall assists heat transfer and generally prevents the build up of deposits. For more viscous liquids proximity impellers such as anchor or helical ribbon types are employed. The principle is that the blades move close to the vessel wall, thereby disturbing the liquid at the wall, and at the same time reducing the propensity to foul. The anchor design is

considered superior [27]. Additionally, the vessel may be fitted with baffles to assist the mixing process.

Agitation may also be achieved by gas sparging but this is not a common practice and furthermore in fouling situations, the technique is unlikely to prevent or reduce, deposit accumulation.

In many of the processing operations in agitated vessels, endothermic chemical or biological reactions take place Unless the agitation is effective, the vessel wall temperature may reach unacceptably high values with a consequent risk of fouling. In polymer production for instance, high temperatures at the wall may encourage polymerization fouling on the heat transfer surface. The problem may be aggravated if the steam pressure in the jacket (or the heating coil for that matter) is controlled by the desired temperature in the bulk liquid. In some operations the quality of the product is governed by the time the contents of the vessel are at the high temperature. Inappropriate choice of either one or both these variables could lead to fouling problems.

The same arguments apply to the fouling of the in vessel coil. Unless a heated coil or tube array, is adequately swept with liquid, chemical reaction fouling is likely to be a problem where this is possible by the reactions involved.

As discussed elsewhere, the quality of the surface is important. The use of glass with its smooth surface, has already been mentioned. In some industries however the vulnerability of glass to mechanical shock may be regarded as an unacceptable risk. In food processing where any foulant released from the surface of a vessel or coil, may affect the quality of the product, it is usual to employ polished stainless steel equipment. Smooth surfaces are also recommended for hygienic design. It was shown qualitatively [27] the advantage of electropolished 213 stainless steel over "as received" material, for biofouling reduction. It has also been demonstrated quantitatively [28] that roughness assists fouling in bioprocessing.

In summary it may be concluded that in general, agitated vessels are used for processing "clean" liquids. The character of the vessel walls as a heat transfer surface, is an important factor since the foulant removal forces associated with liquid movement are limited. Where fouling resulting from chemical reactions, is possible careful control of the operating conditions (i.e. temperature) is necessary. The issue of control assumes even greater importance where polymer manufacture is involved, otherwise a polymerised fouling layer may be produced which can be extremely difficult to remove. It may be necessary to remove these deposits by painstaking hand methods, with all the attendant safety hazards. The complexity of the inside of an agitated vessel, including impeller, baffles, and possibly internal coils adds to the problem of cleaning.

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F. Evaporators

(by D. I. Wilson)

This section focuses on heat exchangers used to concentrate solutions or effect crystallization. Direct contact evaporators are discussed in section 3.17.7.K, and other vapour generation units are discussed in section 3.17.7.H. Evaporator fouling is a major problem because: (1) the increased thermal resistance of the deposit layer must be countered by using higher utility temperatures in order to maintain the temperature conditions required for evaporation, and (2) the deposit often traps process liquor at the evaporator surface leading to severe corrosion.

The heat source in an evaporator is commonly condensing steam. Boiler house steam has a low fouling tendency, but utility side fouling can arise where the steam is generated from process sources, such as another evaporator unit in a multiple effect system. These streams can contain process liquid, entrained as mist, which causes deposition on the condensing surface. Demisters are therefore usually installed in order to prevent liquid carryover.

Deposition on the process (liquid) side is usually more significant. Table 3 gives a summary of evaporation processes reported to be subject to severe fouling.

(a) Fouling Mechanisms

The conditions encountered in evaporators, namely increasing concentrations of solids and solute species, and temperatures near the boiling point, give rise to

- Crystallization fouling, caused by the concentrations of dissolved salts (including soluble species) exceeds their solubility limits. Where a number of inverse solubility salts are present, it is quite common for the dominant species involved in scaling to differ between units in a multiple-effect system, due to the variation in solubilities with temperature [29,33].
- Chemical reaction fouling caused by the increased concentration of reactive species, at high temperatures, giving increased rates of generation of fouling precursors. Reactions involving dissolved gases, such as oxygen in gum formation [34], are sensitive to temperature and pressure as these determine the solubility of the gaseous species in the liquid.
- Particulate fouling caused by the increased concentration of solids in the system. The solids may be the products of crystallization or chemical reaction in the bulk liquid.
- Combinations of the above, and corrosion fouling promoted by deposition.

Fouling considerations frequently impose limits on the solids or solute concentrations in an evaporator. Rapid fouling occurs above these threshold values, resulting in uneconomically short operating periods between cleaning operations [30,33].

 Table 3
 Cases of Evaporator Fouling

| Application | Fouling mechanism(s) | Species involved | Ref. |
|---|---------------------------------------|---|---------|
| Sugar (concentration of thin juice) | Primarily crystallization | Alkaline scales; silicates; hardness salts introduced by color removal processes | [29] |
| Pulp and paper (concentration of black liquor in alkali Kraft process) | Chemical reaction/ crystallization | Insoluble - fibers, sand, flaked scale; Moderately soluble - CaCO ₃ , silica, aluminum silicates; Soluble - 2Na ₂ SO ₄ - Na ₂ CO ₃ (burkeite) | [30] |
| Aluminum refinery (Bayer process) | Crystallization | Desilication product scale (DSP - Na ₂ O.Al ₂ O ₃ .2SiO ₂) | [31] |
| Desalination (vapour recompression and multi-effect units: not multi-staged flash units) | Crystallization | Alkaline and calcium sulfate scales | [33] |
| Hydrocarbons | Chemical reaction | e.g. auto-oxidation gums in kerosene vaporizers | [34] |
| Food(milk concentration) (fruit juice concentration) | Chemical reaction and crystallization | Proteins and calcium phosphate | [35,40] |



Table 3 shows that crystallization and chemical reaction fouling were identified as the major types of fouling involved in these systems. Several studies [30,34] have reported that the fouling rate was much more sensitive to temperature than flow velocity over the range of conditions studied. The solubility of dissolved species (solutes and gases) and reaction rates are both strongly dependent on absolute temperature; furthermore, the temperature difference at the heat transfer surface ($\Delta T_{Sb} \equiv T_{Surf} - T_{bulk}$) determines the mode of heat transfer and the fouling mechanism. At low values of ΔT_{Sb} , where heat transfer is governed by natural or forced convection, the fouling mechanism is similar to that involved in sensible heat transfer.

Significantly larger fouling rates are observed when ΔT_{sh} is high enough to promote nucleate boiling, where heat transfer is augmented or dominated by bubble formation at nucleation sites. Increased deposition occurs around these nucleation sites, in the form of rings, footprints and other patterns. This effect has been attributed to enhanced supersaturation in the microlaver under growing bubbles [37,38] and precipitation at the solid-liquid-vapour interface [39, 40]. The initial growth of deposit may cause an initial rise in the number of nucleation sites, but continued deposition has been shown to drastically alter the character of the heat transfer surface, reducing the number of such sites and thus the rate of heat transfer [37]. Porous deposits can give rise to 'wick boiling' from fissures in the fouling layer. Deposits formed under nucleate boiling conditions are also harder to

Reducing the extent of, or avoiding, nucleate boiling can therefore mitigate fouling. This can be achieved by operating at lower heat fluxes (i.e. increasing the area of the exchanger and using a lower temperature utility), or by using either enhanced surfaces or exchanger designs (e.g. plate heat exchangers) which increase the rate of heat transfer at low ΔT_{SD} . Nucleate boiling cannot be avoided in many applications, particularly where the fluid contains particulates, which reduce the value of ΔT_{S} for the onset of nucleate boiling.

Induction periods are often observed in new units, whereby no fouling occurs until the heat transfer surface is conditioned to support deposit growth. Induction periods frequently decay to zero after prolonged service. A wide range of fouling resistances and rates may be encountered in evaporator units. Fouling resistances for spent alkaline pulping liquors have been reported in the range 7-14 \times 10⁻⁴ m²K/W [41], while typical fouling resistances for desalination plants range from 7.6 to 15 \times 10⁻⁵ m²K/W [42]. Wilson *et al.* [42] reported linear fouling rates ranging from 5 to 45 \times 10⁻¹² m²K/J, and observed fouling

resistances up to 1.5×10^{-3} m²K/W, in sugar solution evaporators. McCabe and Robinson [43] observed that scaling in evaporators operating at low velocity and constant ΔT_{wb} ($\equiv T_{wall} - T_{bulk}$) exhibited the following behavior of the fouling resistance with time, $R_f(t)$

$$\left(R_f(t) + \frac{1}{U(0)}\right)^2 = \left(\frac{1}{U(t)}\right)^2 = at \tag{2}$$

Branch and Müller-Steinhagen [30] showed that equation (2) was consistent with a chemical reaction/crystallization fouling mechanism where velocity effects are not important. The constant a will thus be determined by the evaporator operating conditions and water quality. Epstein [44] derived expressions for the optimal running period for a single evaporator subject to fouling given by a more generalized form of equation (2). Müller-Steinhagen [30] has reported studies of fouling mechanisms, combined with process plant simulation, to optimize the performance of systems of evaporators [33].

(b) Process Modification

Mitigation of evaporator fouling by process design or selection of appropriate operating conditions requires information about the deposition mechanism, particularly the type of fouling involved and identification of the precursors (Sections 3.17.2,3). This is particularly important where chemical antifoulants are to be used, as selection of the wrong dopant can be expensive and even deleterious [30,46]. Chemical treatment is widespread (see Section 3.17.8.A (b)) outside the food industry. Another form of 'chemical' treatment is to add particles (e.g. calcium carbonate) to the bulk liquid, these 'seeds' act as preferential nucleation centers and reduce the amount of deposition on the heat transfer surface [33,47,48]. Equipment for removing the particles must also be installed in order to prevent them causing blockage. corrosion or fouling downstream.

Vacuum evaporation can be used to mitigate fouling where the fouling is sensitive to high temperatures, e.g. chemical reaction fouling in food streams, and scaling caused by inverse solubility salts. Temperature reduction is not appropriate where scaling is caused by a mixture of normal and inverse solubility species, such as with Kraft process black liquor. Selection of the configuration in multiple-effect systems involves similar considerations, but must also include the effect of concentration on viscosity (and heat transfer coefficient) and boiling point elevation. Sugar systems commonly use forward feed, while pulp and paper liquor systems use backward feed. Müller-Steinhagen

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intermediate black liquor with the feed to reduce froth formation and fouling.

Flash evaporation designs have been used to reduce fouling caused by boiling and bubble generation. The process liquid is heated under increased pressure, suppressing boiling, and the solvent flashed off as it enters the vapour/liquid separator. Recirculation of the liquid around the system increases the velocity through the exchanger, improving the rate of sensible heat transfer and in some cases reducing the fouling rate. Multi-staged flash units are used extensively in desalination [33].

(c) Selection of evaporator type

Rising forced convection and falling film units are the most common configurations used under fouling conditions: falling film units are often used for severe fouling conditions and are the standard evaporator in dairy applications [35]. Horizontal tube units are difficult to clean so are rarely used. Film evaporators usually employ relatively low values of ΔT_{SD} , but rising film units often feature a nucleate boiling region near the bottom of the tube to generate a sufficiently high vapour flow upwards and a low liquid residence time in the tube. The flow rate upwards can also be increased by forced convection. Falling film units have low liquid residence times but care must be taken to avoid poor flow distribution, as this can cause severe local fouling and dryout. Evaporator configurations tailored for fouling conditions include (1) basket evaporators. featuring an easily removable tube bundle for ease of cleaning and (2) agitation [47]. Plate heat exchangers are now available in falling, rising and flash evaporation configurations. These units are suitable for solutions and suspensions with particle sizes less than \sim 500 µm and have been reported to show superior fouling performance [30]. The selection of evaporator designs for pulp and paper liquors was reviewed by McCann [49].

Enhanced heat transfer surfaces can help to achieve reasonable heat fluxes and reduce the need for nucleate boiling. Bergles and Somerscales [50] reviewed the use of such surfaces for single phase liquid, pool boiling and flow boiling applications. They concluded that although fouling does have a significant effect on the performance of enhanced surfaces, fouled enhanced tubes were still superior to fouled plain tubes. Bandelier, et al. [51] found that fluted tubes gave both enhanced heat transfer and satisfactory fouling performance in a sugar refinery, and reported that the installation cost was recouped after 8000 hours of operation. The use of surface modification to prevent or reduce the adhesion of deposit has not been demonstrated for large scale applications, either because

of durability issues (e.g. Teflon wear [30]) or scale up of the technology (e.g. ion beam implantation [52]). Furthermore, both enhanced surfaces and surface modification techniques must be compatible with the type of deposit formed and the cleaning methods likely to be used.

Cleaning of evaporators is discussed in Section 3.17.7.B. Kraft process black liquor is unusual in that the principal fouling species at high solids concentration is burkeite, a normal solubility salt. The feed liquor can therefore be used to clean the final evaporators, which have been fouled by burkeite. This is achieved in practice by installing duplicate units and switching the flows on a regular basis.

G. Furnaces and air preheaters: fouling locations

(by E. R. Miller)

As might be expected, each zone of a combustion system is likely to be more susceptible to certain types of gas side fouling than others. The following outline indicates the fouling processes most apt to be found in a given location.

(a) Radiant Sections

I. Scaling

Tube oxidation occurs primarily at the hot face of the tubes nearest the flame envelope and where tubes may be subjected to direct flame impingement. A secondary location is elsewhere in the firebox where secondary combustion might be taking place because of the presence of unburned fuel and intrusion of tramp air.

II. Particulate fouling

Deposition of particulates from the flue gas can take place almost anywhere in the radiant zone. This is especially true of fuel derived substances that are near their fusion point yet cool enough to not have dissociated. It is not unusual to find particulate fouling concentrated in the cold end of the firebox and on the backside of single-fired tubes where the velocity and/or turbulence may be lower. This is particularly insidious because it further reduces the heat flux in areas where that parameter is already the lowest.

Although soot is generally classified as particulate fouling, one special sub-case deserves recognition. If a luminous reducing flame strikes a cold tube, carbon may plate out directly on the surface. This would be found in close proximity to the burners and is normally the result of a defective burner.



III. Corrosion Fouling

Depending on composition and flue gas temperature, acid salt particulates may begin to be found at the radiant section outlet, especially where there is a sharp temperature gradient from burner end to outlet. Such deposits foul both as particulates and as corrosives.

(b) Convective sections and heat recovery units

I. Scaling

Because of their dual role as both radiant and convective tubes, shock tubes at the convection section entrance are most susceptible to high temperature oxidation. In fire side units, the most severe location in the tube is the upstream stagnation point. With the heat flux enhancement, the first extended surface rows are also vulnerable. Depending on conditions and construction materials, either the tube or the extended surface may burn preferentially.

II. Particulate Fouling

Given the high collision probability between particulate and surface, this mechanism is a major fouling contributor in any furnace or boiler convection section with an appreciable flue gas particulate loading. As might be expected for shell side flow, deposit patterns are circumferentially non-uniform and highly dependent on velocity and turbulence associated with the tube layout in question.

Extended surface is particularly prone to fouling. In dirty systems, the space between fins or studs may fill with deposits, defeating the very purpose of the extended surface. And the deposits may eventually cake and continue to build until they bridge the gap between adjacent tubes.

Flow disparity across a tube bank due to poor baffling, plenum and/or breaching design invites particulate fouling. Low flow regions, which undercontribute to their share of the heat load in the clean condition, become even worse when fouled, without the self limiting effect of adequate velocity.

Low melting point deposits may accumulate where the flue gas temperature exceeds the fusion point. Because they are sticky, they will entrap other particulates.

Shell side heat recovery units generally foul in a manner similar to convection sections. With in-tube units, deposits are more uniform, but may show the effect of non-uniform velocity distribution.

III. Corrosion Fouling

Acid salt particulates may foul convective surfaces at any point in the bank. Since these salts tend to be

deliquescent, they are apt to be more corrosive toward the cold end.

Dew point corrosion is likewise a cold end problem. It is totally independent of acid salt particulate fouling but, given both environments, the effect on corrosivity is synergistic.

(c) Air Preheaters

I. Particulate Fouling and Corrosion Fouling

In dirty flue gas systems, both types of fouling might be anticipated throughout the air preheater be it regenerative or recuperative. With sulfur bearing fuels, the potential for dew point corrosion fouling must be anticipated at the cold end of the preheater, and the unit designed and operated so as to avoid it.

Regenerative preheaters are unique in that the air and flue-gas share the same surface for alternate parts of the cycle so that each flow path experiences flow reversal.

H. Boilers

(a) Industrial Boilers

(by K. W. Herman)

Industrial boilers operate over a wide range of pressures and temperatures. For boilers that include superheat, turbine drives or process restriction on steam purity, the suggested water chemistry limits are shown in Table 7 of Section 3.17.6. For units with out these restrictions and operating below 30.7 bar pressure, the suggested water chemistry is issued by the American Society of Mechanical Engineers in 1944 are shown in Table 4.

In the preboiler section no phase change takes place, and fouling and corrosion must be avoided through the various process shown in Table 8 in section 3.17.6. Orthophosphates should be avoided in the preboiler, since they could form calcium phosphate, which is slightly insoluble.

In the boiler itself, deposits on the water side of the tubes can reduce the rate of heat transfer, cause high metal temperatures, and frequently can rupture the tubes.

I. Treatment Techniques

Three treatment techniques used to prevent fouling on the tube side of boilers are phosphate, chelate, and all organic treatments [53].

(i) Phosphate treatment.

Calcium ions are precipitated by adding phosphate and alkali to the water. Magnesium ions are precipitated by

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Table 4 Suggested Water Quality In Modern Water Tube Boilers With No Superheater, Turbine Drives or Process Restriction On Steam

| Drum Pressure, bar | 0 - 20.4 | 20.5 – 30.6 |
|---------------------------------|----------|-------------|
| Feedwater | | |
| Dissolved O ₂ (mg/l) | <0.007 | <0.007 |
| Total iron (mg/l as Fe) | 0.1 | 0.05 |
| Total Copper | 0.05 | 0.025 |
| (mg/l as Cu) | | |
| Total Hardness (mg/l*) | 0.5 | 0.3 |
| рН @, 25 °С | 8.3-10.5 | 8.3-10.5 |
| Boiler Water | | |
| Silica (mg/)l | 150 | 90 |
| Total. Alkalinity (mg/l*) | <1000 | <850 |
| Free OH Alkalinity (mg/l*) | NS | NS |
| Specific Conductivity | < 7000 | <5000 |
| (μSiemens/cm 25°C) | | |
| Unneutralized | | |

as CaCO₃

NS = Not Specified

alkali and silicates. The precipitates formed are sludges of calcium hydroxyapatite $[3Ca_3(PO_4)_2\,Ca(OH)_2]$ and serpentine $[2MgSiO_3\,Mg(OH)_2\,H_2O]$. These sludges settle into a mud drum and are removed periodically. Sludge conditioners containing polymers, organics, sequesterants, and iron sequesterant-dispersant are used to retard deposition by conditioning the boiler sludges so that they are less adherent to the tube walls. Antifoam agents are also frequently used to minimize potential boiler water carry over into the steam.

(ii) Chelate treatment.

Chelation is a scale prevention treatment by which soluble, heat-stable complexes are formed. The most common chelating agents are ethylenediamine tetraacetic acid (EDTA) and trisodium salt of nitrite triacetic acid (NTA). The chelant concentration must be well controlled, as an excess can cause corrosion And a deficiency can cause scaling. Oxygen must be completely removed from the system.

(iii) Organic treatment.

Certain synthetic polymers serve as effective deposit control agents. The side groups of these polymers generally carry a negative charge and attach themselves to an active site in a growing crystalline scale. The presence of the large electronically charged polymer molecule distorts the growing crystal, disrupts bonding and creates internal stresses that causes the structure to break apart. The net result is an aborted scale fragment that remains dispersed in the boiler water. Each polymer chain contains many functional groups and

thus does not require precise ratios of product to impurity such as phosphate and chelants that must be fed stoichiometrically. The effectiveness of a polymer is characterized by its molecular weight, functionality and concentration. In order to improve effectiveness blends of various polymers have been formulated in recent years.

I. Control of iron oxide

Iron oxide is particularly troublesome in many boilers. It acts as a binder for boiler sludges, which in turn is deposited on the tube wall. The source of iron is corrosion in other parts of the system. This problem can be mitigated by inhibiting the corrosion at its source, removing the iron oxide by filtration, and treating the iron oxide to minimize deposition. [54]. Use of an iron dispersant along with other organic compounds has found effective in controlling iron oxide deposits.

II. Corrosion control

Corrosion in the feed water system and boiler is promoted by the presence of dissolved oxygen. Oxygen is effectively removed by deaeration followed by the addition of a chemical oxygen scavenger. Sodium sulfite, hydrazine and methyl ethyl ketoxime are three common oxygen scavengers. Proprietary formulations of these chemicals are available and some contain a catalyst.

Corrosion in the after boiler system is normally caused by oxygen or the formation of carbon dioxide that is released in the boiler from the breakdown of

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3.17 FOULING IN HEAT EXCHANGERS / 3.17.7 Types of Heat Exchanger and Fouling Potential

carbonate or bicarbonate alkalinity in the boiler feed water. When the steam condenses, carbonic acid is formed which causes low pH corrosion. These causes can be mitigated by removing these impurities at the source or treating the system with either a volatile neutralizing amine of a film forming amine. Morpholine and cyclohexylamine are the most common used neutralizing amines: others include diethylaminoethanol, methylpropanol methoxypropylamine. Filming amines are high molecular weight amines or amine salts which contain straight carbon chains of 10 to 18 atoms, such as octadecylamine, hexadecylamine and dioctadecylamine.

(b) Fouling in reboilers

(by J. W. Palen)

3.17.7-14

I. Introduction

Fouling in reboilers may be the second most misunderstood topic (after fouling in condensers) in the discipline. Most reboilers are designed with a significant fouling factor that may be necessary, but more often is either a known safety factor or a factor that originally emanated out of a poor performance caused by a bad design or by an upset operation. Because the heat transfer coefficients, except for wide boiling mixtures, tend to be very high in reboilers, even what seems like a moderate fouling resistance, such as 0.00018 m²K/W can cause a significant amount of excess area. Therefore, economically it is very important to give serious thought to whether a highspecified fouling resistance actually is needed or can be reduced. In addition to the economics incentive, good operation also requires careful selection of an appropriate fouling resistance and careful consideration of how the unit will operate on startup, when clean. Unfortunately there are not many reliable guidelines published. The best an engineer can do presently is to review past history of similar units in the company and try to assess whether fouling has been a problem or not. Basically the situation usually boils down to one of two cases: 1) fouling has not been a reported problem with these reboilers, but we have always used these fouling resistances for design, or 2) these reboilers have had severe fouling problems, must be cleaned frequently and represent a limitation to performance in this section of the plant. In case 1) perhaps all that is needed is a lower fouling resistance. In case 2) the design should be inspected and probably a different type of reboiler or different operating conditions, should be used.

These following Sections will offer no data for determination of reboiler fouling factors, but will discuss and hopefully clarify some of the concepts leading to more thoughtful specification of reboiler fouling factors.

II. Types of reboiler fouling

Basically reboilers are subject to all the same types of fouling as single-phase exchangers plus some additional; the most prevalent types in real fouling situations are:

- Polymerization (temperature sensitive)
- Coking (wall temperature sensitive)
- Sedimentation (velocity sensitive)
- Dryout deposition (vapor fraction sensitive)

While it is a useful exercise for model building to consider the various types separately, usually more than one type of fouling is taking place at once, and such models would have to be extremely complex to be able to predict the true situation. At present, sufficient data to test such a model are not available. Even with a good data based model, the reliability is likely to be erratic because it is virtually impossible to cover all possible combinations of possible mechanisms in a general way. Therefore, presently it is necessary to back off from predictive fouling models, take a "broader brush" approach, and review what measures can be applied in general to minimize all types of fouling.

III. Methods of mitigation

Whether fouling in reboilers or any other type of heat exchangers, the most important factors, which, if controlled, will significantly affect fouling rates, are the following

(i) Wall temperature.

Most types of fouling are to some extent sensitive to surface temperature. For reboilers, of course, the surface temperature is always higher than the bulk temperature. This tends to promote fouling from any substances that deposit due to chemical change such as polymeric substances. Since chemical reaction rates follow the Arrhenius exponential function of temperature, deposition of this type of fouling is extremely sensitive to surface temperature. Therefore, an effective mitigation method is to use the lowest practical surface temperature. Of course, this provides a difficult economic analysis problem because the heat transfer rate tends also to increase as an exponential function of the wall temperature. The trend in fouling research now is to attempt to determine threshold wall temperatures as a function of velocity, at which fouling is negligible. Presently few data of this type exist, and those that do are mostly proprietary, so determination of the economic balance normally is not possible. Even if

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it were, however, often the heating medium temperature is set by the process and cannot be changed. The exception is when the heating medium is steam that can be throttled to provide a lower saturation temperature. When the heating medium temperature is set the reboiler wall temperature can still be decreased, however, by increasing the boiling fluid velocity, as discussed next.

(ii) Velocity.

High flow velocity is probably the most effective practical means of fouling mitigation. This is because it affects both fouling removal through the wall shear effect, and fouling deposition through lowering the wall temperature, as mentioned above. Wall shear is most effective on soft deposits, which can be virtually eliminated by high enough velocity. Some deposits, e.g. coke deposits, are too hard to be affected by velocity. Wall temperature is decreased when higher velocity increases the boiling heat transfer coefficient. Theoretically, the wall temperature approaches the bulk temperature as the boiling heat transfer coefficient approaches infinity. Therefore, even when the heating medium temperature is fixed, increasing boiling fluid flow velocity can still lower the wall temperature. Practically, however, the velocity is limited by pressure drop, which can be quite high per unit of velocity for a vaporizing fluid. Designing the reboiler for as high as possible uniform flow velocity is a most important challenge in providing maximum fouling mitigation.

(iii) Vapor fraction.

The shear force at the solid interface at a given liquid flow rate increases as the fraction vapor increases, and according to the above discussion, this should help mitigate fouling. However, the vapor fraction must be limited since high vapor fraction promotes two tendencies that increase fouling. Higher vapor fraction causes a higher concentration of nonvolatile and potentially fouling components in the liquid phase. Also, vapor fractions above about 0.5 can easily cause local areas where the vapor is in direct contact with the surface (dry spots). Dry spots cause particularly bad fouling problems in reboilers if fouling components are present. This is because as the wall becomes dry the local boiling side heat transfer coefficient becomes very low and the wall temperature approaches the heating medium temperature. Dry spots tend to be intermittent, and when liquid periodically contacts the hot dry surface reaction rate fouling is greatly accelerated through the exponential temperature effect mentioned above. Therefore, with potentially fouling fluids, not only should the velocity be as high as possible but the vapor fraction should be kept low; a

good rule of thumb for hydrocarbons is 20 weight percent or less. This requires a well designed thermosiphon reboiler with good circulation or in critical cases it may require a tube-side boiling forced circulation reboiler.

(iv) Fluid composition.

The singly most important factor affecting fouling, yet the one least possible to control, is the concentration of potential fouling components in the boiling fluid. Some fluids simply do not foul at normal process temperatures; for example aliphatic or aromatic light hydrocarbons, especially C_1 - C_8 . If such fluids foul when boiled at normal processing temperatures it can only be due to heavy impurities, and usually fouling factors specified for the design only function as "safety" factors (which can be self defeating, as covered in a later section).

On the other hand, olefins can readily foul, since they are created to polymerize. So fouling tendency of light hydrocarbon streams can be related to their olefin concentration. Some heavier streams, the extreme cases of which are crude oil heavy cuts, contain very large potentially unstable molecules. A good example is the asphaltenes (see Section 3.17.6.A). These polycyclic molecules remain in solution in the presence of aromatics but in the presence of aliphatics flocculate into suspended particles that decompose on the hot surface. Fouling enhancers of this type are called precursors and need be present in only trace amounts to cause eventual heavy fouling buildup. Other possible precursors are sulfur-organic compounds, metal-organic compounds and immiscible aqueous phases, which accelerate corrosion.

Of course, the best way to mitigate fouling is to remove or neutralize all fouling components. For cooling water, antifoulant additives are now available that may largely neutralize fouling components. In hydrocarbon processes, although some additives are now being sold, it is more difficult to use an additive because it then becomes part of the process. It is possible that molecular sieves could remove suspended solids but at this time this has not been viewed as practical. When the fouling material is a necessary part of the process, as in the case of olefin separation column reboilers, nothing can be done with composition except to use it to predict how serious the fouling might be to aid in specifying the best reboiler type and conditions.

IV. False fouling indications

What appears to the operator as a decrease in performance with time, is usually attributed at first to fouling. Even when subsequent inspections reveal no

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visible fouling, the tendency is to add an increased fouling factor to future designs in lieu of any better ready explanation. The following sections describe some alternative reasons for performance decreases.

(i) Heavy component concentration.

This phenomenon is especially prevalent in large kettles operating on wide boiling mixtures and vaporizing a large percentage of the feed. Since there is a small bottoms draw, the heavy components concentrated in the liquid do not get well flushed from the reboiler and build up over time. As the concentration of heavy components increases the equilibrium saturation temperature increases and the temperature difference between the hot and cold fluids correspondingly decreases. The resulting decrease in effective boiling side temperature difference with time requires a counteracting increase in the heating medium temperature to maintain required performance exactly as would occur for fouling. Concentration of the trace heavy fouling precursors may also cause true fouling at the same time, but regardless of whether true fouling takes place or not the performance decrease is observed. This phenomenon has been reported not only for kettles but even for very large wide boiling range vertical tube-triggered not by high vaporization but by a vapor fraction too low for good circulation caused by a very low design heat flux. Since the liquid was not circulated well back into the distillation column, the "heavies" concentrated as in the kettle case. For both of these cases, using a larger fouling factor for the next design just accentuates the problem by making the reboiler further over-sized with lower liquid velocities and more potential for "heavies" concentration. Rather than using a large fouling factor the kettle design can be improved by designing for a larger bottoms draw or providing for periodic blowdown. The thermosiphon can be made much worse by a large fouling factor, which decreases the design heat flux and decreases the liquid circulation rate. For wide boiling mixtures, especially if there is no appreciable real fouling, a shellside boiling horizontal thermosiphon should be used instead of the vertical thermosiphon. The better mixing provided will permit a smaller unit and the lower static head requirement will permit a higher liquid circulation rate. If the vertical thermosiphon is already built and not working because of this phenomenon, installing a line from the bottom channel for periodic blowdown should solve the problem.

(ii) Condensate inert blanketing.

Sometimes what appears to be fouling may have nothing to do with either fouling or the boiling fluid. A

mirror image of the heavy component buildup phenomenon on the boiling side is the inert gas accumulation phenomenon on the condensing side. Even though the severely detrimental effect of inert gas on condensation heat transfer rates is well known, cases of poor performance are still reported where the fault is inadequate venting. This may be because venting was not considered necessary since the heating medium vapor was a pure component, e. g. steam, or because the vent was simply forgotten. In actual fact, all condensers need to be vented because all fluids are subject to trace amounts of inert gases that eventually build up in the condenser, unless they can be vented. Another reason for inadequate venting is poor placements of the vents. Contrary to intuition, inert vents should not be placed at the top of the condenser, but in the vapor space nearest the condensate drain nozzle; this is where the noncondensables will accumulate. For a reboiler heated by a non-vented condensing heating medium, e. g. steam, the observed effect on performance is qualitatively the same as if the reboiler were fouling; performance gradually falls off, requiring higher and higher steam pressures until the reboiler must be shut down for "cleaning". Opening the unit removes the noncondensable problem and even though the reboiler appeared relatively clean, the "cleaning" process restores normal operation, thus confirming the need for a "fouling" resistance. As stated above, the same scenario takes place with inadequate blowdown or recirculation for wide boiling mixtures.

In summary, what appears to be fouling is not always fouling, and the specification of excessive fouling factors to cover such eventualities can be self-defeating, as discussed in the next section.

(iii) Self-fulfilling prophesy.

Many are already familiar with the condenser cooling water self fulfilling prophesy case, where excess fouling resistances and associated over-performance at the startup, cause controls to decrease water velocity, which in creases the fouling rate. A different scenario with a similar end result is seen for reboilers. Excessive fouling factors make a reboiler greatly oversized on startup. In a well-designed system, the intent is for the control system to decrease the steam pressure and lower the saturation pressure to decrease the excessive vapor generation rate. However, if the design steam pressure is high enough to cause film boiling at the zero fouling resistance start up condition (often the case), the reboiler may start up with the much lower heat transfer coefficient of the film-boiling regime. The performance will not be excessive and it may not be understood that the reboiler is operating with dry wall rather than wet wall conditions. The problem with this situation is that the wall temperature is much higher than expected.

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approaching the steam temperature, so as liquid intermittently contacts the hot surface fouling can occur at a higher than expected rate. Therefore, instead of the fouling factor appearing from performance to be too high, it actually appears too low, and may be further increased for the next design. The author knows of a case where the plant engineers were adamant that their reboiler was fouling and that the fouling factor of the boiling fluid needed to be checked by an experimental program. The boiling fluid in this steam-heated reboiler was pure propane. Needless to say culprit was not really fouling.

V. Fouling factor specification

This document does not intend to recommend design of reboilers with zero fouling factors. Usually even in clean reboilers there is a certain amount of deposition on the tubes, which, if the boiling and heating medium heat transfer coefficients are high, can cause a noticeable decrease in performance. However, assigning as much as 50 percent of the exchanger surface to an unknown and arbitrarily chosen fouling factor, as is often done, is usually wasteful and self-defeating, as stated above. In fact, if the amount of excess area required for fouling is greater than about 25-30 percent, the fouling factors should be re-examined for source and reliability. An alternative design with higher velocities and lower wall temperatures should be investigated if the high fouling factors are realistic and not just "safety" factors. However, the fouling resistances chosen must be related to the reliability of the heat transfer coefficients used. The reason for this is explained below.

(i) Reasons for excessive design fouling.

In the past, reboiler fouling resistances may have evolved as necessary correction factors that made up for inadequate predictive methods. The main reason for inadequacy of early methods was failure to recognize

the detrimental effect caused by boiling mixture mass transfer limitations on the heat transfer coefficient. When literature methods or rules of thumb, gave inadequate performance, it was natural to attribute the reason to fouling and for the next design assign a compensating fouling factor, whether or not there was any physical evidence of deposition. This worked fine as a "stopgap" measure before technology further developed, and many working reboilers were designed by this crude method. However, as economics began to require better design methods, correlations appeared which took into account the very strong mixture effect on the boiling heat transfer coefficient. What was completely overlooked in most cases, was the fact that, with use of the better methods, the "fouling" resistance used before was either no longer necessary or could be greatly decreased. Failure to take this step probably accounts for the largest percentage of reboiler over-surface seen in present day specifications.

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(ii) Recommended ranges.

Fouling is a very complicated and often process that is not reproducible involving trace materials, process upsets, and other unforeseen events, which cannot be accounted for in the design stage. Therefore, prediction of exact design fouling factors is not possible and the values actually used must be tempered by engineering judgement. This could involve such factors as experience with cleaning cycles of similar units and the seriousness of being slightly short of surface, if fouling actually does turn out to be more than expected. However, due to the above considerations, it is the author's opinion that the level of fouling factor specification is too high, especially for light hydrocarbons if modern methods using mixture corrections are employed for the boiling heat transfer coefficient. Table 3 gives suggested design value ranges if state-of-the-art methods are used for the boiling heat transfer coefficient.

Table 5 Recommended ranges of fouling resistances for reboilers

| Fluids Fouling resistance, R _f | | ance, R _f | |
|--|--------------------|--------------------------|--|
| | m ² K/W | ft ² F hr/Btu | |
| В | Soiling side | | |
| C ₁ -C ₈ normal hydrocarbons | 0 - 0.00009 | 0 - 0.0005 | |
| Heavier normal hydrocarbons | 0.00009 - 0.00025 | 0.0005-0.0015 | |
| Diolefins and polymerizing hydrocarbons | 0.00025 - 0.00045 | 0.0015-0.0025 | |
| Heating Side | | | |
| Condensing steam | 0 - 0.000045 | 0 - 0.00025 | |
| Condensing organics | 0.000045 - 0.00009 | 0.00025 - 0.0005 | |
| Sensible heating, organic fluids | 0.000045 - 0.00018 | 0.00025 - 0.001 | |



VI. Conclusion

In conclusion, fouling in reboilers contains all the same elements as fouling in other exchangers, except vaporization can make potentially fouling fluids foul even more. This is especially true for cases with too a high temperature difference causing film boiling, or inadequate liquid flow, causing dry out. The normal mitigation rules, high liquid shear, uniform flow distribution, and low wall temperatures, apply even more so for reboilers. There is tendency, because of simplified design methods used in the past, to specify excessively high fouling resistances for reboilers. This is no longer necessary with state-of-the-art computer based design methods that include proper multicomponent boiling fluid heat transfer corrections. In fact use of excessive reboiler fouling resistances has been shown repeatedly to cause not only wasted heat transfer surface but also poor control characteristics, in some cases leading to even more fouling than expected.

I. Evaporative Coolers

(by G. F. Hays, J. G. Knudsen)

Evaporative coolers (sometimes known as serpentine coolers) consist of a bank of horizontal tubes arranged in horizontal rows either on a square or triangular pattern. The fluid to be cooled flows inside the tubes and cooling water is sprayed from distributors arranged at the top of the bank of tubes. An attempt is made to distribute evenly the water so that the outside of each tube is well covered with a uniform film of water. The water flows over the first bank of tubes on to the second bank and thence to the third bank becoming warmer as it progresses down through the bank of tubes.

Depending on the water quality and the temperature of the fluid to be cooled, fouling may occur on the outside of the tubes. Deposits may be corrosion products, scale or biological growth particularly algae where the cooler is exposed to natural light. Fouling may be exacerbated on the lower rows of tubes where the water is the hottest and high wall temperatures may contribute to fouling. Fouling can also occur due to drying of the outer tube surfaces if there is maldistribution of the water as it is sprayed onto the tubes. Clogged spray nozzles may be responsible for lack of complete coverage of the surface of the tubes.

Many of the problems are similar to those experienced with cooling tower water (see Section 3.17.6.F (a)).

J. Water-cooled tubular condensers

(by J. G. Knudsen)

Tubular condensers for condensing steam or other process vapors are usually arranged so that the vapor to

be condensed is on the shell-side of the condenser with the cooling water flowing inside the tubes. Usually, unless polymerization or freezing occurs, fouling on the vapor side (shell side) is negligible. Fouling on the shell side of power plant steam condensers may occur if there are contaminants (such as oil) in the steam being condensed. Traces of air that leak into condensers retard heat transfer and may also be regarded as "fouling." Many condensers used in petroleum that are condensing light hydrocarbon fractions have very little fouling on the vapor side.

Fouling on the tube side where the cooling water is flowing can occur under certain conditions (see Section 3.17.6.F(a)). Here the problem of fouling is the same as for any heat exchange process in which water is used as the cooling fluid. All forms of fouling may occur. Here again, the proper water velocity and tube surface temperatures are essential as well as knowledge of the water quality and proper treatment of the water.

Biofouling is a common problem in power plant steam condensers because the temperatures involved are conducive to the growth of biological material. A small amount of biofouling can have a very adverse effect of the performance of the condenser. This is because the thermal conductivity of the biofilm is very low (of the order of that of water and much lower than the thermal conductivity of calcium carbonate films). Because of the heat transfer coefficients in steam condensers are very high a small amount of fouling can seriously affect condenser performance. A water-side fouling allowance of 0.00006 m² K/W (0.00035 hr ft² F/Btu) are routinely used in the design of the condenser.

K. Direct Contact Heat Transfer

(by J. G. Knudsen)

Direct contact heat transfer (sometimes known as quenching) in which both the hot and the cold fluid are in direct contact with each other is often used in cases in which there is a severe potential for fouling. Direct contact heat transfer is, therefore, one of the means for the avoidance or mitigation of fouling. The process involves intimately mixing the two streams together and afterwards separating them. The pairs of fluids may be two liquids, a gas and a particulate solid, a liquid and a particulate solid and a gas and a liquid.

There is a possibility of contamination of one or both of the streams, which may later lead to fouling problems. Barometric condensers operating on a cooling water loop may contaminate the cooling water with hydrogen sulfide (geothermal), organic matter (HPI/CPI) or a number of other materials. Thus, while fouling is usually avoided or minimized in direct contact heat transfer, the potential for fouling of other

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equipment in the process is increased depending on the materials involved.

L. Fouling of enhanced surfaces

(by C. B. Panchal)

(a) Types of enhanced surfaces

Heat transfer enhancements inside and outside of tubes (such as fins, ribs, and flutes) are proven methods of increasing the thermal performance of heat exchangers. Finned tubes are commonly used to compensate the low heat transfer coefficients for air and combustion gases: serrated fins enhance the heat transfer coefficient in addition to providing extended areas. Major mechanisms of enhancing single-phase and phasechange heat transfer are: (1) boundary-layer disruption, (2) swirling or secondary flows, (3) improved distribution of liquid and vapor phases, and (4) surface tension induced condensation and evaporation. The interactive effects of enhancement and fouling mechanisms determine fouling propensity of enhanced surfaces. Due to lack of knowledge for the prediction of the fouling characteristics of enhanced surfaces. operating experiences provide a basis for selection for a given application. Better understanding of fouling mechanisms and the effects of physical, as well as chemical parameters, would greatly help to make a proper selection in terms of type and geometry. Furthermore, new and improved mitigation and cleaning techniques could be developed for enhanced surfaces to maintain their thermal performance.

Major types of commercial enhanced surfaces are summarized in Table 6, along with their known applications. Enhanced surfaces are applied either on one side or both sides of tubes, depending on materials and cost effectiveness. Finned tubes are extensively used in air-cooled heat exchangers, furnaces and boilers to compensate for the low heat transfer coefficient. The refrigeration industry has aggressively used enhanced surfaces for single phase, as well as convective condensation and boiling applications. indented tubes have been installed in several powerplant condensers. The desalination industry commonly uses axially fluted tubes in the multi-effect evaporation process. Application of enhanced surfaces in the process industries has been relatively slow; except that porous surfaces and low-finned tubes, are used in reboiler applications with non-fouling conditions. Recently, tube inserts have been promoted for mitigating fouling in petroleum processing [55-57].

(b) Fouling characterization

The influence of enhanced surfaces on transport processes, shear stress distribution, secondary flows in the vicinity of walls, phase distribution in multi-phase

flows, and wall temperatures can alter the fouling process. Depending on the controlling step for a given fouling mechanism, enhancement could increase or decrease the rate of fouling and the effectiveness of chemical additives. The secondary flows generated by certain types of enhancement could contribute to removal of fouling deposits formed either at the wall or in the boundary layer. Watkinson [58] discussed the effects of heat and mass transfer enhancement on some of the fouling mechanisms. If diffusion of the fouling species, such as dissolved metals in hydrocarbons, is a controlling step, the high wall shear may not be adequate to reduce fouling. On the other hand, if formation of a foulant by chemical reaction or crystallization in the thermal-boundary layer, or at the tube-wall is a controlling step, altering the tube-wall temperature can significantly reduce fouling. For example, lowering the tube-wall temperature is known to reduce fouling of crude oil and olefin-induced hydrocarbon fouling [59,60] while increasing temperature would reduce paraffin deposition [61]. The mechanisms associated with threshold conditions, at which a sudden change in fouling rates has been observed, are not fully understood. However, some enhancement is expected to change the thermo-physical conditions in the vicinity of the heat transfer surface below threshold fouling condition and thereby reduce the fouling rate significantly.

The key issue to be considered for enhanced surfaces is that most enhancement devices produce a non-uniform shear-stress distribution and transport coefficients. Therefore, preferential fouling can occur between consecutive enhancement geometric shapes [58,62]. The preferential deposition in turn, will alter the enhancement shape and thereby change mechanisms. In some fouling mechanisms, such as biofouling, relatively uniform fouling occurs without a significant drop in the performance [63] as compared to that for plain surfaces. However, in some fouling mechanisms, such as particulate fouling, the preferential deposition might continue rapidly and thereby eliminating the improved heat transfer effects [64].

The interactive effects of tube-wall temperature and wall shear produced by enhanced surfaces are reflected in their crystallization fouling characteristics. Watkinson [58] reported that the asymptotic fouling resistance for a longitudinal finned tube was 15 - 30 % greater than that for the plain surface. On the other hand, the spirally indented tube showed 25 - 50 % lower fouling resistances than that for the plain tube. Knudsen and Roy [64] showed similar results for spirally indented tubes. Moore [65] described several applications in which radial finned tubes had distinct advantages over plain tubes under fouling conditions. He contended that irregular thermal expansion on the

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 Table 6
 Enhanced Surfaces for Single-Phase and Phase-Change Heat Transfer

| Enhanced Surface | Enhancement Mechanisms | Known Applications | Schematic View |
|---|--|--|----------------|
| Spirally indented | Boundary layer disruption | Refrigeration water side; Power plant condensers | |
| Spirally Finned: low pitch to height ratios | Boundary layer disruption and/or swirling flows; Phase distribution for two phase flows | Flow boiling and condensation in refrigeration | |
| Spirally ribbed (high pitch to height ratio) | Phase distribution for two phase flows | Steam boilers | |
| Low fins – Outside of tube | Surface tension | Boiling and condensation in refrigeration | |
| High fins – Outside of tube | Extended surface | Air cooled heat exchangers; Boilers and furnaces | |
| Twisted tubes | Secondary flows | Liquid to liquid | |
| Porous surface | Reentrant boiling | Reboilers | |
| Spirally fluted | Swirling flows; Surface tension | Single phase flows: Flow boiling and condensation | |
| Axially fluted | Surface tension | Condensation and falling-film evaporation | |
| Spiral wire - Fixed | Boundary layer disruption | Single phase flows | |
| Spiral wire – Oscillating | Secondary flows | Anti-fouling device | NY IV |
| Wire matrix | Intensification of turbulence | Anti-fouling device | |
| Spiral ribbon and Static mixture | Swirling flows; Bulk flow interruption | Low Reynolds numbers; Non-Newtonian flows | |

fins tends to produce a looser scale that is easier to remove

The interactive effects of fouling and enhancement in two-phase flow applications are complex and the long-term data are limited. The fouling mechanism is further complicated by the distribution of liquid and vapor phases in different flow regimes. In addition to producing secondary or swirling flows in the liquid phase of two-phase flows, enhancement devices that reduce the phase separation and dryout of the heated wall would reduce fouling significantly. Coking and scale formation in petroleum furnaces and boilers, show preferential deposition in some part of the heating coil, where cyclic dryout can occur. Spirally ribbed tubes

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(commonly known as rifle tubes) are now commonly used in steam boilers to minimize the localized scale deposition. Axially fluted tubes are commonly used in desalination processes for thin film evaporation, where chemical treatment is a primary mode of mitigation method. Porous surfaces have been successfully used in the process industry to enhance nucleate boiling. It is claimed that the vigorous nucleate boiling on the porous surface repel foulant away from the surface.

(c) Design methods

Design methods for fouling conditions should follow the three basic steps:

- 1. Selection of enhancement type for a given application,
- 2. Performance analysis for clean and fouled conditions, and
- 3. Mitigation and cleaning techniques.

Selection of enhanced surfaces for non-fouling conditions are generally based on the overall performance and costs. Rabas [66] consolidated much of the literature of common enhancement devices for single-phase heat transfer and compared their performance using the figure of merit index, η , defined as

$$\eta = (\alpha_e/\alpha_p) / (f_e/f_p) \tag{3}$$

Where

 α_e = the heat transfer coefficient on the enhanced surface

 α_p = the heat transfer coefficient on the plain surface

 f_e = the friction factor on the enhanced surface

 f_p = the friction factor on the plain surface

The ratio of heat transfer coefficients is compared with that of friction factors for enhanced and plain surfaces. The merit index should be compared for clean and expected fouled conditions. The objective is to maximize the integrated benefits of enhanced surfaces between cleaning schedules, which might be different from those for plain surfaces. The fouling propensity of the process stream governs the choice of enhancement geometry. For rapid fouling conditions where frequent cleaning is required, the choice should be moderately enhanced surfaces, such as spirally indented tubes.

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Tube inserts can be used as retrofits and they can be taken out, if their effectiveness in controlling fouling is not satisfactory. The choice of tube inserts should be evaluated, also, on the basis of known fouling mechanisms. In retrofitting applications, tube inserts are used either to enhance the performance and/or reduce fouling. Although little data are available, the combined effects of chemical treatment and the use of some of the enhancement devices, may reduce fouling significantly. Tube inserts used for fouling control in petroleum applications may extend cleaning cycles by a factor of two or more [55,57].

Chemical cleaning and hydroblasting are commonly used in the process industry; therefore, the choice of geometry should be such that chemicals or water jets can penetrate the complex enhancement surfaces. On line cleaning is evaluated for cooling water applications [67,68] and the results showed that the performance of spirally indented tubes can be restored with mechanical cleaning. Finned tubes in boiler applications are routinely cleaned with soot blowers with predictable performance. Some fins are easier to clean using soot blower technologies than others.

The major objective for the development of enhanced surfaces in the past was to maximize the heat transfer performance without significant increase in pressure drop. Future research should focus on developing geometry for mitigating fouling. Table 7 provides a summary of successful applications of some of the enhanced surfaces listed in Table 6 under fouling conditions. Enhanced surfaces and tube inserts have the potential to mitigate fouling by either reducing the rate of fouling, compensating the fouling resistance with improved performance, or increasing the effectiveness of chemical additives. However, until the long term performance, similar to that shown by Rabas et al. [69], of enhanced surfaces and tube inserts is achieved, the industry acceptance of enhanced surfaces would be slow.

 Table 7 Successful Applications of Some Enhanced Surfaces

| Enhanced Surfaces | Applications | Fouling Mechanisms |
|------------------------------|-----------------------------------|--------------------------|
| Spirally Indented | Refrigeration, Utility Condensers | Biofouling |
| Axially Fluted | Desalination | Crystallization of salts |
| Wire Insert: | Crude oil | Chemical reaction |
| Matrix, Vibrating | | |
| Finned Tubes | Air and Combustion Gases | Particulate |
| Low Fins and Porous Surfaces | Reboilers | Chemical |
| Spiral Ribs | Boilers | Crystallization of salts |

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M. Scraped Surface Heat Exchangers

(by T. R. Bott)

In general a scraped surface heat exchanger (used for processing liquids) involves a rotating shaft on which are mounted blades (usually spring loaded) that move across the surface through which the heat is passing. The blades are thrown outwards by the rotation of the shaft and scrape the heat transfer surface; hence the name. The shaft is usually mounted on the axis of a suitable tubular geometry. The tube through which the liquid is pumped may be running full of liquid and can therefore be mounted vertically or horizontally. In other examples the liquid is pumped to the tube inlet and falls as a film down the inside of the tubular body (e.g. in evaporation) which necessitates a vertical mounting. Heating or cooling of the liquid in contact with the blades may be accomplished e.g. with stem or chilled water.

The scraped surface heat exchanger is generally used for viscous liquids, the scraping action of the blades removes the viscous sub layer from the heat transfer surface thereby improving the heat transfer compared to the situation when there is no scraping action.

Due to the relatively high capital cost and maintenance charges (due to rotating parts and blade wear), scrapped surface heat exchangers are only used for special applications usually clean conditions, particularly in the food industry for cooling margarine and ice cream for instance. In the unlikely event that fouling is a potential problem, the action of the blades provided they operate at a suitable rotary speed, is likely to eliminate the problem.

A modification of the scraped surface heat exchanger is when the blades are fixed and there is in consequence, a small gap between the blade and the surface. The improvement in performance of this design is not so great as when the rotating blades are in direct contact with the heat transfer surface. Nevertheless, the close clearance design does disturb the liquid at the heat transfer surface. If fouling is a problem, again with sufficient rotary speed, the fouling is likely to be restricted to a relatively thin layer. The thermal resistance of this layer is not likely to be much different from a slow moving liquid layer between the blade tip and the heat transfer surface.

N. Fixed/fluidized beds

(by H. Müller-Steinhagen)

(a) Fluidized bed heat exchangers

An effective solution for heat transfer involving severely fouling liquids is the fluid bed heat exchanger

which has been described by Klaren [70] and Kollbach [71]. Small solid particles (glass, ceramic, metal) are fluidized inside parallel tubes by the upward flow of liquid. The solid particles regularly break through the viscous boundary layer, so that good heat transfer is achieved in spite of relatively low flow velocities [72]. For water and "particles" of 2.5 mm x 2.5 mm stainless steel cylinders, the heat transfer coefficient at 0.35 m/s superficial velocity is equal to that for 1.3 m/s with water flow only. More importantly, the solid particles have a slightly abrasive effect on the wall of the heat exchanger tubes, thus removing most deposits at an early stage. A schematic diagram of a fluid bed heat exchanger is shown in Figure 4.

Fluid bed heat exchangers can also be operated as falling film, rising film or circulating bed heat exchangers. They have been installed in water treatment plants, paper mills, food and dairy plants, geothermal plants and in various chemical and mineral processing plants. Figure 5 shows the heat transfer coefficient as a function of time for measurements with a fluidized bed test heat exchanger on a side-stream of an Alcoa of Australia Ltd. refinery [73].

Because of the hard and adherent nature of the silica deposit, scaling could not be eliminated completely and the heat transfer coefficient decreased almost linearly with time. However, the fouling resistance after 8 days is $0.2\times10^{-4}~\text{m}^2\text{K/W}$, which is only 15% of the fouling resistance observed without the fluidized bed over the same time span. There was no deposition on the particles, even after 24 days of operation.

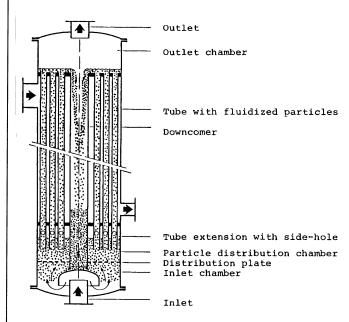
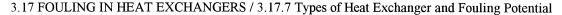


Figure 4 Circulating fluid bed heat exchanger [70]





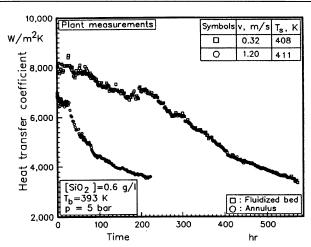


Figure 5 Reduction in heat transfer coefficient from Bayer liquor, with and without fluidized bed [73]

(b) Fixed Beds

The formation of deposits during flow of liquids and gases through fixed beds or porous media, is a common problem. Examples range from fouling of catalysts during hydrocarbon processing to deformation during secondary oil recovery. In most cases, the deposition occurs within the porous matrix, rather than at the interface between the bed and a solid containment. While scale formation and biological growth may be observed if natural waters are used, by far most common fouling problem is caused by particles suspended in the fluid. If the size of the particles is of the same order of magnitude as the pore size, filtration theory applies. For submicron particles, the interaction energy between particles and surface is due to Londonvan der Waals attraction [74], electrostatic interactions [75] and Born repulsion at very close distances. The latter does not need to be considered in normal deposition processes. If no electrostatic interaction occurs, the deposition process can be described by a diffusion model, i.e.

$$k(diff) = 0.624D^{2/3}r^{-2/3}(\beta u)^{1/3}$$
 (4)

where, the porosity term β for a column packed with spherical particles is [76]

$$\beta = [1 - (1 - \Phi)^{5/3}]/[1 - 1.5(1 - \Phi)^{1/3}]$$

$$+1.5(1-\Phi)^{5/3} - (1-\Phi)^2 \tag{5}$$

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When the diffusion process is affected by the interaction forces, the discrepancy in the prediction of the above equation may be accounted for by a so-called stability coefficient W which is defined as [77]

$$W = k(diff)/k \tag{6}$$

With this one obtains

$$\ln \frac{C_{in}}{C_{out}} = 1.87 D^{2/3} W^{-1} M r^{-5/3} \rho^{-1} \beta^{1/3} S^{-1/3} \dot{V}^{-2/3}$$
(7)

Experiments with particles and surfaces of opposite charge where found to agree with the diffusion-only case [78]. Figure 6 shows the effect of pH on the deposition of spherical α -Fe₂O₃ and rod-like β -FeOOH particles on steel at 25°C [77].

The arrows indicate the isoelectric points. Obviously, the shape of the particles has some effect on deposition. Rapid deposition occurs if particles and steel surface are of opposite charge. The fact that not the full pH-range of opposite charge is used is explained by the gradual accumulation of particles on the steel surface [77].

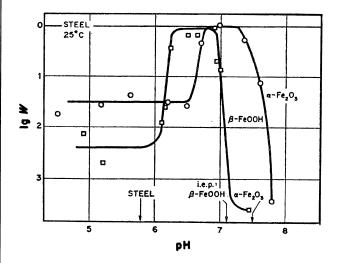


Figure 6 The effect of pH on the deposition of α -Fe₂O₃ (O) and β -FeOOH (\square) particles

NOMENCLATURE

- a coefficient in Equation (2), m²K/J
- A_c heat exchanger area not taking account of fouling, m²
- A_f heat exchanger area taking account of fouling, m²

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| 3.17.7- | 2.7-24 3.17 FOULING IN HEAT EXCHANGERS / 3.17.7 Types of Heat Exchanger and Fouling Potential | |
|-------------------|---|--|
| C | particle concentration, 1/m ³ | |
| D | diffusivity of colloidal particles, m/s ² | |
| f_a | friction factor for enhanced surface | |
| f_n | friction factor for plain surface | |
| $\overset{Jp}{k}$ | mass transfer coefficient, m/s | |
| k(diff) | · | |
| M | mass of particles in bed, kg | |
| r | diameter of particles, m | |
| R_f | fouling resistance, m ² K/W | |
| $R_{f}(t)$ | fouling resistance at time t , m ² K/W | |
| S | cross sectional area of packed bed, m ² | |
| t | time, s | |
| U | superficial velocity, m/s | |
| U(0) | overall heat transfer coefficient at $t = 0$, W/m ² K | |
| U_{c} | clean overall heat transfer coefficient, W/m ² K | |
| U(t) | overall heat transfer coefficient at time t , W/m 2 K | |
| W | stability coefficient (Equation (6)) | |
| $lpha_e$ | heat transfer coefficient for enhanced surface, W/m ² K | |
| α_p | heat transfer coefficient for plain surface, W/m ² K | |
| β^{ν} | porosity function (Equation (5)) | |
| η | figure of merit defined by Equation (3) | |
| ρ | density of particles, kg/m ³ | |
| Φ | void volume fraction | |
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Fouling mitigation and heat exchanger cleaning

T. R. Bott, G. F. Hays, J. G. Knudsen, E. R. Miller, A. P. Watkinson, D. I. Wilson

A. Fouling control measures

(a) Physical Mitigation Techniques (by T. R. Bott)

The removal of deposits from heat exchanger surfaces may be achieved by the application of suitable forces that dislodge the accumulation of unwanted material. In many instances the removal forces are applied through a fluid medium, often it is the process fluid itself that provides the means of applying the removal force. In other situations, deposits are prevented from forming or are knocked from the surface, by a solid agent. Some of the techniques lend themselves to on line cleaning i.e. the process is continued while the mitigation takes place. Other techniques may require that the plant is shut down, or at any rate the particular heat exchanger in question is taken out of service for cleaning. Many of the techniques are not universal and have been developed to meet particular requirements and processes.

I. Circulation of Sponge Rubber Balls

In the power industry the maintenance of steam condenser performance is essential to maintain generation efficiency and competitiveness. In order to maximize the output from the turbine generation set, it is necessary to ensure that the lowest possible pressure in the steam condenser is retained. Condensation is achieved by the circulation of cooling water through the

tubes of very large shell and tube exchangers. The system may be once through or recirculating. Since in general, the water system is open to the atmosphere it is likely to become contaminated with microorganisms and particulate matter that accumulate in the condensers where the conditions favor the formation of biofilms (see section 3.17.2). In addition, scale formation is possible, where the concentration of dissolved solids reaches saturation levels (due to evaporative cooling of the water). In addition particulate products of corrosion may also accumulate on the surface, or the surface itself may become corroded. The consequence, if mitigation techniques are not applied, is the formation of slime layer (due to microbial colonization) in conjunction with particulate deposition, products of corrosion and crystal formation where conditions are suitable.

The large size of power station condensers, with a uniform tube diameter lends itself to the circulation of slightly oversize sponge rubber balls, with the water flow. The passage of the balls through the tubes is effective in wiping the insides of the tubes clean. The balls are filtered out of the discharge water by a suitable strainer, returned to the circuit via a collector, which removes worn and undersized balls. Replacement balls are added as required. Balls with an abrasive outer layer may be employed for tenacious deposits, or where preliminary cleaning is needed following the installation of the circulating ball system. The continuous use of abrasive balls is to be discouraged due to the erosion that will inevitably occur with time.

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Indeed the use of the softer sponge rubber balls over long periods of time may also cause erosion of the heat exchanger surfaces, over which they pass. The effectiveness of the system depends on the probability that each tube in the heat exchanger will see a ball on a regular basis. A typical frequency is twelve times per hour [1]. Circulation of the balls can either be continuous or intermittent depending on the severity of the problem.

Metal corrosion resistance is often achieved by the presence of a passive micro-layer on the surface. It is essential therefore that the circulation of the sponge rubber balls does not impair this protection. It is possible to optimize the corrosion resistance of condenser tubes by the use of the ball recirculation system, in conjunction with chemical additives by maintaining protection and at the same time minimizing resistance to heat transfer.

The installation cost of the system is relatively high compared to the equipment used for chemical dosing, but pay back times in terms of improvements in efficiency and reduced energy consumption, of the order of 3-5 years have been reported [2].

In general, the system is only applicable to large heat exchangers with a uniform tube diameter (as in power station condensers). The system is not suitable for smaller individual heat exchangers due to the high capital cost involved, nor is it suitable for other heat exchangers that do not have a single tube pass, e.g. multipass shell and tube exchangers, or plate types. The system is not applicable to the shellside of shell and tube exchangers. It also has to be remembered that the system only applies to the heat exchanger, other parts of the system e.g. pipelines, cooling tower and basin, are likely to require chemical treatment to keep them free of deposits.

II. Brush and cage system

The brush system of on-line cleaning is similar in principle to sponge rubber ball cleaning. It also carries the same limitation that it is only applicable to the inside surfaces of tubes. The technique however, is applicable to individual heat exchangers and it can handle fouling from other liquid streams as well as water flows.

The method involves the transport of a brush, fabricated from metal or polymer fibers (depending on the prevailing conditions), from one end of the tube to the other and back again. Located at either end of each tube there is a cage to catch the brush on completion of its travel. Oscillation of the brush projectile is accomplished by flow reversal in the heat exchanger. The frequency of oscillation is determined by the severity of the fouling problem, usually on a trial and

error basis. Flow reversal is generally made automatic, based on the results of the trials.

The principal drawbacks to this technology are the initial cost, which will include the complex piping arrangements to accommodate the flow reversal, and the necessary automatic control. A further complication may result from the momentarily interrupted flow when the changeover occurs, which may have implications for steady state conditions in process operation and the effect on subsequent product quality.

For reasons of cost and integration into plant operation, the system is generally not amenable to retrofit situations, unless possibly a piping system is in place to provide back washing facilities that may be utilized. The same general philosophy applies in regard to tube side wear, as for the sponge rubber ball system. It is to be expected however, that the brush and cage system will require less maintenance.

III. Backwashing

In some installations it is possible to remove accumulated deposits on heat transfer surfaces, by reversing the fluid (usually liquid) flow for a short period of time. A suitable arrangement of valves, pumps, piping and tank to retain the wash liquid will be necessary. The back flow rate will generally need to be higher than the normal process flow (in the opposite direction).

IV. Air or gas injection

A technique that has been used for many years to dislodge deposits from surfaces of heat exchangers processing liquids, is the injection of air into the liquid stream. The method has been given the name of "rumbling". The concept of the method is that a slug of air in a liquid system (i.e. a two-phase flow), disrupts the liquid near the solid/liquid interface and causes removal forces to be applied to the deposit. Rumbling is often applied to otherwise inaccessible locations, such as the shell side of tubular exchangers. For many deposits the method is not likely to be successful except for loose particulate deposits, due to the relatively small removal forces that can be generated in this way. A further drawback is the installation costs and the availability of compressed air (or gas). Often the method is used to provide a temporary respite in severe problems of fouling and restricted flow. Care has to be exercised under these circumstances to ensure that the operation is executed safely. Where flammable process liquids are involved it is necessary to use an inert gas. such as nitrogen, to eliminate the risk of generating explosive mixtures of vapors. In broad terms gas rumbling must be regarded as a last resort solution and may only be suitable for certain specific problems. On

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the shell side of shell and tube heat exchangers it may be the only technique that is applicable for on-line cleaning.

V. Soot blowing

The technology of soot blowing, as the name implies, is generally confined to combustion systems. (Soot Blowing is also discussed in Section 3.17.8.B.(b)I.(i)). During the burning of combustibles e.g. fossil fuels, flammable waste and biomass, the mineral content originally contained in the fuel, may go forward with the flue gases. Deposition of these compounds on heat transfer surfaces can cause a serious fouling problem. Two conditions are apparent. In high temperature regions the mineral matter is molten and the phenomenon is generally known as "slagging." In the cooler regions, the mineral matter exists as particulate matter that is likely to settle by convection or impaction, on the heat transfer surfaces; for instance preheater and superheater tube banks. After deposition chemical reactions may occur making the deposit more difficult to remove. Although the technology of soot blowing is generally applied in combustion plant, there is no reason why it could not be applied to problems of a similar nature and where there is suitable access. Soot blowing is frequently employed in coal fired boilers and often found in smelter hoods.

A soot blower consists essentially, of a jet of steam or air directed towards the deposit and made to impinge on it. The force created by the jet as it strikes the solid material is designed to knock the deposit off the surface. If this is carried out on a frequent basis it is possible to maintain reasonably clean surfaces and retain heat transfer efficiency. Because of the extent and relatively complex geometry of the heat recovery equipment, it is often necessary to install a number of soot blowers. Manual or more usually automatic, rotating and traversing will be required to ensure that the soot blower may "see" the entire heat transfer surface. In general soot blowers are not operated continuously but intermittently, the frequency of operation depending on the severity of the fouling problem.

Soot blower designs have evolved from experience particularly in the light of the fuels being burnt in the equipment. Different impingement pressures to accommodate different deposit characteristics may be obtained by the choice of nozzle size.

Two broad types of soot blower are used, i.e. long retractable or rotary devices. Retractable designs are used where temperatures are high and long exposure times would cause material damage, such as might occur deep into the flue gas space in the region of radiant superheaters. Adequate cooling from circulating air or steam will be necessary to maintain the integrity of the equipment. Rotary designs are generally

restricted to applications where the prevailing temperature is below 500°C, and consist of a multinozzle head, capable of rotation, but permanently located in the flue gas stream.

The usual arrangement for the operation of soot blowers is to use high-pressure steam directly from the superheaters of the boiler plant. If compressed air is used this will entail the installation of a suitable compressor and air receiver, with the attendant capital and running costs. High-pressure water jets may be used instead of steam or air, since the momentum of the denser water, will provide a greater removal force. The thermal shock produced by the relatively cold water in contact with the hot deposit may assist the removal process. There is however, some reluctance to employ water jets, since the thermal shock combined with the large forces involved, may damage the heat transfer surfaces and the associated structures. The problem of damage could be overcome by a combination of water and steam or air jets, but potential erosion effects due to high velocity water droplets, may be a problem. Furthermore the injection of cold water into the combustion area will have the effect of reducing the overall thermal efficiency of the combustor and reducing the steam temperature.

In any event, it is advisable to check surfaces swept by jets from soot blowers, for signs of erosion. If there is evidence of damage, modifications to the equipment or cycle times may be necessary.

Although the discussion has been confined to combustion systems, there is no reason why the technology should not be used for other suitable fouling gas systems.

VI. Acoustics

The use of acoustics, or sonic technology, has found application in the removal of deposits from surfaces. Its widest application perhaps, has been in combustion systems in a similar way to soot blowers.

The principle underlying the technology is that the agitation or vibration, caused by the propagation of sound, is sufficient to dislodge deposits and shake it from the surface. Low and high frequency sound emitters have been used to dissipate deposits in heat exchangers. Good results are possible in dealing with loose friable deposits, such as particulate accumulation in the convection sections of combustors. The effectiveness is likely to be much less, where sticky deposits are found e.g. where slagging of mineral matter occurs in high temperature regions.

A common application of sonic technology is to supplement the use of soot blowers to deal with regions that are not accessible by conventional equipment. At the same time, there is some hesitation in respect of using the technology, due to the potential risk to the

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integrity of the installation from vibration. Noise pollution in the vicinity of the plant may also present health risk to employees in the area.

Recent studies [3,4] have demonstrated that the application of ultrasound (20kHz frequency) may be valuable for the control of biofilms in aqueous systems. There is no reason to suppose that this technique could not be applied to other liquid systems.

VII. Shot impingement

An additional technique that has been employed in combustion plant, is that of shot cleaning to control mineral deposits on heat transfer surfaces. The principle is simple and depends on the ability of the kinetic energy, contained in falling metallic spheres, to dislodge any deposit attached to surfaces. The shot cascades under gravity, in a vertical chamber in which the heat exchanger tubes are located. After collection at the bottom of the chamber the shot is returned to the release point at the top of the plant. The technique has been used for boiler plant economizers and recuperative air heaters. It is suitable for regions where temperatures are below 800°C.

The concept of the method is to prevent significant accumulations of deposit rather than remove significant formations. Where soft or molten deposits exists, there is the distinct possibility that the shot may become incorporated in the deposit; rather than alleviating the problem, but adding to it!

Local damage may occur to surfaces that are subject to shot impingement. It may be necessary to retrofit deflection plates or shields, if evidence of damage is found.

VIII. Water washing

The manual application of water jets or sprays, for online cleaning, has been employed for many years in order to restore heat transfer efficiency in flue gas systems. (Water washing is also discussed in Sections 3.17.8.B. (b) I. (ii) and II. (ii)). The use of water washing to restore heat transfer efficiency is often associated with off-line cleaning (see section 3.17.8.B. (b) II.), but it may also be used for on-line cleaning. In some plants permanent equipment has been installed but the technology is much less sophisticated than the use of soot blowers (see Section 3.17.8.A (a) V. and 3.17.8.B. I. (i))). In many installations, water washing has been a last resort where other methods have failed. It is necessary to employ good quality water, since if there is a high concentration of dissolved solids, as the water evaporates an additional foulant will be deposited on the heat transfer surfaces. If for instance, seawater is used as wash water, serious problems could occur.

Water jets may be used but in regions of lower temperature it is more usual to employ water sprays. The technique is applicable to economizers with horizontal tubes and air preheaters, involving the installation of a water distribution system above the top bank of tubes to provide a curtain of water. Soluble rather than insoluble deposits are more amenable to this approach.

Consideration has to be given to the effluent liquid produced as a result of water washing; it is possible to generate corrosive solutions. Disposal of the liquid effluents may also represent a problem. A modification of the simple water washing technique is to use chemical solutions to facilitate softening and removal of deposits. There are, of-course, implications in the safe disposal of the effluent produced by this treatment.

IX. The use of inserts

Inserts are generally applied to the inside of heat exchanger tubes. Although the primary concern with the use of inserts is to enhance heat transfer it has been found, in some applications, that inserts also reduce the incidence of fouling. Some inserts however, are primarily designed to reduce fouling e.g. wire spring like configurations that are free to move under the influence of the fluid flow. The rubbing action of the insert against the heat transfer surface has the effect of maintaining a clean surface. A problem that may result from this approach is that repeated flexing of the insert may give rise to fatigue failure of the structure. Disconnected pieces of insert may then pose a problem downstream from the exchanger. A more robust design of insert is that manufactured by Cal Gavin, which is held tightly within the tube by a push fit as well as anchorage at the end.

Gough and Rogers [5] demonstrated that with the use of inserts in a tar oil heater after 4.5 years operation the fouling resistance was only 30% of that allowed for using tubes with no inserts, and yet using plain tubes the design fouling resistance was reached in 2 months!

Laboratory studies by Crittenden et al [6] using a light Arabian crude oil showed that with inserts in place, fouling resistance to heat transfer reached a steady value after 10 hours. Furthermore the values of the fouling resistance at the asymptote were only about 2-7% of the revised recommended TEMA value [7].

Crittenden et al [6] suggest that the benefits in respect of fouling, are due the hydrodynamic disturbance created by the presence of the inserts. There are potentially four advantageous effects:

• A reduction in the residence time of the fouling precursors along the heat transfer surface.



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- A reduction in the quantity of liquid, which is heated to a temperature in excess of the bulk liquid.
- Elimination of nucleation at the heat transfer surface that reduces deposition.
- An increase in the release of deposits from the wall.

There is also some evidence of the beneficial effects of inserts in aqueous systems in respect of biofouling [8].

The use of inserts carries with it the penalty of increased resistance to flow and the associated increase in pressure drop, for a given flow rate. However, in conjunction with the enhanced heat transfer, it is possible to reduce the length of liquid flow path, with the attendant beneficial effect on pressure drop.

X. Vibrating tubes

It is possible to use plastic tubes (e.g. PVC) in shell and tube heat exchangers operating at temperatures below 90°C. Under the influence of the flow conditions, the tubes vibrate. The continual movement of the tubes has the effect of making it difficult for deposits to accumulate. Furthermore the character of the polymer surface makes it less hospitable to the accumulation of solids. There appears to be little reported in the literature on the effectiveness of the technique.

XI. Magnetic devices

The use of magnetic devices to reduce or eliminate scale formation from sparingly soluble salts in aqueous solutions has been attempted for many years. Despite testimonial claims, a search of the available literature shows that there is no substantial evidence of any long term scientifically measured benefit in reducing or eliminating, deposition or fouling with magnetic devices in place.

(b) Chemical treatment

I. Aqueous streams

(by J. G. Knudsen & G. F. Hays)

Although the designer can mitigate fouling through proper design of a heat exchanger and knowledge of the fluids being handled, there still exists the need for a well-organized, well controlled water treatment program to attain trouble-free operation of a well-designed heat exchanger. There are three types of cooling water systems: once-through, open recirculating and closed. In once-through systems, the water is drawn from a source and passes through the heat exchanger only one time before it is either returned to the original source or empties into another system. An open-

recirculating cooling water system uses the evaporation of water as it passes through a cooling tower or a spray pond to cool the remaining water. In the process, the mineral and organic matter, in the recirculating water, increase in concentration. In some instances, such as fossil fuel fired or nuclear power plants, water from a lake or river is used to cool heat exchangers in a service water system, then is used as make-up water for the plant's open recirculating system. The evaporative cooling tower and associated circulating system provide and excellent environment for biofouling, scaling and particulate deposition. Closed systems, which are discussed in 3.17.6.K, use the same makeup water quality, but generally have very limited makeup.

Chemical treatment of cooling water is widely used. There is a large amount of information available on the effectiveness of various treatment chemicals and treatment techniques in reducing or preventing fouling. Several practical guides to water treatment are available [9-11].

The chemical treatment of water can generally be categorized into two major areas, scale and particulate control and biofouling control.

(i) Scale and Particulate Control

Various methods are used to prevent the deposition of inverse solubility salts and other constituents such as clays, silts and metallic oxides.

Removal of Foulants

Scaling and particulate species are removed from the water to the extent that they no longer have the potential for deposition, under the conditions that the water is being used.

Mechanical prevention

Steps are taken during the design of the heat transfer equipment, in which geometric configurations and process variables are selected to minimize deposition.

pH control. The solubility of scale-forming constituents in water is affected by the pH of the water and conditions are adjusted so that these constituents are more soluble and, thus, have less potential for deposition on the heat transfer surface. Use of pH control often requires that a corrosion inhibitor be used particularly in all-steel systems, in order to minimize corrosion.

Scale inhibitors and dispersants. A number of proprietary compounds are available to inhibit scale formation and to disperse particulate materials in the water.

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Corrosion inhibitors. Corrosion inhibitors can be considered as treatment of water, not only to prevent corrosion, but also to mitigate fouling. Corrosion products, which adhere to heat transfer surfaces, constitute hindrances to heat transfer. In addition, corrosion products, which are removed from corroded surfaces, may cause particulate fouling or agglomerate other foulants causing them to foul heat transfer surfaces.

(ii) Biofouling control

The environment in cooling towers and cooling systems is particularly conducive to the growth of microorganisms in the water and on heat transfer surfaces. Power plant condensers in which the heat transfer surface is at a temperature in the range 35-50° C (95-120° F) are subject to biofouling. The biofilm deposited not only adds to the resistance to heat transfer but often has a structure such that a significant increase in pumping power occurs as well.

Biological growths can be controlled destroying the microorganisms with biocides. An effective biofoulng control program should be initiated at the time a new heat exchanger is placed in operation. Biocides are effective only if they reach the bacteria deposited on the heat transfer surfaces.

A summary of chemical additives used in mitigating or eliminating cooling water fouling is shown in Table 1 [12].

(iii) Process control

Cooling water systems are dynamic processes, which are subject to process disturbances such as changes in

heat load, airborne contamination, process leaks and agglomeration of biomass. After selection of the proper treatment chemistries, the next critical factor in mitigating fouling of heat exchangers in cooling water service is to feed properly the chemicals and control the system chemistry.

(iv) Economics

Assessing the economics of fouling of operating heat exchange equipment is a relatively easy task if there is only one heat exchanger on the cooling water system. When there are a number of heat exchangers and the process also has process to process heat exchangers, then the task becomes very difficult and time consuming. In either case, the following factors should be included:

- Volume of makeup water used in cooling system
- Volume of waste water from cooling system
- Cost of makeup water and waste treatment
- Cost of treatment (chemicals & services)
- Length of production runs
- Maintenance down time (time and cost)
- Unabsorbed overhead during maintenance downtime
- Product throughput
- Any product quality problems.

Table 1 Summary of typical chemical additives used for different fouling conditions

| Fouling Type | Additive Type | Additive Chemistry |
|-----------------|---|---|
| Biofouling | Biocides, biodispersants, biostats (to reduce activity) | Chlorine, bromine, chlorine dioxide, ozone |
| Crystallization | Dispersant, crystal modifier, chelating agent | EDTA (ethylene diamine tetra-acetic acid) PH control by addition of acid HEDP (1-hydroxyethylidine-1, 1-bisphonic acid) |
| Particulate | Dispersant or coagulator (for settling) | EDTA, various polymers |
| Corrosion | Inhibitor or surface filming | Orthophosphates, Polyphosphates, Azoles |



(b) Chemical treatment

II. Hydrocarbon streams

(by A. P. Watkinson)

(i) Introduction

Hydrocarbon process fouling involves either the presence of insoluble impurities such as corrosion products, coke particles or water droplets in the fluid to be heated, or the production of new species by chemical or physical processes during heating, which then become insoluble in the remainder of the hydrocarbon fluid. For polymerization fouling, insolubility may result from an increase in chain length. In autoxidation-induced fouling, the highly polar nature of the gums formed leads to their insolubility in the parent fluid. In the case of asphaltene deposition in oil systems, the lack of sufficient peptizers due to changes in temperature, pressure or composition leads to phase separation. In the case of thermal decomposition reactions of heavy hydrocarbon molecules, reactions in which side groups are stripped off lead to formation of asphaltene cores which have a solubility limit, and precipitate leading to coke formation. At sufficiently high temperatures, coking of light hydrocarbons occurs through series of free radical reactions. The unifying link in all of these fouling situations is the formation of insoluble species by either chemical or physical processes. The insoluble species may form on the exchanger surface, or if formed in the fluid, attach to the surface either directly or after some agglomeration steps. The effectiveness of chemical treatments lies in the ability of the additives to either interfere in the formation of the insoluble species, or to prevent the agglomeration steps by which the incipient fouling material forms substantial deposits, or to prevent the attachment of the agglomerated foulant to the surface. Attachment prevention of organic foulants can also be effective in minimizing fouling by inert insoluble impurities such as suspended corrosion products, fine clays or catalyst particles.

(ii) Minimization of undesired reactions

Autoxidation-induced fouling, in either liquid or gaseous systems, occurs by a chain reaction possibly initiated by metal ions, and proceeding via propagation steps in which perhydroxy radicals undergo abstraction and addition reactions ultimately leading to polymeric peroxides gums. Metal deactivating additives can act by chelating metal species, preventing their catalysis of the initiation reactions. Alternately, anti-oxidants such as hindered phenols or aromatic amines may be used to interrupt the chain reactions in the propagation stage. The formation of fouling precursors is prevented by

converting hydroperoxides to stable products, or by scavenging peroxy radicals and forming species that cannot take part in further chain reactions. In [13], the action of a commercial anti-oxidant, BHT (di tert butyl 4 methyl phenol), was studied in the inhibition of heat exchanger fouling. Indene dissolved in a carrier fluid was continuously oxygenated as the fluid was recirculated around a lab heat transfer loop. The BHT prevented fouling until it was all consumed, after which fouling proceeded at the uninhibited rate. Others [14,15] have reported similar delays in the onset of fouling of jet fuels with inhibitors present. At high concentrations or at elevated temperatures, the inhibitor may itself contribute to fouling [13,15], thus there is a ceiling temperature above which a given inhibitor should not be used.

As in autoxidation fouling, in polymerization fouling where chain reactions occur which do not necessarily involve oxygen, a similar approach is used. Treatment includes additives that deactivate metals to prevent initiation reactions, and those that scavenge free-radicals such that inert products rather than additional active free radicals are formed.

(iii) Dispersants and surfactants

Surfactants are attracted to the metal surface where they minimize sticking of organic particles. Once a gum or polymeric precursor is formed in the fluid, some agglomeration may be necessary for significant amounts of fouling to occur. Dispersants or detergents, such as alkyl phenolates, sulphonates or succinates can be used to prevent the sticking of fine insoluble particles onto other particles, acting as particle size limiters. Sticking of particles onto the heat exchanger surface is minimized by surfactants and dispersants [16,17]. Dispersants and surfactants do not prevent the precursor from forming, but by adsorbing onto particle surfaces apparently prevent the finely dispersed polymerised species from agglomerating, converting them to stable colloidal dispersions which flow through the system without depositing. Dispersants generally contain polar groups which adsorb on the particle surface, and nonpolar hydrocarbon-soluble groups to effect dispersion by their solublization. They may also be effective for rust or coke particles.

(iv) Anti-foulants

Commercial anti-foulants for both liquid and gaseous hydrocarbon systems, usually contain components in their formulation which cover the above three actions: metal-deactivator, anti-oxidant, and dispersant. A separate corrosion inhibitor may also be present. In ethylene production systems, anti-polymerants are also used to hinder polymerization reactions of specific

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alkenes [18]. Compositions of anti-foulants are usually proprietary, although the patent literature describes large numbers of chemicals that have been developed and tested for fouling minimization. Some examples are given in Table 2. At concentrations of 50-100 ppm, reductions in fouling up to 95 % are reported. Economics of anti-foulant use are described in [16,19]. Evidence of the complexity of action of additives (particularly in blended formulations) is found in the detailed jet fuel stability studies where metal deactivators and anti-oxidants are used together [14,20]. For other fouling systems, the user must rely on reports of laboratory or industrial scale case studies, many of

which either fail to identify the anti-foulant formulation, or lack essential details of dosage rates, or exchanger conditions, or the composition of the hydrocarbon stream [16,19,21]. Unlike the situation for cooling waters, there is no available study comparing a wide range of generic anti-foulants for hydrocarbon systems. Because of the bewildering array of possible chemicals, and their interactions with each other, the hydrocarbon stream, and the exchanger surface, users should contact a supplier when contemplating the use of additives to reduce fouling [22].

 Table 2 Some Anti-foulant Components from the Patent Literature

| Role | Component | Patent or Reference No. |
|--------------------------------|--|-------------------------|
| Anti-oxidant / Anti-polymerant | Hindered phenols, cresols, catechols | Reference 13-15 |
| | | US 5,183,554 |
| | Amines, Thiophenes | US 4,824,601 |
| | Organic Acids | US 4,941,926 |
| | Substituted benzoquinone oximes | US 4,237,326 |
| Metal Deactivator | N,N' Disalicylidene-1-2-propane diamine | Reference. 20 |
| | Alkoxylated Mannich reaction products | US 4,810,354 |
| | Oxamides, Benzimidiazole | |
| | Triazoles and Thiadiazole | US 4,810,397 |
| | compounds | |
| Dispersant | Polyalkyl thiophosphonic acid or ester | US 4,775,458 |
| | Polyalkenyl succinic anhydrides | US 4,483,886 |
| | Alkyl phosphonate phenate sulfide | US 4,927,519 |
| | Bridged alkyl phenates | US 5,821,202 |
| | Di-alkyl hydroxylamine plus organic surfactant | US 4,440,625 |
| Tri-t-butyl phosphate esters | | US 5,593,568 |
| | Di-alkyl metal sulfo-succinates | US 5,169,545, |
| | | UK 2,017,747 |
| | N,N' Di-ethylhydroxylamine | US 4,551,226 |
| | Hydro-carbonaceous sulfonic acids | US 4,902,824 |

(c) Gas-side fouling prevention

(by E. R. Miller)

Given the impact of combustion side fouling on equipment performance and service life, it is prudent to address this issue relative to both design and operation. When properly anticipated, much can be done to minimize the degree of fouling and mitigate its effect. The discussion that follows addresses the main features to be considered in minimizing the impact of gas side fouling. The brackets at the close of each paragraph or section identify the fouling mechanism(s) in question.

I. Design factors

(i) Stream location

Assignment of stream location plays an important role in determining the fouling characteristics of combustion equipment. In most fired equipment, the combustion products are outside the tubes. Waste heat boilers (which are usually unfired) are the exception, placing the flue gas inside the tubes for mechanical reasons.

Combustion gas fouling is usually more severe shell side than tube side because of flow patterns and because



that is where most of the extended surface is located. Tube side extended surface is rare, except in specialty equipment where compactness is required. Theoretically, uniform fouling has a lower impact on extended surface than on prime surface. However, gas side fouling, especially from particulates that are deposited by gravity, seldom is uniform. Upward facing fin/stud gaps fill from the bottom, eventually to the point that the gas no longer has access to the surface. Corrosion fouling related to acid salts or dew point preferentially occurs at the base of the fin/stud where the metal temperature is lowest. [Particulate; Corrosion]

(ii) Burner-to-tube spacing

For each fuel type and burner heat release, there is a recommended minimum spacing between the burner and the nearest tube row. This serves to prevent tube overheating in the area of the flame envelope. [Scaling/Oxidation]

(iii) Firebox volume

Similarly, for each fuel type there is a recommended minimum ratio of firebox volume to heat release. This is to ensure that there is adequate space to contain all flame envelopes without impingement and that all combustibles will be consumed within the firebox. [Scaling/Oxidation; Particulate Formation, i.e., Soot]

(iv) Shock tube rows

To shield the convection section extended surface tubes from the severity of direct firebox radiation combined with high convective flux, it is standard to use two or three rows of bare tubes at the inlet. [Scaling/Oxidation]

(v) Extended surface geometry

In fouling services, it is important to limit the density and height of the extended surface (fin or stud) in the convection section. This serves to minimize the risk of filling the fin or stud gaps with particulate deposits, thus deactivating that surface. [Particulate]

(vi) Convection bank flow distribution

Poor distribution of gas side flow in crossflow convection banks is detrimental to both general performance and fouling. If necessary, multiple plenum distribution points and breaching collection points, should be provided in order to ensure good flow uniformity. [Particulate, Corrosion]

(vii) Tube and extended surface metallurgy

Tube and fin/stud materials should be selected to be compatible with the service conditions. Chrome-molybenum or austenitic steels will usually provide the necessary oxidation resistance should carbon steel tubes not be suitable. Since extended surface must be hotter than the base tube, it is often of higher alloy than the tube material itself. Standard fin materials in the direction of increased oxidation resistance are carbon steel, 11-Chromium steel and Type 304 Stainless Steel. [Scaling/Oxidation; Corrosion]

Corrosion resistant metals could be used to protect against acid salt corrosion and sub-dew point H_2SO_4 corrosion. In process heaters and boilers this is rarely done, however, because the cost of suitable materials is prohibitive. Other treatments are more cost effective. In air preheaters, the story is somewhat different. Since these are low pressure non-code devices, less costly corrosion resistant materials can be used effectively. Regenerative units typically use low chrome steel baskets in the cold end. Recuperative units are available with stainless sheet or pyrex tube cold end sections. [Corrosion]

In commercial and residential HVAC (Heating, Ventilating and Air conditioning) units, sub-dew point design and operation is now standard. For H_2CO_3 protection, the cold end of the heat exchanger is normally stainless. [Corrosion]

(viii) Surface coatings

The concept of applying corrosion and oxidation resistant tube coatings (such as bimetal spraying) has been around for some time. One commercial process that claims to be effective and competitive with upgraded metallurgy is the application of a thin diffusion layer of aluminum. This is then fired to Al_2O_3 , which provides the scaling resistance and protection against certain corrosion processes. [Scaling/Oxidation; Corrosion]

(ix) Convection section flow arrangement

Whether or not the cold end tube surface is below the dew point often depends on the temperature of the incoming process stream. At the sacrifice of some heat recovery, this may be corrected by reversing the convection section process stream to make it co-current, rather than countercurrent. [Corrosion]

(x) APH (air preheater) cold air bypass and tempering air heater

Under winter conditions or extreme turndown, the cold end metal temperature may be below the acid dew



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point. There are two common ways to deal with this. First, a cold air bypass with damper control is usually provided by which a portion of the incoming air can be shunted around the APH thus raising the outlet flue gas temperature. For more severe conditions, a steam heated tempering coil may be needed. [Corrosion]

(xi) Electrostatic precipitators

Process off-gases such as from refinery catalytic cracker regenerators may provide waste heat for steam generation and/or low-level residual fuel value (CO) for recovery in process heaters or boilers. These types of gases often contain appreciable particulate loading of catalyst fines that, although dry and friable, tend to drop out on convection bank extended surfaces. For environmental reasons, the streams must be cleaned up before discharging to the atmosphere. Most often this is accomplished by means of electrostatic precipitators, although bag filters or scrubbers are used in some processes.

The location of the cleanup device is important in terms of equipment cleanliness. Particulate removal upstream of the combustion equipment would be preferable both in the interest of cleanliness and the size of the gas stream to be treated. However, in many cases the political decision dictates that the cleanup takes place immediately before discharge to the atmosphere. [Particulate]

II. Operating factors

(i) Burner maintenance

Poorly maintained burners contribute to gas side fouling in several respects. Where flame pattern is distorted. tube impingement may occur, with accelerated scaling rate. Poor fuel oil atomization, or fuel/air mixing are primary causes of soot formation and unburned hydrocarbons. Burner maintenance programs should be ongoing, and revised according to experience, with the plant on-stream as well as during turnarounds. [Scaling/Oxidation; Particulate]

(ii) Fuel treatment

Fuel selection and the way in which it is prepared are important fouling considerations. Residual oils will be much lower in both solids and sulfur if they come from crude oils that have been desalted. Distillate oils should be essentially metals free and hydrotreated oils should also be sulfur free. Fuel cost, of course, escalates with the degree of treatment. Highly treated oils normally have alternate product values and are used only as backup fuels.

Residual oils whose ash produces low-melting oxides or salts can be treated to raise the melting point by the addition of MgO. This also serves to neutralize the acidity of the particulates and render them less hygroscopic.

Desulfurization significantly improves the fouling characteristics of coal.

Utility (natural) gas is clean and needs no treatment. Byproduct gases are usually desulfurized by amine (or other) scrubbing procedures. Heavy ends that may condense in the fuel line should be avoided, since liquid to a gas burner will cause sooting as well as a number of safety problems. [Particulate: Corrosion]

(d) Fouling mitigation in aqueous systems (by G. F. Hays)

I. Mechanical modifications to maintain cooling water velocity

There are two mechanical modifications, which can be made to reduce the heat duty of a specific heat exchanger while maintaining cooling water velocity. The first is to install a recirculating loop on the cooling waterside, which is controlled by the process outlet temperature and/or pressure. The recirculating loop recycles a portion of the water exiting the heat exchanger back to the inlet. To do so, will require a motive means such as an eductor and a control valve or a variable speed pump. The valve or pump speed control would be adjusted to maintain a constant process outlet temperature or pressure. If lowering the temperature of the process stream is critical and specifically, if excessive cooling is detrimental, then, this is the only means to maintain the water velocity. However, if the heat exchanger is a process cooler and only reason not to cool the process further is a waste of energy, then a process bypass could be used. A process bypass would allow a fraction of the process stream to bypass the heat exchanger and be blended together with the cooled process stream after the heat exchanger. In this case, a control valve on the bypass stream would be controlled by a temperature measurement located down stream from the blending point.

II. Use of thermal bypasses and cooling tower fans to

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increase the propensity of fouling to occur in the throttled heat exchangers. A better means to compensate for the cooler ambient conditions would be to make adjustments to the cooling tower operation thus affecting simultaneously all of the heat exchangers. There are two approaches to adjusting the cooling tower operation - (a) adjust fan speed and, where possible, fan blade pitch, and (b) install a thermal bypass on the hot return to divert a portion of that water into the tower basin. Both adjustments result in an increase in the temperature of the water returning to the process heat exchangers.

III. Chemical treatment

The purpose of chemical treatment is to protect the economic life of heat exchange equipment by inhibiting corrosion and to maximize heat transfer by inhibiting fouling. As previously noted, the water used as a cooling medium is generally a natural water, such as sea water used in once-through cooling or surface, well or treated city water used as makeup to open recirculating cooling water and chilled water systems. In addition to the impurities in the makeup water, all three types of systems are subject to contamination from the processes that they serve. Such contamination may be the result of leaks in the heat exchangers themselves or from heat exchangers which mix the water with the process such as barometric condensers. Open recirculating cooling water systems, which use cooling towers, are also subject to airborne contamination. Foulants such as process contaminants, biomass, suspended matter and the products of various reactions such as corrosion and crystallization concentrate in the cooling water and, without chemical treatment, result in deposition and/or further corrosion.

IV. What is wrong with throttling cooling water flow?

The easiest and quickest means to balance a heat exchange process, which uses cooling water to cool a process stream, is to throttle the cooling water flow. Unfortunately, that is also the action, which is most detrimental to the long-term operation of heat exchangers. Throttling the cooling water flow has the effect of raising the surface temperature of the heat exchanger and, at the same time, reducing shear stress of the water against the heat exchange surface. Both the higher surface temperature and the lower shear stress will increase the propensity for fouling to occur. There are better methods of balancing heat exchangers.

V. Hydraulic balance of the operating cooling water system

The addition of a single heat exchanger into an existing cooling water circuit can upset thermal and hydraulic balance of the existing heat exchangers. The new heat exchanger will require cooling water, which means that the flow through existing heat exchangers will be reduced. At the same time, the amount of cooling water flow available may not be sufficient for the new heat exchanger. Depending on the size, heat duty and location and size of the new heat exchanger, and the number and size of those already installed, the new heat exchanger may have anywhere from a slight to a significant effect on the rest of the system.

VI. Booster pumps

As processes are modified, some heat exchangers may be added and others removed. These changes may upset the thermal and hydraulic balance of an operating cooling water system. Booster pumps may be used to overcome such upsets, without having to replace large sections of the cooling water supply and return lines. Booster pumps may be used to increase the flow through, one or more of the heat exchangers, particularly those at the far end of the cold water supply line or new heat exchangers, which may be installed at elevated locations. Booster pumps should be sized to provide sufficient flow of cooling water to the heat exchanger which they serve, without reducing the flow to other heat exchangers on the same cooling loop.

VII. Process/energy balance

One common practice in the effort to minimize capital expenditure, has been to design a process industry facility with a single cooling tower servicing two or more parallel trains, or two or more production units. While this saves on capital, it adds to process complexity. For example, process contamination entering the cooling water system from a single train or unit, has an adverse effect on all the units serviced by that cooling water system. Another complexity arises when one of the trains or production units is taken out of service. The reduction in heat load and, in the case of a maintenance turnaround, the cooling water flow rate, can, and usually does, upset the balance for all of the units remaining on that cooling water loop.

Another effect is the change in ambient conditions - day to night and season to season. Generally, cooling systems are designed to provide the required amount of cooling in the afternoon on the hottest summer days normally expected at that site. Which means, that on a cool evening or in the dead of winter, the cooling system is capable of rejecting too much heat. If the

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process is adversely affected by colder cooling water, the cooling system operation must be modified - fan speeds reduced or thermal bypasses installed - in order to balance the process.

VIII. Relationship of temperature and residence time:

As noted above, heat exchangers operating in cooling water service are susceptible to various forms of fouling. Two key parameters which may be used to predict the fouling tendencies of all heat exchangers operating in a single cooling loop are the residence time of the cooling water in a heat exchanger and the surface temperature at the outlet of the heat exchanger. For ease of evaluation, these two parameters may be combined into the Hydrothermal Stress Coefficient (HTSC) using the following relationship:

HTSC =
$$(T_s \times t_R) / 1000 (T_s \text{ in } ^\circ\text{F}) \text{ or}$$

HTSC = $((T_s \times 1.8 + 32) \times t_R) / 1000 (T_s \text{ in } ^\circ\text{C})$

Where.

 T_s = temperature of the heat exchange surface at the outlet (°F or °C)

 t_R = residence time of the water in the heat exchanger (seconds)

1000 = conversion factor (°F - seconds)

If the HTSC is greater than 2.0 then there is a probability that there will be some type of fouling. The higher the HTSC, the greater the fouling problem. The type of fouling is a function of the outlet temperature as follows:

- For outlet temperatures below 80 °F, a combination of biofouling and cold water scale deposits
- for outlet temperatures between 80 and 115 °F, biofouling; for outlet temperatures between 115 and 125 °F, otherwise a combination of biofouling and hardness deposits;
- for outlet temperatures above 125 °F, hardness deposits.

All the heat exchangers operating on a single cooling water loop, should be evaluated at the same time in order to eliminated the role of water chemistry.

The HTSC may be used to predict changes in fouling which may occur should the cooling water flow through the heat exchanger be throttled to control the

process temperature. Throttling will increase residence time, surface temperature and outlet temperature. Thus, it will increase both the HTSC and drive the fouling toward hardness deposits. In applications where excessive cooling of a product must be avoided, cooling water recirculating loops are the preferred method for controlling cooling water temperature and limiting process cooling, particularly where the ambient temperature may vary widely with the seasons. A recirculating cooling water loop passes a portion of the heat exchanger outlet water back into the inlet. Such a system may be controlled by an independent process control loop based on the outlet process temperature, which may control either a valve or the speed of a pump, to recirculate the water and overcome the pressure difference between inlet and outlet streams. Other mechanical means, which may be employed to limit the cooling, are partial process and thermal bypasses installed around the cooling tower.

IX. Hydraulic balance of the operating cooling water system

Processes, which utilize open recirculating cooling water systems for cooling, normally have multiple heat exchangers cooled by the same water system. Initially, when a process is designed, one of the design criteria is to assure that each heat exchanger has sufficient water flow to provide at least the design cooling capacity. Today, there are several commercially available software programs to assist the designer in completing a balanced design of the entire cooling water system.

When the process goes into operation, process engineers are constantly in search of means to improve process efficiencies. This may involve adjustments to process streams, which may require one or more additional heat exchangers to operate on the same cooling water system. The cooling water system capacity, line sizing and location of the new heat exchanger(s) with respect to the existing ones, must all be considered to ensure that the addition(s) will have enough flow and, at the same time, not disrupt the cooling system balance. Thus, a thorough analysis of the existing system balance should be completed as well as an analysis of the proposed addition(s) should be conducted prior to the modification. Analysis of the existing system should be done based on actual operating data taken during periods of high loads and high ambient temperatures, not on the original design.

X. Coatings

One means of preventing corrosion in heat exchanger water boxes is to cover the exposed water box surfaces with a corrosion resistant coating. Such techniques are

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widely used. If the surfaces are properly prepared and the coating expertly applied, such coatings will reduce both in-situ corrosion and the amount of corrosion products, which migrate through the cooling system adding to the mass of foulants which may deposit elsewhere in the system. In order to work effectively, the coating must be uniform and cover 100% of the exposed surface. Any voids will accelerate localized corrosion. Failure to provide a 100% effective bond between the coating and the surface may cause the coating to rupture in operation. Also, coatings may be subject to damage from debris, which enters the heat exchanger from the cooling water system. In all three instances, the accelerated corrosion rate will release corrosion products into the cooling water, thus increasing the concentration of foulants in the circulating cooling water and increasing the rate of agglomeration of foulants.

XI. Sacrificial anodes

Sacrificial anodes have been used to inhibit corrosion in operating heat exchangers, particularly those, which operate on seawater. Anodes may be made of either zinc or magnesium. While they do retard corrosion, they do so by sacrificially releasing the zinc or magnesium into the circulating water. In the process, they are slowly consumed. Depending on the water chemistry, particularly the pH, hardness salts and phosphate ions, either material may react and precipitate in the cooling water system.

XII. Environmental impact

Windage and drift emitted by cooling towers include impurities, which may have an undesirable impact on the environment. The same is true for circulating waters discharged through blowdown or bleedoff. Treatment chemistries may be designed to minimize their impact on the environment, in compliance with government regulations. However, the fluids on the process side of the heat exchangers are a function of the process. Thus it is very important and, at times, critical that process contamination be minimized or, better yet, totally prevented, for any process material that enters the cooling water may be expected to be released to the environment at some time. (See Section 3.17.5 for a complete discussion of the environmental impact of fouling.)

B. Cleaning of Heat Exchangers

(a) Cleaning of Heat Exchangers that Handle Liquids

(by D. I. Wilson)

I. Introduction

If fouling mitigation methods such as those described in Section 3.17.8.A are not effective, the heat exchanger will need to be cleaned. On-line cleaning methods, whereby deposit is removed without interrupting the process, have been discussed in 3.17.8.A.(b). This section will focus on liquid-side cleaning operations that require the exchanger to be taken out of service. Section 3.17.8.B.(b) is a discussion of the particular problem of cleaning heat exchangers subject to gas side fouling.

Methods for cleaning off-line, usually feature some form of mechanical action, which may be augmented by chemical treatment of the deposit. Techniques for cleaning exchangers in situ, often termed cleaning-in-place (CIP) methods, involve circulation of cleaning chemicals that react with, or promote the dissolution of, the deposits. Selection of an appropriate cleaning method is dictated by the following:

(i) Deposit nature

The chemical composition, hardness, homogeneity, thickness and environmental impact of a deposit will determine which cleaning methods are appropriate. It is therefore essential to obtain samples of deposit, or consider the likely nature of a deposit, in planning cleaning operations.

(ii) Type of heat exchanger

Some deposits require cleaning methods that are incompatible with certain exchanger designs, and some types of heat exchanger are very difficult to clean. The nature of deposit likely to be generated in an exchanger will therefore restrict the choice of possible exchanger types. The material of construction will also restrict the choice of possible cleaning methods or chemicals.

(iii) Frequency of cleaning

Cleaning methods that require disassembly of a heat exchanger, e.g. removing a tube bundle, are not appropriate for applications where cleaning occurs on a regular basis after short operating periods, unless standby units are available.

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(iv) Extent and efficiency of cleaning

The process may require 'physical cleanliness', such that thermal performance and pressure drop are restored. Some applications require surfaces to left in a condition of chemical or biological cleanliness. Food and bio-process applications frequently require cleaning to standards set by sterility or hygiene considerations.

(v) Cost

The process-related costs of taking an exchanger offline are often much larger than the cost of cleaning the exchanger. Similarly, the cost of preparing an exchanger for cleaning can be greater than the cost of cleaning chemicals etc.

II. Cleaning off-line

These techniques require the exchanger to be taken out of service. Most off-line cleaning techniques employ mechanical methods to break down the structural integrity of the deposit and are labor intensive. Mechanical methods may be augmented by chemical or thermal treatment in order to render the deposit suitable for cleaning. Several of the on-line cleaning methods described in Section 3.17.8.A.(a), particularly soot blowing, acoustics, shot impingement and water washing are also used for cleaning off-line.

Table 3 gives a summary of frequently used mechanical cleaning methods. Water jets, augmented by brushes or abrasive particles (e.g. sand), are used extensively. Most of the methods in the table require the exchanger to be disassembled so that the cleaning equipment can access the fouled areas. This will have implications for exchanger construction methods, layout and safety. If it is expected that the shell side of a shell and tube unit will require cleaning, it is necessary to use a square-pitch tube layout.

The choice of an appropriate mechanical method is determined by the hardness of the deposit and the hardness of the exchanger materials. Since most mechanical methods rely on abrasive action, there is always a risk of surface erosion during cleaning so an appropriate corrosion allowance should be used and tube thicknesses etc. should be monitored. Abrasive methods can also remove protective passivating layers and damage refractories. Mechanical cleaning is sometimes followed by water or chemical rinsing, treatment with passivating chemicals and/or drying before returning the unit into service.

Non-mechanical methods also used include thermal shock and steam soaking, used to spall off brittle deposits and biofilms, and controlled combustion of hydrocarbon foulants. Care must be taken with such insitu methods that the deposit removed does not

accumulate elsewhere in the system, or cause blockages downstream.

III. Chemical cleaning

These methods feature the exposure of deposits to chemical reagents which either react with the deposit or cause it to be dissolved in the cleaning fluid. Chemical cleaning methods may be augmented by mechanical action (e.g. brushing) and frequently require heating in order to improve the cleaning rate. French [23] presented a good discussion of chemical cleaning, including several case studies. The advantages of chemical cleaning are

- 1. It is relatively rapid
- 2. It is effective, particularly where tailored cleaning formulations are used.
- 3. Heat transfer surfaces are not damaged mechanically
- 4. Both heat transfer surfaces can be cleaned simultaneously.
- 5. The cleaning fluids usually reach otherwise inaccessible areas.
- 6. It is less labor intensive than mechanical cleaning (but can be more capital intensive).
- 7. Cleaning can be performed in situ. CIP is practised widely in boiler systems [23], furnaces and the food industry [24,25].

The disadvantages of chemical cleaning are

- 1. Cost of cleaning chemicals.
- 2. Potential corrosion of surfaces caused by aggressive chemicals.
- 3. Difficulty in guaranteeing complete cleaning.
- 4. Environmental impact and disposal of spent chemicals.

Certain types of deposit are not normally removed by chemical cleaning. These include glasses, inert polymers, ceramics, vulcanised and latex rubber.

A specialized case of chemical cleaning is the thermal decoking of the inside of furnace tubes. The tubes are isolated, purged of air and hydrocarbons using steam, and then heated to furnace temperatures with steam inside. After a period whereby the steam has spalled coke off, air is introduced to burn off the remaining coke. Wall temperatures have to be monitored throughout the process in order to avoid hot spots or loss of tube integrity.

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Table 3 Types of Off-line Mechanical Cleaning

| Method | Examples of deposits | Features | Requirements |
|--|--|--|---|
| Chipping | Hard water scales | Labour intensive | • |
| High pressure water jetting Hydroblasting | Dust and grit Biological growth Mud Heavy organic deposits | Augmented by brushes or abrasive solids Erosion | Clean water required Surface abrasion Requires working space |
| Shot cleaning and sandblasting – abrasive solid cleaning Nutshell blasting | | Erosion | Little solvent waste Dust hazards |
| Water/steam lance | Waxes | | |
| Drilling Brushes and scrapers Blow guns – brushes and plugs Rodding and bulleting of tubes | Boiler scale inside tubes Silicates | Labour intensive | Requires straight tubes or ducts |
| Explosive | Boiler scale | Very hard deposits | Strong tubes; safe area Heating utility |
| Steam soaking | Steam raising units Biofouling | Can damage equipment | Steam supply |
| Thermal Shock | Boiler scale, biofilms | Brittle or thermally sensitive deposits | Temperature control |
| Air bumping | Soft shell side deposits | Cleaning shell side deposits | |
| Ultrasound | | Limited use in heat exchanger cleaning | Short range; difficult to incorporate into large exchangers |

Most cases of chemical cleaning feature the circulation of cleaning liquids through the exchanger; heating may also be required. Circulation is essential to ensure that the chemicals are well mixed, to avoid dead zones and prevent re-deposition of entrained material. Circulation velocities are usually in the range 0.3-1.5 m/s and are provided by pumping or gas injection. Most operations involve several stages, separated by rinsing steps. A typical sequence would feature an initial rinse to remove process fluid and debris, followed by a number of cleaning steps, surface reconditioning

steps and a final rinse. Adequate drainage and provision of rinse water etc. are therefore essential.

Table 4 shows a selection of cleaning chemicals in common usage. Typical cleaning formulations contain wetting agents; active agents, detergents and emulsifiers for breaking down deposits; antifoaming agents; stabilizers; and dispersants to ensure that deposit, once removed, does not precipitate elsewhere in the system. Cleaning chemicals are frequently corrosive so most formulations contain anti-corrosion inhibitors, and may also require the surface to be treated immediately afterwards by passivating oxidants such as nitric acid.



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 Table 4 Summary of common chemical cleaning reagents

| Cleaning Reagents | Types of deposit | Comments |
|---|---|--|
| Kerosene, chlorinated and aromatic hydrocarbon solvents | Degreasing of oils, grease, fats, waxes, solvents etc. | |
| Trisodium orthophosphate, sodium metasilicate, sodium hydroxide | Light oils, degreasing | |
| Surfactants | Fats, waxes | Emulsification of fats |
| Alkaline solutions of potassium permanganate | Coke/carbon | |
| Inhibited hydrochloric, sulphuric, phosphoric acids | Removal of alkaline scales and metal oxides from mild steel | Calcium carbonate, sulphat phosphate; magnesium hydroxide, iron oxides, coppo oxides, nickel oxide. |
| Inhibited hydrochloric acid containing fluoride, hydrofluoric acid | Removal of silicates from carbon steels | |
| Inhibited citric, formic, sulfamic, phosphonic acids | Removal of alkaline scales and oxides | Use on austenitic, high allo steels, aluminium and coppe Biodegradable. |
| Ammoniated citric acid/sodium bromate | Copper plated out by HCl | post acid treatment |
| EDTA, gluconates, polyphosphates, NTA and MGDA salts | Alkaline scales, salts | Sequestrants. Gluconates are biodegradable |
| Alkaline sodium nitrite solution Hydrazine/ammonia Solution Nitric acid | | Passivation of metal surface |
| Sodium hydroxide | Food and biofilms | Dissolves proteins |
| Polyphosphates | Organics, food | Suspending agents |
| Enzyme cleaners | Food, biofilms | Expensive, often slow, requineutral pH and heating |
| Potassium permanganate, sodium bromate, sodium hypochlorite, ammonium persulphate | Oxidants – biocides, passivation | Hypochlorite can be used to degrade proteins |
| Ozone solutions | Biofilms | Oxidant, sterilising agent |



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Strong acids such as HCl also dissolve copper, which subsequently deposits on carbon steel surfaces. Postacid cleaning with ammoniated citric acid solutions is used to remove these plated copper layers.

The rate of cleaning frequently varies with time, as the chemicals may need to be absorbed and/or react with the deposit before significant removal occurs. Selection of appropriate cleaning reagents and operating conditions will thus require information on the composition and nature of the deposit, and the likely cleaning mechanism. The appropriate concentration of reagent will depend on (1) corrosive action; (2) the minimum value required to remove all deposit and keep it in solution; (3) temperature; and (4) deposit/detergent chemistry, particularly for organic deposits. A notable example is the use of NaOH-based solutions for cleaning dairy protein deposits [25]. In this case, the proteins swell on contact with the alkali and the nature of the gel formed determines the rate of cleaning, giving rise to an optimal concentration for cleaning. The alkali does not remove calcium phosphate scale present in the deposit, so the alkali wash is either followed by an acid stage (two stage cleaning), or accompanied by sequestrants (mixed action formulations). Low temperature cleaning usually requires prolonged cleaning times, whereas high temperature cleaning requires an energy input and can cause corrosion damage. Further information about cleaning mechanisms and chemical formulation can be found in references [24-27].

Most CIP systems employ appropriate sensors to track the extent of cleaning. For example, monitoring conductivity, pH, free acid and inhibitor concentrations is recommended during boiler de-scaling. Pressure drop recovery and thermal measurements can be used to establish 'physical cleanliness', but these measurements are not sensitive enough to characterize surfaces as clean for biological or sterility purposes. Flow maldistribution in the exchanger, which gives rise to severe fouling, also renders those slow to clean. Stagnant zones are particularly difficult to clean as the transport of chemicals and solubilised deposit is then limited by diffusion.

Biofouling is frequently controlled on-line by periodic dosing of the water stream with biocides such as chlorine and hypochlorite, biodispersants, complexing agents or oxidants such as ozone. Biocides and oxidants kill the biological growth, causing detachment of significant fractions of the biofilm, but do not remove it completely. The remaining biofilm can re-establish itself so biocide methods are effectively used to control film growth. Complete biofilm removal can be achieved using food cleaning agents based on sodium hydroxide, which dissolve the proteins present. Biofilm cleaning and control is discussed by Bott [27]. Enzyme cleaning agents are available but are rarely

used on a large scale owing to their relatively high cost. Biofilms may also be disrupted by osmotic shock, where a saline environment is temporarily replaced by fresh water (and vice versa). This is only feasible where the alternate water supply is available and switching would not accelerate corrosion.

The disposal of spent cleaning solutions is becoming increasingly important owing to the environmental impact of the foulant materials and the cleaning chemicals. Reagents such as citric acid and gluconates are biodegradable alternatives for scale removal. There is particular concern over complexing agents such as EDTA, which pass through municipal wastewater treatment plants. Re-use and recovery of cleaning solutions is practiced in some cleaning-in-place installations [25]. The cost and requirements of disposal of cleaning chemicals must be considered where these solutions cannot be recycled into the process or existing waste streams.

IV. Design for cleaning

It should be obvious that cleaning must be considered at the design stage of any exchanger which is likely to experience significant fouling over its lifetime. Some exchanger types are not suitable for handling fluids likely to cause fouling as they are very difficult to clean, whereas fluidized bed and scraped surface heat exchanger units feature continuous cleaning of the heat transfer surfaces in order to give good anti-fouling performance. The nature of the fouling deposit will determine the range of possible cleaning options to be considered, which will in turn dictate which type of exchanger can be used. Table 5 is a summary of the cleaning features of some exchanger types which should be considered at the design stage. Selection of the wrong exchanger type or cleaning method, can prove very expensive, so information on related cases of fouling and cleaning requirements should be sought wherever possible.

The designer must incorporate features required by the chosen cleaning method. The corrosion resistance must contain an allowance for cleaning, and the materials used in the exchanger, gaskets, seals etc. must be compatible with both the operating fluids and the cleaning fluids. There is a large body of literature on materials selection (e.g. [28]); Table 6 shows the compatibility of some common cleaning chemicals and materials of construction. Metal erosion, stress corrosion cracking and hydrogen damage are common metallurgical problems associated with cleaning. Where mechanical cleaning is likely to be used, the layout must include space so that a bundle can be removed, or to allow access to the fouled surfaces. For example, streams that give rise to hard fouling deposits requiring harsh mechanical cleaning conditions, or the

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use of aggressive cleaning chemicals, are usually put on the tube side of shell and tube exchangers. U bends can be very difficult to clean mechanically. Chemical cleaning may require additional nozzles, instrument points, pumps, valves and drains. Most cleaning methods require a supply of good quality water for washing, rinsing or soaking.

Design and operating guidelines for heat exchangers and CIP systems for processes requiring hygienic conditions are published regularly by the European Hygienic Equipment Design Group (EHEDG) [29]. Dead spaces and stagnation zones should be avoided, and all surfaces need to be constructed from non-toxic, non absorbent, corrosion resistant materials. Lines

should be built with a positive slope and should drain completely.

The designer should seek to minimize hazards during cleaning wherever possible; this is particularly important in the nuclear industry. Finally, attention must be given to cleaning the unit in the commissioning stage to remove any debris introduced during construction and installation.

V. Scheduling of cleaning

The need to remove a heat exchanger for cleaning will usually have significant effects on the process. If no alternate capacity is available, a complete plant shutdown may be necessary. This is a costly occurrence

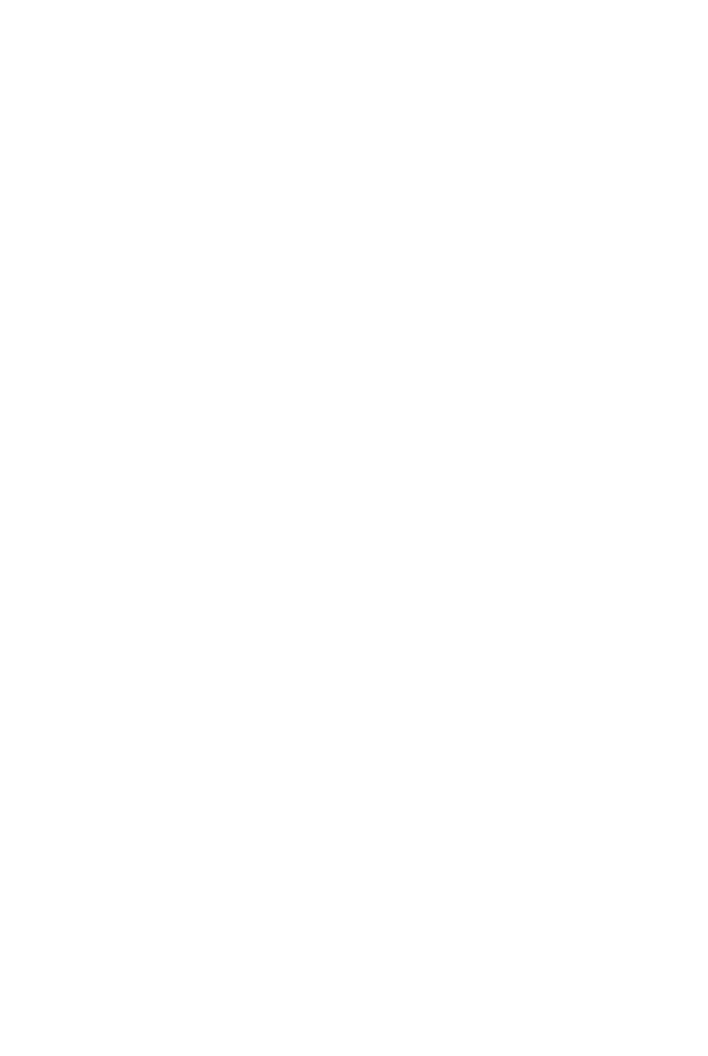
Table 5 Cleaning characteristics of common types of heat exchanger

| Heat Exchanger Type | |
|--------------------------|--|
| Spiral | Not suitable for some mechanical cleaning methods |
| Shell and tube | U-bends pose difficulties for mechanical cleaning |
| | Cleaning tube side deposit is usually easier |
| Teflon heat exchangers | Chemical cleaning only |
| Graphite heat exchangers | Chemical cleaning only. Danger of brittle mechanical failure |
| Scraped surface | Self cleaning; readily cleaned by most methods |
| Plate and frame | Easily disassembled for cleaning; check compatibility of gaskets |
| | with cleaning chemicals |

Table 6 Compatibility of commonly used metals with cleaning reagents

| Material | Compatible cleaning agents |
|--|--|
| ATAMERAAMA | Companior Cicuming agents |
| Carbon steel | Inhibited mineral or organic acids, NaOH, organic solvents, alkalis and sequestrants |
| Austenitic steels | Inhibited HF, HNO ₃ , H2SO ₄ , H ₃ PO ₄ , organic acids, NaOH, sequestrants and non-chlorinated organic solvents. Not HCl. |
| Copper, nickel and their alloys (e.g. brass) | Inhibited sulphuric or organic acids, organic solvents |
| Cast iron | Inhibited mineral or organic acids, organic solvents |
| Chrome/molybdenum steels | Inhibited citric acid, organic solvents. Not HCl |
| Titanium and its alloys | Very resistant to chlorides, caustic and chemical pulping liquors. Inhibited mineral acids. Avoid crevices. |
| Aluminium | Weak acids (citric, sulphamic), organic solvents |
| adapted from Bott [5] | |

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and should be avoided wherever possible. Most industrial plants shut down for periodic maintenance, and heat exchanger cleaning should be planned to coincide with these shutdowns. In cases where rapid fouling causes exchangers to be taken off-line and cleaned regularly, process and economic considerations will determine whether a standby unit should be provided. A number of smaller exchangers is often more robust than two large exchangers in such cases; the actual number will depend on the economics of the design.

Fouling may require a heat exchanger to be cleaned because of reduced thermal efficiency, excessive pressure drop, poor control performance or concern for process sterility and/or hygiene. Oversizing the exchanger at the design stage may allow the unit to operate for longer periods before cleaning is required, but this approach is not advisable where the deposits can undergo aging, rendering them more difficult to clean. (See Section 3.17.6.M)

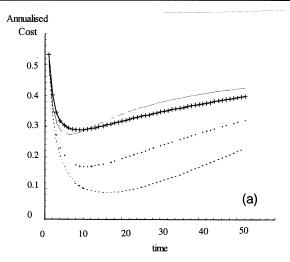
In cases where an exchanger undergoes heavy fouling and requires regular cleaning, consideration should be given to the scheduling of cleaning operations. Where information on the fouling behavior is available, it is possible to perform an economic analysis for the best cleaning schedule, based on minimizing the total fouling cost given by

$$C_{foul}(t) = C_{cleaning} + C_{maintenance}$$

$$+ \int_{0}^{t} C_{extra\ fuel}\ dt + \int_{0}^{t} C_{process\ losses}\ dt \tag{1}$$

The process and energy costs due to fouling are often larger than cleaning and maintenance costs. Figure 1 shows how the annualized cost of cleaning an exchanger varies with the length of the operating period for different types of fouling behavior. The cost calculation here is based on the extra energy required due to fouling. The figure shows that there is an optimum length of operating period for each case. The cost of cleaning is not recovered in short operating periods, while the cost of extended operation increases as the efficiency of the unit continues to decrease.

Detailed descriptions of scheduling calculations and methods are given in references [30-36]. The methods described in [30-33] feature deterministic approaches using a fouling model with known rate parameters to calculate the cost of fouling in equation (1). The probabilistic approach described in [34-36] treats fouling as a time-dependent random process, where uncertainty in fouling behavior is incorporated into the parameters of the fouling model. For example, a heat exchanger exhibiting linear fouling may best be described by a linear fouling model where the rate parameter is normally distributed about a mean value. The likelihood of such an exchanger subject to fouling reaching a certain performance level in a given time is then described by a risk level. Reliability-based cleaning and maintenance strategies can therefore be calculated



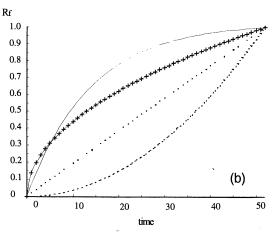


Figure 1 (a) Annualized cleaning cost, based on energy consumption, for a single heat exchanger operating at constant ΔT_h (log mean ΔT) subject to fouling behaviour shown in (b). Downtime = one time unit. Dotted line - linear fouling, $R_f = a_1 t$; solid line, asymptotic fouling, $R_f = a_2 (1 - \exp(-a_3 t))$; crosses, falling rate fouling, where $R_f = a_4 t^{0.5}$; dashed line, accelerating fouling, $R_f = a_5 t^2$ ($R_f =$ fouling resistance, t = time).

for given risk levels. This approach has obvious applications for systems with considerable scatter in fouling rate.

(b) Cleaning of gas-side fouling (by E. R. Miller)

I. Cleaning – on-line

Although elimination of fouling would be most desirable, this end is seldom attainable. Means and procedures have been developed for on-stream cleaning, when fouling must be limited for economic reasons or to avoid aborting run length. These are described below.

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(i) Soot blowing

In convection banks and boiler screen tubes, periodic steam soot blowing is a common way to restore cleanliness. (Soot Blowing is also discussed in Section 3.17.8.A (a) V.). Soot blowing is most effective on dry friable particulate deposits, less so on hygroscopic corrosion products. Ceramic fiber linings should not be used where soot blowing is contemplated.

Two types of soot blower are available, rotary and retractable. Both mount through the furnace or boiler casing into soot blower "cavities," i.e., gaps between adjacent tube rows of 0.5 to 1 m (1.5 to 3 ft). A choice of drive is available: air, steam or electric motor.

A rotary blower has numerous small jets in its lance, which remains in the gas stream at all times. When activated, the steam is turned on and the lance rotated through its cycle. Deposits are removed by jet action, most effectively in the region of the lance.

A retractable blower has just two large jets (opposed) at the tip of the lance. It operates at higher steam pressure than does the rotary. When inactive, the lance lies in a housing outside of the furnace casing. During operation, the lance rotates and advances (then retracts) helically across the width of the tube bank. Compared to rotary units, I have found retractable blowers more effective and more reliable. They are also more expensive and require deeper cavities.

(ii) Water Washing

Since the 1950's, water washing has proven a successful cleaning technique for some convection bank fouling deposits. (Water washing is also discussed in Section 3.17.8.A. (a) VIII.) Water sprays work best on soluble deposits but are also effective on loose insoluble particulates that can be flushed out. The cleaning action of water can be described as a combination of dissolving, flushing and fracturing by thermal shock. Jetting is not considered essential in this process.

The system consists of fixed spray nozzles located in the soot blower cavities and directed both up and down. Full core square pattern nozzles are used to give most effective coverage. The refractory walls are lined with 11-Chromium sheet metal for protection from water damage and water patterns are arranged so as to avoid direct impingement on intermediate tube supports. Spray densities of 2.0-3.4 kg/m² s (3-5 GPM per sq. ft. of cross section) are typical. Tolerance of the process to upset will fix the total water rate. As a guideline, the latent heat of the wash water should not exceed about 1/3 of the furnace heat release. If necessary, the system can be divided into multiple manifolds in order to meet that constraint. Firing controls should be placed on manual and the draft increased in preparation for the wash cycle.

Several words of caution need to be mentioned about on-stream water washing based upon my experience. Upon metallurgical examination after many cycles, some tubes were found to show early signs of thermal fatigue failure. Awareness of this should be built into the inspection program. Also, loose and friable particulates that are not completely removed may tend to cake, rendering them more difficult to remove by further washing or soot blowing. Applications of water wash systems to hardenable alloy tubes operating at high wall temperatures should be avoided unless constraints can be imposed to limit the thermal shock. For washing austenitic steel tubes, chloride-free water containing about 2% by weight of low chloride soda ash should be used to minimize the risk of stress cracking by chlorides or polythionic acids.

(iii) Vibration and Sonic Cleaning

Sonic cleaning has been successfully applied for many years in the dislodgment of dry and friable particulates mostly in water wall boilers and electrostatic precipitators. Horns are strategically placed so as to resonate throughout the system. It is my understanding that the horns do have temperature constraints that define their limits of application. Sonic cleaning must be applied with caution in refractory lined settings to avoid refractory damage.

Efforts to dislodge deposits by mechanical vibration have not generally been successful because of the high mass that must be accelerated. In addition, the risk of damage to refractory and other components is perceptible.

(iv) Erosives

Injection of erosive materials on an intermittent basis for cleaning has been used in some processes. Erosives in the general sense are broadly defined to include sand, crushed walnut hulls, steel shot, pellets and balls. Propulsion may be by entrainment in the gas stream or by gravity.

Applications are quite limited. For example, radiant sections and extended surface tube banks are not good candidates. In the former, it is difficult to achieve sufficient impact velocity to do much good. In the latter, the smaller gas borne erosives are more likely to add to the fouling rather than to reduce it, while the larger gravity dominated agents cannot reach the fouled surfaces

In-tube cleaning with gas carried erosive has found use in vertical and horizontal equipment, while the denser media are best suited for vertical in-tube units or horizontal shell side (bare) units. Inert materials that are injected must be recovered at the outlet, while (in

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hot services) walnut hulls might be expected to burn up enroute.

II. Cleaning off-line

When equipment is off-line for inspection and maintenance, cleaning is an essential activity for restoring lost performance. Common cleaning procedures for fouled combustion equipment include the following.

(i) Abrasive blasting

Blasting with sand, grit or other erosives is a standard way of cleaning radiant tubes. Care must be exercised to protect the tubes from metal loss. For single-fired tubes in refractory lined settings, protection for the refractory is usually provided. It is also important to keep the abrasives from reaching a refractory floor. At operating temperatures, sand is likely to flux the refractory, or buckle the floor if allowed to penetrate any cracks.

Abrasive blasting can also be used for in-tube cleaning. For convection bank extended surface fouling that responds to no other procedure, it may be necessary to remove the tubes for individual blasting.

(ii) Water washing

Water washing can be a very effective cleaning procedure for almost all combustion heat transfer surfaces. (Water washing is also discussed in Section 3.17.8.A. (a) VIII.) Most of the sulfur related deposits are water soluble, and much of the insoluble particulates can be flushed away. For these materials, water quantity, rather than pressure, is the important parameter. A 1-1/2 in. fire hose with a fog nozzle can do a marvelous job. The floor (and any other up-facing refractory surfaces) should be covered with plastic sheet to collect the water and route it out of the setting. This will keep the washed deposits out of the refractory. Vertical walls may or may not be protected, according to preference. Thoroughly cured hard refractory will not suffer significant damage provided a suitable dryout is taken. To minimize the time exposure of metal components such as tiebacks and casing, washing should be deferred until just before startup. Tubes in ceramic fiber lined settings should be washed only if the linings can be kept dry.

Deposits that are not soluble or flushable may be removed by hydroblasting. For external tube surfaces, this is a labor-intensive process usually reserved for localized deposits. For internal tube surfaces, hydroblasting is probably the preferred general cleaning method. It must be remembered that hydroblasting is a high-pressure operation that involves increased risk to personnel. In confined quarters, such as convection banks, taking this risk is usually considered unacceptable.

(iii) Air lancing

Depending on the nature of the deposits and possible restrictions on the use of other cleaning materials, air lancing may be the method of choice. Use of protective personnel gear is usually required.

(iv) Vacuum cleaning

Vacuuming is an alternate to air lancing. Although not capable of directing as much energy to a localized area, it has the advantages of being less offensive to personnel and less likely to redistribute the deposits on cleaned surfaces.

(v) Mechanical methods

An assortment of mechanical methods has been used for cleaning the fireside of combustion equipment. This includes such things as hand scraping for external surfaces and power brushing for inside tubes. For the hard-to-reach back side of single fired tubes (against a wall), a piece of chicken wire has often proven effective. Chicken wire may also be used to remove orange-peeled scale. Firmly attached unbroken scale is usually left undisturbed.

(vi) Explosive devices

A relatively new technology is the use of controlled explosions that are above the energy required to remove the deposit [37]. It may be applied to superheaters, reheaters, and economizers. The equipment treated must be of a non-brittle nature. Among the advantages claimed for the method are: rapid cleaning, improved safety and no corrosion problems. Risks to the integrity of the plant must be recognized and it is imperative that a company specializing in the technology be engaged to conduct the work.

III. Fuel trends

For environmental and economic reasons, much has changed in the last three decades, or so, with respect to fuel quality, particularly in the developed nations. Prior to that time, high sulfur, high ash residual oil was a common industrial fuel. By-product fuel gases (the mainstay refinery diet) were largely untreated. containing high sulfur and (possibly) ammonia levels. And coal was burned as it came out of the ground.

Now, there are ever tightening emission controls on particulates, opacity, unburned hydrocarbons, H₂S, SO₂,



3.17.8-22 3.17 FOULING IN

CO, NH₃ and NO_x. The fallout significant. Residual fuel oil burn States has been reduced to a trickle. like vacuum flashing, cracking hydroprocessing have allowed upgrading of this material to gas By-product fuel gases have been utility gas quality. These and natu most of the fuel gap. Coal desult

cost of fouling, e.g cost of cleaning, e. cost of maintenance $C_{\it extra fuel}$ cost of extra fuel, $C_{process\ losses}$ cost of process loss time, s

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| HEAT EXCHANGER | S / 3.17.8 Fouling Mitigation and Heat Exchanger Cleaning | | |
| therefrom has been rning in the United Refining processes ing, coking and conversion and soline and jet fuel. cleaned up to near ural gas have filled furization processes | have improved the quality of solid fuels still used by public utilities and industry. Where the cleanup has taken place upstream (i.e., fuel vs. flue gas), the heat transfer equipment has become the direct beneficiary in terms of improved performance and reliability. Already there are many that don't remember, or never knew what combustion side fouling "used to be like!" | | |
| NOMENO | CLATURE | | |
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