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**ARGENTINE - U.S.A.
WORKSHOP ON BIODETERIORATION
(CONICET-NSF)
April 21-27, 1985 La Plata, Argentina**

A bilateral workshop on Biodeterioration with special emphasis on microbiologically influenced corrosion has been held at the Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA) in La Plata, Argentina, within the cooperation program between the National Science Foundation (NSF) and the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET). The objective of the workshop was to create a channel for exchange of information on the basic and applied aspects of Biodeterioration between scientists from the United States and Argentina. Particular attention has been paid to basic aspects on the mechanisms on microbiological corrosion and biofilm formation, biodeterioration problems in Argentine and United States industries, its influence on biomedical implant materials and finally to a discussion of control and prevention methods.

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INFLUENCE OF MICROBIAL FILMS ON INDUSTRIAL PROCESSES

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THE OBJECTIVE OF THIS PAPER

The objective of this paper is to offer a unified, systematic framework for dealing with all problems of fouling deposition in any environment. The approach presented is necessarily quite fundamental and will entail classification and description of contributing processes, influence of important process variables, and presentation of expressions describing the various process rates. The final result will be a [mathematical] model describing the fouling process. The intent of the paper is to provide a conceptual basis for analyzing fouling problems in a rational way. Any presentation of mathematical model development will be restricted although illustrations developed from the mathematical model will be used throughout the paper.

THE OPERATING PLANT ENVIRONMENT

An industrial (power or process) plant contains numerous environments where corrosion and fouling processes are potentially troublesome including cooling water systems (recirculating and once-through), storage tanks, water and wastewater treatment facilities, and piping. Fouling and corrosion have been reportedly found in turbulent flows and stagnant waters, on smooth surfaces and crevices, and on metals and concrete (Figure 1).

Corrosion is one of the costly results of fouling in addition to energy losses resulting from increased heat transfer resistance and frictional resistance. In the plant, biofouling frequently occurs in conjunction with other types of fouling including crystalline or precipitation fouling (e.g. scaling) and particulate fouling (frequently due to sedimentation). Figure 2 schematically illustrates processes occurring in a hypothetical water conduit and depicts processes occurring in the bulk water phase as well as transformations occurring at the liquid-solid interface. The diagram also depicts "under-deposit" corrosion that is frequently reported in relation to many types of deposit.

Microbial activity has been found in calcareous deposits and in deposits of particulate material resulting from sedimentation or adsorption. Increased corrosion rates are frequently reported in these circumstances.

A recirculating cooling tower system (Figure 3) provides an illustration of a plant environment in which fouling and corrosion can occur. The fill material is generally wooden and its "corrosion" rate is generally controlled by microbial degradation (fungi) or measures to control microbial activity (chlorine). In the heat exchanger, scaling (under certain conditions) and microbial film development on the tubes and areas around flow obstructions can increase heat transfer resistance and [metal] corrosion rates.

FOULING. A DEFINITION

Fouling refers to the formation of deposits on equipment surfaces which significantly decreases equipment performance and/or the useful life of the equipment.

TYPES OF FOULING DEPOSITS

Several types of fouling, and their combinations, may occur and have been

conveniently classified¹:

1. biological fouling: the attachment and metabolism of macroorganisms (macrobial fouling) and/or microorganisms (microbial fouling)
2. chemical reaction fouling: deposits formed by chemical reaction in which the surface material (e.g. condenser tube) is not a reactant. Polymerization of petroleum refinery feedstocks is an important example of type fouling
3. corrosion fouling: the surface material itself reacts with compounds in the liquid phase to produce a deposit or degrade the surface material
4. freezing fouling: solidification of a liquid or some of its higher melting point constituents on a cooled surface
5. particulate fouling: accumulation on the equipment surface of finely divided solids suspended in the process fluid. Sedimentation fouling is an appropriate term if gravity is the primary mechanism for deposition
6. precipitation fouling: precipitation of dissolved substances on the equipment surface. This process is termed scaling if the dissolved substances have inverse temperature solubility characteristics (e.g. CaCO_3) and the precipitation occurs on a superheated surface.

In most operating plant environments, more than one type of fouling will be occurring simultaneously. For example, microbial fouling is not limited to processes related to biological activity. The term may also include the interaction of the microorganism and the associated slime layer with both the chemistry of the equipment surface and the bulk fluid. The interaction can enhance some of the more commonly observed phenomena such as particulate, sedimentation, and corrosion fouling.

The interactions between the various types of fouling are poorly understood and, consequently, provide a challenge to the water treatment chemist or engineer in terms of diagnosis and treatment.

PROBLEMS CAUSED BY FOULING

The economic consequences of fouling are the essential reason for industrial and research interest in the fouling of heat transfer equipment. To assess the importance of a fouling situation, the economic and energy penalties arising from the operation of heat transfer and process equipment subject to fouling must be considered. The deleterious effects of fouling include the following:

1. energy losses due to increased fluid frictional resistance and increased heat transfer resistance
2. increased capital costs for excess surface area in heat exchange equipment to account for fouling heat transfer resistance
3. increased capital costs for premature replacement of equipment experiencing severe under-deposit corrosion
4. unscheduled turnarounds or downtime, resulting in loss of production, to clean heat exchange equipment which fouled at an unanticipated rate.
5. quality control problems resulting from fouling of heat exchange equipment or fouling of product stream (e.g., sliming of paper mills or rolled steel)
6. safety problems resulting from "leakers" caused by corrosion pits which penetrate the entire tube thickness in heat exchange equipment.

In summary, the anticipated presence of significant fouling can offset the size and other design features of operating equipment. The operation of this equipment subject to fouling is constrained by the need to formulate economically justifiable cleaning schedules.

COST OF FOULING

An estimate of the economic consequences of fouling was presented by Britchard² for fouling in Britain and suggests the cost was between \$600-1,000 million per year (about 0.5% of the British 1976 GNP). Van Nostrand et al.³ have estimated, that for petroleum refining in the non-Communist countries, the total cost of fouling is \$4.4 billion per year. Both these figures are bound to increase with increasing fuel and material costs.

In virtually every type of heat exchange equipment, fouling of heat exchange surfaces is the main cause of any progressive reduction in performance and efficiency. Accumulation of slime, dirt, and debris in other parts of the plant environment rarely causes concern and, perhaps, is the cause for the limited attention focused on fouling in the past. However, the cost of problems related to fouling are significant and must be emphasized to designers and operators of heat exchange equipment.

BENEFITS OF THE RATIONAL APPROACH TO FOULING

"A distinguished German physicist has said -if my memory serves me aright- that it is the office of theoretical investigation to give the form in which results of an experiment may be expressed"

J. Willard Gibbs

"Experience enables one to apply things that one knows; theoretical science enables one to apply things that have never been dreamed of"

Robert H. Goddard

Fouling is a complex phenomenon resulting from several processes occurring in parallel and in series. The rate and extent of these processes, in turn, are influenced by numerous physical, chemical, and biological factors in the immediate environment of the surface. Many laboratory experiments and field observations have resulted in volumes of data without deducing relationships of wide, general use. Much of the historical data available, in addition to future experimental fouling work would benefit from a conceptual framework for describing fouling processes. If the conceptual framework could be stated in mathematical terms, more benefits would accrue including the ability to mathematically simulate fouling processes on the computer... computer "experiments" frequently being cheaper than laboratory experiments.

A rational approach, as contrasted with an empirical approach, develops the conceptual framework by resorting to fundamental processes which are reasonably well understood. These fundamental processes can usually be described mathematically which is necessary for computer simulation. Consequently, such "models" can be used to extrapolate and generalize experimental results.

The difficulty in generalizing or extrapolating experimental fouling data is related to the complexity of the process which frequently involves heat transfer, mass transfer, momentum transfer, as well as physical, chemical, and biological processes at the surfaces. The rational approach attempts to elucidate each of the fundamental processes that contribute to the overall fouling process. Once these fundamental processes are properly understood, they are incorporated into a mathematical model of the overall fouling process. This requires experiments designed

specifically to investigate particular fundamental processes rather than experiments which consider only the overall process. This approach is clearly more time consuming than research which only considers the overall fouling process, but it ultimately leads to results that can be applied with greater confidence to a wider range of fouling situations.

This type of "process analysis" has been described previously by Characklis⁴ for the specific case of microbial fouling. Burrill⁵ presents another illustration of the power of this technique in explaining a practical problem of fouling and the decisions necessary to minimize its effects.

These procedures can also lead to computer simulation "experiments" which can be used to test design concepts such as the influence of metallurgy, shear stress, heat flux, geometry, etc., on fouling processes and their influence on equipment performance. Simulation can also be used to test operating and maintenance procedures such as internal treatments and cleaning schedules. The process analysis technique may also lead to a more systematic method for developing and evaluating fouling control techniques, regardless of whether they employ physical, chemical, or even biological methods. These ideas will be discussed below.

In summary, the rational approach to fouling entails a process analysis which identifies the contributing fundamental processes and determines the influence of process variables on process rate and extent. The approach requires experimental measurement techniques which permit the elucidation of the specific processes.

THE ITERATIVE NATURE OF THE PROCEDURE

Developing a rational understanding of the fouling process is an iterative process. Figure 4 schematically describes some of the interrelationships between four of the important activities within this iterative process:

Cycle 1 - EFFECTS OF FOULING are MEASURED by some appropriate instruments to test the performance of the equipment. The extent of the problem is determined and a FOULING CONTROL PREVENTION TREATMENT is applied. Any change in the EFFECTS OF FOULING are observed and the cycle is repeated.

Cycle 2 - A process analysis is accomplished to determine the RATE AND STOICHIOMETRY of the process from which a model is developed. The influence of treatment procedures on rate and stoichiometry may be critical. The model is tested with a SIMULATION of the real system in which process variables can be carefully controlled. Reformulation or modification of the model may follow.

The overlap between the two cycles is MEASUREMENT AND SIMULATION. Simulating the process environment, in the laboratory or in the field, is critically important to the rational approach and cannot be overemphasized. The usefulness of a model, and its ability to describe reality, is strictly dependent on the accuracy of the data used to develop and test the model.

RATE AND STOICHIOMETRY ANALYSIS OF FOULING PROCESSES

The physical, chemical and biological transformations resulting in fouling deposit accumulation are completed in a certain period of time. For example, some specific change may signal the shutdown of manufacturing operations and the beginning of cleaning operations. The time required for this specified change is inversely proportional to the rate at which the process occurs. Thus, the rate is the most important quantity in process analysis. If the process involves a change of process

ses in series, the slowest step of the sequence exerts the greatest influence and controls the overall process rate. This step is called the "rate-determining process" or "rate-controlling process".

Stoichiometry is the application of the law of conservation of mass and the chemical laws of combining weights to chemical processes. Stoichiometry provides information about extent of reaction, composition, and yields.

Rate and stoichiometry are determined by measuring concentrations of reactants and products. In the case of fouling, the reactions take place in the microenvironment of the surface and interfacial concentrations are extremely difficult to measure. Consequently, rate and stoichiometric relationships must be developed as functions of concentrations in the bulk fluid environment. To do so requires a thorough understanding of the fluid flow regime, the nature of the surface, and, when applicable, the temperature gradient at the wall.

The remainder of this section will discuss the environment in which fouling reactions occur and provide an outline of methods for its description and analysis.

SYSTEM DEFINITION

Figure 5 schematically describes the fouling environment. Important features include the following four "phases":

1. fluid phase
2. suspended particulates
3. solid or semi-solid fouling deposit
4. the substratum

The fluid phase contains dissolved organics and inorganics as well as the suspended particulates. The fouling deposit frequently contains a larger percentage of water (e.g., as much as 80-90% in biofouling deposits) but is still considered a solid phase due to lack of convective fluid motion. The substratum is the equipment surface of concern (e.g., metal condenser tube). In many cases of interest, the fluid phase is in turbulent flow and the substratum is at an elevated (or reduced) temperature from that of the bulk fluid phase.

CONSERVATION EQUATIONS AND CONSTITUTIVE PROPERTIES

Analysis of this relatively complex system requires consideration of mass transfer, momentum transfer (i.e. fluid dynamics), and heat transfer as well as physical, chemical, and biological processes. Required tools include the equations for conservation of momentum, energy and mass which are a result of Newton's laws and the laws of thermodynamics.

Table 1 indicates the intensive variables (i.e., variables independent of system mass or volume) and examples of thermodynamic properties that must be measured to utilize the conservation equations effectively. The intensive variables and thermodynamic properties are relatively easy to measure accurately.

Constitutive principles deal with the rates of physico-chemical processes. Conservation and thermodynamic principles do not deal with mechanism, but constitutive principles do: constitutive principles deal with mechanism as it is influenced by the constitution of matter. Examples of constitutive principles are the laws that govern rates of transport and rates of chemical reactions.

Since conservation principles do not depend on the constitution of matter, a mathematical model expressing a conservation principle is "correct" if all flows, sources, and sinks have been included. The usefulness of the model, however, depends

TABLE 1

Relationship between conservation equations and commonly employed variables and properties.

	<u>Momentum</u>	<u>Energy</u>	<u>Mass</u>
Intensive variable	$\dot{v}$	T	c
Thermodynamic properties	ρ	C_p	K_{eq}
Constitutive properties			
- transport	v	α	D
- chemical reaction	•	•	$K_1 A_i$
- microbial reaction	•	•	μ_{max}, K_s, Y

primarily on two things:

1. The choice of the system
2. Availability of constitutive principles for description of unknown quantities which appear in the model (e.g. reaction rates)

Mechanisms and constitutions are often poorly understood. Therefore, constitutive relations present the most difficulty in modelling. Transport coefficients (Table 1), for example, are difficult to measure and accuracy is generally poor, yet, transport coefficients are essential to determining rates of mass, heat and momentum transfer in fouling environments. Reaction rate coefficients (K_1 , μ_{max} , K_s) in table 1 depend on many environmental factors. In fact, reaction rate coefficients are most often inferred from conservation equations by assuming a kinetic or rate model (e.g., power law or saturation rate equation). The stoichiometric coefficients (A_i and Y in Table 1) are also constitutive properties and related the rate of consumption or production of one reactant to another.

In modelling a fouling environment, it may be necessary to deal simultaneously with all three conservation equations as well as reaction kinetics. The interrelationships between these various processes often provide the greatest challenge to the investigator. A useful illustration is a recirculating cooling tower (RCT) system in which significant momentum, mass and heat transfer is occurring in the condenser (heat exchanger) as well as the tower (Figure 3). These aspects of the RCT system have been adequately described in a mathematical form by Sherwood et al.⁶. However, the constitutive relationships describing fouling in the RCT system have received much less attention. The critical concern to equipment operators is the influence of fouling on heat and momentum transfer in the RCT system. With reasonably accurate constitutive relationships for fouling processes, these influences can be predicted and, thereby, avoided.

FUNDAMENTAL RATE PROCESSES

The constitutive fouling relationships can be classified into four rate processes which are fundamental to all types of fouling. Fouling deposit accumulation can be considered the net result of the following physical, chemical and biological processes (Table 2):

1. transport of soluble and particulate material to the wetted surface
2. attachment of soluble or particulates to the wetted surface
3. chemical or microbial reaction at the surface or within the deposit, and
4. detachment, sloughing, or spalling of portions of the deposit from the wet-

TABLE 2

Summary of fundamental processes contributing to fouling.

Transport	. Soluble . Particulate
Attachment	. Adsorption . Adhesion
Reactions	. Particulate . Precipitation . Corrosion . Microbiological - growth, etc. - corrosion
Detachment	. Desorption . Sloughing . Spalling

The overall result is a progression of events characterized by three identifiable periods (Figure 6):

1. an induction period,
2. a rapid increase in accumulation, and
3. an asymptotic or plateau period.

Because fouling rate can be controlled by many process variables, one of the three periods may be negligible in duration compared to the other two.

Transport to the Wetted Surface

Transport of soluble and particulate materials to the wetted surface is the first step in the overall fouling process. Transport rates for soluble materials can be predicted reasonably well with accepted empirical relationships⁶. Predicting transport rates of particulates from the bulk fluid to the wetted surface is more difficult, primarily because of the numerous forces which may influence particle movement in flowing fluids⁷.

Transport has frequently been combined with deposition which is easier to measure but is the net result of deposition and detachment⁸. Frequently, investigators focus on transport rates and incorporate a "sticking probability" to rationalize measurements of deposition rates. Experimental observations, even with inert particulates⁸, indicate that sticking probability changes as deposition alters the characteristics of the wetted surface.

Transport processes can conveniently be classified by consideration of the fluid flow regime: turbulent, laminar, or a combination thereof. For example, in turbulent pipe flow two regions can be differentiated: the turbulent bulk fluid and the laminar or viscous sublayer. Transport rates are quite different in these two regions.

Transport may be the rate-limiting process in some cases of particulate fouling. However, it appears doubtful that transport will limit the rate of deposition for any other type of fouling except in the very early stage of accumulation (i.e. the induction period in Figure 6) or in very dilute environments.

Interfacial phenomena

Once material is transported to the surface, it absorbs/adheres or is re-entrained in the fluid. The concept of "sticking probability" accounts for the fraction remaining at the wall.

Considerable effort has been invested in the study of microbial cell adhesion and its role in biofouling⁹. Much of the work stems from the assumption that this process must be inhibited in order to eliminate biofouling problems. Interfacial phenomena have also been investigated for particulate fouling¹⁰, freezing fouling¹¹, chemical reaction fouling¹², and crystallization fouling¹³.

Interfacial processes and transport processes are difficult to distinguish in experimental systems. Accumulation or deposition, however, are relatively easy to measure and represent the net effect produced by transport followed by adsorption/adhesion. Deposition can generally be described by a hyperbolic progression (Figure 7) and is probably the rate-limiting step, dominating the overall process during the induction period of any type of fouling (Figure 7).

Reactions at the Surface or Within the Deposit

Chemical or biochemical reactions at the surface or within the deposit can contribute significantly to the accumulation of the fouling deposit. Reactions within the deposit will influence biological fouling⁴, chemical reaction fouling^{12,13}, and precipitation fouling¹⁴. Reactions at the surface will influence corrosion fouling⁷. In some cases, there will be significant interactive effects such as illustrated by microbially-mediated corrosion fouling. In this case, microbial (metabolic) products may diffuse to the metal surface and cause deterioration (corrosion) of the surface.

Relevant biochemical reactions include microbial growth, extracellular polymer formation, and death/lysis. Microbial cells, once attached to the surface, grow, multiply and form products from chemical energy (chemosynthetic organisms) derived from the bulk water. In most cases, organic compounds (heterotrophs) provide the energy but reduced inorganic compounds (e.g., Fe^{++} , NH_3 , $\text{S}^{=}$) can also be used (autotrophs). Photosynthetic organisms can sometimes provide the organic compounds for heterotrophic growth as has been observed in recirculating cooling tower systems. The relative extent to which cells or product (primarily extracellular polymer substances, EPS) dominate the deposit will significantly influence the effectiveness of any chemical treatment in preventing or removing a biological fouling deposit. Trulear¹⁵ has studied the processes of cellular reproduction and extracellular polymer formation in biofilms and observed the influence of several environmental factors on their relative rates. The biological deposit, an adsorptive surface, will frequently enhance the accumulation of other fouling deposits such as particulate deposits¹⁶, precipitation deposits¹⁷, and corrosion deposits¹⁸.

Chemical reaction fouling is a result of reactions at the surface and within the deposit. Illustrations of chemical reaction fouling include coke formation in petrochemical reactors¹² and organic deposits in the food processing industry¹³. Reactions also occur in precipitation fouling deposits as the precipitates change their crystalline form¹⁹.

Precipitation fouling is caused by a chemical reaction (precipitation) at the surface¹⁴ and the rate is influenced primarily by the amount of precipitate present (i.e., autocatalytic). The kinetics of this process have been studied in great detail¹⁴. Reactions which alter the crystalline form of the precipitates occur within the deposit and can alter the porosity and thermal conductivity of the deposit. The calcium salts have received the most attention in this fouling category.

Corrosion fouling can increase deposit accumulation and results from two identifiable processes²⁰: (1) reactions at the surface which cause its deterioration and (2) adsorption of corrosion products released from other locations in the system. In the latter case, transport and detachment play significant roles in determining the effect on performance.

In many cases, chemical and biochemical reactions are responsible for the phase of rapid increase in deposit accumulation (see Figure 6).

Detachment

Detachment is a significant process in at least two stages of fouling deposit accumulation. In the first case, detachment is intimately related to the "sticking probability" discussed in relation to transport and interfacial phenomena. Secondly, as the deposit becomes thicker, fluid shear stress will play a more significant role⁴. This has been observed in biological fouling⁴, chemical reaction fouling¹³, and precipitation fouling¹. The detached material often deposits in other parts of the system as has been observed with corrosion products⁷.

Detachment processes are mostly responsible for the asymptotic phase of a typical fouling progression (see Figure 6). During this phase, detachment rate is equal to the combined effects of transport, adsorption/adhesion, and reaction on deposit accumulation.

FACTORS INFLUENCING FUNDAMENTAL RATE PROCESSES

Physical, chemical and biological factors influence the fundamental rate processes. These factors influence the rate as well as the extent to which fouling deposits accumulate.

Physical factors

The most important physical factors affecting the fundamental processes are shear stress, temperature (bulk fluid and surface) and surface (micro) roughness. All three factors influence transport, interfacial phenomena, detachment and reactions at the interface. Only temperature will influence reactions within the deposit. Other factors influence fouling processes at the macroscopic system level including geometry or configuration of the heat exchanger, residence time, and physical treatment methods (e.g., Amertap, MAN brushes).

Chemical factors

The chemical factors influencing the fundamental rate processes are too numerous to list. However, some of the more important are pH, Ca^{++} , Fe^{+++} , Si, dissolved oxygen, and organic carbon. These factors do not affect transport rates but may affect interfacial phenomena and certainly influence reaction rate and extent in the deposit and at the metal surface. Another chemical factor influencing fouling processes is the metal alloy. There have been numerous tests which have evaluated the fouling and/or corrosion potential of various alloys. The influence of surface (micro) roughness versus surface chemical composition, however, is not always clear. Internal chemical treatment programs to minimize fouling provide a multitude of other chemical compounds which influence fouling processes. Chemical treatment programs depend on the type of deposit and, in some cases, treatment for one condition may be antagonistic to control of another. For example, phosphorous compounds added to minimize precipitation fouling may enhance biological fouling. Many chemical compounds exert a significant influence on fouling processes at relatively low concentrations which further complicates analysis.

Biological factors

Biological factors have their greatest influence on biochemical reactions within the deposit where bacterial cell numbers, physiological state of the cells, and microbial community structure determines the influence of the deposit on equipment performance⁴. However, biological factors may also influence interfacial adsorption/adhesion as well as detachment. For example, microbial deposits contain significant quantities of extracellular polymer substances (EPS) which increase the adsorptive capacity of the wetted surface and trap particulates¹⁵. Microbial activity within the deposit may also increase the cohesiveness of the deposit¹⁶ forming an organic matrix which provides resistance to fluid shear forces. Biological factors probably influence the effectiveness of chemical treatment programs in minimizing other types of fouling (e.g., precipitation and corrosion fouling) although the author has found no literature documentation for this statement.

EFFECTS OF FOULING

The problems caused by fouling at the macroscopic level (i.e., the operating plant) have been discussed above. This section will concentrate on the effects of fouling within the heat exchanger tube. Accurate measurement of effects under controlled thermohydrodynamic conditions can be extremely useful for monitoring the progression of fouling as well as determining the type of deposit forming.

Fluid Frictional Resistance

Fouling deposits cause increased fluid frictional resistance by decreasing the effective diameter of the heat exchange tube and by increasing the effective roughness of the tube. Picologlou et al.²¹ have indicated that biofilms increase frictional resistance primarily by increasing the effective roughness. Other data¹⁷ indicate that inorganic scales produce much lower effective tube roughness.

Frictional resistance measurement has several advantages as an indicator of fouling:

1. very simple and inexpensive
2. in water distribution systems, it monitors the quantity of most concern... head loss or loss in carrying capacity.

However, in some situations, frictional resistance measurements alone are of limited value and sometimes misleading:

1. Frictional resistance measurements are relatively insensitive until the fouling deposit thickness exceeds a certain value, approximately the thickness of the viscous sublayer²¹. The thickness of the viscous sublayer is inversely proportional to flow velocity.
2. Some deposits such as CaCO_3 scale, exhibit a relatively low relative roughness (Table 3) but have a low thermal conductivity¹⁷. Therefore, frictional resistance will be relatively low but heat transfer resistance will be high.
3. In heat exchangers or condensers, the major concern is heat transfer resistance.

Frictional resistance measurements, in conjunction with heat transfer measurements, however, do yield valuable information.

Overall Heat Transfer Resistance

Overall heat transfer resistance is the sum of conductive and convective heat transfer resistance. Convective heat transfer resistance results from fluid motion

and generally decreases as the fouling deposit accumulates since the "roughness" of the deposit increases turbulence in the interfacial region. Conductive heat transfer resistance results from insulating layers formed by the deposits and generally increases as the fouling deposit accumulates. The relative changes in convective and conductive heat transfer resistance will depend on the following:

- deposit thickness, roughness, and thermal conductivity
- fluid flow rate
- radial temperature gradient in the tube

Characklis and his co-workers have reported the influence of fouling deposits on conductive and convective heat transfer resistance in tubes in the laboratory²² and also in operating plant-scale equipment^{16,17}.

If deposit thickness is measured along with convective and conductive heat transfer resistance and fluid frictional resistance, the effective deposit thermal conductivity and effective deposit roughness can be determined. Effective deposit thermal conductivity and roughness have been determined in several cases by this method¹⁷. Results are presented in Table 3.

Corrosion

The loss of material due to corrosion of a heat transfer surface can lead to failure of that surface in operation. However, there is reason to believe that in situations where metal damage is not important, corrosion products can introduce a significant heat transfer resistance²⁰. Poor control of other types of fouling deposits can lead to accelerated corrosion-under-deposit corrosion. Corrosion in such cases can result from oxygen differential cells. The water-deposit interface contains oxygen but the microenvironment of the deposit-metal interface is oxygen-deficient and becomes the anode of the differential aeration cell. A self-perpetuating corrosion cycle is established frequently leading to rapid failure. Corrosion probes are frequently unable to predict such occurrences because the probes reflect conditions in the bulk water rather than at the heat transfer surface. The accurate prediction of corrosion fouling and under-deposit corrosion progression will require more research effort.

MEASUREMENT AND SIMULATION

"When you can measure what you are speaking about and express it in numbers, you know something about it; and when you cannot measure it, when you cannot express it in numbers, your knowledge is of meagre and unsatisfactory kind. It may be the beginning of knowledge, but you have scarcely in your thought advanced to the stage of a science".

Lord Kelvin

NEED AND PURPOSE

The experimental investigation of fouling is a necessary and important route to obtaining an understanding of the fundamental processes. If reliable fouling data could be obtained on full-scale heat exchange equipment using the actual fluids, other measurements and simulation would be unnecessary. However, many of the parameters of interest vary considerably throughout the equipment and, in addition vary with time. As a result, measurements in the laboratory and in field locations are necessary at specified and constant values for critical parameters.

Laboratory measurements

The laboratory provides the proper environment for conducting mechanistic

studies which lead to useful models in terms of simulating real systems. These tests are a "starting point". Physical, chemical and biological factors can be controlled at desired levels. Valuable information can be obtained related to design concepts such as influence of alloy¹⁸, fluid velocity, tube geometry (e.g., enhanced heat transfer surfaces), and temperature profiles²³. The effect of water quality (chemical and biological) on these factors can also be evaluated. Operation and maintenance procedures can be evaluated. For example, laboratory tests can evaluate the effectiveness of a treatment (chemical or physical) procedure applied at varying frequency^{24,25}. These tests frequently identify the operating conditions which are best for a given treatment procedure. Laboratory experimentation frequently results in development of measurement techniques useful for field tests and monitoring¹⁷.

Aside from mechanistic data and testing, laboratory tests are generally less^o expensive than field tests based on value of the information obtained.

Field measurements

Measurements at the operating plant are essential because no system can be simulated perfectly. But the purpose of field measurements is generally monitoring equipment and/or warning of impending problems. Field measurements which simulate the equipment environment could be used to evaluate the effectiveness of internal chemical treatment programs but this activity, for reasons unknown, is rare. Field tests have been used to evaluate the influence of physical factors and a limited number of chemical factors on fouling and corrosion. For example, the performance of different alloys is presently being tested at a power plant site using an instrument which simulates the heat exchange equipment¹⁶. Field tests are also useful in evaluating the performance of contemplated changes in treatment programs and/or process modifications^{17,26}. Of all factors influencing fouling, biological variables are most difficult to control in the field as is also frequently the case with some chemical components generally contributing to water quality.

Laboratory and field measurements are intimately related within the iterative procedure described in Figure 8.

Laboratory observations under carefully controlled conditions provide the framework for evaluating and interpreting field results where control of all parameters is not possible. On the other hand, field results indicate inconsistencies in the models and provide the impetus and experimental hypotheses for further laboratory work.

MEASUREMENTS RELATED TO FOULING

Measurements related to fouling processes include methods for monitoring the progress of the fouling process, methods for characterizing the fouling deposit, and methods for describing and/or controlling the fouling environment. In some cases, methods for monitoring progress can also be used to characterize the deposit.

Monitoring the Progression of Fouling

Methods available for monitoring the progress of fouling processes can be conveniently classified as follows²⁷:

1. direct measurement of deposit quantity
2. indirect measurement of deposit quantity
 - a. specific constituent within the deposit
 - b. for biofilms, microbial activity within the deposit
 - c. effects of deposit on transport processes (i.e., heat transfer and fluid frictional resistance).

Direct measurement includes deposit mass and deposit thickness and is essential for several reasons. Calibration of any indirect method involves comparison with actual quantity of accumulated deposit. Direct measurements are a necessity when using mass conservation equations to determine process rates and stoichiometry. Direct methods are also useful in relating deposit accumulation to fluid frictional resistance and heat transfer resistance in a rational way.

Indirect methods provide significant benefits including increased sensitivity. For example, organic carbon analysis of biofilm is as much as 25 times as sensitive as biofilm mass measurements²⁷. In this case, the specific constituent of the deposit (i.e., organic carbon) provides an excellent measure of accumulation. However, if the deposit contains a large amount of silt and sediment, organic carbon may not be representative.

Indirect methods include monitoring the influence of deposits on heat transfer and fluid frictional resistance as discussed above. These techniques have been discussed in more detail by others¹⁷ and indicate that the influence of deposits on heat and momentum transfer depends strongly on deposit characteristics (e.g., composition, thermal conductivity, roughness).

Characteristics of Fouling Deposits

Fouling deposits can exhibit a wide range of chemical and microbial composition. Not surprisingly then, two deposits of equal thickness can influence heat and momentum transfer in drastically different ways. The reason for this behavior is widely varying deposit thermal conductivity and roughness as indicated in Table 3. Characterization of deposits is a necessary preliminary to choosing control strategies as indicated by Table 4.

Presuming an *in situ* deposit thickness measurement is possible, effective deposit thermal conductivity and roughness, can be determined through measurements of conductive and convective heat transfer resistance, fluid frictional resistance, and engineering correlations. This *in situ* diagnostic method is presently being incorporated into an on-line fouling monitor. Such a diagnostic tool would find advantage as a feedback control device in an operating plant as illustrated in Figure 9. As more data accumulates, deposit composition could be estimated from thermal conductivity and roughness determinations in much the same way as chemical composition is determined from "libraries" of spectral data associated with gas chromatography/mass spectrometry. Field data of this type would also contribute to empirical relationships useful for predicting fouling processes as a function of environment... providing that the appropriate environmental factors are known or measured. A library file of deposit properties and compositions of this type exists and is being expanded at regular intervals.

Important Environmental Factors

There are many factors which influence the rate and extent of fouling processes but the primary ones certainly include bulk water quality (chemical and biological), temperature (bulk water and surface), fluid shear stress at the surface, and the nature of the surface (alloy). Superimposed on these factors is any chemical or physical treatment program regularly employed to minimize the effects of fouling.

Fouling is a heterogeneous process in that it requires both a liquid and solid phase. Consequently, concentrations and compositions at the liquid-solid interface determine the processes which control deposition.

Unfortunately, interfacial conditions are extremely difficult to measure except under controlled laboratory conditions and interfacial processes must be related to

TABLE 3

Properties of fouling deposits indicating the significant variations between various types of deposits¹⁷

Type deposit	Deposit Thickness (cm)	Relative Roughness (dimensionless)**	Thermal conductivity (watt m ⁻¹ °C ⁻¹)
Roughness characteristics of biofilms and scale deposits			
Biofilms ⁴	0.0040	0.003	
	0.0165	0.014	
	0.0300	0.062	
	0.0500	0.157	
CaCO ₃ Scale ⁷	0.0165*	0.0001	
	0.0224*	0.0002	
	0.0262*	0.0006	
Thermal conductivity of scales and biofilm			
Scale ⁶			
Calcium carbonate			2.26-2.93
Calcium sulphate			2.31
Calcium phosphate			2.60
Magnesium phosphate			2.16
Magnetic iron oxide			2.88
Alcalcite			1.27
Biofilm ⁵ (Water)			0.63

* Calculated from overall heat transfer resistance assuming a thermal conductivity for CaCO₃ of 0.026 watts cm⁻¹°C⁻¹.

** Inside tube diameter is 1.27 cm.

TABLE 4

Categorization of various fouling control methods by their influence on the fundamental processes contributing to fouling.

Fundamental process	Biofouling	Scaling	Corrosion
Transport	.Filtration .Coagulation	.Water .Softening	.Oxygen .Removal
Interfacial process	.Biodispersants .Biocide .Coatings	.Dispersant	.Coatings
Reaction	.Tube alloy .Biocide	.Crystal .Growth .Inhibitor	.Coatings .Electrolytic .Protection .Corrosion .Inhibitors (e.g., Cr)
Detachment	.Oxidizing .Biocides .Physical .Removal	.Chelant .Acid	.Chelant

to the bulk water environment. Under these limitations, data interpretation must proceed with caution and a thorough process analysis must be accomplished before valid conclusions can be drawn. As an illustration, consider biofouling in an open recirculating cooling tower (RCT) system. It was believed for many years that biofouling was related to the colony-forming units (CFU) measured by a plate count procedure. Recently, data was presented¹⁷ which indicated no relationship between CFU's in the bulk water and fouling as measured by heat transfer or fluid flow measurements. The lack of correlation can be attributed to the number of processes contributing or removing organisms from the bulk water phase (Figure 10). Organisms enter the cooling tower bulk water through the make-up water, by growth and reproduction within the bulk water, from the air, and by detachment from bio-fouled surfaces. Organisms leave the RCT system bulk water in the blowdown and drift, by adsorption to surfaces within the RCT system, and by "death", at least partially due to biocide application. Obviously, the number of CFU in the cooling water is not strictly related to the extent of biofouling in the RCT system.

Key chemical constituents which influence fouling processes include Ca^{++} , Mg^{++} , Fe^{+++} , Fe^{++} , Si, O_2 , PO_4^{-3} , CO_2 (and related forms), $\text{SO}_4^{=}$, Cl^- , and organic carbon.

Bulk temperature influences most chemical and biochemical reaction processes as well as transport rate processes. Fouling processes are no exception as indicated in Figure 11 which indicates the progression of fluid frictional resistance as a function of bulk water temperature in a biofouling environment²⁸. The most deleterious effects are observed at 40°C (104°F). Surface temperature also influences fouling processes as indicated in Figure 12 which indicates the maximum biofouling deposit thickness attained as a function of surface temperature and nutrient loading rate²³. One important observation from these data is the significant interaction between variables, in this case, surface temperature and nutrient loading rate.

Fluid shear stress is critical in fouling environments since it strongly influences transport and detachment rates. Figure 13 indicates the influence of fluid shear stress on biomass accumulation rates²⁹. Accumulation rates are higher at the higher flow rate suggesting that transport dominates over detachment in this system during the early stages of deposit formation. Figure 14 indicates the influence of shear stress on fluid frictional resistance changes caused by biofilm accumulation³⁰.

Finally, the composition of the surface material influence the rate of deposition. Figures 15 and 16 depict the progress of biofouling deposition on copper-nickel and titanium in a laboratory seawater system¹⁸. If only total deposit mass is considered, the copper-nickel alloy fouled to a much greater extent than titanium. However, consideration of volatile deposit mass suggests that "biofouling" was essentially the same in the two alloys. Other analyses indicated that much of the total deposit mass on copper-nickel could be attributed to corrosion products¹⁸.

PREVENTION/CONTROL

The impetus for developing a rational approach to problems of fouling deposition is the expectation that such an approach will lead to more satisfactory methods for preventing and/or controlling fouling.

PRESENT FOULING PREVENTION/CONTROL METHODS

There are physical and chemical methods available for preventing/controlling fouling deposition. Table 4 illustrates the numerous methods and indicates the type of fouling deposit and the fundamental process presumably inhibited. For example, filtration/coagulation is effective in reducing the concentration of microbial cells thereby reducing transport of cells to surfaces and inhibiting biofouling.

However, none of these methods are totally satisfactory or fouling would no longer be a problem.

Controlling Specific Types of Fouling

Significant success has been achieved in controlling certain specific types of fouling deposition when they exist in a relatively homogeneous form. For example, calcium carbonate crystallization fouling can be controlled quite effectively by phosphonate compounds (or other inhibitors) as long as no interfering compounds are present (see below). Laboratory and field observations indicate that these same compounds are not as effective in preventing scaling when biofouling exists. It is apparent that very little is known about the interactive effects between different types of fouling deposits and effective means for their control. For example, do polyphosphate corrosion inhibitors remain effective when significant biofouling has occurred on the corroding surface?

Interferences

Frequently, other reacting components interfere with the intended control procedure. Chlorine is a useful biofouling control compound. But in heavily contaminated waters, chlorine is consumed in side reactions (chlorine demand reactions) and is rendered ineffective. Even copper-nickel alloys possess a significant chlorine demand¹⁸. Therefore, water quality are at least two environmental factors which must be considered in choosing a treatment program to minimize fouling.

Environmental Quality

Some chemical treatments are quite effective but are undesirable due to their impact on environmental quality. Chlorine has been used for years as a reasonably

effective method for controlling biofouling. But recently, concern over toxicity of chlorine and its reaction products has spurred the search for alternatives. Biocides, in general, are toxic materials and must be evaluated thoroughly prior to their large scale use. Chromate corrosion inhibitors have suffered a similar fate. However, thoughtful engineering approaches will permit use of compounds such as chlorine and chromate so the environmental concentrations are within satisfactory limits.

Treatment Effectiveness and Its Quantitative Measurement

The effectiveness of various treatments in actual field applications is rarely assessed in a meaningful, accurate, and sensitive manner unless a catastrophe occurs. Unfortunately, treatment programs are frequently ineffective and, in some cases, may enhance fouling. "Cleanliness" factors are sometimes reported using heat transfer rate measurements from full-scale heat exchangers but these data are generally useless for predictive purposes or for analytical purposes due to the "noise" in the system. Some simplistic sidestream devices depend only on visual observations or frictional resistance measurement frequently ignoring the real concern...heat transfer. Measurement of fundamental engineering quantities are necessary to provide the operations engineer with a clear picture of the effects of fouling on equipment performance, influence of operating variables on fouling rates, and effectiveness of treatment programs.

DEVELOPING NEW METHODS FOR FOULING PREVENTION/CONTROL

The nature of this paper suggests that systematic methods exist for developing novel, more effective treatment methods. The approach presented here inherently assumes the following:

- . There is no universal remedy for fouling.
- . An effective treatment in one operating environment may be quite ineffective in another environment.
- . A treatment effective in controlling one type of fouling (e.g., biofouling) may enhance another type of fouling (e.g., corrosion).
- . A treatment effective against one type of fouling (e.g., scaling) may be rendered ineffective by the presence of another type of fouling (e.g., bio-fouling).

Hypothetical Procedure

Select a candidate treatment program to prevent or inhibit one of the fundamental processes (Table 4) and test its ability to do so in the laboratory. For example, choose a chemical which inhibits EPS formation in microorganisms because it may inhibit cell adhesion. The laboratory tests are conducted in a system engineered to simulate the operating equipment in which the program will be applied. Measure the appropriate variables. Heat transfer and frictional resistance are important from the operational standpoint but offer little in terms of determining process characteristics. In the case of microbial cell attachment, measure the number of attached cells and their EPS content. Run appropriate controls. Evaluate the dosage requirements in the simulated system and use scale-up procedures to estimate the environmental concentrations which may result. Determine whether the system, not the program, can be engineered to minimize the environmental impact of the treatment. Test the treatment program with the same simulated system in the field under relevant operating conditions. Measure the changes in heat transfer and fluid frictional resistance as well as corrosion losses. Analyze the physical, chemical, and biological characteristics of the deposit to determine the effectiveness of the treatment and to detect possible interferences to the program. Repeat the cycle if necessary.

A program of this type can be planned in great detail using statistical experimental design techniques to provide the most useful data for statistical analysis and confidence limits with which to base decisions.

SUMMARY

A rational approach to problems of fouling have been presented. Text limitations have necessitated that mathematical details be limited. However, the intent was to propose an approach. The usefulness and relevance of this approach will be judged by the reader from whom the author enthusiastically solicits questions, comments, and suggestions.

ACKNOWLEDGMENTS

The author gratefully acknowledges the National Science Foundation (CPE 80-17439), Office of Naval Research (N00014-80-C-0475), Calgon Corporation, and Montana State University Engineering Experimental Station for partial financial support. Thanks to Jean Julian and Glenda Farnes for helping to prepare the manuscript.

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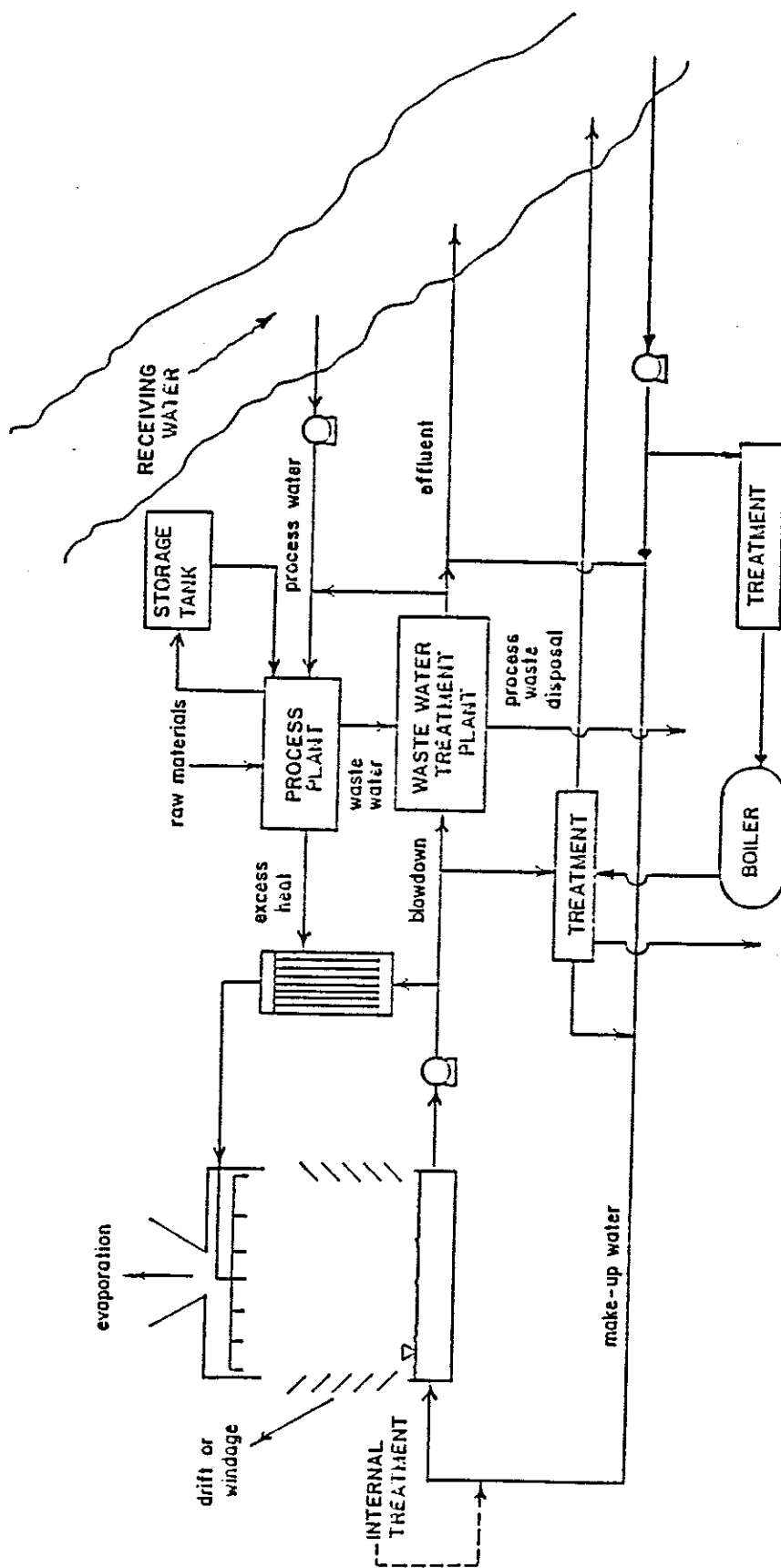


Fig. 1.- A generalized schematic diagram of the water system in an industrial facility.

FACTORS AFFECTING TRANSPORT RATES:

1. FLOW RATES
2. VARIATION IN FLOW RATES
3. TEMPERATURE, PH
4. PIPE ROUGHNESS
5. CONCENTRATION

FACTORS AFFECTING TRANSFORMATION RATES:

1. CONCENTRATION
2. TEMPERATURE, PH
3. SURFACE AREA / VOLUME RATIO
(FOR INTERFACIAL PROCESSES)

FACTORS AFFECTING "PROCESS" STOICHIOMETRY:

1. CONCENTRATION
2. TEMPERATURE, PH
3. RESIDENCE OR REACTION TIME IN PIPE

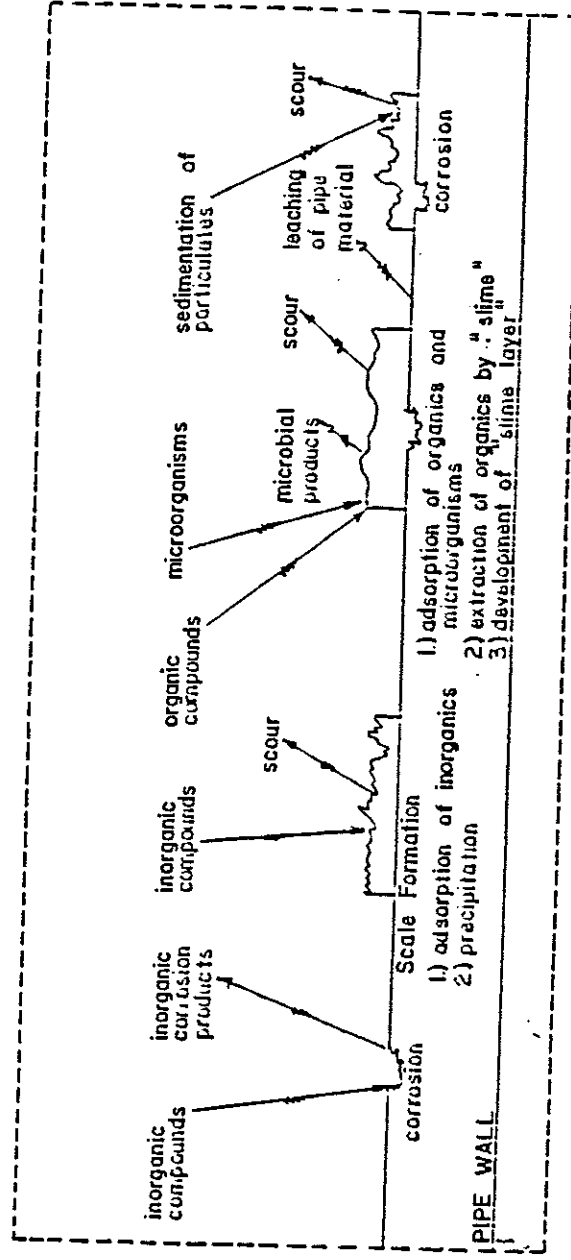


Fig. 2.- Schematic representation of various types of fouling processes and deposits which can form on equipment surfaces.

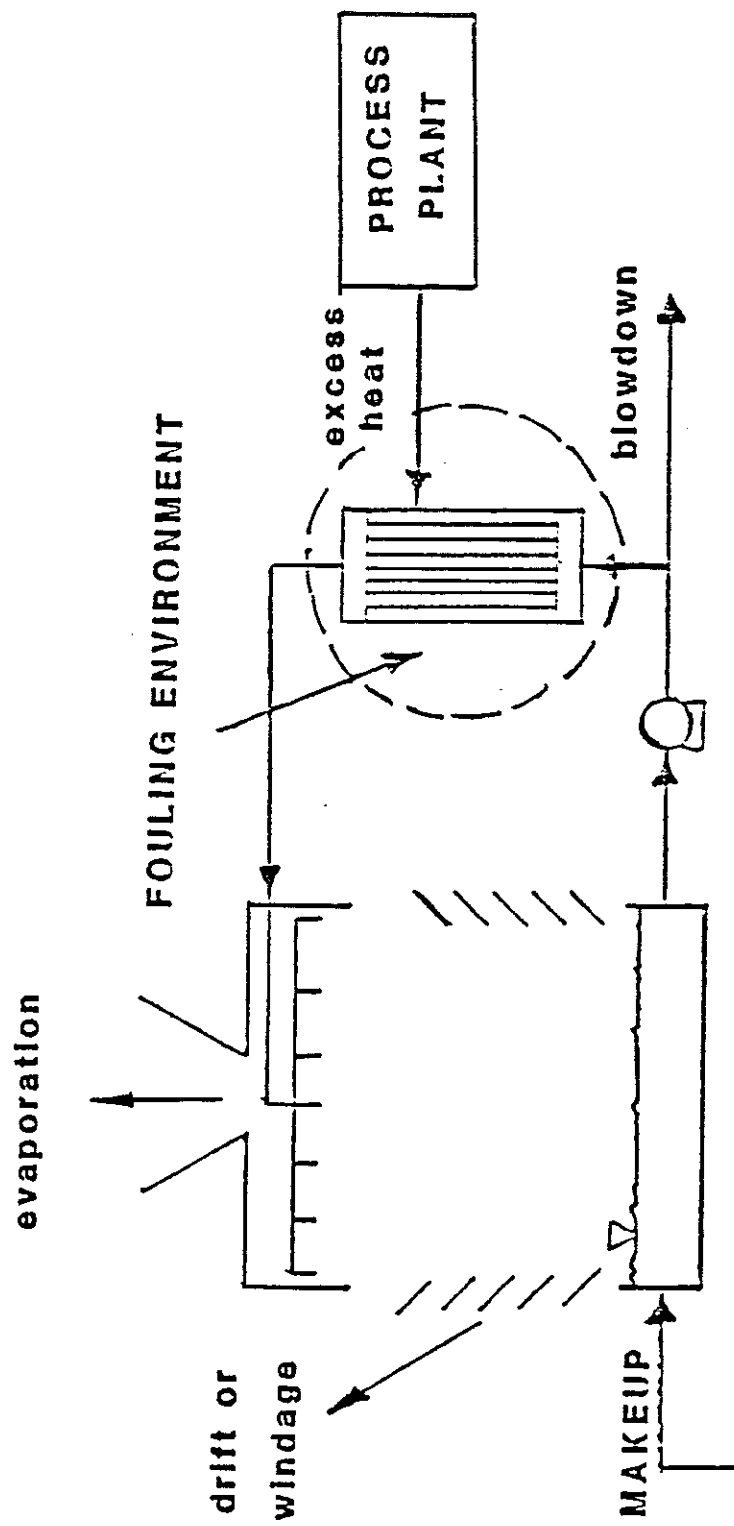
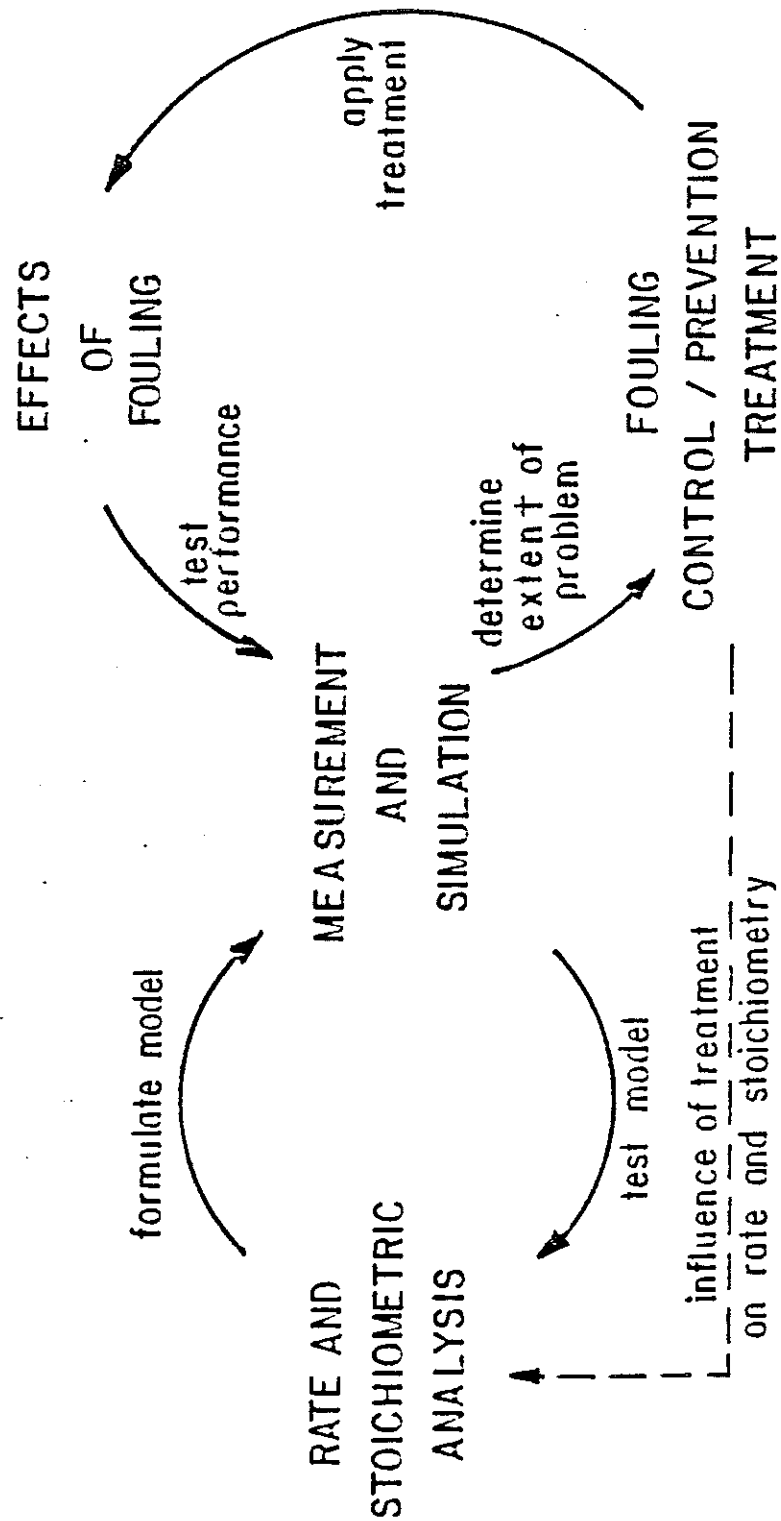
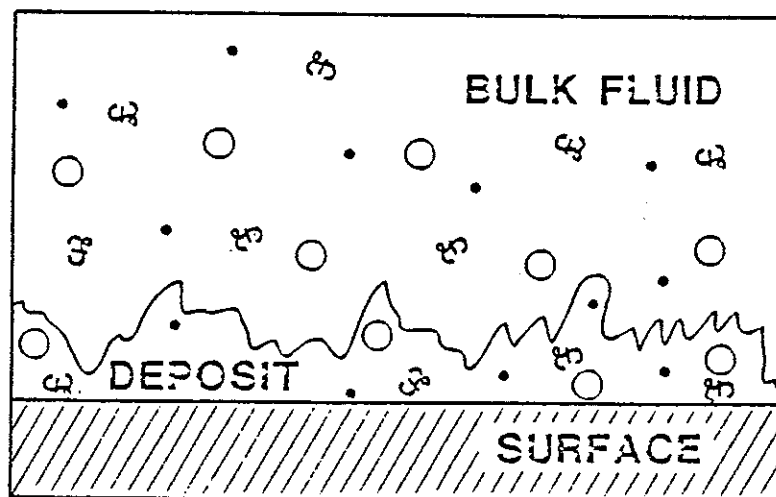


Fig. 3.- Schematic diagram of an open, recirculating, cooling tower system.

DEVELOPING UNDERSTANDING ... AN ITERATIVE PROCESS





"PHASE DIAGRAM"

Fig. 5.- A schematic diagram of the environment in which fouling occurs.

- Soluble inorganics
- Soluble organics
- Suspended particulates

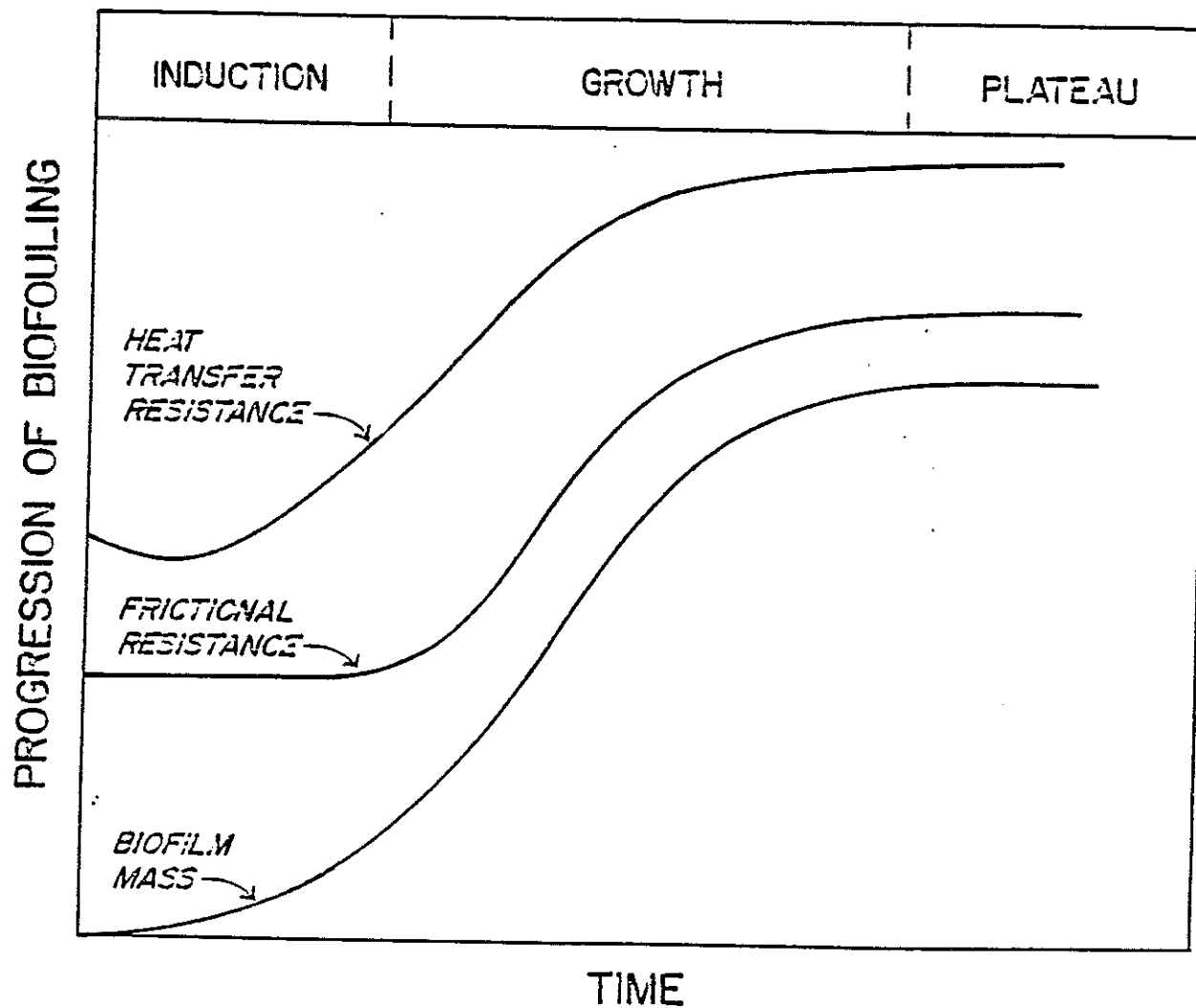


Fig. 6.- A schematic representation of the progression of fouling deposition.

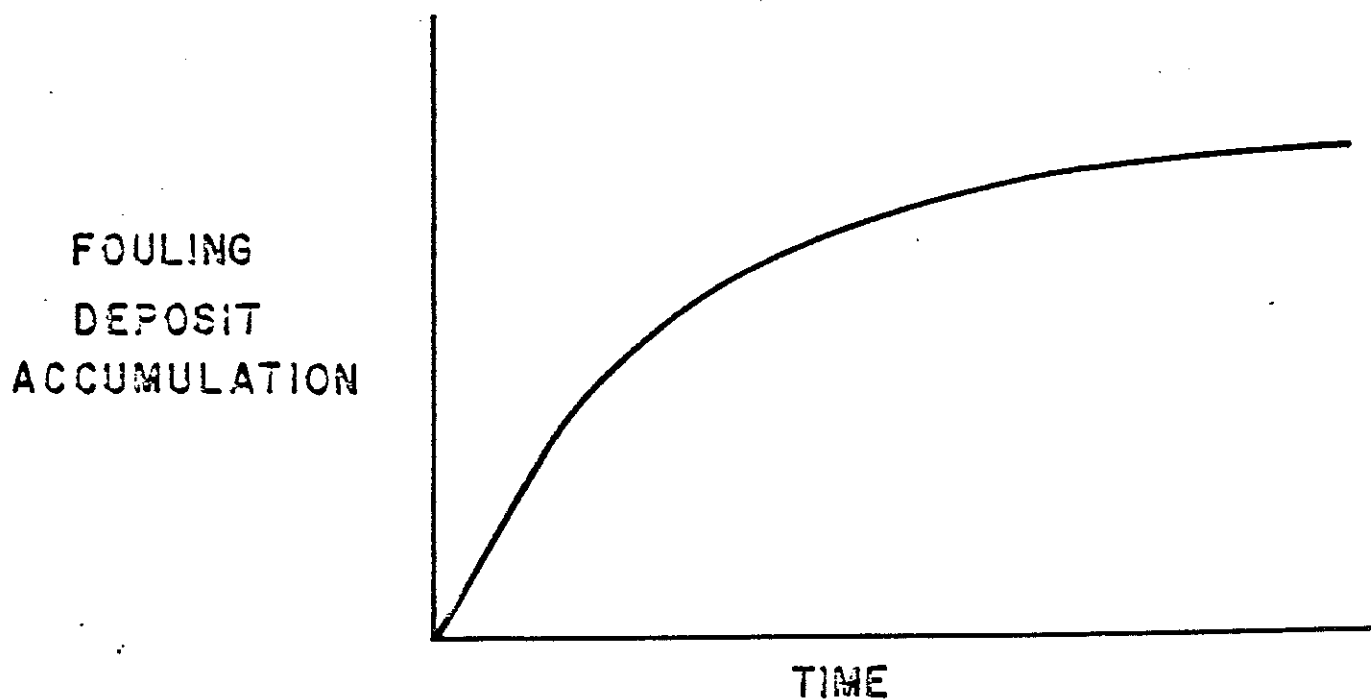


Fig. 7.- A typical progression, due to transport and adsorption/adhesion, observed during the initial stages; or induction period (see inset of Fig. 7).

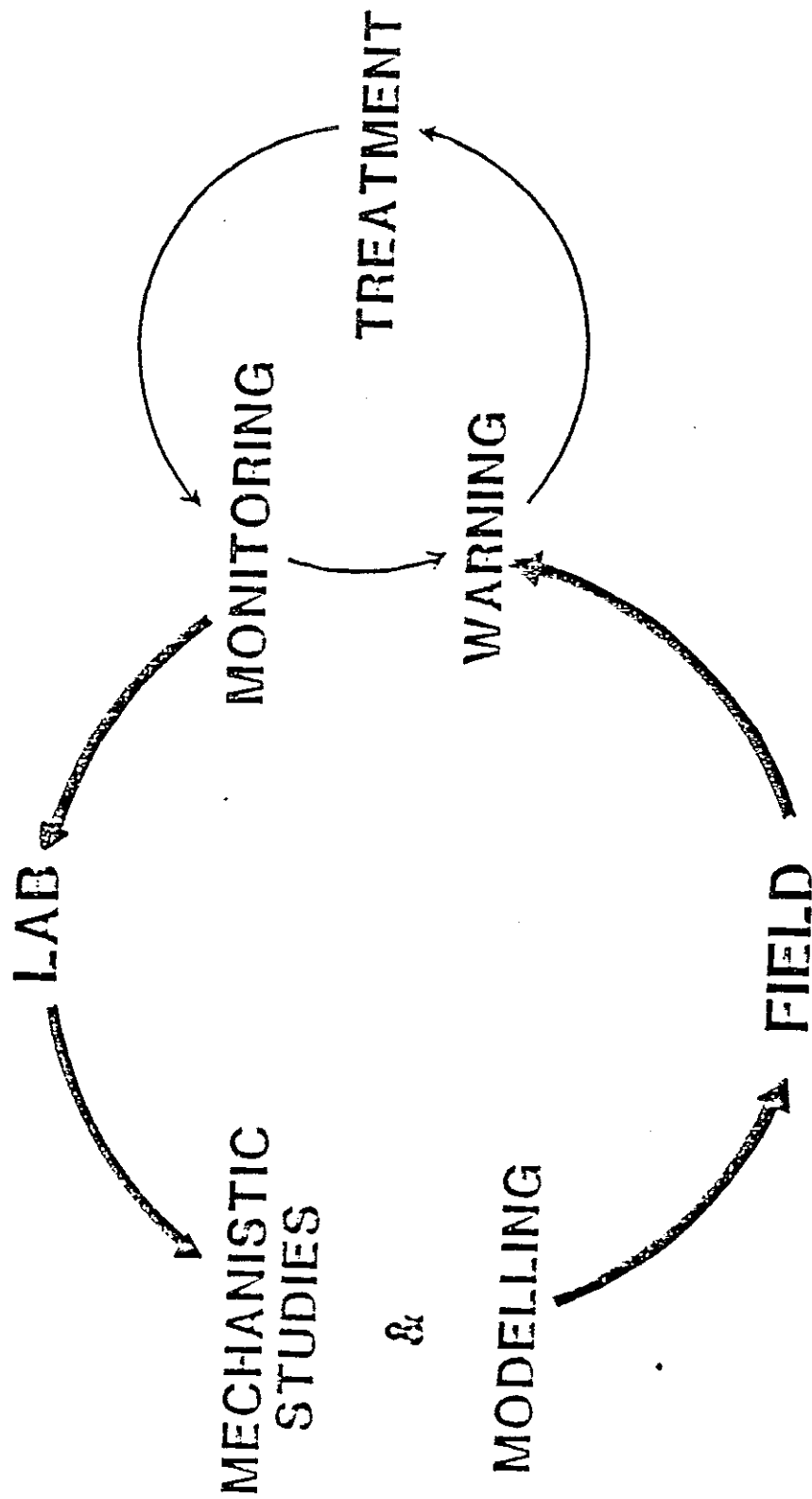


Fig. 8.- The relationship between field testing and laboratory experimentation related to fouling processes.

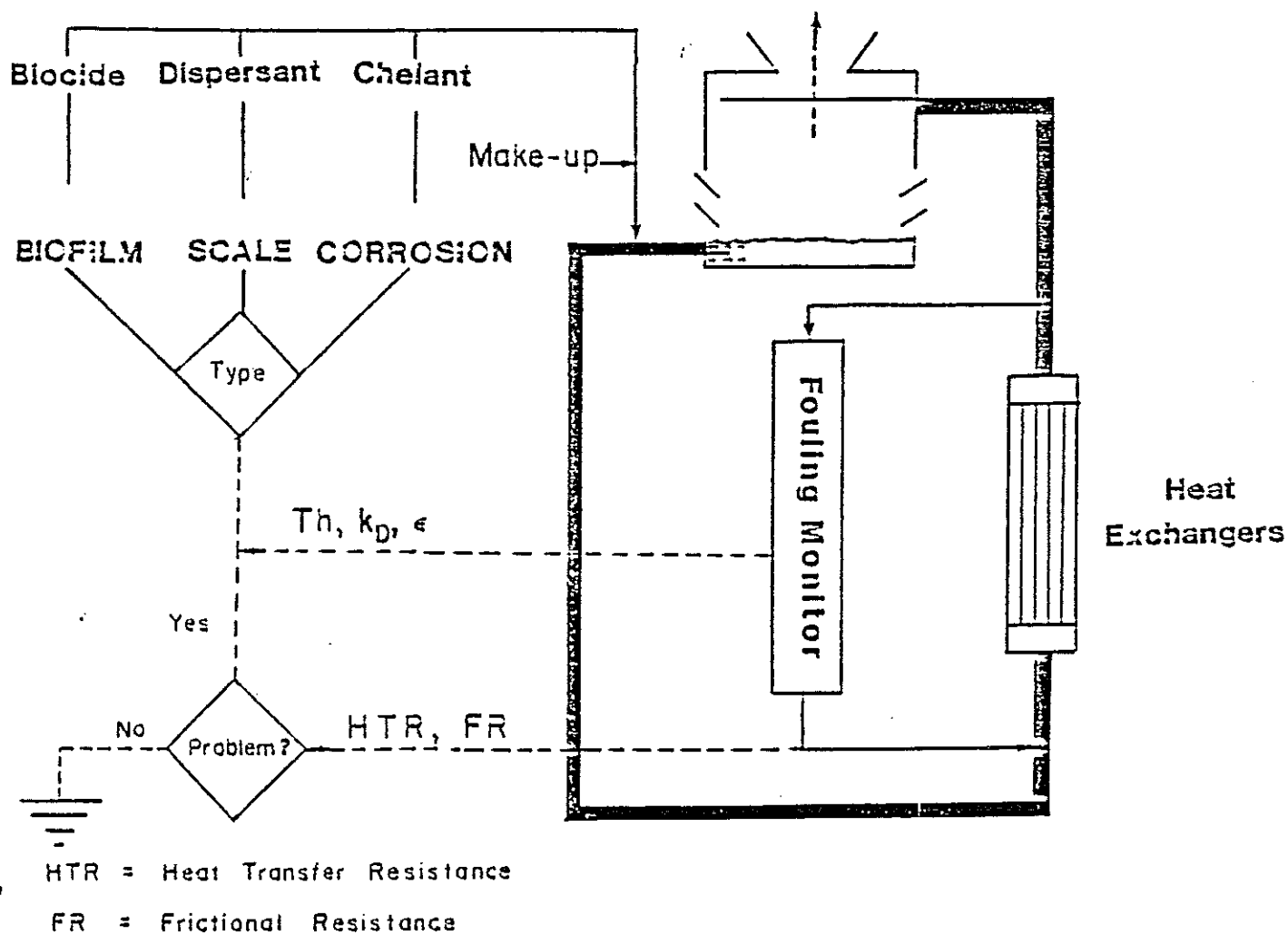


Fig. 9.- An illustration of the use of a diagnostic, on-line fouling monitor as a feedback control device in an open, recirculating cooling tower system³⁰.

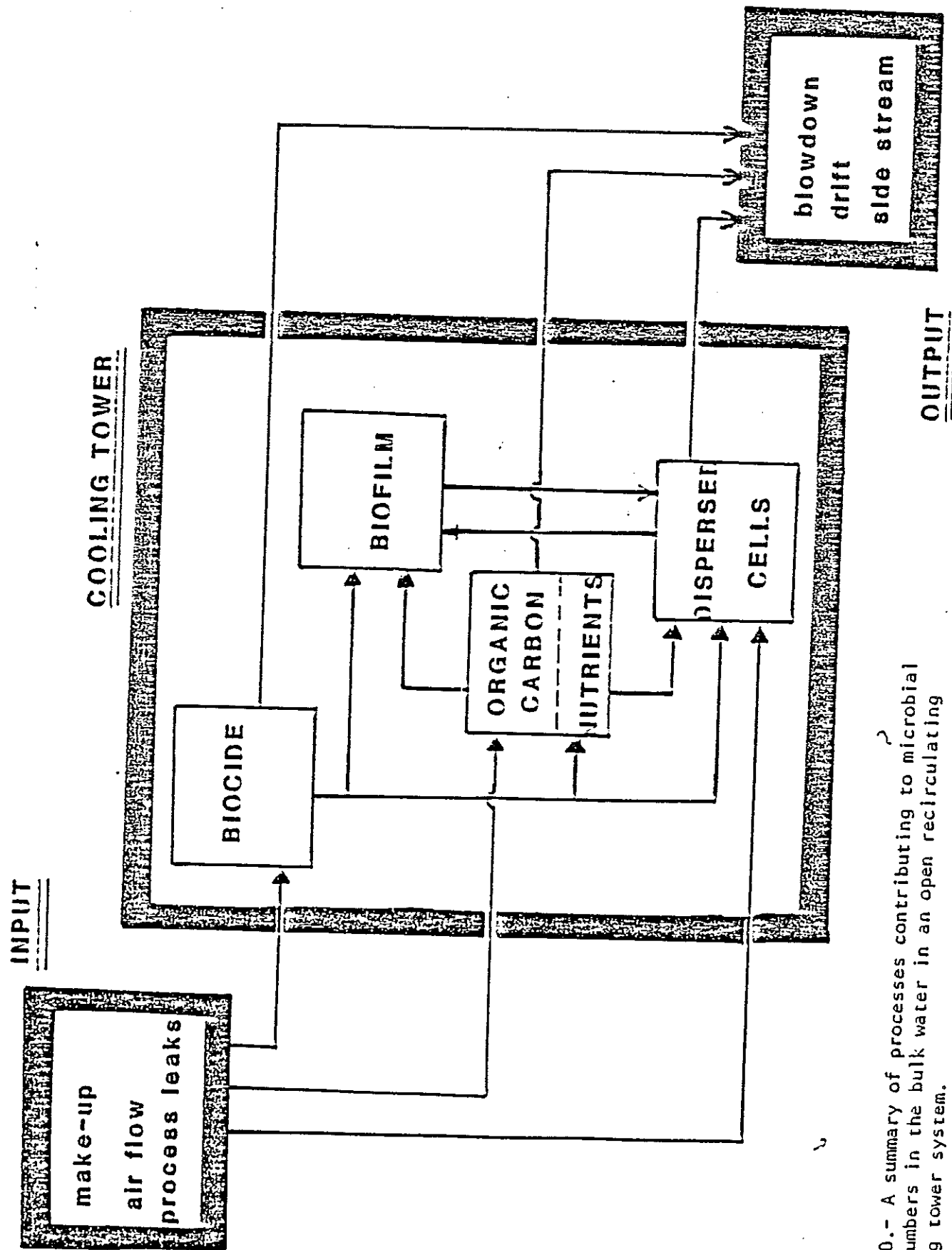


Fig. 10.- A summary of processes contributing to microbial cell numbers in the bulk water in an open recirculating cooling tower system.

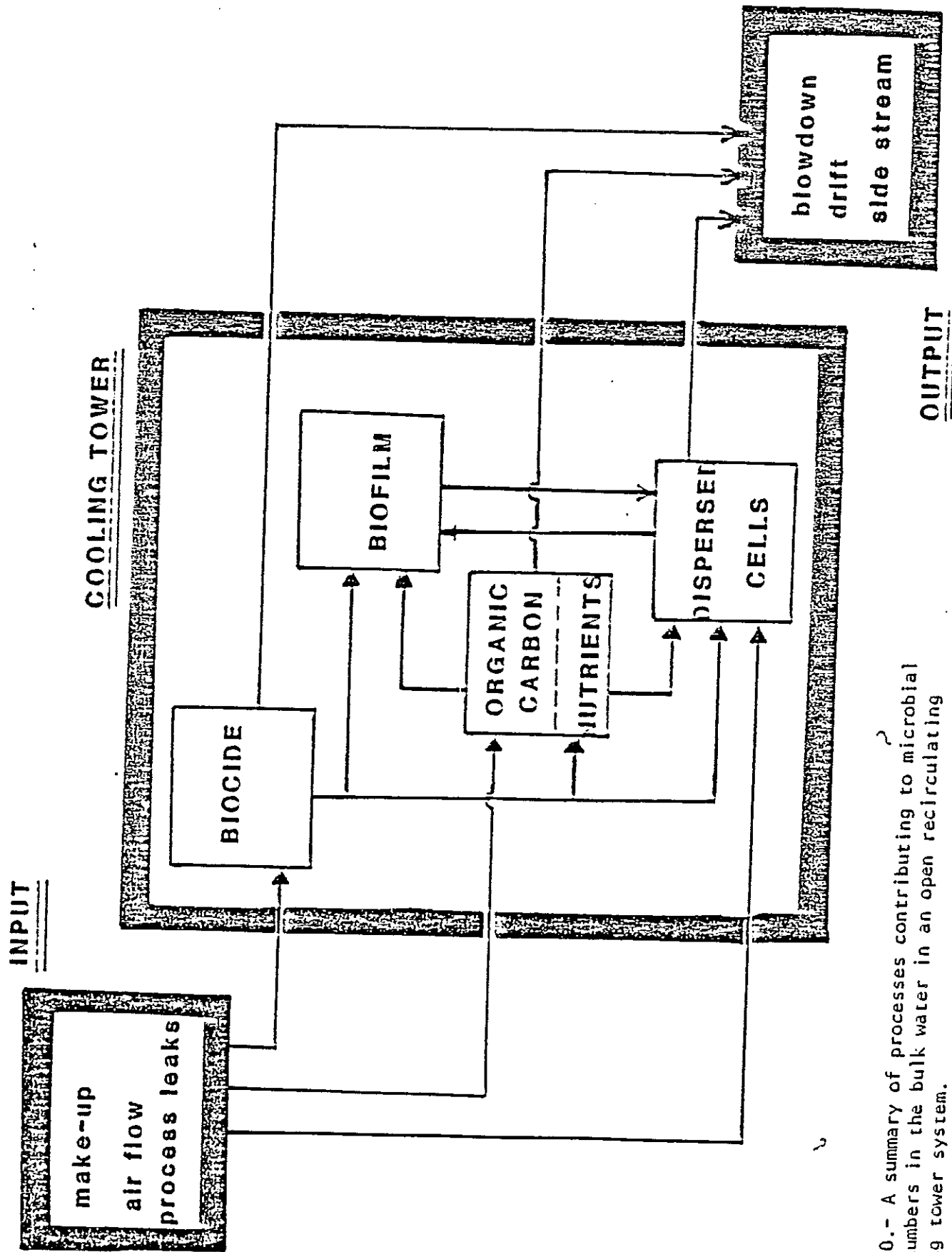


Fig. 10.- A summary of processes contributing to microbial cell numbers in the bulk water in an open recirculating cooling tower system.

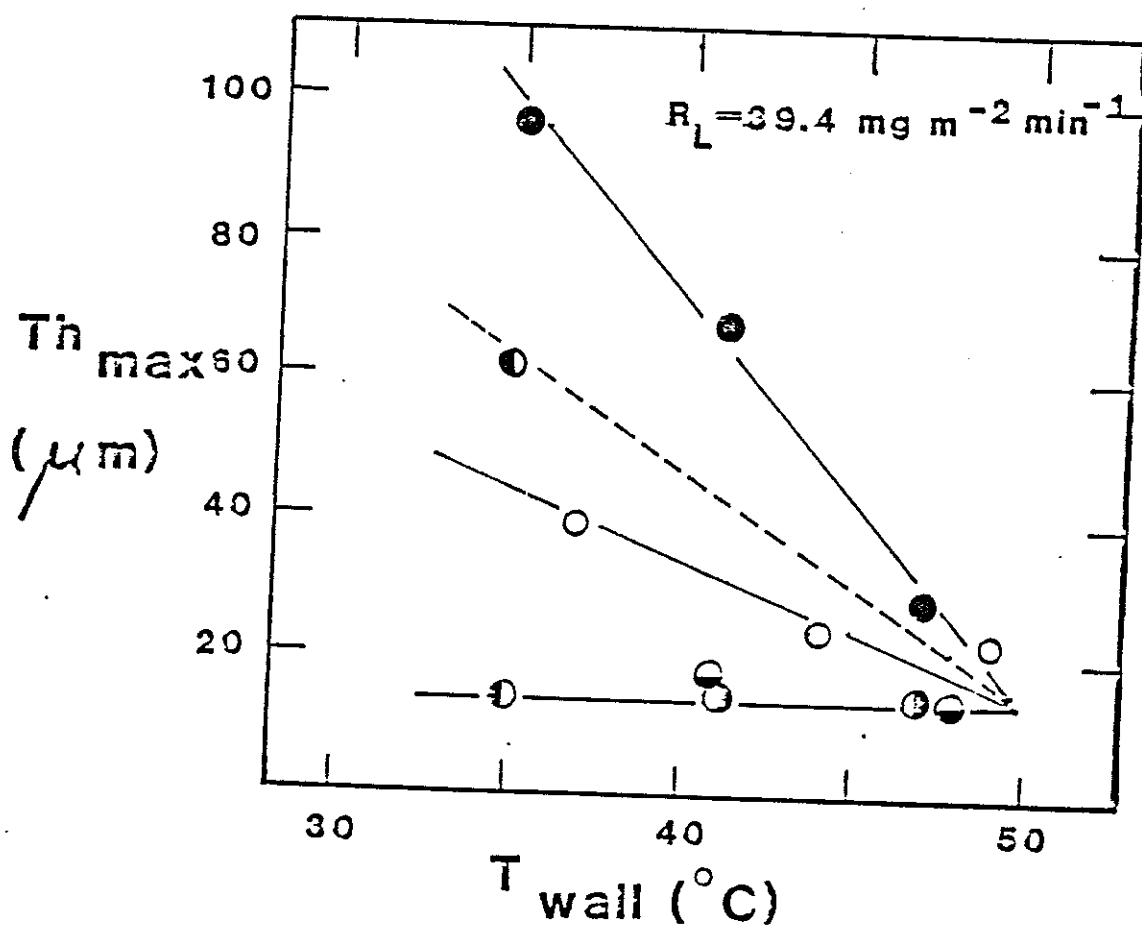


Fig. 12.- The influence of wall temperature and nutrient loading rate on maximum biofouling deposit thickness in a laboratory system²³.

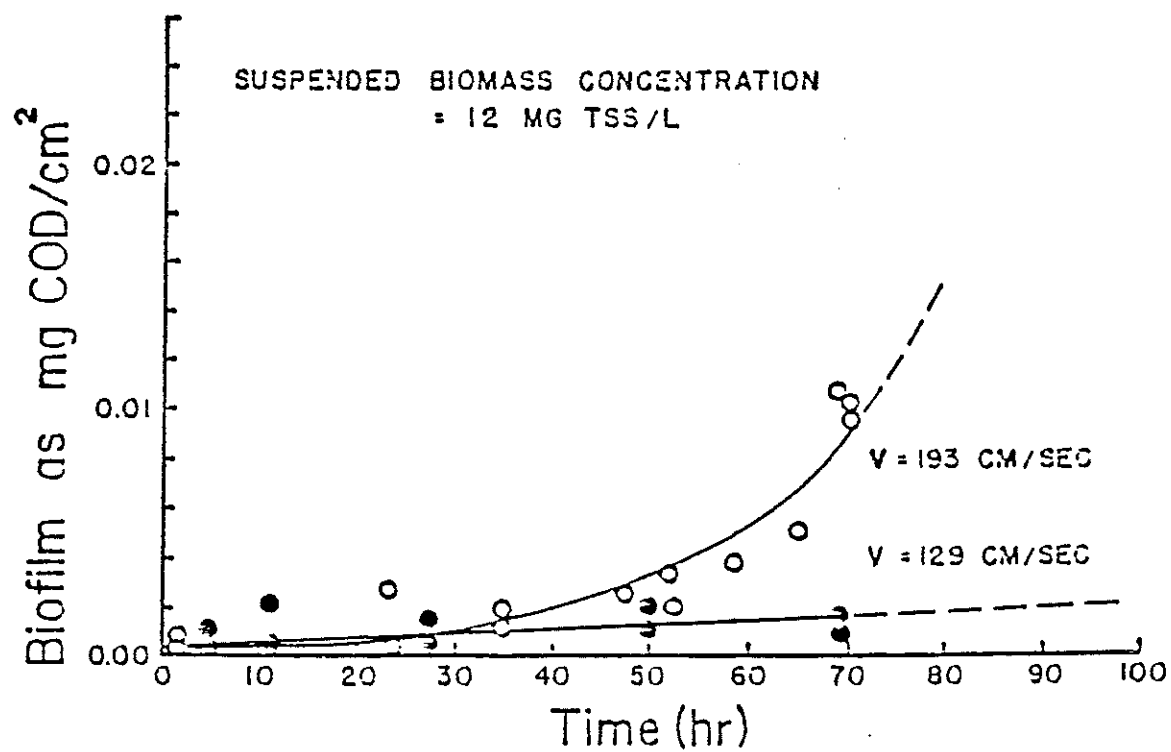


Fig. 13.- Influence of fluid shear stress on biofilm development²⁹.

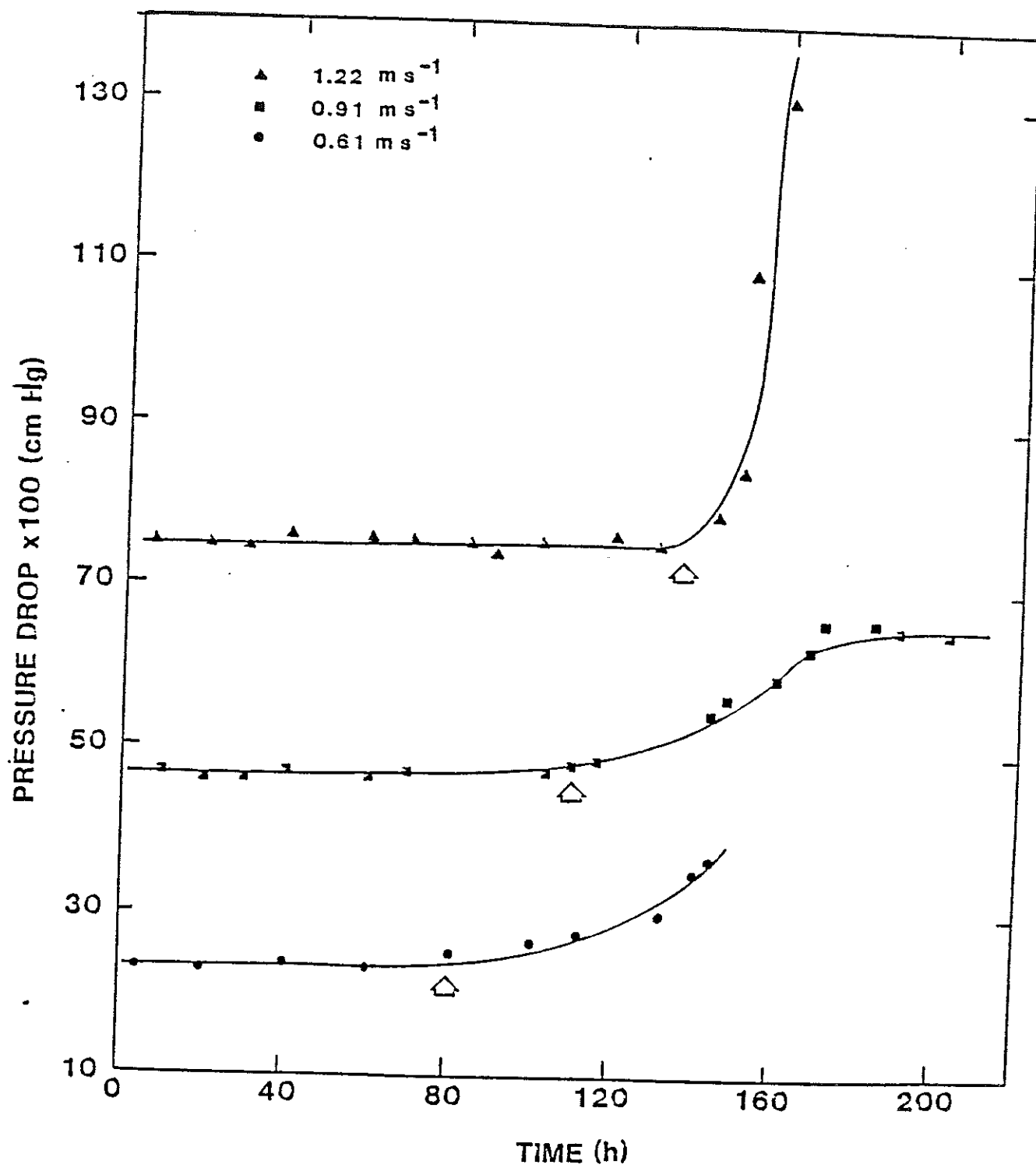


Fig. 14.- Influence of fluid shear stress on fluid frictional resistance due to biofilm development³⁰.

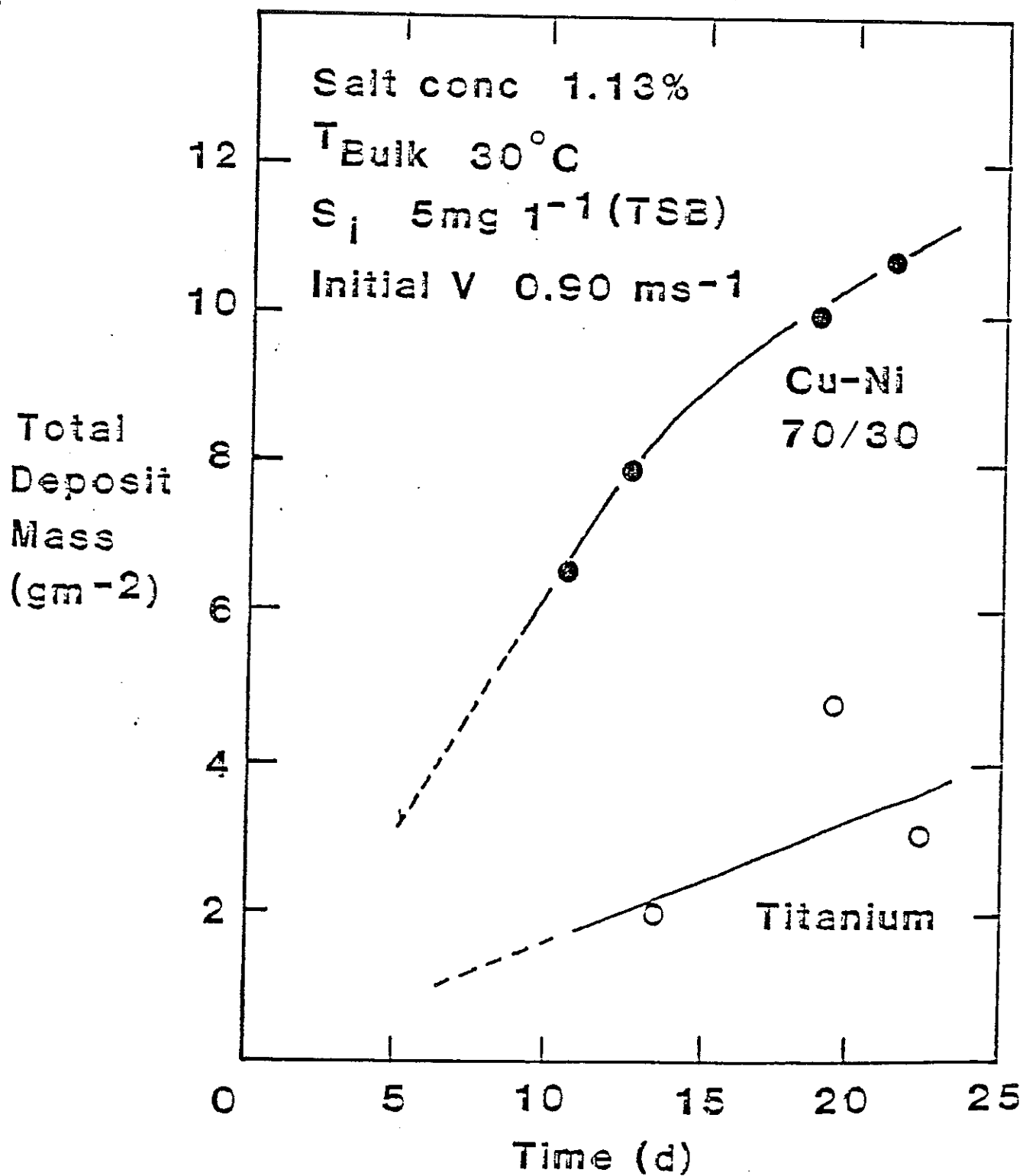


Fig. 15.- Accumulation of fouling deposit on two alloys¹⁹.

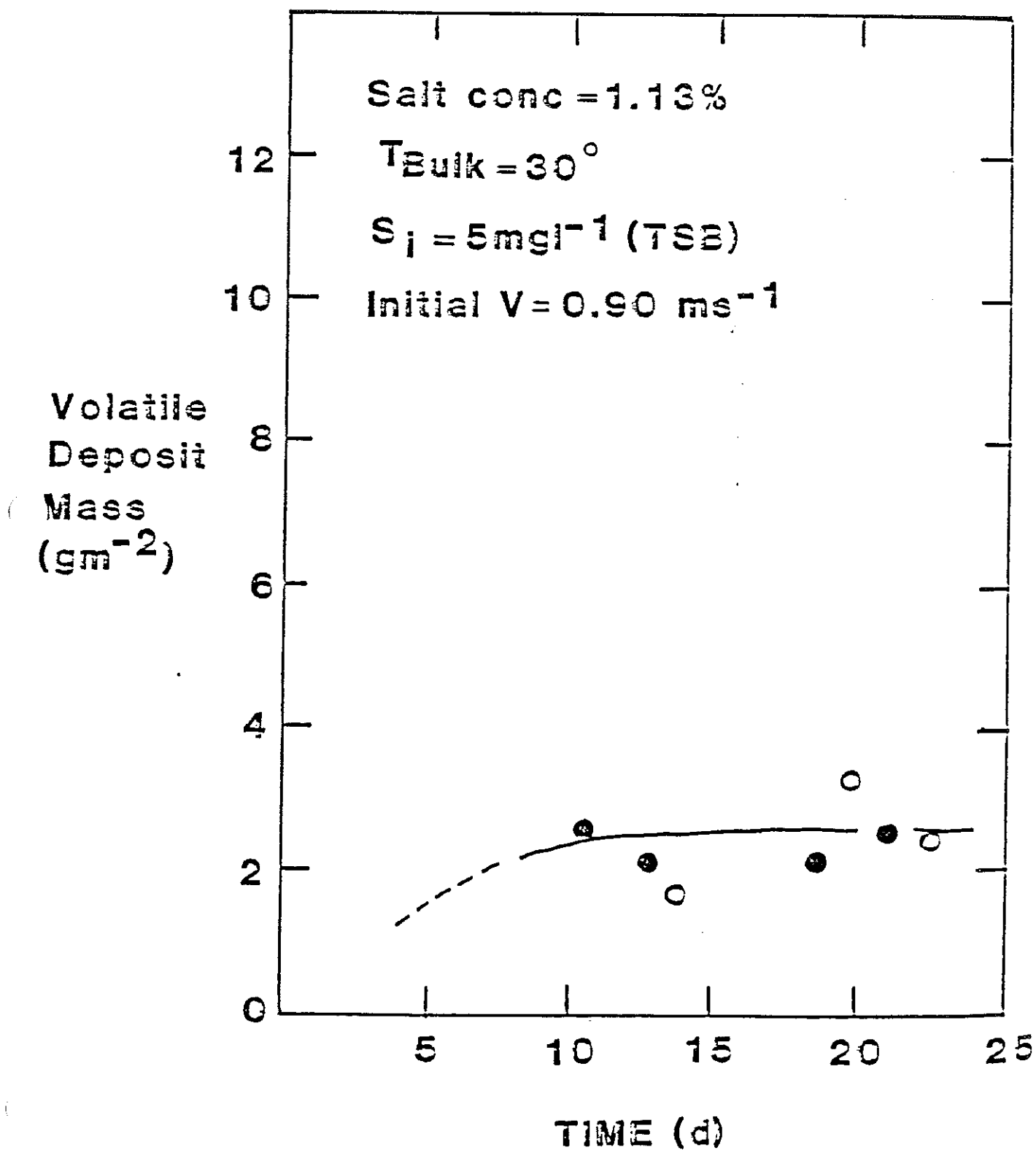


Fig. 16.- Accumulation of volatile deposit mass on two alloys¹⁸.

ANTICORROSIVE PROTECTION BY PAINTS IN MARINE AND INDUSTRIAL ENVIRONMENTS

Juan José Caprari

CIDEPINT - Research and Development Center for Paint Technology

The microbiological corrosion can be considered, in light of the present knowledge on the subject, as one of the greater and more subtle dangers for the metallic and non-metallic structures used in media where there exists the possibility of bacteria development. From the standpoint of protection by paints, the industries more affected by the microbiological corrosion phenomena are the petroleum industry, the equipment for the purification of industrial and sewage water wastes and those industries that develop their activities in marine areas.

The action of the microbiological corrosion includes a greater quantity of metallic materials, as naval steel, aluminium and its alloys, copper and its alloys, stainless steel and besides non-metallic materials such as concrete, plaster, etc.

The study of the action of these corrosive bacteria has taken a great impulse during the last years, specially from the moment when it is raised as a problem in the marine medium, due to its influence on the deterioration of fixed structures (harbour platforms, buoys) and mobile structures (ships hulls, off-shore constructions) and for the importance relating maintenance and replacement costs.

The bacteria role in materials corrosion is associated with a chemical activity that develops on the substrate due to the presence of aggressive substances coming from the metabolic processes of the microorganisms, during their growth and reproduction. A increase of both vital functions accelerates parallelly the chemical reactions and increases the surface attack.

Even when a bacteria may be determined as responsible for the deterioration, the attack that takes place is generally a consequence of different species associations, complemented by enzymes that catalyse the reaction.

The corrosion effects on the substratum may be attributed to different factors: a direct chemical action of metabolites (sulfuric acid, organic and inorganic sulfides, organic acids that act as chelating agents, etc.); a cathodic depolarization related to an anaerobic growth and development; changes in the oxygen potential, in the pH values and in the saline concentration, with the formation of local electrochemical cells; action over certain corrosion inhibitors (nitrite and ammine oxidation); action over some of the components of the protective coatings (bitumen in the case of bituminous paints); presence of variable biomass quantities; or, finally, to hygroscopic salts deposits. In all the cases the chemical substances submit the protective coating to extreme exigencies.

The following topics were considered in this paper: bacteria nature and characteristics; reactions which take place; bacterial corrosion on concrete and metallic materials; protection by paint systems; design as an important factor in the corrosion processes; the influence of metallic surface preparation; selection of coating application method; physical and chemical properties of paint formulations and its relation with bacteria and fungi action and paints for the anticorrosive protection in highly aggressive media are mentioned.