INDUSTRIAL CHEMICAL CLEANING

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Preface

This book has been written to provide information for chemists, process engineers, and management personnel who deal with industrial chemical cleaning contractors. Because of the specialized equipment required, chemical cleaning is seldom done in-house, but, even so, the client should be qualified to discuss the details of proposed procedures with the contractor when negotiating a contract. Furthermore, several of the methods discussed in the book are protected by patents, so they are best left to qualified contractors who have made the necessary licensing arrangements. As with any purchased service, however, it is to the purchaser's advantage to have a good understanding of the work to be done and the methods to be used. The principles and practice of industrial cleaning described here will enable any technically trained individual to understand chemical cleaning operations.

Chapter I contains a discussion of the sources and composition of various types of fouling deposits; the mechanism of corrosion; hazards that are encountered in chemical cleaning; and a brief description of the special equipment used by contractors. Chapters II, III, and IV contain detailed descriptions of the numerous chemicals used for industrial cleaning including alkalis, acids, corrosion inhibitors, and wetting agents, as well as some special agents. Several patented processes are also considered, as are nonaqueous solvents, foams, and a few nonchemical procedures, the most useful of which is high pressure water blasting.

Chapter V explores the principles and practice of the very important subject of passivation. Chapter VI deals with planning and contracting of chemical cleaning jobs with emphasis on safety and the proper disposal of hazardous wastes.

The next four chapters, VII-X, contain specific procedures for deoiling, cleaning, and passivating steam generators, heat exchangers, columns, reactors, and furnaces. The directions given here are intended as general information and should not be applied indiscriminately without the advice of a qualified professional contractor. Great care must be taken, for instance, to take account of specific metallurgical considerations to avoid major damage to equipment by incompatible chemicals.

Chapter XI includes laboratory procedures for measuring the strength of cleaning solutions, estimating solubilities, sampling fouling deposits, and evaluating industrial cleaners.

Although I must assume responsibility for any errors, I wish to thank my associate, Mr. Donald A. Alexander, for his thorough reading of the manuscript and his many suggestions that led to improvements in the work. He is widely recognized in the petroleum refining industry for his detailed knowledge of chemical cleaning processes and for his outstanding safety record as a supervisor of these inherently hazardous operations. Mr. Robert J. Hammond, who is unusually talented in piping layout work, kindly provided the piping diagrams. Finally, I am most grateful to my wife, Dolores, for her many contributions to the success of my books.

Richmond, California
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James W. McCoy

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I

Principles of Chemical Cleaning

The formation of various types of scales, sludges, and deposits in process equipment of the petroleum refining and chemical processing industries occurs frequently. Some of these present serious problems—for example, the scaling of boiler tubes, or corrosive attack on the metals of which various types of reactors and similar vessels are constructed. Others are less significant—for instance, the phosphate sludges formed in boiler drums as the result of over-treatment with phosphate, or the formation of deposits of coke and salts on the floors of furnaces.

When such equipment is taken out of service, preferably on a scheduled shut-down for maintenance, but sometimes because of failure or loss of heat transfer capacity, the engineer in charge of operations often obtains a chemical analysis of any fouling material found. This is done for any of several reasons: to find whether the deposit resulted from corrosive attack on the vessel or from foreign material brought into the vessel; to indicate the reason for failure of equipment; or to assess the extent to which a vessel has been attacked during a certain period of operation. More often than not, however, all that is desired is an indication of the conditions necessary for the removal of the deposit from the site of formation. In this case, no analysis is required, but rather a report on the loosening effect of water, steam, detergents, dilute inhibited acids, alkalis, or other agents on the material.

Within the past 30 years it has become apparent that in-place cleaning of industrial equipment by means of chemical solutions is, in many instances, safer and more economical than the older, labor-intensive, mechanical methods. As the choice of cleaning agent is to some extent empirical, laboratory performance tests with representative samples are desirable to determine solubility in various solutions, the most effective temperature, and the efficiency to be expected in cleaning the fouled equipment. Specific directions for sampling are difficult to provide because of the many different circumstances encountered. Nevertheless, it is evident that the interpretation of analytical and solubility data depends upon a knowledge of the normal operation of process units and upon information concerning the location, consistency, distribution, and other features of the deposit. In vessels containing sections, baffles, or trays, for instance, the distribution of fouling is often significant, and samples from different locations may vary greatly in composition and solubility.

I.1 SOURCES AND COMPOSITION OF FOULING

Before any attempt is made to dissolve or loosen scales or deposits with a chemical solution, it is necessary to characterize the material as to its composition, which in some measure is related to its origin. For the purpose of a systematic discussion, fouling material is here arbitrarily classified by origin as water-formed, corrosion, microbiological, organic, or combustion deposits.

I.1.a Water-Formed Scales and Deposits

Scales and deposits are regularly encountered in aqueous cooling systems, mixers, solution tanks, boilers, and other steam generators, surface condensers, and in equipment in which heat is transferred from a process stream to water. The term scale describes a continuous, adherent layer of foreign material crystallized on the water side of a surface through which heat is exchanged. In principle, by adding certain chemicals the growth of scales can be inhibited and the insoluble particles can be dispersed in the recirculating water and removed by blowdown. Should the particles come out of suspension, however, they can accumulate as sludge in quiet sections of a boiler or cooling system. Deposit is a general term applied to more-or-less loose accumulations often found in less-turbulent sections of boilers, cooling systems, and water-treating facilities.

Scales are objectionable because of their insulating effect. In a boiler tube, for instance, they cause overheating and eventual failure of the metal. Deposits often cause plugging in critical areas such as waterwalls, waterwall headers, in blowdown lines, and in gauge glasses. Many different mineral structures have been identified in boiler scales by the methods of x-ray diffraction, electron diffraction, and polarizing microscopy. Examples of silicate scales are: acmite, $Na_2O \cdot Fe_2O_3 \cdot 4SiO_2$; analcite, $Na_2O \cdot Al_2O_3 \cdot 4SiO_2 \cdot 2H_2O$; pectolite, $Na_2O \cdot 4CaO \cdot 6SiO_2 \cdot H_2O$; serpentine, $3MgO \cdot SiO_2 \cdot 2H_2O$; sodalite, $Na_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot 2NaCl$; xonotlite, $5CaO \cdot 5SiO_2 \cdot H_2O$. When phosphate is used for internal treatment, ferric phosphate, $FePO_4$, basic magnesium phosphate, $Mg_3(PO_4)_2 \cdot Mg(OH)_2$, and hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, may also be precipitated, as well as the more common anhydrite, $CaSO_4$, and aragonite, $CaCO_3$. As already noted, the presence of these and other scales impedes the circulation of water and reduces heat transfer, both of which cause overheating and failure of tubes.

Scales and deposits form in a boiler because the compounds of which they are composed are insoluble under the conditions prevailing there. Two factors combine to make calcium salts especially troublesome: certain anhydrous calcium salts, notably the sulfate, decrease in solubility as temperature and pressure increase, and increasing temperature shifts the equilibrium of the following reaction to the right, causing $CaCO_3$ to precipitate.

$$Ca^{++} + 2HCO_3^{-} = CaCO_3 + CO_2 + H_2O \tag{I-1}$$

In addition, hydrolysis of excess bicarbonate increases the concentration of hydroxyl ion, precipitating $Mg(OH)_2$, the solubility product of which is 5.5×10^{-12}. The solubility of $CaSO_4$ decreases rapidly with increasing temperature, producing an extremely hard, adherent, insoluble coating on boiler tubes, especially in locations where heat flux is high. The compositions of several scales containing aluminum, magnesium, calcium, and silicate have been given above. Analcite and acmite, which form at high temperature, are invariably found beneath sludges of hydroxyapatite or serpentine, or under porous deposits of iron oxides. Occasionally, other extremely insoluble iron or magnesium silicates are also encountered, and now and then α-quartz, SiO_2, appears, usually originating from colloidal silica, finely divided silt, or sand in the feed water.

The precipitate formed by calcium in phosphate-treated boiler water is usually represented as the normal phosphate, $Ca_3(PO_4)_2$. Attempts to precipitate this salt in the laboratory, however, invariably produce hydroxyapatite, the formula of which can be written in various ways including $Ca_{10}(PO_4)_6(OH)_2$, $3Ca_3(PO_4)_2 \cdot Ca(OH)_2$, and $Ca_5(PO_4)_3OH$. A consideration of the solubility products $(Ca^{++})(CO_3^{--}) = 4.8 \times 10^{-9}$, $(Ca^{++})^3(PO_4^{---})^2 = 1.3 \times 10^{-32}$, and $(Ca^{++})^5(PO_4^{---})^3(OH^-) = 3 \times 10^{-58}$, indicates that the basic salt forms in boiler water. Magnesium forms similar salts such as $Mg_3(PO_4) \cdot Mg(OH)_2$ and $Mg_5(PO_4)_3OH$, which are undoubtedly much less soluble than $Mg(OH)_2$.

Latimer[1] notes that in aqueous solution silicic acids participate in complex equilibria on account of the small differences in free energy between the numerous polyacids and their salts. Thus, a variety of mineral types have been identified in boiler scales and deposits. Acmite, $Na_2O \cdot Fe_2O_3 \cdot 4SiO_2$, and analcite, $Na_2O \cdot Al_2O_3 \cdot 4SiO_2$, both of which are quite insoluble, require high temperature to form and, thus, are seldom found in boilers operated at less than 300 psi. On the other hand, serpentine, $3MgO \cdot SiO_2 \cdot 2H_2O$, and hydrated magnesium orthodisilicate, $Mg_3Si_2O_7 \cdot 2H_2O$, can form at any pressure. Garrels and Christ[2] show that magnetite, Fe_3O_4, is unstable relative to ferrous metasilicate, $FeSiO_3$, so that if an aqueous solution contains sufficient silica to satisfy all of the iron present, ferrous metasilicate forms in preference to magnetite. Iron silicate scales are exceedingly insoluble and adherent. Table I-1 summarizes the components of deposits most commonly found in boilers and related equipment.

In addition to the inorganic components mentioned, boiler deposits may also contain organic material including starch, quebracho, pyrogallol, sodium alginate, sodium mannuronate, chestnut tannin, and carbonized sulfonated lignins, all of which have been used as sludge conditioners. When oil is present as a contaminant in boiler water, loose scales may form, particularly in water wall tubes. Oil serves as a nucleus and binder for scaling at hot spots, although these scales are often merely baked mud that is easily dislodged by hammering the tubes. The "oil balls" found in steam drums and water wall headers are typical formations in turbulent sections; they are especially common in steam drums, where they are formed by the rolling motion of the water.

A large proportion of the fouling that occurs in recirculating cooling systems is occasioned by mishaps related to pH control and contamination of the water by reducing agents. Failures in some part of the acid injection system are the source of most acid contamination. When the pH falls below 5.5 corrosion inhibitor films are damaged; at about pH 4 hydrogen begins to evolve, and iron dissolves rapidly.

$$Fe + 2H^+ = Fe^{++} + H_2 \tag{I-2}$$

In a system treated with chromate, ferrous ion formed in Eq. (I-2) is oxidized to ferric ion.

TABLE I-1

Components of Boiler Deposits

Mineral	*Formula*	*Nature of Deposit*	*Usual Location and Form*
Acmite	$Na_2O \cdot Fe_2O_3 \cdot 4SiO_2$	Hard, adherent	Tube scale under hydroxyapatite or serpentine
Alpha quartz	SiO_2	Hard, adherent	Turbine blades, mud drum, tube scale
Amphibole	$MgO \cdot SiO_2$	Adherent binder	Tube scale and sludge
Analcite	$Na_2O \cdot Al_2O_3 \cdot 4SiO_2 \cdot 2H_2O$	Hard, adherent	Tube scale under hydroxyapatite or serpentine
Anhydrite	$CaSO_4$	Hard, adherent	Tube scale, generating tubes
Aragonite	$CaCO_3$	Hard, adherent	Tube scale, feed lines, sludge
Brucite	$Mg(OH)_2$	Flocculent	Sludge in mud drum and water wall headers
Copper	Cu	Electroplated layer	Boiler tubes and turbine blades
Cuprite	Cu_2O	Adherent layer	Turbine blades, boiler deposits
Gypsum	$CaSO_4 \cdot 2H_2O$	Hard, adherent	Tube scale, generating tubes
Hematite	Fe_2O_3	Binder	Throughout boiler
Hydroxyapatite	$Ca_{10}(PO_4)_6(OH)_2$	Flocculent	Mud drum, water walls, sludge
Magnesium phosphate	$Mg_3(PO_4)_2$	Adherent binder	Tubes, mud drum, water walls
Magnetite	Fe_3O_4	Protective film	All internal surfaces
Noselite	$4Na_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot SO_4$	Hard, adherent	Tube scale
Pectolite	$Na_2O \cdot 4CaO \cdot 6SiO_2 \cdot H_2O$	Hard, adherent	Tube scale
Serpentine	$3MgO \cdot 2SiO_2 \cdot H_2O$	Flocculent	Sludge
Sodalite	$3Na_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot 2NaCl$	Hard, adherent	Tube scale
Xonotlite	$5CaO \cdot 5SiO_2 \cdot H_2O$	Hard, adherent	Tube scale

$$3Fe^{++} + CrO_4^{--} + 8H^{+} = 3Fe^{+++} + Cr^{+++} + 4H_2O \qquad \text{(I-3)}$$

Above a pH of about 3 ferric ion is hydrolyzed to the hydrous oxide.

$$Fe^{+++} + 3H_2O = Fe(OH)_3 + 3H^{+} \qquad \text{(I-4)}$$

If caustic soda is now added, as it often is in an acid spill, excess ferrous ion and chromic ions in the system precipitate as the hydrous oxides when the pH reaches about 7.

$$Fe^{++} + 2OH^{-} = Fe(OH)_2 \qquad \text{(I-5)}$$

$$Cr^{+++} + 3OH^{-} = Cr(OH)_3 \qquad \text{(I-6)}$$

Ferrous hydroxide is then oxidized rapidly by oxygen in the water to ferric hydroxide, producing heavy, slimy fouling.

$$2Fe(OH)_2 + \tfrac{1}{2}O_2 + H_2O = 2Fe(OH)_3 \qquad \text{(I-7)}$$

The voluminous and insoluble hydrous oxides settle in places where the flow of water is slow, then under-deposit corrosion ensues, adding further to the mass of fouling.

When reducing agents contaminate chromate-treated cooling water chromate is reduced to chromic hydroxide and corrosion rates increase rapidly. Two especially troublesome reducing agents are hydrogen sulfide and sulfur dioxide, both of which are common in chemical processing and petroleum refining. Catalytic cracking, for example, produces hydrogen sulfide and hydrogen cyanide from sulfur and nitrogen compounds in petroleum feed stocks. These acidic gases are evolved in process gas (methane and ethane). Admiralty brass exchangers used to cool the mixed gases are occasionally penetrated, allowing hydrogen sulfide and hydrogen cyanide to leak into the cooling water.

Hydrogen cyanide reacts with any ferrous ion in the water to form ferrocyanide [hexacyanoferrate (II) ion].

$$6HCN + Fe^{++} = Fe(CN)_6^{-4} + 6H^{+} \qquad \text{(I-8)}$$

Hydrogen sulfide is oxidized to sulfur by chromate ion, which is itself reduced to chromic hydroxide.

$$3H_2S + 2CrO_4^{--} + 2H_2O = 3S + 2Cr(OH)_3 + 4OH^{-} \qquad \text{(I-9)}$$

If, as is usual, the chromate treatment also contains zinc ion, it is precipitated as ZnS, destroying the cathodic corrosion barrier. When an admiralty brass cooler is penetrated by hydrogen sulfide a tough, gelatinous sludge of ZnS, CuS, $Cr(OH)_3$, and elemental sulfur accumulates in the tubes and on the tube sheets.

Sulfur dioxide from stacks, SO_2-treating, and other sources occasionally is drawn into cooling towers. In addition to reducing chromate ion, the pH of the water is lowered by the hydrolysis of the gas.

$$SO_2 + H_2O = H^+ + HSO_3^- \qquad \text{(I-10)}$$

$$3SO_2 + 2CrO_4^{--} + 4H_2O = 3SO_4^{--} + 2Cr(OH)_3 + 2H^+ \qquad \text{(I-11)}$$

Process leaks occur frequently in petroleum refining that contaminate cooling water. Usually the bulk of a heavier oil collects on the surface of the water in the basin, from which it can easily be skimmed into a vacuum truck. Compounded lubricating oils, however, from leaking oil coolers, form extremely tight, thick emulsions of water, dirt, dispersant, and sometimes calcium salts; these emulsions tend to plug tubes and foul tube sheets of heat exchangers. Leaking oil seldom reduces chromate, but it coats the filling material in the cooling tower, particularly if it contains film packing, and interferes with the air/water contact.

Wind-borne dust is blown into cooling towers, dispersed in the water, then carried along until it reaches a place where the velocity of the water slows enough for the solids to settle and build up a deposit. This is especially troublesome during land filling, road work, or excavation, but every dry, windy day adds a great deal of dirt to a cooling system. Much of this settles in the basin of the cooling tower, but enough is carried into the cooling system to cause difficulties. Clays, for instance, are so finely divided that they readily form colloidal solutions, or sols, in cooling water that under certain circumstances undergo gelation, setting to a more-or-less homogeneous, firm, elastic gel containing 2–3 percent clay with the remainder water.[3] Particles of clay also tend to adhere to each other when wet, and deposit as impervious, sticky masses. Oil leaks further complicate matters, as clay and other soils have a marked affinity for oil.

If polyacrylamides are used to disperse mud through a cooling system, it is possible for soft, gelatinous masses to form if the polymer is added too rapidly. When this material enters the tubes of a heat exchanger, the heat transforms it to a hard, plastic mass that is most difficult to remove. Mechanical blockage also occurs frequently when wood fibers from cooling tower deterioration or chips from carpentry repairs lodge in heat exchanger tubes or upon the faces of tube sheets.

Calcium, magnesium, and ferric phosphate are commonly found in scales and deposits in phosphate-treated cooling systems. A particularly voluminous and insoluble salt is formed in cooling water treated with, or contaminated by, ferrocyanide. This is the familiar, intensely blue ferric ferrocyanide, $Fe_4[Fe(CN)_6]_3$, also called Prussian blue ($K_{SP} = 3.3 \times 10^{-41}$). Other organic salts that occur in water-formed deposits include calcium carbonate, calcium sulfate, and magnesium silicate.

I.1.b Corrosion Deposits

Corrosion is the result of the oxidation of metal by some oxidizing agent in the environment. The area over which the metal is oxidized is called the anode and that at which the oxidizing agent is reduced is called the cathode. These areas are separated, but usually are not far apart. As corrosion proceeds, electrons flow through the metal between these areas and ions flow from one area to the other through the solution. This system constitutes an electrochemical cell.

The oxidation (corrosion) of iron by hydrogen ion is represented by the following equation:

$$2H^+ + Fe = Fe^{++} + H_2 \tag{I-12}$$

This reaction is opposed by an irreversible potential called the hydrogen overvoltage, which is markedly affected by the condition of the surface of the metal. Agents that raise the overvoltage oppose or inhibit corrosion, while conditions that facilitate the escape of hydrogen from the cathodic surface (roughness, debris, etc.) augment corrosion. Table I-2 lists several anodic–cathodic couples that can occur in aqeuous environments, for example, cooling systems or boilers.

Much iron corrosion is caused by failure to clean and passivate new equipment properly, and also by allowing metallic surfaces to become scaled or fouled. In general, the corrosion product of mild steel is ferric oxide, Fe_2O_3. In boilers under sulfite or hydrazine treatment magnetite, Fe_3O_4, is the usual product.

$$3Fe_2O_3 + SO_3^{--} = 2Fe_3O_4 + SO_4^{--} \tag{I-13}$$

Oxides of iron are often mixed with other inorganic compounds, oil, tar,

TABLE I-2

Anodic–Cathodic Couples

Anode	*Cathode*
Stressed metal	Unstressed metal
Low oxygen concentration	High oxygen concentration
Clean metal	Fouled metal
Iron	Copper

wax, or coke and, if old, are likely to be quite insoluble. Copper and cuprous oxide derived from corrosion of copper alloys in preboiler equipment are also frequently seen in boiler corrosion deposits. Cupric ions dissolved from stage heaters, condensers, and evaporators subsequently plate on steel boiler tubes, become a cathode, and the surrounding and underlying steel corrodes.

Hydrogen sulfide is a source of corrosion in petroleum refineries, where reflux drums, stripping columns, and heat exchangers fabricated of admiralty brass, monel, and cupro-nickel alloys are exposed to it. Corrosion deposits from these units may contain sulfides of copper, nickel, zinc, and iron. Regenerators in hydrofluoric alkylation plants, which are also made of monel, are often found to contain nickel, copper, and iron fluorides as products of corrosion.

I.1.c Microbiological Deposits

Water in an open recirculating cooling system is continuously infested with a variety of nuisance microorganisms indigenous to soil including bacteria, algae, and fungi.(4) These organisms are introduced in wind-borne dirt and once in the water they proliferate unless checked by the addition of microbicides. Algae are often visible as green, felt-like mats in internal sections of cooling towers that are wet and accessible to sunlight. Filamentous and capsulated colonial algae coat splash packing and interior structural members, thereby interfering with the formation of droplets that is essential for intimate contact between water and air; they are otherwise innocuous. As these microorganisms require sunlight to live, they are not found within heat transfer equipment. Although in the field of water treatment there is frequent reference to "dead algae," as a practical matter,

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