IPS

ENGINEERING STANDARD

FOR

CHEMICAL CONTROL OF CORROSIVE ENVIRONMENTS

GENERAL

1. SCOPE

This Engineering Standard which is contained in 3 parts deals with the control of corrosive environment by inhibitor.

Part 1: Covers general requirements for controlling of corrosive environments.

Part 2: Specifies requirements for controlling of corrosive environments involved in petroleum and petro-chemical industries.

Part 3: Specifies requirements for controlling corrosive environments involved in utility systems (cooling water and boiler water systems).

This Standard may involve hazardous materials, operation, and equipment, but the standard does not purpant to address all of the safety problems, it is the responsibility of the user of the standard to establish appropriates.

2. REFERENCES

Throughout this Standard the following standards and codes are referred to. The editions of these standards and codes that are in effect at the time of publication of this Standard shall, to the extent specified herein, form a part of this Standard. The applicability of changes in standards and codes that occur after the date of this Standard shall be mutually agreed upon by the Company and the Vendor/Consultant/Contractor".

API   (AMERICAN PETROLEUM INSTITUTE)

API-RP-38   "Recommended Particle for Biological Analysis of Subsurface Injection Waters"

ASTM (AMERICAN SOCIETY FOR TESTING AND MATERIALS)

ASTM Method   "Water Separation Characteristics of Aviation Turbine Fuel. ASTM Standard
2250-66T,   Part 17.P. 965"

ASTM Standard GS-87

ASTM Standard D-1660

IPS   (IRANIAN PETROLEUM STANDARDS)

IPS-E-TP-100   "Paint"
IPS-E-TP-270   "Coating"
IPS-E-TP-350   "Lining"
IPS-E-TP-740   "Corrosion Consideration in Material Selection"
IPS-E-TP-760   "Corrosion Consideration in Design"
IPS-E-TP-820   "Electrochemical Protection"
IPS-M-TP-673   "Acid Inhibitor"

NACE (NATIONAL ASSOCIATION OF CORROSION ENGINEERS)

NACE Standard   "Laboratory Corrosion Testing of Metals for the Process Industries"
TM-01-69 (1976 Revision)

NACE Standard   "Laboratory Screening Tests to Determine the Ability of Scale Inhibitors to Pre-
TM-03-74   vent the Precipitation of Calcium Sulfate and Calcium Carbonate from Solution"

NACE Standard RP-02-729 (1972)	"Economy Evaluation"
NACE Report 10182	"Wheel Test Procedure Utilizes a Revolving Wheel to which Sample Bottles Are Attached"
NACE TPC-8	"Industrial Cleaning Manual"
NACE Committee T-8 (Sep. 1971)	"Refinery Corrosion"

Other References

1) C.C Nathan and C.L Dulaney.

Statistical Concepts in Testing of Dispersants, I. & E.C. Prod. Res. and Dev. (1970), December.

2) C.C. Nathan and C.L. Dulaney.

Statistical Concepts Facilitate Evaluation of Corrosion Inhibitors, Materials Protection 10, 21-25 (1971), February.

3) Economic Data on Chemical Treatment of Gulf Coast Cooling Waters, Corrosion 11, 61-62 (1965), Nov., reported by NACE Recirculating Cooling Water Sub-committee.

Publications

a) Source Book (a collection of outstanding articles from the technical literature). Seymour. K. Coburn NACE, third printing, July 1985.

b) Corrosion Control and Monitoring in Gas Pipelines and Well Systems. Robert G. ASPE NGFR NACE, Copyright 1989, NACE.

c) Corrosion Engineering Mans. Fontana, Copyright 1986.

d) Corrosion Prevention in the Process Industries R.N. Parkins, NACE, Copyright 1990.

e) Corrosion Prevention NACE, Course No. 2. Frank E. Rizzo, 1974.

f) Corrosion Inhibitor for Oil and Gas Products from Metals handbook, Ninth Edition, Volume 13, Corrosion.

g) Plant Design and Economics for Chemical Engineers, Copyright 1981, Timmeuhous, Kalus D.

h) ISO 9003: 1993, Quality Systems-Model for Quality Assurance in Final Inspection and Tests.

i) Corrosion Inhibitors, An Industrial Guide, Copyright 1987 by Ernest W. Flick, published in the U.S.A.

j) International Approaches to Reducing Corrosion Costs (sponsored by the NACE, International Relations Committee).

k) Oil and Gas Journal, 117 (1965) May, 3, Entitled "New Fast Approach to Reduced Preheat Exchanger".

l) "Refinery Corrosion", September 1971, Meeting of NACE T-8.

3. DEFINITIONS AND TERMINOLOGY

Additive

A Substance added in a small amount, usually to a fluid, for a special purpose, such as to reduce friction, corrosion, etc.

Aqueous

Pertaining to water; an aqueous solution is a water solution.

Bactericide

Chemicals that kill hactena.

Bacteriostat

A substomce which prevents or retards the growth of bacteria.

Biocide

A chemical which kills other of life in addition to bacteria.

Biological Corrosion

Biological corrosion is not a type of corrosion; it is the deterioration of a metal by corrosion processes that occur directly or indirectly as a result of the activity of living organisms. These organisms include micro forms such as bacteria and macro types such as algae and barnacles. Microscopic and macroscopic organisms have been observed to live and reproduce in mediums with pH values between 0 and 11, temperatures between -1.1°C (30°F) and 82.2°C (180°F), and under pressures up to 1020 bar (15,000 lb/in²). Thus biological activity may influence corrosion in a variety of environments including soil, natural water and sea water, natural petroleum products, and oil emulsion-cutting fluids.

Biostat

A chemical which retards growth of other forms of life in addition to bacteria.

Cathodic Inhibitor

A chemical substance or combination of substances that prevent or reduce the rate of cathodic or reduction reaction by a physical, physico-chemical or chemical action.

Cathodic Polarization

Polarization of the cathode; a reduction from the initial potential resulting from current flow effects at or near the cathode surface. Potential becomes more active (negative) because of cathodic polarization.

Cavitation

Cavitation is a particular kind of erosion-corrosion caused by the formation and collapse of vapor bubbles in a liquid contacting a metal surface. The resultant shock forces reach high levels in local areas and can tear out jagged chunks of brittle materials or deform soft metals. Where the environment is corrosive, severity of cavitation damage increases.

Cell

A circuit consisting of an anode and a cathode in electrical contact in a solid or liquid electrolyte. Corrosion generally occurs only at anodic areas.

Corrosion

The destruction of a substance; usually a metal, or its properties because of a reaction with its surroundings (environment) i.e. physiochemical interaction between a metal and its environment which results in changes in the properties of the metal and which may often lead to impairment of the function of the metal, the environment, or the technical system, of which these form a part.

Note:

This interaction is usually of an electrochemical nature.

Corrosion Damage

Corrosion effect which is considered detrimental to the function of the metal, the environment or the technical system, of which these form a part.

Corrosion Inhibitor

An inhibitor is a substance which retards or slows down a chemical reaction. Thus, a corrosion inhibitor is a substance which, when added to an environment, decreases the rate of attack by the environment on a metal. Corrosion inhibitors are commonly added in small amounts to acids, cooling water, oil wells and other environments, either continuously or intermittently to prevent serious corrosion.

Corrosion Rate

The speed (usually an average) with which corrosion progresses (it may be linear for a while); often expressed as though it were linear, in units of mg/dm²/d (milligrams per square decimeter per day) for weight change or M.P.Y. (mils per year) or μm/y (microns per year) for thickness changes or grams per square meter per day (g/m²/d), or millimeters per year (mm/y).

Corrosive Agent

Substance which when in contact with a given metal will react with it.

Corrosive Environment

Environment that contains one or more corrosive agents.

Cracking

When a metal part fails by cracking, it is generally obvious that it cracked, but the exact type of cracking and the cause are less obvious. To determine the type of cracking, microscopic examination is necessary. In some instances the environment plays a minor role, while in others its role is major.

Crevice Corrosion

Crevice corrosion is a special type of pitting. The anode of a corrosion cell is fixed by the geometry in a crevice or under a deposit. To function as a corrosion site, a crevice must be wide enough to permit entry of the liquid, but narrow enough to maintain a stagnant zone. Metals or alloys that depend on oxide films or passive layers for corrosion resistance are particularly susceptible to crevice corrosion.

Deposit

A foreign substance which comes from the environment, adhering to a surface of a material.

Embrittlement

Severe loss of ductility of a metal (or alloy).

Environment

The surroundings or conditions (physical, chemical, mechanical) in which a material exists.

Erosion and Erosion-Corrosion

Erosion is a strictly mechanical phenomenon, while erosion-corrosion is a combination of mechanical action and chemical or electro-chemical reaction. Pure erosion seldom occurs in aqueous systems. Erosion-corrosion is characterized by grooves, gullies, waves, rounded holes and valleys, and usually exhibits a directional pattern. In copper alloy heat exchanger tubes, the attack frequently results in the formation of horseshoe-shaped depressions. Erosion-corrosion is the acceleration of metal loss because of the relative movement between a fluid and a metal surface. Generally, the movement is rapid, and the effects of mechanical wear are involved. Metal is removed as dissolved ions or as solid corrosion products that are swept from the surfaces.

Exfoliation

Exfoliation is a type of subsurface corrosion that occurs and propagates as cracks approximately parallel to the surface. It leaves the metal in a laminated, flaky, or blistered condition, and appears most frequently in aluminum alloys or Cupro-Nickels.

Fatigue

Subjecting a material to repeated stresses ultimately results in cracking. The environment may have an effect on the fatigue limit of a metal, though this is usually a minor factor. Generally, a fatigue failure is a single fracture, which is transgranular in most common metals. There is normally only a single fracture because stresses on other regions are relieved when the fracture occurs. Characteristic chevron patterns or beach marks can appear on the fracture face.

Fretting Corrosion

Another special case of erosion-corrosion, fretting corrosion, occurs when two heavily loaded metals rub rapidly together, causing damage to one or both metals. Vibration is usually responsible for the damage, but corrosion is also a factor because the frictional heat increases oxidation. In addition, mechanical removal of protective corrosion products continually exposes fresh metal. Fretting corrosion occurs more frequently in air than in water.

Galvanic Corrosion

When two dissimilar metals are in contact with each other and exposed to a conductive environment, a potential exists between them, and a current flows. The less resistant metal becomes anodic, and the more resistant, cathodic. Attack on the less resistant metal increases, while on the more resistant one, it decreases.

Hydrogen Damage

At moderate temperatures, hydrogen damage can occur as a result of a corrosion reaction on a surface or cathodic protection. Atomic hydrogen diffuses into the metal and collects at internal voids or laminations where it combines to form more voluminous molecular hydrogen. In steels, blisters sometimes occur. At higher temperatures and pressures, atomic hydrogen can diffuse into steel and collect at grain boundaries. Either molecular hydrogen is then formed, or the hydrogen reacts with iron carbides to form methane, resulting in cracking and decarburization. Hydrogen cracking is Intergranular and highly branched, but not continuous.

Hydrogen Embrittlement

Embrittlement of a metal caused by hydrogen; sometimes observed in cathodically protected steel, electroplated parts, pickled steel, etc. Hydrogen embrittlement process results decrease of toughness or ductility of a metal due to absorption of hydrogen.

Intergranular Corrosion

Metals are composed of grains or crystals which form as solidification occurs. A crystal grows until it meets another advancing crystal. The regions of disarray between crystals are called grain boundaries, which differ in composition from the crystal center. Intergranular corrosion is the selective attack of the grain boundary or an adjacent zone. The most common example of intergranular corrosion is that of sensitized austenitic stainless steels in heat affected zones at welds. Intergranular corrosion usually leaves the surface roughened, but definite diagnosis must be made by microscopic examination.

Overload

When a metal part has been subjected to a single stress beyond its tensile strength, it can fail by overload. The fracture can be either ductile or brittle, depending on factors such as the metal's hardness and operating temperature. In most cases, a single fracture results.

Passivation

A reduction of the anodic reaction rate of an electrode involved in electro-chemical action such as corrosion.

pH

A measure of the acidity or alkalinity of a solution. A value of seven is neutral; low numbers are acid, large numbers are alkaline. Strictly speaking, pH is the negative logarithm of the hydrogen ion concentration.

Pickle

A solution, usually acid, used to remove mill scale or other corrosion products from a metal.

Pitting

Highly localized corrosion resulting in deep penetration at only a few spots.

Rusting

Corrosion of iron or an iron-base alloy to form a reddish-brown product which is primarily hydrated ferric oxide.

Selective Leaching

Selective leaching describes a corrosion process also called "parting" or de-alloying. More specifically, it can be called de-zincification in the case of brasses, de-nickelification in cupro-nickels, etc. Selective leaching may occur in a plug form or in a more evenly distributed layer type. Stagnant conditions and regions under deposits are conductive to selective leaching. In brasses it can occur at pH extremes in water; high dissolved solids and high temperature also promote selective leaching. The overall dimensions of a part do not change drastically, but appreciable weakening can occur.

Stray-Current Corrosion

Stray-current corrosion differs from other forms in that the source of the current causing the corrosion is external to the affected equipment. This cause of metal deterioration is frequently mis-diagnosed. Stray-current corrosion can cause local metal loss in buried or submerged metal structures, but it occurs much less frequently in underwater transporting equipment than in underground structures. Stray-current corrosion is almost always associated with direct current. At the anodic areas, metal goes into solution and the electrolyte tends to become acidic. It is most commonly encountered in soils containing water.

Stress Corrosion Cracking

Stress corrosion cracking is the result of the combined action of static stresses and corrosion. The static stresses may be residual or applied service stresses. The environment plays an important role in this type of cracking. The resulting cracks are branched, and can propagate either transgranularly or intergranularly, and sometimes both ways. Caustic cracking of steel is a case of stress corrosion cracking that is sometimes called caustic embrittlement. Generally speaking, it is not necessarily the concentration of the corrodent in the bulk environment that causes the cracking, but the increased concentration occurring in crevices or in alternately wetted and dried regions.

Uniform Corrosion

General corrosion is characterized by a chemical or electro-chemical reaction that occurs uniformly over the exposed surface. Anodic and cathodic sites shift constantly so that corrosion spreads over the entire metal surface. Identifying general corrosion is usually simple, but determining its cause is often difficult. Chemical dissolution by acids, bases or chelants frequently results in general corrosion.

4. UNITS

This Standard is based on International System of Units (SI), except where otherwise specified.

PART ONE

GENERAL REQUIREMENTS

CONTENTS :

APPENDICES:

1. SCOPE

This IPS-E-TP-780 specifies general requirement to be considered for controlling of corrosive environments by chemicals.

2. REFERENCES

See general.

3. DEFINITIONS AND TERMINOLOGY

See general.

4. UNITS

See general.

5. GENERAL RULES FOR CORROSION CONTROL

5.1 A component in operating oil and petrochemical industries will require replacement when:

- Corrosion or other deterioration has made it unfit for further service.
- It no longer performs satisfactorily, although it may still be operational.
- It has become completely non-operational.

Based on the results of a failure analysis, certain corrective measures can be implemented. These include, for example, the use of alternative materials of construction, changes in equipment design and process conditions, application of protective coatings and linings, cathodic and anodic protection and the use of corrosion inhibitors.

5.1.1 Materials selection

For material selection see IPS-E-TP-740.

5.1.2 Design changes

For design changes see IPS-E-TP-760.

5.1.3 Protective coatings and lining

For protection of metallic substrates by coating and lining reference is made to IPS-E-TP-100, IPS-E-TP-270 and IPS-E-TP-350.

5.1.4 Cathodic and anodic protection

For corrosion protection of metallic substrate by cathodic protection see IPS-E-TP-820.

5.1.5 Process changes

Process changes that can be considered for reducing corrosion and other failures include the following:

5.1.5.1 Temperature can be decreased to decrease corrosion rates.

5.1.5.2 Concentrations of critical corrosive species can be adjusted.

5.1.5.3 Flow velocity can be reduced to prevent erosion-corrosion.

5.1.5.4 Oxygen (air) can be removed by the use of scavenging chemicals.

5.1.5.5 Water entry can be controlled by installation of calcium chloride drying equipment, settling drums, or de mister screens.

5.1.6 Corrosion inhibitors

Corrosion inhibitors can be grouped into several common types or mechanistic classes: passivating, vapor phase, cathodic, anodic, film forming, neutralizing, and reactive. Inorganic inhibitors, such as disodium arsenite (Na_2HAsO_3) and ferrocyanide, have been used to inhibit carbon dioxide (CO_2) corrosion in oil wells, but the treatment frequency and effectiveness have not been satisfactory. This has led to the development of many organic chemical formulations that could almost be reduced to a single type of organic molecule: film-forming amines and their salts. These organic corrosion inhibitors can be classified as cathodic, anodic, or cathodic-anodic.

The consensus is that organic compounds inhibit corrosion by adsorbing at the metal/solution interface. Three possible types of adsorption are associated with organic inhibitors: π-bond orbital adsorption, electrostatic adsorption, and chemisorption. A more simplistic view of the mechanism of corrosion inhibitors can be described as controlled precipitation of the inhibitor from its environment (water and hydrocarbons) onto metal surfaces.

During the past 30 years, the primary improvements in inhibitor technology have been the refinement of formulations and the development of improved methods of applying inhibitors. The methods of evaluating the performance during their use have also advanced considerably (see IPS-I-TP-802).

5.2 Implement of Protective Measure

With reference to Subclause 5.1 the best corrosion protective measures shall be implemented accordingly, on the basis of technical and economical aspects when establishing new constructions.

6. TYPES OF INHIBITORS

Inhibitors are usually grouped in six different classes as follows:

6.1 Anodic Inhibitors (Passivators)

There are two types of passivating inhibitors: oxidizing anions such as chromate, nitrite and nitrate which can passivate steel in the absence of oxygen; and the non-oxidizing ions such as phosphate, tungstate, and molybdate which require the presence of oxygen to passivate steel.

6.2 Cathodic Inhibitors

Cathodic inhibitors either slow the cathodic reaction itself, or they selectively precipitate on cathodic areas to increase circuit resistance and restrict diffusion of reducible species to the cathodes.

Acid inhibitors such as arsenic and antimony compounds and also oxygen scavengers are examples of cathodic inhibitors.

6.3 Ohmic Inhibitors

Ohmic inhibitors usually increase the ohmic resistance of the electrolyte circuit by the formation of a film on cathodic areas.

6.4 Organic Inhibitors

Organic inhibitors constitute a broad class of corrosive inhibitors which can not be designated specifically as anodic, cathodic, or ohmic. As a general rule, organic inhibitors affect the entire surface of a corroding metal when present in sufficient concentration.

6.5 Precipitation-Including Inhibitors

These inhibitors are film forming compounds which have a general action over the metal surface and which, therefore, interfere with both anodes and cathodes indirectly. The most common inhibitors of this class are the silicates and phosphates.

6.6 Vapor Phase Inhibitors

Vapor Phase Inhibitors (VPI), also called Volatile Corrosion Inhibitors (VCI) are compounds which are transported in a closed system to the site of corrosion by volatilization from a source. In boilers, volatile basic compounds such as morpholine or octadecylamine are transported with steam to prevent corrosion in condenser tubes by neutralizing acidic carbon dioxide. Compounds of this type inhibit corrosion by making the environment alkaline. In closed vapor spaces, such as shipping containers, volatile solids such as the nitrite, carbonate, and benzoate salts of dicyclohexylamine, cyclohexylamine, and hexamethyleneimine are used.

For more information about the basic types of inhibitors and their actions (see Appendix A.1).

7. CORROSIVE ENVIRONMENTS

Corrosive environments to which corrosion inhibitors apply are as follows (see also Appendix B.1).

7.1 Aqueous Systems

Aqueous systems are by far the most common corrosive environments to which corrosion inhibitors are applied. Water is a powerful solvent capable of carrying many different ions at the same time, so requirements for corrosion inhibition may vary greatly, depending on the type and amount of dissolved species present. Because there is no universal inhibitor for water systems, an inhibitor which may be satisfactory for one system may be ineffective or even harmful in another. The main factors which may be considered in the application of corrosion inhibitors to aqueous systems are salt concentration, pH, dissolved oxygen concentration, and the concentration of interfering species.

7.2 Strong Acids

High acid concentrations are encountered in pickling processes, oil well acidizing, and during the transportation of acids for use in chemical processes. Hydrochloric acid of all concentrations requires an inhibitor if steel is to be used. The use of inhibitor in pickling processes also allows the acid to dissolve scale from steel without appreciable attack on the metal.

7.3 Non-aqueous Systems

Corrosion in non-aqueous liquids such as fuels, lubricants, and edible oils is usually caused by the small amounts of water often present. Water is slightly soluble in petroleum products, and its solubility increases with temperature. If a non-aqueous solvent is saturated with water and the temperature is lowered, then some of the water will separate to attack steel that it contacts. Oils that have been subjected to high temperatures in air will contain organic acid that will be extracted by any water present to increase the rate of attack on steel.

Corrosion in steel systems handling wet oils can be inhibited with both organic and inorganic compounds. Effective organic compounds include various amines, lecithin, and mercaptobenzothiazole. The inorganic inhibitors include sodium nitrite and sodium nitrate. Chromate's are not used because of their instability in the presence of organic.

Small amounts of water inhibit corrosion in some non-aqueous solvents. Halogenated (containing chlorides, fluorides, bromides, or iodides), non-aqueous solvents can be particularly troublesome. Organic amines are effective inhibitors for steel degreasing vessels that contain hot chlorinated solvents.

7.4 Gaseous Environments

Gaseous environments include the open atmosphere, the vapor phase in tanks, natural gas in wells, and the empty space in packaging containers. Here again, water and oxygen are the principal corrosive agents, but the main problem in providing inhibition is to transport the inhibitor from a source to the sites where corrosion may occur.

7.5 Effect of Elevated Temperatures

Most effects of elevated temperatures are adverse to corrosion inhibition. High temperatures increase corrosion rates (about double for a 15°C rise at room temperature), and they decrease the tendency of inhibitors to adsorb on metal surfaces. Precipitate-forming inhibitors are less effective at elevated temperatures because of the greater solubility of the protective deposit. Thermal stability of corrosion inhibitors is an important consideration at high temperatures. Polyphosphates, for example, are hydrolyzed by hot water to form orthophosphates which have little inhibitive value. Most organic compounds are unstable above about 200°C hence, they may provide only temporary inhibition at best.

8. TECHNIQUES FOR APPLICATION OF INHIBITORS

8.1 Continuous Injection

Continuous injection of corrosion inhibitors is practiced in once-through systems where slugs or batch treatment can not be distributed evenly through the fluid. This method is used for water supplies, oil field injection water, once-through cooling water, open annulus oil or gas wells, and gas lift wells. Liquid inhibitors are injected with a chemical injection pump. These pumps are extremely reliable and require little maintenance. Most chemical injection pumps can be adjusted to deliver at the desire injection rate.

Another form of continuous application is by the use of slightly soluble forms of solid inhibitors. The inhibitor (such as glassy phosphate or silicate in the form of a cartridge) is installed in a flow line where the inhibitor is continuously leached out by passage of fluid through the cartridge. Inhibitors in the form of sticks or pellets are used in oil and gas wells to supply inhibitor continuously by their natural slow dissolution.

Boilers, closed cooling water systems, and other closed circulating fluid systems can be treated with inhibitors with continuous injection. When such systems are started up after construction or major maintenance, the inhibitor is often injected at higher-than-normal concentration to permit rapid development of protective films.

8.2 Batch Treatment

The most familiar example of batch treatment is the automobile cooling system. A quantity of inhibitor is added at one time to provide protection for an extended period. Additional inhibitor may be added periodically, or the fluid may be drained and replaced with a new supply. In most aerated, closed loop cooling systems, it is important that the inhibitor concentration be measured occasionally to ensure that a safe level is maintained.

Batch treatment is also used in treating oil and gas wells. An inhibitor is diluted with an appropriate solvent and injected into the annuals of open hole wells or into the tubing of gas wells that have a packer. In this application, it is important that the inhibitor contacts all surfaces and that it has good persistence. Most wells require treatment about every two weeks.

8.3 Squeeze Treatment

The squeeze treatment is a method of continuously feeding an inhibitor into an oil or gas wells. A quantity of inhibitor is pumped into a well and is followed by sufficient solvent to force the inhibitor into the formation or mixing inhibitor in oil, aromatic solvent, or water at the proper ratio, pump the mix into the tubing and displace it to the bottom, followed by sufficient fluid to over displace the mixture into the formation by 3500 to 11500 liters. The inhibitor is absorbed by the formation from which it slowly escapes to inhibit the produced fluids. Protection applied in this manner has been known to last for a year.

8.4 Volatilization

Volatilization has already been discussed under vapor phase inhibitors in connection with boilers and closed containers. Another application is the inhibition of gas consendate corrosion. However, the treatment here is essentially the same as used in batch or squeeze treatments.

8.5 Coatings

Inhibitors are used in coatings exposed to the open atmosphere. When moisture contacts the paint, some inhibitor is leached out to protect the metal. Thus, the inhibitor must be soluble enough to be leached out in sufficient amounts to protect the metal, but not so soluble that it will be lost rapidly.

The most common coating inhibitors are zinc chromate and plumbous orthopulmbate (red lead), which passivate steel by providing chromate and plumbate ions, respectively, as well as the zinc and lead cathodic inhibitors. These inhibitors are not effective against attack by sea water or brines because the high chloride concentration prevents passivation of steel.

Recently, heavy coatings, which act as sealants for crevices have been developed for the aircraft and aerospace industries. These coatings contain proprietary inhibitor formulations which are especially effective in minimizing corrosion associated with dissimilar metal fasteners.

9. INHIBITOR MECHANISMS

9.1 Neutralizing Inhibitors

Neutralizing inhibitors lessen the corrosivity of the environment by decreasing hydrogen ion (H^+) concentration, which reduces the concentration of the corrosive reactant. Neutralizers function by controlling the corrosion caused by acidic materials, such as hydrogen chloride, carbon dioxide (CO_2), sulfur dioxide (SO_2), carboxylic acids, and related compounds. These materials are found in small quantities in many process streams. However, because of such separation processes as distillation, one or more of these acidic species can concentrate in specific areas and cause severe corrosion. The area most susceptible to corrosion in the refinery is the heat exchanger, where the first drops of water condense (the initial condensate). An effective neutralizer will exhibit the same distillation/condensation properties as the acid is designed to control.

A variety of neutralizers are used in many applications in the refinery. The list includes ammonia (NH_3), and various proprietary alkyl-amines and polyamines. The physical characteristics of each neutralizer determine its application. A strong alkali, such as NaOH, is an excellent neutralizer when injected into the desalted crude, but it can not be used in overhead heat exchangers. Ammonia is an inexpensive overhead neutralizer, but it has no solubility in the initial condensate.

9.2 Filming Inhibitors

Most of the inhibitors used are of the film-forming type. Instead of reacting with or removing an active corrodent species, filming inhibitors function by creating a barrier between the metal and the environment. They consist of one or more polar groups based on nitrogen, sulfur, or oxygen that are attached to the metal surface by chemisorption or electro static forces.

Filming amine chemistry in the refinery includes amides, diamides and imidazoline salts. Each type is known to be effective in selected environments. The amino group is the important functional and salt-forming species. For readily handled commercial products, the amide intermediate is reacted with an imidazoline salt to enhance solubility in carrier solvents and to decrease gelling or phase separation. However, both groups are effective inhibitors.

9.3 Scavengers

Perhaps the most widely used scavenger system is employed in boilers to remove oxygen from the feed water. Techniques such as steam stripping can be used to remove most of the dissolved oxygen from water; however, such methods become increasingly costly when the last traces of oxygen must be removed from the boiler feed water. In these cases, chemical techniques for oxygen removal become more attractive. Hydrazine and sodium sulfite are the two most widely used scavengers in boiler systems.

9.4 Miscellaneous Inhibitors

Miscellaneous inhibitors include such materials as scale inhibitors, which minimize deposition of scale on the metal surface, and biocides, which kill living organisms that can foul equipment.

10. CRITERIA FOR CORROSION CONTROL BY INHIBITORS

The use of corrosion inhibitors has grown to be one of the foremost methods of combating corrosion. To use them effectively, the corrosion engineer must, first of all, be able to identify those problems which can be solved by the use of corrosion inhibitors. Second, the economics involved must be considered, i.e., whether or not the loss due to corrosion exceeds the cost of the inhibitor and the maintenance and operation of the attendant injection system. Third, the compatibility of inhibitors with the process being used must be considered to avoid adverse effects such as foaming, decreases in catalytic activity, degradation of another material, loss of heat transfer, etc. (see also 12.1.11). Finally, the inhibitor must be applied under conditions which produce maximum effect, see IPS-I-TP-802. Similar criteria shall be used when combating the scale problems alone.

11. SYSTEM CONDITION

11.1 A system must be carefully examined before a program of corrosion inhibition can be planned effectively. The examination must include a survey of any adverse effects an inhibitor may have on the process in which it is to be used and an analysis to detect the presence of interfering substances.

11.2 Another possible adverse effect of inhibition is an increased rate of corrosion of a metal in the system other than the one for which the inhibitor was selected to protect. For example, some amines protect steel admirably, but will severely attack copper and brass. Nitrites may attack lead and lead alloys such as solder. In some cases, the inhibitor may react in the system to produce a harmful product. An illustration of this is the reduction of nitrite inhibitors to form ammonia which causes stress corrosion cracking of copper and brass. The only way to avoid these problems is to know the metallic components of a system and be thoroughly familiar with the properties of the inhibitor or to be used (see Tables 1.1 and 2.1 as general information).

11.3 The examination must include preparation of a complete list of materials, both metallic and non-metallic, which will be in contact with the fluid that will be inhibited. Such small items as gaskets, instrument probes, and control devices may be made from materials that will not be compatible with some inhibitors. The results from this examination may suggest that certain parts of a system should be changed to permit the use of a particular inhibitor.

11.4 The examination must also include a determination of the cleanliness of the surfaces of the system that will be in contact with the inhibited fluid. A system can be plugged as the result of an inhibitor loosening scale and suspending it in the fluid. This problem is best avoided by planning ahead. The best preventive measure is to clean the system thoroughly, if possible, before an inhibitor is applied.

11.5 Cleaning may be accomplished with chemical cleaners, mechanical cleaners, ultrasonic energy, or thermal shock. Inhibitors can reach cleaned metal surfaces much more easily than they can reach heavily fouled or scaled surfaces.

TABLE 1.1 - SOME CORROSIVE SYSTEMS AND THE INHIBITORS THAT HAVE BEEN USED TO PROTECT THEM

SYSTEM	INHIBITOR	METALS PROTECTED	CONCENTRATION
Water, Potable	$Ca(HCO_3)_2$	Steel. Cast Iron + Others	10 ppm
	Polyphosphate	Fe, Zn, Cu Al	5-10 ppm
	$Ca(OH)_2$	Fe, Zn, Cu	Sufficient for pH 8.0
	Na_2SiO_3	Fe, Zn, Cu	10-20 ppm
Water, Cooling	$Ca(HCO_3)_2$	Steel. Cast Iron + Others	10 ppm
	Na_2CrO_4	Fe, Zn, Cu	0.1%
	$NaNO_2$	Fe	0.05%
	NaH_2PO_4	Fe	1%
	Morpholine	Fe	0.2%
Boilers	NaH_2PO_4	Fe, Zn, Cu	10 ppm
	Polyphosphate	Fe, Zn, Cu	10 ppm
	Morpholine	Fe	Variable
	Hydrazine	Fe	O_2 Scavenger
	Ammonia	Fe	Neutralizer
	Octadecylamine	Fe	Variable
Brines	$Ca(HCO_3)_2$	Fe, Cu, Zn	10 ppm
	Na_2CrO_4	Fe, Cu, Zn	0.1%
	Sodium Benzoate	Fe	0.5%
	$NaNO_2$	Fe	(NaCl 5%)
Oil Field Brines	Na_2SiO_3	Fe	0.01%
	Na_2SO_3 (or SO_2)	Fe	O_2 Scavenger $(O_2 \times 9)$ ppm
	Quaternaries	Fe	10-25 ppm
	Imidazoline	Fe	10-25 ppm
	Rosin Amine Acetate	Fe	5-25 ppm
	Coco Amine Acetate	Fe	5-15 ppm
	Formaldehyde	Fe	50-100 ppm
Seawater	Na_2SiO_3	Zn	10 ppm
	$NaNO_2$	Fe	0.5%
	$Ca(HCO_3)_2$	All	pH Dependent
	$NaH_2PO_4 + NaNO_2$	Fe	10 ppm + 0.5%
Engine Coolants	Na_2CrO_4	Fe, Pb, Cu, Zn	0.1 - 1%
	$NaNO_2$	Fe	0.1 - 1%
	Borax	Fe	1%

(to be continued)

TABLE 1.1 (continued)

SYSTEM	INHIBITOR	METALS PROTECTED	CONCENTRATION
Glycol/Water	Borax + Mercaptobenzothiazole	All	1% + 0.1%
Acids, HCl	Ethylaniline	Fe	0.5%
	Mercaptobenzothiazole	Fe	1%
	Pyridine + Phenylhydrazine	Fe	0.5% + 0.5%
	Rosin Amine + Ethylene Oxide	Fe	0.2%
H_2SO_4	Phenylacridine	Fe	0.5%
Con. H_3PO_4 Most Acids	NaI	Fe	200 ppm
	Thiourea	Fe	1%
	Sulfonated Castor Oil	Fe	0.5 - 1%
	As_2O_3	Fe	0.5%
	Na_3AsO_4	Fe	0.5%
Vapor Condensate	Morpholine	Fe	Variable
	Ammonia	Fe	Variable
	Ethylenediamine	Fe	Variable
	Cyclohexylamine	Fe	Variable
Enclosed Atmosphere	Cyclohexylamine Carbonate	Fe	1 lb per 500 cu ft
	Dicyclohexylamine Nitrite	Fe	1 lb per 500 sq ft
	Amylamine Benzoate	Fe	Variable
	Diisopropylamine Nitrite	Fe	Variable
	Methylcyclohexylamine Carbonate	Fe	Variable
Coating Inhibitors	$ZnCrO_4$ (yellow)	Fe, Zn, Cu	Variable
	$CaCrO_4$ (white)	Fe, Zn, Cu	Variable
	Red Lead	Fe	Variable

TABLE 2.1 - CORROSION INHIBITOR REFERENCE LIST

Metal	Environment	Inhibitor
Admiralty	Ammonia, 5%	0.5% hydrofluoric acid
Admiralty	Sodium hydroxide, 4° Be	0.6 moles H_2S per mole NaOH
Aluminum	Acid hydrochloric, 1 N	0.003 M α-phenylacridine, β-naphthoquinone, acridine, thiourea, or 2-phenylquinoline
Aluminum	Acid nitric, 2-5%	0.05% hexamethylene tetramine
Aluminum	Acid nitric, 10%	0.1% hexamethylene tetramine
Aluminum	Acid nitric, 10%	0.1% alkali chromate
Aluminum	Acid nitric, 20%	0.5 hexamethylene tetramine
Aluminum	Acid phosphoric	Alkali chromates
Aluminum	Acid phosphoric, 20%	0.5% sodium chromate
Aluminum	Acid phosphoric, 20-80%	1.0% sodium chromate
Aluminum	Acid sulfuric, conc.	5.0% sodium chromate
Aluminum	Alcohol anti-freeze	Sodium nitrite and sodium molybdate
Aluminum	Bromine water	Sodium silicate
Aluminum	Bromoform	Amines
Aluminum	Carbon tetrachloride	0.05% formamide
Aluminum	Chlorinated aromatics	0.1-2.0% nitrochlorobenzene
Aluminum	Chlorine water	Sodium silicate
Aluminum	Calcium chloride, sat.	Alkali silicates
Aluminum	Ethanol, hot	Potassium dichromate
Aluminum	Ethanol, commercial	0.03% alkali carbonates, lactates, acetates, or borates
Aluminum	Ethylene glycol	Sodium tungstate or sodium molybdate
Aluminum	Ethylene glycol	Alkali borates and phosphates
Aluminum	Ethylene glycol	0.01-1.0% sodium nitrate
Aluminum	Hydrogen peroxide, alkaline	Sodium silicate
Aluminum	Hydrogen peroxide	Alkali metal nitrates
Aluminum	Hydrogen peroxide	Sodium metasilicate
Aluminum	Methyl alcohol	Sodium chlorate plus sodium nitrite
Aluminum	Methyl chloride	Water
Aluminum	Polyoxyalkene glycol fluids	2% Emery's dimer acid (dilinoleic acid), 1.25% $N(CHMe_2)_3$, 0.05-0.2% mercaptobenzothiazole

(to be continued)

TABLE 2.1 (continued)

Metal	Environment	Inhibitor
Aluminum	Seawater	0.75% sec. amyl stearate
Aluminum	Sodium carbonate, dilute	Sodium fluosilicate
Aluminum	Sodium hydroxide, 1%	Alkali silicates
Aluminum	Sodium hydroxide, 1%	3-4% potassium permanganate
Aluminum	Sodium hydroxide, 4%	18% glucose
Aluminum	Sodium hypochlorite contained in bleaches	Sodium silicate
Aluminum	Sodium acetate	Alkali silicates
Aluminum	Sodium chloride, 3.5%	1% sodium chromate
Aluminum	Sodium carbonate, 1%	0.2% sodium silicate
Aluminum	Sodium carbonate, 10%	0.05% sodium silicate
Aluminum	Sodium sulfide	Sulfur
Aluminum	Sodium sulfide	1% sodium metasilicate
Aluminum	50% sodium trichloracetate soln.	0.5% sodium dichromate
Aluminum	Tetrahydrofurfuryl alcohol	1% sodium nitrate or 0.3% sodium chromate
Aluminum	Triethanolamine	1% sodium metasilicate
Brass	Carbon tetrachloride, wet	0.001-0.1 aniline
Brass	Furfural	0.1% mercaptobenzothiazole
Brass	Polyoxyalkene glycol fluids	2.0% Emery's acid (dilinoleic acid), 1.25% $N(CHMe_2)_3$, 0.05-0.2% mercaptobenzothiazole
Brass	50% sodium trichloracetate soln.	0.5% sodium dichromate
Cadmium plated steel	55/45 ethylene glycol—water	1% sodium fluorophosphate
Copper	Fatty acids as acetic	H_2SO_4, $(COOH)_2$, or H_2SiF_6
Copper	Hydrocarbons containing sulfur	p-hydroxybenzophenone
Copper	Polyoxyalkene glycol fluids	2% Emery's acid (dilinoleic acid), 1.25% $N(CHMe_2)_3$, 0.05-0.2% mercaptobenzothiazole
Copper & brass	Acid sulfuric, dil.	Benzyl thiocyanate
Copper & brass	Ethylene glycol	Alkali borates & phosphates
Copper & brass	Polyhydric alcohol anti-freeze	0.4-1.6% Na_3PO_4 plus 0.3-0.6 sodium silicate plus 0.2-0.6% sodium mercaptobenzothiazole
Copper & brass	Rapeseed soil	Succinic acid
Copper & brass	Sulfur in benzene solution	0.2%, 9, 10-anthraquinone
Copper & brass	Tetrahydrofurfuryl alcohol	1% sodium nitrate or 0.3% sodium chromate
Copper & brass	Water-alcohol	0.25% benzoic acid, or 0.25% sodium benzoate at a pH of 7.5-10

(to be continued)

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TABLE 2.1 (continued)

Metal	Environment	Inhibitor
Galvanized iron	Distilled water	15 ppm. mixture calcium and zinc metaphosphate
Galvanized iron	55/45 ethylene glycol—water	0.025% trisodium phosphate
Iron	Nitroarylamines	Dibenzylaniline
Lead	Carbon tetrachloride, wet	0.001-0.1% aniline
Magnesium	Alcohol	Alkaline metal sulfides
Magnesium	Alcohol. methyl	1% oleic or stearic acid neutralized with ammonia
Magnesium	Alcohols, polyhydric	Soluble fluorides at pH 8-10
Magnesium	Glycerine	Alkaline metal sulfides
Magnesium	Glycol	Alkaline metal sulfides
Magnesium	Trichlorethylene	0.05% formamide
Magnesium	Water	1 pc potassium bromolnate
Monel	Carbon tetrachloride, wet	0.001-0.1% aniline
Monel	Sodium chloride, 0.1%	0.1% sodium nitrite
Monel	Tap water	0.1% sodium nitrite
Nickel & silver	Sodium hypochlorite contained in bleaches	Sodium silicate
Stainless steel	Acid. sulfuric. 2.5%	5-20 ppm. $CaSO_4 5H_2O$
Stainless steel	Cyanamide	50-500 ppm, ammonium phosphate
Stainless steel. 18-8	Potassium permanganate contained in bleaches	Sodium silicate
Stainless steel, 18-8	Sodium chloride. 4%	0.8% sodium hydroxide
Steel	Acid citric	Cadmium salts
Steel	Acid sulfuric, dil	Aromatic amines
Steel	Acid sulfuric. 60-70%	Arsenic
Steel	Acid sulfuric, 80%	2% boron trifluoride
Steel	Aluminum chloride—hydrocarbon complexes formed during isomerization	0.2-2.0% iodine. hydriodic acid, or hydrocarbon iodide
Steel	Ammoniacal ammonium nitrate	0.2% thiourea
Steel	Ammonium nitrate—urea solns.	0.05-0.10% ammonia 0.1% ammonium thiocyanate
Steel	Brine containing oxygen	0.001-3.0 methyl ethyl. or propyl substituted dithiocarbamates
Steel	Carbon tetrachloride, wet	0.001-0.1% aniline
Steel	Caustic—cresylate solution as in regeneration of refinery caustic wash solutions, 240-260 F	0.1-1.0% trisodium phosphate
Steel	Ethyl alcohol. aqueous or pure	0.03% ethylamine or diethylamine
Steel	55/45 ethylene glycol—water	0.025% trisodium phosphate
Steel	Ethylene glycol	Alkali borates & phosphates
Steel	Ethylene glycol	Guanidine or guanidine carbonate
Steel	Ethyl alcohol, 70%	0.15% ammonium carbonate plus 1% ammonium hydroxide
Steel	Furfural	0.1% mercaptobenzothiazole
Steel	Halogenated dielectric fluids	0.05-4% $(\gamma C_4 H_3 S)_4$ Sn. $\gamma(C_4 H_3)_2 Sn$. or $\gamma C_4 H_3 S$ $SnPh_3$
Steel	Halogenated organic insulating materials as chlorinated diphenyl	0.1% 2, 4$(NH_2)_2 C_6 H_3 NHPh$, o—$MeH_4 NH_2$. or p—$NO_2 C_6 H_4 NH_2$

(to be continued)

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TABLE 2.1 (continued)

Metal	Environment	Inhibitor
Steel	Herbicides as 2, 4-dinitro-6-alkyl phenols in aromatic oils	1.0-1.5% furfural
Steel	Isopropanol, 30%	0.03% sodium nitrite plus 0.015% oleic acid
Steel	1:4 methanol—water	To 4l. water and 1l. methanol add 1 g. pyridine and 0.05 g. pyragallol
Steel	Nitrogen fertilizer solutions	0.1% ammonium thiocyanate
Steel	Phosphoric acid, conc.	0.01-0.5% dodecylamine or 2 amino bicyclohexyl and 0.001% potassium iodide, potassium iodate, or iodacetic acid
Steel	Polyoxyalklene glycol fluids	2% Emery's acid (dilinoleic acid) 1.25% $N(CHMe_2)_3$ 0.05-0.2% mercaptobenzothiazole
Steel	Sodium chloride, 0.05%	0.2% sodium nitrite
Steel	50% sodium trichloracetate soln.	0.5% sodium dichromate
Steel	Sulfide containing brine	Formaldehyde
Steel	Tetrahydrofurfuryl alcohol	1% sodium nitrate or 0.3% sodium chromate
Steel	Water	Benzoic acid
Steel	Water for flooding operations	Rosin amine
Steel	Water saturated hydrocarbons	Sodium nitrite
Steel	Water, distilled	Aerosol (an ionic wetting agent)
Tin	Carbon tetrachloride, wet	0.001-0.1% aniline
Tin	Chlorinated aromatics	0.1-2.0% nitrochlorobenzene
Tinned copper	Sodium hypochlorite contained bleaches	Sodium silicate
Tin plate	Alkali cleaning agents as tri-sodium phosphate, sodium carbonate, etc.	Diethylene diaminocobaltic nitrate
Tin plate	Alkaline soap	0.1% sodium nitrite
Tin plate	Carbon tetrachloride	2% mesityl oxide, 0.001% diphenylamine
Tin plate	Sodium chloride, 0.05%	0.2% sodium nitrite
Titanium	Hydrochloric acid	Oxidizing agents as chromic acid or copper sulfate
Titanium	Sulfuric acid	Oxidizing agents or inorganic sulfates
Zinc	Distilled water	15 ppm. mixture calcium and zinc metaphosphates

[SOURCE: Maxey Brooke, Corrosion Inhibitor Checklist, Chem. Eng., pp. 230-234 (December, 1954).]

12. SELECTION OF INHIBITORS

12.1 Many factors are involved in the selection of inhibitors, including the following:

12.1.1 Identification of the problem to be solved.

12.1.2 Type of corrosion(s) present, see definitions and terminology.

12.1.3 Type of system (which influences the treatment method), (see Clause 8).

12.1.4 Pressure.

12.1.5 Temperature.

12.1.6 Velocity.

12.1.7 Production composition.

12.1.8 System condition, (see Clause 11).

12.1.9 Efficiency of inhibitor, (see Clause 12.2.2.3).

12.1.10 Economy, (see Clause 13 of this Part).

12.1.11 Compatibility with other chemicals and inhibitors

The inhibitor must be able to treat in the presence of other materials such as phosphonates, polymers, bisulphites, and surface active agents, and must not interfere with their functions.

12.2 Procedure for Selection

12.2.1 General

There are several approaches to be followed in selecting a proper inhibitor for a given system. An outside consultant can be asked for advice. Various suppliers can be asked for advice. Tabulations such as 1 and 2 can be consulted. Table 1.1 is arranged by environment, while Table 2.1 is arranged by material and indicates the broad range of material-environment-inhibitor combinations that are possible.

Often, the particular combinations at hand can not be found in the literature. Hence, in addition to experience in the area (see Clause 12.2.1.1), testing must be conducted to determine which inhibitor and what concentration to use. Standard tests can be found in American Society for Testing and Materials (ASTM) publications and in NACE Standard Test Method, some of which are described in Clause 12.2.2.

A frequent cause of ineffective inhibition is loss of the inhibitor before it has a chance to contact the metal surfaces or effect the desired changes in the environment. An inhibitor might be lost by precipitation, adsorption, reaction with a component of the system, or by being insufficiently soluble or too slow to dissolve.

Typical examples of losses of an inhibitor due to these factors are precipitation of phosphates by the calcium ion, reaction of chromates with sulfides or organic, adsorption of inhibitors on suspended solids, and injection of a poorly soluble inhibitor without an adequate dispersing agent. To avoid these problems, inhibitors shall be tested in the actual fluids to be treated rather than in simulated environments. If possible, testing shall be done in the process stream or in a small side stream.

12.2.1.1 Experience in the area

It is always advantageous to check with other operators in the area to determine what chemicals and treatment methods are being used and the results being achieved from these treatments. This information can be extremely valuable in providing a starting point for an inhibition program.

12.2.2 Evaluation test of inhibitor

The nominated inhibitor(s) shall be evaluated (tested) with regard to its function before selecting for a system. Test(s) shall be include the laboratory test(s) as well as field or operational test.

12.2.2.1 Laboratory evaluation tests for nonqueous systems (two-phase systems)

The laboratory test(s) shall include one or more of the following test method(s) as required by the system to be treated.

12.2.2.1.1 Static test for corrosion inhibitor

In the static test, the weight loss of a mild steel coupon after exposure to an inhibited solution is compared to the results obtained in an unhibited solution with the same condition.

12.2.2.1.2 Dynamic test method for corrosion inhibitor

The wheel test is a dynamic weight loss test, wherein a weighed coupon is immersed in the test fluids and rotated on a wheel at fixed rpm and temperature for a set period of time. This coupon is the "blank" or "control". In a system using the identical technique, a known concentration of the inhibitor is used. This test is run simultaneously with the control. At the end of the test period, the amount of weight loss suppression afforded by the inhibitor is determined. Wheel test is a widely accepted laboratory test for two-phase systems such as crude oil. This test is very useful, but not always reliable because of the restricted volume of the solvents and the difficulty in duplicating velocity and stagnation effects in real systems. Wheel test procedure is described in the NACE Report 10182.

12.2.2.1.3 Flow tests

A recirculating dynamic test method can be used when it is desired to simulate field flow or operational conditions. Some of the parameters which shall be controlled are velocity of the corrosive medium, oil-water ratio (in case of oil field inhibitors), temperature, and dissolved gas and/or air concentration. Variables which can be imposed are the type of corrosive medium, concentration of inhibitor, effect of precorrosion of the test specimen, and type of inhibitor treatment.

This type of flow test provides a more severe test of inhibitor film life than the static bottle test. It furnishes a useful technique for the study of variable affecting inhibitor performance. Correlation between laboratory tests and field use of inhibitors is better using this technique than it is using data from the static test.

12.2.2.1.4 The test for foaming is to obtain a sample of the fluid and gas from the process step, add the inhibitor in question, adjust the temperature to that corresponding to the process step and shake vigorously. If this test produces a stable foam, a potential problem exists. Pressure suppresses foam; some foams which exist at atmospheric pressure will not exist at system pressure. The test for emulsion formation is the same as for foams; the solution for the formation of an emulsion is to add a demulsifier, use another inhibitor or inhibit the slugs during shut-down. Most inhibitors will not cause emulsion formation at concentrations up to 250 ppm. Above this, be careful.

The best preventative measure for the loosening of scale is to clean the system thoroughly, if possible, before inhibitor is applied. An alternate or supplementary method in systems which are very sensitive to suspend solids is to protect the sensitive parts with temporary filters.

12.2.2.1.5 Similar laboratory evaluation tests shall be performed for other systems (see Clause 7). The standard test methods shall be in accordance with appropriate test methods of ASTM and NACE Standards such as "NACE Standard" TM-01-69 (1976 Revision).

12.2.2.1.6 The scaling inhibitors and biological inhibitors shall be tested in accordance with "NACE Standard TM-03-74" and "API-RP-38" accordingly.

12.2.2.2 Operational or field tests

After initial selection of the inhibitor(s) by means of laboratory tests the operational or field tests shall be conducted for final selection. Tests shall be conducted in the field or plant by monitoring the corrosivity of the fluid of interest in the presence of inhibitor(s) initially selected. This is normally accomplished by treating the medium and measuring the effectiveness of the inhibitor with the appropriate standard methods. The initially selected inhibitor(s) shall pass operational or field test of 90 days minimum.

12.2.2.3 Concentration and performance of inhibitor (inhibitor efficiency)

12.2.2.3.1 Corrosion inhibitors are sold in solid or liquid form. Most solids are relatively pure, but sometimes a solid inhibitor is fused with another ingredient or encapsulated where a controlled rate of solubility is required. Liquids are usually preferred because of the ease with which they can be transported, measured, and dispersed.

12.2.2.3.2 Liquid inhibitors are rarely pure for several reasons. Organic inhibitors seldom have optimum characteristics of viscosity, or freezing or boiling points; therefore, they are dissolved in an appropriate solvent to achieve the properties desired. Furthermore, it is often desirable to blend the inhibitor with a demulsifier, dispersant, surfactant, antifoaming agent, or synergistic agent.

12.2.2.3.3 Liquid inhibitors are sold by the gallon, part of which is solvent. The amount of inhibitor present is expressed as percent active, i.e., a gallon of inhibitor which is 20%, active contains 20% by weight of inhibitor. In cold climates where inhibitors are likely to be stored or used in subfreezing temperatures, it may be impossible to use as concentrated a solution as in warmer climates without resorting to more expensive solvents.

12.2.2.3.4 Corrosion inhibitors are usually compared on the basis of their inhibitor efficiency, which is the percentage that corrosion is lowered in their presence as compared with the corrosion rate which occurs in their absence. The inhibitor efficiency is calculated from the formula:

$$E = \frac{R_o - R_i}{R_o} \times 100 \qquad \text{(Eq. 1)}$$

Where:

E is inhibitor efficiency.
R_o is corrosion rate in absence of inhibitor.
R_i is corrosion rate in presence of inhibitor.

Example:

Mild steel corroded in a cooling, water at a rate of 1650 μm/y (65 mpy). When 10 ppm of an inhibitor was added, the corrosion rate dropped to 380 μm/y (15 mpy). What is the inhibitor efficiency?

$R_o = 1650$ and $R_i = 380$

substituting in Equation (1),

$$E = \frac{1650 - 380}{1650} \times 100 = 77\%$$

12.2.2.3.5 Inhibitor concentrations are expressed as parts per million (ppm); for solids the units are on a weight basis, e.g., kilograms (or pounds) of inhibitor per million kilograms (or pounds) of fluid; and for liquid inhibitors, volumes are used, e.g., liters of inhibitor per million liters of fluid. To obtain the amount of inhibitor required for a given system, simply divide the amount of fluid to be inhibited by 1,000,000 and multiply by the ppm desired:

$$Q = \frac{V}{1,000,000} \times ppm \qquad \textbf{(Eq. 2)}$$

Where:

Q   is quantity of inhibitor required.

V   is the amount of fluid to be inhibited, and ppm is the inhibitor concentration in parts per million.
            Note that the quantity of inhibitor must be in the same units as those for the amount of fluid.

Example:

What is the dosage of sodium chromate (a solid) required to add 10 ppm to 620,000 liters (165,000 gallons) of water? The volume of water is first converted to weight.

kilograms of water	= 620,000 liters × 1
(pounds)	= (165,000 gallons × 8.316/gal)

then:

V	= 620,000 kg (1,369,500 Ibs.)
ppm	= 10

substituting in Equation (2):

$$Q = \frac{620,000}{1,000,000} \times 10 = 6.2 \text{ kg}$$

$$(\text{or } Q = \frac{1,369,500}{1,000,000} \times 10 = 13.7 \text{ Ibs.})$$

A typical evaluation method of inhibitor is included in Appendix A.1.

12.3 In conclusion, the inhibitor must meet certain requirements for each specific application such as stability against temperature, time, and exposure to the corrosive environment. It must function at low concentration and be easy to apply. Solubility characteristics must be designed for each application, and the inhibitor must be pumpable at the system temperature. It must be compatible with other chemicals in use, and must meet performance specifications. It must inhibit corrosion. It must also be compatible with the system in which it is used, and not cause system upsets. It can not be too toxic, and the flash point must be within specifications. Raw materials must be readily available and not too expensive, and manufacturing processes capable of control and reproducibility.

12.4 A typical corrosion inhibitor selection and testing for high temperature, high pressure systems is included in Appendix B.2.

13. ECONOMICS OF INHIBITION

13.1 Prevention of corrosion by inhibition may be desirable for several reasons:

13.1.1 To extend the life of equipment.

13.1.2 To prevent shutdowns.

13.1.3 To prevent accidents resulting from brittle (or catastrophic) failures.

13.1.4 To avoid product contamination.

13.1.5 To prevent loss of heat transfer.

13.1.6 To preserve an attractive appearance.

13.2 Potential savings for each of those goals must be evaluated to determine if a program of corrosion inhibition will be economical. Because costs are sometimes difficult to estimate, the best method is to obtain data on maintenance, replacement, etc., from past history of the system which is to be protected or from a similar system. Literature on the economics of inhibition is a tremendous aid in estimating costs.

13.3 There are several costs associated with the use of inhibitors. In fact, the cost of one or more of the following must be factored into any economic evaluation of corrosion inhibition:

13.3.1 Installation of injection equipment.

13.3.2 Maintenance of injection equipment.

13.3.3 Purchase of inhibitor chemical(s).

13.3.4 Monitoring inhibitor concentration(s).

13.3.5 System changes to accommodate the inhibitor.

13.3.6 Operational changes to accommodate the inhibitor.

13.3.7 System cleaning.

13.3.8 Waste disposal.

13.3.9 Personnel safety equipment.

13.4 Economics of inhibitor use is an important requirement, but in cases where major shutdowns can be avoided through the use of inhibitors, the economic advantages of inhibition undoubtedly will be clear. Other cases will require detailed economic evaluations. Economic evaluation shall be made through the use of formulas given in NACE Standard RP-02-72, 1972.

APPENDICES

APPENDIX A.1
BASIC TYPES OF INHIBITORS AND HOW THEY WORK

A.1.1 Polarization diagrams

In this Appendix, the relationship of corrosion inhibitors to anodic and cathodic polarization will be explained.

Of the four components of a corrosion cell (anode, cathode, electrolyte, and electronic conductor), three may be affected by a corrosion inhibitor to retard corrosion. The inhibitor may cause:

A.1.1.1 Increased polarization of the anode (anodic inhibition),

A.1.1.2 Increased polarization of the cathode (cathodic inhibition), or it may

A.1.1.3 Increase the electrical resistance of the circuit by forming a thick deposit on the surface of the metal.

Of course, the bulk film-formers also restrict diffusion of depolizers (such as dissolved oxygen) to the surface of the metal; hence, they may play a dual role. The resistance of the electronic conductor connecting the anodes and cathodes (i.e., usually the resistance of the metal itself) is very low and can not be changed by corrosion inhibitors.

The effects of a corrosion inhibitor on a corrosion cell are conveniently determined by polarizing the corroding metal in a suitable electrolyte with varying amounts of current from an external source such as a battery. A simple laboratory apparatus for polarization measurements is shown in Fig. A1.1. The force which must be applied to stimulate the anodic or cathodic reactions is measured by the potential difference between the working electrode and a reference electrodes. No current is applied to the reference electrode; hence, it is used as a standard against which the potential of the working electrode is measured.

In an experiment to compare the effects of several inhibitors on the polarization of steel in a corrodent, such as dilute acid, the apparatus would be assembled using steel as the working electrode, dilute acid as the electrolyte, and an inert material such as carbon or platinum as an auxiliary electrode. Then the current would be increased in steps by means of the variable resistor, and the potential of the working electrode read at each step. A plot of the current versus potential in the absence and presence of an inhibitor shows the effects of the inhibitor on the polarization characteristics of the steel. Typical curves are shown in Fig. A.1.2.

When no current is applied and the working electrode has achieved a steady state, then the potential is the corrosion potential, E_c, of the electrode material. The corrosion potential is the mixed potential to which the anodes and cathodes are polarized by the corrosion reaction. It is also an indication of the effects of corrosion inhibitors.

(to be continued)

APPENDIX A.1 (continued)
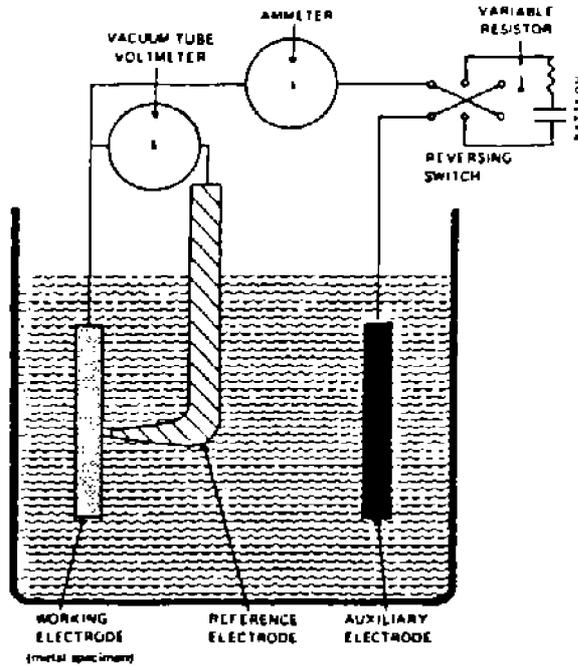
LABORATORY APPARATUS FOR POLARIZATION MEASUREMENTS
Fig. A.1.1
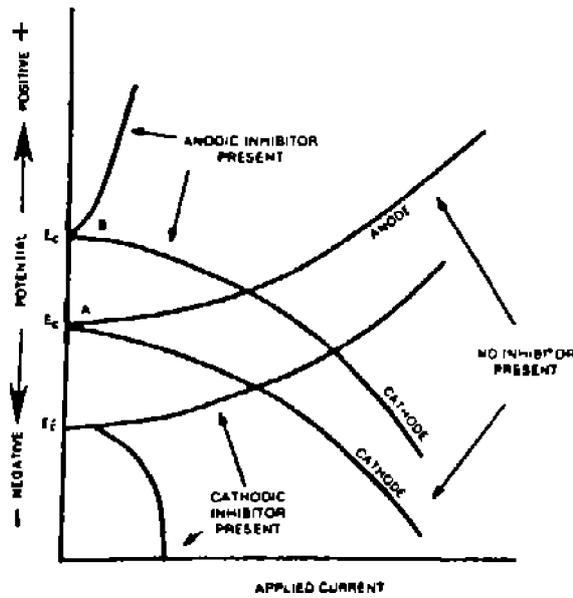
EFFECTS OF INHIBITORS ON POLARIZATION CURVES
Fig. A.1.2

(to be continued)

APPENDIX A.1 (continued)

A.1.2 Types of inhibitors

Six classes of inhibitors will be discussed:

1) passivating (anodic);
2) cathodic;
3) ohmic;
4) organic;
5) precipitation inducing;
6) vapor phase inhibitors.

While some authors may use slightly different classes, these will illustrate the complexity of the inhibitor picture.

A.1.2.1 Anodic passivating inhibitors

Anodic inhibition is illustrated in Fig. A.1.2, which shows an increase in the polarization (a large potential change results from a small current flow) of the anode in the presence of an anodic inhibitor. Addition of the inhibitor causes the corrosion potential to shift in a cathodic direction from E_c to E'_c.

Anodic inhibitors which cause a large shift in the corrosion potential are called passivating inhibitors. They are also called dangerous inhibitors because, if used in insufficient concentrations, they cause pitting and sometimes an increase in corrosion rate. There are two types of passivating inhibitors: oxidizing anions such as chromate, nitrite, and nitrate which can passivate steel in the absence of oxygen; and the non-oxidizing ions such as phosphates, tungstate, and molybdate which require the presence of oxygen to passivate steel. With careful control, however, passivating inhibitors are frequently used because they are very effective in sufficient quantities.

Passivating inhibitors such as sodium chromate (Na_2CrO_4) and sodium nitrite ($NaNO_2$) do not require oxygen to be effective. They increase the rate of anodic passivation to the extent that the anodes are polarized to a passive potential (or Flade Potential), indicated by E_f in Fig. A.1.3. The cathodes will be depolarized, as indicated by the cathodic lines in Fig. A.1.3. The depolarized cathodic curve then intersects the anodic curve in the passive region at E_c. Adsorption of the inhibitor on anodic areas also plays a part in the process because it decreases the current (or corrosion rate) required for the anode to reach the critical passive potential (E_f).
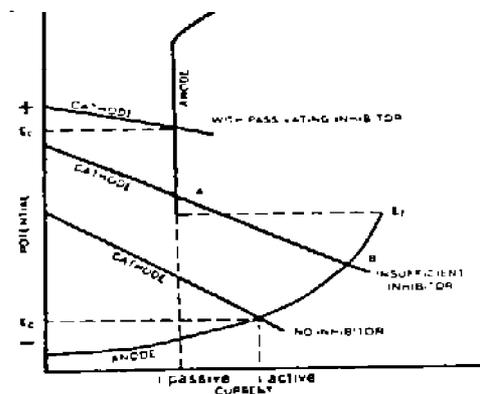
EFFECT OF PASSIVATING INHIBITORS ON THE CORROSION OF IRON
Fig. A.1.3

(to be continued)

APPENDIX A.1 (continued)

Note that when an insufficient amount of inhibitor is used, the cathodic curve will intersect the anodic curve in an active region or in both active and passive regions, indicated by A and B in Fig. A1.3. In the former case, corrosion will proceed at a high rate; in the latter case, passivity is unstable, and the corrosion potential will oscillate between A and B, usually resulting in pitting of the metal. Measurement of the corrosion potential when using passivators is a good way to determine if the inhibitor is doing its job because a large positive shift in potential should occur if the metal passivates. Passivation by inhibitors is more difficult at higher temperatures, higher salt concentrations, lower pH, and lower dissolved oxygen concentrations.

Mechanism

The mechanism by which chromate passivates steel has been studied extensively, and it appears likely that protection is afforded by a combination of adsorption and oxide formation on the steel surface. Adsorption helps to polarize the anode to sufficient potentials to form very thin hydrated ferric oxides which protect the steel. Because the oxide film is invisible on steel, articles protected by chromate remain bright in otherwise aggressive environments. The oxide film is a mixture of ferric and chromic oxides and is kept in good repair by adsorption and oxidation with very little loss of metal as long as sufficient chromate remains in solution.

Chromates are accelerators of corrosion at low concentration because they are good cathodic depolarizers. The passive oxide film is conductive and cathodic to steel; therefore passive steel consists almost entirely of cathodic areas. When the passive film is penetrated by scratching or by dissolution, and when insufficient chromate is present to repair the film, the exposed steel becomes a small anodic area on which accelerated localized corrosion can occur, resulting in pitting of the metal. Mechanisms similar to that proposed for chromate are believed to apply to nitrites and nitrates.

It is practical to passivate steel in any aqueous solution, except those which contain easily oxidized substances in solution or high concentrations of chloride ions. For example, chromate should not be used in hydrogen sulfide, (H_2S)-containing (or sour) environments because it is lost by oxidation of the sulfide to free sulfur. High concentrations of chloride ions prevent passivation because they compete with chromate for adsorption, thus preventing polarization of the anodes. They also prevent deposition oxides by forming a soluble complex with ferric ions.

For a given concentration of passivating inhibitor, there is a concentration of chloride and sulfate ions which will cause depassivation. Table A.1.1 lists the "critical concentrations" of sodium chloride (NaCl) and sodium sulfate (Na_2SO_4) required to cause pitting of steel in the presence of various concentrations of sodium chromate and sodium nitrite. The critical concentrations will vary depending on other factors; for example, more chloride or sulfate will be required for depassivation as the temperature is lowered, the oxygen concentration is increased, or the pH is increased.

Chromate concentration should be maintained at at least twice the level required to prevent pitting. In calculating the amount of chromate needed for passivation, allowance should be made for the inhibitor which is consumed initially in establishing the passive film. The amount of sodium chromate consumed in passivating steel in sodium chloride solutions is given in Table A.1.2. For example, if it is desired to maintain 250 ppm of sodium chromate in water containing 1000 ppm of sodium chloride, then referring to Table A.1.2, 6.35 kg of sodium chromate per thousand square meters of exposed steel should be added in addition to the quantity required to achieve a concentration of 250 ppm.

Non-oxidizing passivators such as sodium benzoate, polyphosphate, and sodium cinnamate require the presence of oxygen to cause passivation. They do not inhibit corrosion in the absence of oxygen. They apparently function by promoting the adsorption of oxygen on the anodes, thereby causing polarization into the passive region. Non-oxidizing passivators are also dangerous when used in insufficient amounts because the oxygen which is required for passivation is a good cathodic depolizer.

(to be continued)

APPENDIX A.1 (continued)

**TABLE A.1.1 - CRITICAL CONCENTRATION OF SODIUM CHLORIDE OR
SODIUM SULFATE ABOVE WHICH PITTING OF ARMCO IRON
OCCURS IN CHROMATE OR NITRITE SOLUTIONS**

5-DAY TESTS, 25°C, STAGNANT SOLUTIONS			
Inhibitor	Concentration ppm	Critical Concentration ppm	
		NaCl	Na_2SO_4
Na_2CrO_4	200	12	25
	500	30	120
$NaNO_2$	50	210	20
	100	460	55
	500	2000	450

[Source: H.H. Uhlig, Corrosion and Corrosion Control, John Wiley & Sons, Inc., New York, N.Y., P.232 (1963).]

**TABLE A.1.2 - AMOUNT OF SODIUM CHROMATE CONSUMED BY STEEL IN 50
DAYS IN ESTABLISHING PASSIVITY IN SODIUM CHLORIDE SOLUTIONS**

SODIUM CHROMATE ppm	SODIUM CHROMATE CONSUMED IN WATER CONTAINING kg/1000 m² (lb/1000 sq ft)	
	10 ppm NaCl	1000 ppm NaCl
25	4.88 (1.0)	—
50	6.35 (1.3)	—
100	2.44 (0.5)	5.37 (1.1)
250	1.46 (0.3)	6.35 (1.3)
500	0.49 (0.1)	3.42 (0.7)
1000	0.49 (0.1)	3.42 (0.7)

[Source: M. Darrin. Ind. Eng. Chem. Vol. 38, p. 368 (1946).]

A.1.2.2 Cathodic inhibitors

Cathodic inhibitors either slow the cathodic reaction itself, or they selectively precipitate on cathodic areas to increase circuit resistance and restrict diffusion of reducible species to the cathodes. The effects of cathodic inhibitors on cathodic polarization are shown in Fig. A.1.2. In this case, where the anodic polarization is unaffected, the corrosion potential is shifted to more negative values from E_c to E''_c.

The cathodic reaction is often the reduction of hydrogen ions to form hydrogen gas. Some cathodic inhibitors make the discharge of hydrogen gas more difficult, and they are said to increase the hydrogen over-voltage. Compounds of arsenic and antimony are examples of this type of inhibitor which are often used in acids or in systems where oxygen is excluded. Another possible cathodic reaction is the reduction of oxygen. The inhibitors for this cathodic reaction are different from those mentioned for the more acidic systems.

Other cathodic inhibitors utilize the increase in alkalinity at cathodic sites to precipitate insoluble compounds on the metal surface. The cathodic reaction, hydrogen ion and/or oxygen reduction, causes the environment immediately adjacent to the cathodes to become alkaline; therefore, ions such as calcium, zinc, or magnesium may be precipitated as oxides to form a protective layer on the metal. Many natural waters are self-inhibiting due to the deposition of a scale on metals by precipitation of naturally occurring ions.

(to be continued)

APPENDIX A.1 (continued)

Inhibition by polarization of the cathodic reaction can be achieved in several ways, and several examples already have been given. The three main categories of inhibitors which affect cathodic reaction are cathodic poisons, cathodic precipitates, and oxygen scavengers.

Cathodic poisons

Cathodic poisons are substances which interfere with the cathodic reduction reactions, i.e., hydrogen atom formation and hydrogen gas evolution. The rate of the cathodic reaction is slowed, and because anodic and cathodic reactions must proceed at the same rate, the whole corrosion process is slowed.

While some cathodic poisons such as sulfides and selenides are adsorbed on the metal surface, compounds of arsenic, bismuth, and antimony are reduced at the cathode to deposit a layer of the respective metals. Sulfides and selenides generally are not useful inhibitors because they are not very soluble in acidic solutions, they precipitate many metal ions, and they are toxic. Arsenates are used to inhibit corrosion in strong acids, but in recent years the trend has been to rely more on organic inhibitors (see also Table A.1.1 of this Standard) because of the toxicity of arsenic.

A serious drawback of the use of cathodic poisons is that they sometimes cause hydrogen blistering of steel and increase its susceptibility to hydrogen embrittlement. Since the recombination of hydrogen atoms is inhibited, surface concentration of hydrogen atoms is increased, and a greater fraction of the hydrogen produced by the corrosion reaction is adsorbed into the steel. Note that hydrogen is adsorbed on the surface, but some of it is adsorbed into the steel.

Hydrogen atoms which penetrate steel may pass through and diffuse out the other side if it also is not corroding to produce hydrogen. Blisters are formed when hydrogen atoms combine to form hydrogen molecules (H_2) inside the steel. Molecular hydrogen does not diffuse through steel; therefore, it collects at defects or voids to create pressures which may reach a million psi or more.

Fig. A.1.4 shows the increase in the fraction of produced hydrogen which penetrates the steel as sulfide or arsenic concentrations are increased. Only small amounts of sulfide or arsenic are required to increase the amount of hydrogen penetrating the steel, which accounts for the frequent occurrence of blistering and hydrogen embrittlement in the presence of these poisons.

It has been suggested that the adsorption of hydrogen by steel could be used to advantage in sealed absorption-type refrigeration machines. Corrosion occurs very slowly in these systems, but sufficient hydrogen is produced to lower the efficiency of the thermal cycle, thus requiring an occasional pump-down of the units. The use of an inhibitor, such as an antimony compound, would cause the hydrogen to pass through the steel piping and vessels so that pumping would not be required. In this application, it would be important to use a steel which is not susceptible to blistering or embrittlement.

(to be continued)

APPENDIX A.1 (continued)
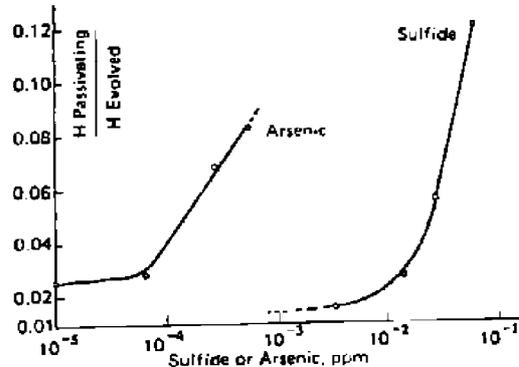
EFFECT OF SULFIDE AND ARSENIC ON THE FRACTION OF CORROSION-PRODUCED HYDROGEN WHICH ENTERS STEEL. [HUDSON, SNAVELY, PAYNE, FIEL, AND HACKERMAN, ABSORPTION OF HYDROGEN BY CATHODICALLY PROTECTED STEEL, CORROSION, VOL. 24, No. 7, PP. 189-196 (1968)]

Fig. A.1.4

A.1.2.3 Cathodic precipitates

The most widely used cathodic precipitation-type inhibitors are the carbonates of calcium and magnesium because they occur in natural waters and their use as an inhibitor usually requires only an adjustment of pH. Zinc sulfate ($ZnSO_4$) precipitates as zinc hydroxide $Zn(OH)_2$ on cathodic areas and is considered an inhibitor of this type. Phosphates and silicates are not distinctively cathodic or anodic inhibitors, but appear to be a combination of both types, so they will be considered later in the section on precipitation inhibitors.

Many natural waters and municipal water supplies contain calcium carbonate (limestone, $CaCO_3$) in solution. Limestone is dissolved in water to form soluble calcium bicarbonate ($Ca(HCO_3)_2$). Limestone can be caused to precipitate again, forming a milky-white suspension by making the calcium bicarbonate solution more alkaline or by adding more calcium. Usually, lime is added to accomplish both objectives.

The objective of corrosion-inhibiting water treatment is to increase the alkalinity of the water to a pH at which precipitation of $CaCO_3$ is just about to occur. If the appropriate pH is exceeded, $CaCO_3$ will precipitate to form a slimy, porous deposit which does not provide corrosion protection and may increase corrosion by creating concentration cells involving oxygen. At the correct pH, the deposit will be fairly hard and smooth and similar to an eggshell. Once a protective deposit is formed, the pH of the water must be maintained at the equilibrium level, because if it is allowed to become acidic, it will redissolve the protective deposit.

A convenient way to express the condition of a water with respect to its tendency to deposit $CaCO_3$ is the Langelier Index, which is the difference between the pH of the water and the pH required to precipitate $CaCO_3$.

Although many metal ions form insoluble hydroxides, few are useful cathodic corrosion inhibitors. Zinc sulfate, which is a good example, when added to neutral water, causes polarization of the cathodic reaction by precipitating zinc hydroxide.

(to be continued)

APPENDIX A.1 (continued)

Oxygen scavengers

Corrosion of steel in waters above about pH 6.0 is due to the presence of dissolved oxygen which depolarizes the cathodic reaction and increases corrosion. Neutral water of low salt content in equilibrium with air at 21°C (70°F) will contain about 8 ppm of dissolved oxygen. The concentration of oxygen decrease with increasing salt concentration and increasing temperature. Only 0.1 ppm of oxygen is required to increase corrosion rates seriously in a dynamic system. In static systems, a higher concentration of oxygen is required to increase the corrosion rate seriously because the corrosion reaction soon depletes the oxygen supply in the immediate vicinity of the metal.

Oxygen scavengers help inhibit corrosion by preventing the cathodic depolarization caused by oxygen. Oxygen scavengers are added to water, either alone or with a corrosion inhibitor, to retard corrosion. Organic corrosion inhibitors alone in aerated brine water will slow general corrosion, but will not always prevent pitting attack. The most common oxygen scavengers used in water at ambient temperatures are sodium sulfite (Na_2SO_3) and sulfur dioxide (SO_2). At elevated temperatures, hydrazine is used to remove oxygen.

The reaction rate of sulfites with oxygen at low temperature is slow, so a catalyst is usually added. Cobalt, manganese, and copper salts are the best catalysts. Cobalt gives the greatest increase in reaction rate. Copper should not be added to water which contacts steel or aluminum because it lowers the hydrogen over-voltage and increases corrosion rate. Consequently, cobalt is preferred and manganese is a close second choice.

Hydrazine reacts very slowly with oxygen in water at low temperatures in the absence of a catalyst, and thus is not often used at low temperatures. The hazards of hydrazine are significant, especially in the hands of untrained personnel. In high-pressure boilers, hydrazine is the preferred oxygen scavenger.

A.1.2.4 Ohmic inhibitors

Inhibitors which increase the ohmic resistance of the electrolyte circuit already have been considered to some extent in discussions of anodic and cathodic film-forming inhibitors. Because it usually is impractical to increase resistance of the bulk electrolyte, increased resistance is practically achieved by the formation of a film, a micro-inch thick or more, on the metal surface. If the film is deposited selectively on anodic areas, the corrosion potential shifts to more positive values; if it is deposited on cathodic areas, the shift is to more negative values; and if the film covers both anodic and cathodic areas, there may be only a slight shift in either direction.

A.1.2.5 Organic inhibitors

Introduction

Organic compounds constitute a broad class of corrosion inhibitors which can not be designated specially as anodic, cathodic, or ohmic. Anodic or cathodic effects alone are sometimes observed in the presence of organic inhibitors, but, as a general rule, organic inhibitors affect the entire surface of a corroding metal when present in sufficient concentration. Both anodic and cathodic areas probably are inhibited, but to varying degrees, depending on the potential of the metal, chemical structure of the inhibitor molecule, and size of the molecule.

The typical increase in corrosion inhibition with inhibitor concentration, as shown in Fig. A.1.5, suggests that inhibition is the result of adsorption of inhibitor on the metal surface. The film formed by adsorption of soluble organic inhibitors is only a few molecules thick and is invisible.

(to be continued)

APPENDIX A.1 (continued)

Organic inhibitors will be adsorbed according to the ionic charge of the inhibitor and the charge on the metal surface. Cationic inhibitors (positively charged, +), such as amines, or anionic inhibitors (negatively charged, -), such as sulfonates, will be adsorbed preferentially, depending on whether the metal is charged negatively or positively (opposite sign charges attract). The in-between potential at which neither cationic nor anionic molecules are preferred is known as the zero point of charge or ZPC. Thus, a combination of cathodic protection and an inhibitor which is adsorbed more strongly at negative potentials gives greater inhibition than either cathodic protection or an inhibitor when used alone.

Synergism with halogen ions

The efficiency of organic amines as corrosion inhibitors is improved when certain halogen ions are present. Halogen ions alone inhibit corrosion to some extent in acid solutions. The iodide (I^-) ion is the most effective, followed by bromide (Br^-).

(Br^-) and chloride (Cl^-). Fluoride (F^-) does not have significant inhibitive properties. Chloride ions, for example, lower the rate of attack on steel by sulfuric acid. A combination of amine and iodide may be more inhibitive than either additive alone, i.e., the two additives are synergistic.

Fig. A.1.6 shows a comparison of corrosion rates of mild steel in 3.0 M phosphoric acid (H_3PO_4) in the presence of n-declyamine, iodide ion, and a combination of n-declyamine and iodide ion. One explanation for synergism is that steel adsorbs iodide ions whose charge shifts the surface potential in a negative direction, thereby increasing adsorption of the cationic amine.

Effects of molecular structure

How the size of organic molecules influences their effectiveness as corrosion inhibitors has been investigated many times. However, the results are not consistent enough to permit formulation of a general rule regarding the effect of increasing molecular weight.

Structures of some organic inhibitors are given in Fig. A.1.7. Primary amines such as n-declyamine become more efficient inhibitors as the chain length is increased, but, in contrast, primary aliphatic mercaptans such as n-butyl mercaptan and some aldehydes decrease in efficiency as the chain length is increased.

These results probably are due to the interaction of various factors which influence the strength of the adsorption bond, compactness of the adsorbed layer, and tendency of the adsorbed molecules to cross-link or otherwise interact with neighboring molecules.

There is little doubt that the bonding of amines to a metal surface is through the nitrogen atom. For example, in the series of saturated cyclic imines, inhibitor efficiency increases, as shown in Fig. A.1.8, as the number of carbon atoms is increased in the ring up to at least 10.

(to be continued)

APPENDIX A.1 (continued)
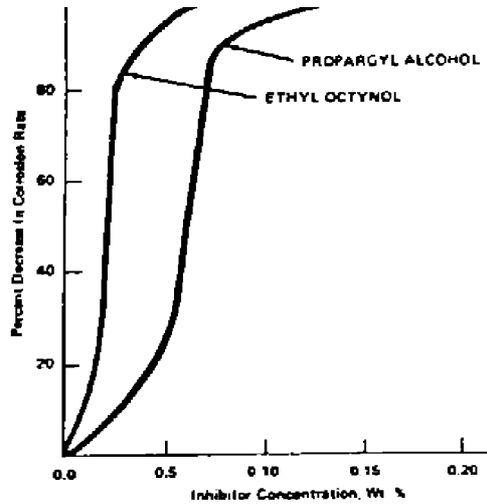
EFFECT OF CONCENTRATION OF ORGANIC INHIBITOR ON CORROSION RATE
[SOURCE: J.G. FUNKHOUSTER, CORROSION, VOL. 17, P. 283 (1961)]
Fig. A.1.5

Adsorption

The observations given previously indicate that for soluble organic inhibitors, the strength of the adsorption bond is the dominant factor. Adsorption of an inhibitor from solution establishes the following equilibrium:

$$I_{solution} \quad \Leftrightarrow \quad I_{surface} \qquad \textbf{(Eq. A.1.1)}$$
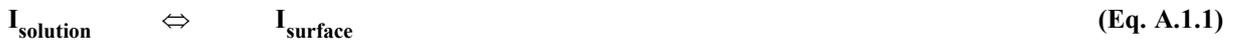
Where:

I is the concentration of a soluble organic inhibitor.

It is characteristic of an equilibrium that if the concentration of one species is changed, then the concentration of species with which it is in balance will change in the same direction to preserve equilibrium. From Equation (A.1.1), it is seen that the amount of inhibitor on the surface is increased by increasing isolution, i.e., the concentration of inhibitor used in the environment to be inhibited. Inhibitor efficiency increases with concentration until the surface is saturated, i.e., it has adsorbed inhibitor molecules on all available sites. Therefore, the stronger the adsorption bond, the lower the concentration of inhibitor in solution required to achieve a given coverage of the surface.

Soluble organic inhibitors form a protective layer only a few molecules thick, but if an insoluble organic inhibitor is added by dispersion as fine droplets, the film may continue to build to a thickness of several thousandths of an inch. Such films show good persistence, i.e., they continue to inhibit corrosion for a time when an inhibitor is no longer injected into the environment. Persistency is an important property when inhibitors can be injected into a system only in slugs.

(to be continued)
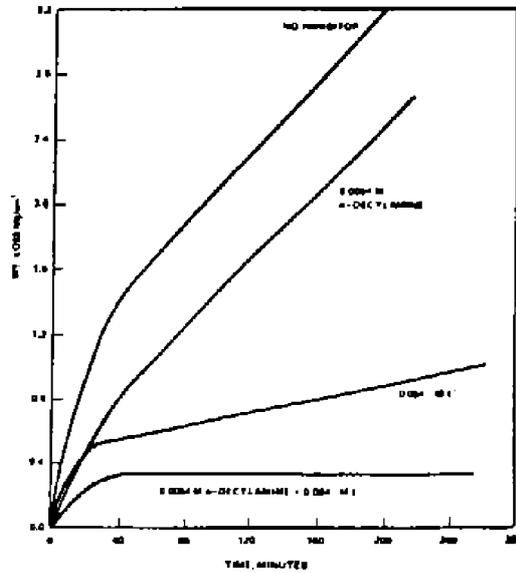
CORROSION OF MILD STEEL IN 3 M PHOSPHORIC ACID (30%) SHOWING SYNERGISTIC EFFECT OF N - DECYLAMINE AND IODIDE ION. [SOURCE: HACKERMAN, SNAVELY, AND PAYNE, J. ELECTROCHEM. SOC., VOL. 113, P. 667 (1966).]
**Fig. A.1.6**
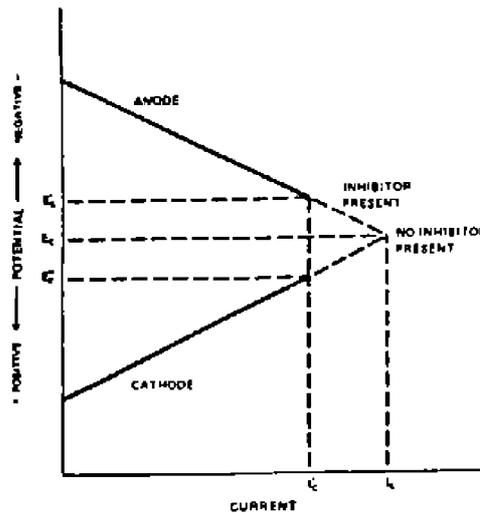
STRUCTURES OF SOME ORGANIC INHIBITORS
Fig. A.1.7

(to be continued)

APPENDIX A.1 (continued)
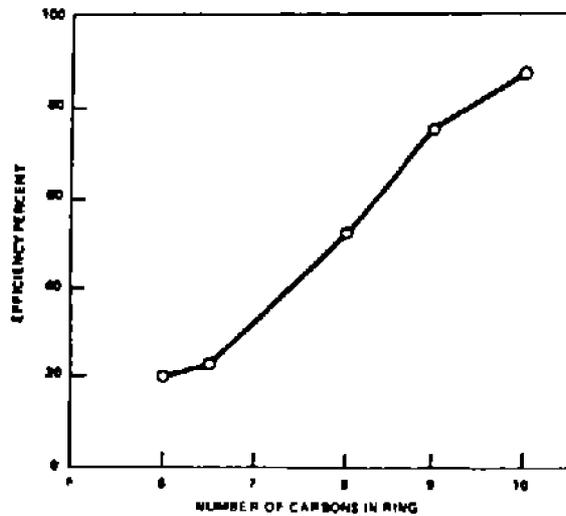
**INHIBITOR EFFICIENCIES OF SATURATED CYCIC IMINES FOR CORROSION OF
STEEL IN 6 M HYDROCHLORIC ACID (22%). [SOURCE: HACKERMAN, HURD,
AND ANNAND, CORROSION, VOL. 18, P. 37 (1962).]
Fig. A1.8**

Precipitation inhibitors

Precipitate-inducing inhibitors are film-forming compounds which have a general action over the metal surface and which, therefore, interfere with both anodes and cathodes indirectly. The most common inhibitors of this class are the silicates and phosphates.

In waters with a pH near 7.0, a low concentration of chlorides, silicates, and phosphates cause passivation of steel when oxygen is present; hence, they behave as anodic inhibitors. Another anodic characteristic is that corrosion is localized in the form of pitting when insufficient amounts of phosphate or silicate are added to saline water. However, both silicates and phosphates from deposits on steel which increase cathodic polarization. Thus, their action appears to be mixed, i.e., a combination of both anodic and cathodic effects.

Silicate is used most often in low salinity waters which contain oxygen. It has the rare property of inhibiting corrosion of steel which is already scaled with rust. While the concentration of silicate required for protection depends on the salinity of the water, for most city water supplies, 5 to 10 ppm are required initially, followed by a gradual reduction to 2 to 3 ppm after a protective deposit is established. High concentrations of calcium and magnesium interfere with inhibition by silicates, but this problem is often overcome by adding 2 to 3 ppm of polyphosphates in addition to the silicates.

Sodium silicate is used in many private water softeners to prevent occurrence of red water or rust water which is caused by suspended ferric hydroxide. The silicates remove iron by precipitation, so they should not be used where formation of scales can not be tolerated.

In aerated hot water systems, sodium silicate protects steel, copper, and brass. However, protection is not always reliable and depends on pH and composition of the water. The best procedure is to adjust the saturation index as already described to facilitate formation of a protective silicate-containing film.

(to be continued)

APPENDIX A.1 (continued)

Phosphates, like silicates, require oxygen for effective inhibition. A concentration of sodium hexameta-phosphate, a typical polyphosphates, of about 10 ppm provides corrosion inhibition in aerated water if the water is in motion. In stagnant areas, corrosion might be increased due to the establishment of oxygen concentration cells.

In addition to motion, the presence of calcium ions is essential to inhibition. Phosphates inhibit the deposition of $CaCO_3$; therefore, the concentration of phosphate and calcium must be in proper balance to obtain effective inhibition. A rule of thumb is that the phosphate must not exceed twice the concentration of calcium carbonate. Therefore, if a water contains 10 ppm of calcium carbonate, then up to 20 ppm of phosphate can be used for inhibition. If the water is exceedingly soft, calcium can be increased by the addition of lime.

If chromate can not be used because windage losses or disposal causes problems due to the toxicity of chromate, industrial cooling towers can be inhibited with about 50 ppm of sodium hexametphosphate. Addition of a soluble zinc salt often improves inhibition by polyphosphates (Fig. A.1.9). Pitting and excessive scale formation are prevented by maintaining the pH in a range of 6 to 7.

The silicates and phosphates do not afford the degree of protection that can be obtained with chromates and nitrites; however, they are very useful in situations where non-toxic additives are required. Their main drawbacks are their dependence on water composition and the careful control required to achieve maximum inhibition.
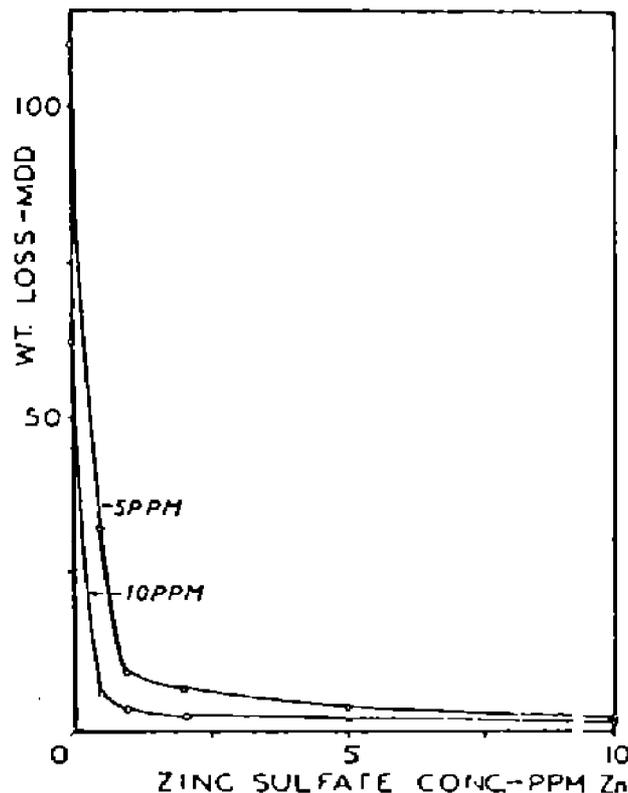
INFLUENCE OF ZINC SULFATE ON INHIBITING CORROSION OF STEEL AT TWO GLASSY PHOSPHATE LEVESLS. TEST 5 DAYS AT 35°C, SOLUTION (PITTSBURGH TAP WATER) HAD pH OF 6.9. [SOURCE: G.B. HATCH AND P.H.RALSTON, OXYGEN CORROSION CONTROL IN FLOOD WATERS, MATERIALS PROTECTION, VOL. 3, No. 8, pp. 35-41 (1964)] Fig. A1.9

(to be continued)

APPENDIX A.1 (continued)

A.1.2.6 Vapor phase inhibitors

Vapor Phase Inhibitors (VPI), also called Volatile Corrosion Inhibitors (VCI), are compounds which are transported in a closed system to the site of corrosion by volatilization from a source. In boilers, volatile basic compounds such as morpholine or octadecylamine are transported with steam to prevent corrosion in condenser tubes by neutralizing acidic carbon dioxide. Compounds of this type inhibit corrosion by making the environment alkaline. In closed vapor space, such as shipping containers, volatile solids such as the nitrite, carbonate, and benzonate salts of dicyclohexylamine, cyclohexylamine, and hexamethylene-imine are used. The mechanism of inhibition by these compounds is not entirely clear, but it appears certain that the organic portion of the molecules merely provides volatility.

On contact with a metal surface, the inhibitor vapor condenses and is hydrolyzed by any moisture present to liberate nitrite, benzoate, or bicarbonate ions. Since ample oxygen is present, nitrite, and benzoate ions are capable of passivating steel as they do in aqueous solution. The mechanism for carbonate may not be the same, and here the organic amine portion of the VPI may serve to aid inhibition by adsorption and by providing alkalinity.

It is desirable for a VPI to provide inhibition rapidly and to have a lasting effect. Therefore, the compound should have a high volatility to saturate all of the accessible vapor space as quickly as possible, but at the same time it should not be too volatile, because it would be lost rapidly through any leaks in the package or container in which it is used. The optimum vapor pressure of VPI then would be just sufficient to maintain an inhibiting concentration on all exposed metal surfaces.

Vapor pressures and other properties of some VPIs are given in Table A.1.3. Note that the vapor pressure of cyclohexylamine carbonate is 2000 times higher than dicyclohexylamine nitrite, thus making it a better choice for containers which are opened occasionally because it will resaturate the vapor space rapidly.

Dicyclohexylamine nitrite is advantageous for once-opened containers which may be stored for extended periods. The amount of VPI required depends on conditions, but 2.2 kg per 100 m² (1 lb per 500 ft²) of surface has been suggested for dicyclohexylamine nitrite and 2.2 kg per 30 m³ (1 lb per 500 ft³) space for cyclohexyalmine carbonate. Vapor phase inhibitors attack nonferrous metals to varying degrees, so it is suggested that a potential user test several of the commercially available VPIs for his particular application. Compatibility of the amines and nitrites with the copper alloys should especially be considered.

TABLE A.1.3 - PROPERTIES OF VAPOR PHASE INHIBITORS

COMPOUND	VAPOR PRESSURE mm Hg AT 25°C	REMARKS
Dicyclohexylamine nitrite	0.0002	Protects steel, aluminum, and tinplate. Increases corrosion of zinc, magnesium, cadmium, lead, and copper. Discolors some plastics.
Cyclohexylamine carbonate	0.4	Protects steel, aluminum, solder, tin, and size. No effect on cadmium. Increases corrosion of copper, brass, and magnesium.

APPENDIX B.1
ENVIRONMENTAL FACTORS

B.1.1 Aqueous Systems

B.1.1.1 Introduction

Aqueous systems are by far the most common corrosive environments to which corrosion inhibitors are applied. Water is a powerful solvent capable of carrying many different ions at the same time, so requirements for corrosion inhibition may vary greatly, depending on the type and amount of dissolved species present. Because there is no universal inhibitor for water systems, an inhibitor which may be satisfactory for one system may be ineffective or even harmful in another. The main factors which must be considered in the application of corrosion inhibitors to aqueous systems are salt concentration, pH, dissolved oxygen concentration, and the concentration of interfering species.

This survey of the use and properties of corrosion inhibitors in aqueous solutions illustrates some common inhibitor-environment interactions. A process shall be analyzed carefully and some tests made before a large-scale program of corrosion inhibition is initiated. When working with natural water, special attention must be given to its composition, particularly in regard to possibilities of natural inhibition and the presence of interfering ions.

B.1.1.2 Effects of various dissolved species

Demineralized water is relatively non-corrosive toward steel because of its high electrical resistance (ohmic control) and low hydrogen ion concentration. However, when demineralized water is in contact with the atmosphere, it will absorb carbon dioxide and form carbonic acid which will decrease its resistance to that significant corrosion of steel will occur, the cathodic reaction being primarily reduction of dissolved oxygen rather than reduction of hydrogen ions. In this case, minimal concentrations of inhibitors such as sodium chromate, sodium nitrite, polyphosphates, sodium benzoate, or borax are effective. Steel is easily passivated in demineralized or distilled water because the pH is neutral and there are no dissolved ions to interfere with formation of the passive layer.

Industrial and domestic waters contain dissolved substances which affect their aggressiveness and corrosion inhibitor requirements in various ways, depending on the nature of the substances. The most common dissolved substances and their effects on corrosion inhibition are as follows:

B.1.1.2.1 Oxygen (O_2)

In neutral water, oxygen causes corrosion; therefore, if it is reduced to less than 0.1 ppm by scavenging compounds or by stripping, sufficient control is thereby provided for some systems; e.g., in boilers and hot water supplies. Oxygen can be utilized in passivating steel by adding a passivating inhibitor. Organic inhibitors are seldom effective against oxygen-caused attack unless they contain passivating groups such as benzoate or nitrite.

B.1.1.2.2 Chloride (Cl^-)

Steel, as well as many other metals, is more difficult to passivate in the presence of the chloride ion; therefore, a higher concentration of passivating inhibitor is required if chlorides are present. Non-passivating inhibitors must be used in higher concentrations also because chloride ions are strongly absorbed by steel.

B.1.2.3 Sulfate ($SO_4^=$)

The effects of sulfate on passivity are similar to those of chloride, but to a lesser degree. Sulfates or chlorides must not be allowed to build up in a system by evaporation because depassivation may occur.

(to be continued)

APPENDIX B.1 (continued)

B.1.1.2.4 Bicarbonate (HCO_3^-)

Bicarbonate in hard waters can be utilized for natural inhibition by forming precipitates. In soft water, corrosion inhibitors must be used if excess carbon dioxide is present because of the acidic condition it produces.

B.1.1.2.5 Sulfides ($S^=$)

Sulfides precipitate many metal ions, e.g., inhibitors which contain zinc can not be used. Oxidizing inhibitors are reduced by sulfide to form free sulfur. They are effective only if an excess above the amount required to react with sulfide is used and the collodial precipitate of free sulfur can be tolerated.

B.1.1.2.6 Metal cations

Sodium (Na^+) and potassium (K^+) ions have no particular effects on inhibitors; calcium (Ca^{++}) and magnesium (Mg^{++}) may be used to form protective precipitates, but at high concentrations they interfere with inhibitors by precipitating nonprotective deposits and also by precipitating inhibitors such as phosphate ($PO_4^=$) and silicate ($SiO_3^=$). Very small concentrations of heavy metal ions, such as copper and mercury, can cause severe interference with inhibitors.

B.1.1.2.7 Acid (H^+)

Hydrogen ions increase corrosion rates and increase the difficulty of passivating steel. Passivation is used in sulfuric (H_2SO_4) and phosphoric acids (H_3PO_4), but not in hydrochloric acid (HCl). Non-passivating organic or cathodic inhibitors (e.g., guanidine or sodium arsenate) are preferred in pickling acids to avoid the disastrous consequences of depassivation.

B.1.1.2.8 Alkali (OH^-)

In alkaline solutions, corrosion of steel is controlled by the rate of oxygen diffusion through the precipitated corrosion product (usually ferrous hydroxide, $Fe(OH)_2$), so corrosion rates are low. Steel is easily passivated in alkaline solutions. Amphoteric metals such as aluminum, zinc, and lead corrode slowly at low alkali concentrations, but above pH 9.0 their rates are very high and inhibitors are required.

B.1.1.3 Waters of low-to-moderate salt concentrations

B.1.1.3.1 Waters of low-to-moderate salt concentrations are encountered in municipal water systems, cooling waters, marine and offshore activities, and oil-field water injection systems. Because metals adsorb ions of dissolved salts in water, an inhibitor has more difficulty in reaching the metal surface and displacing adsorbed ions than it has in diminer- alized water; hence, a higher concentration of inhibitor is required. Furthermore, chloride ions have a depassivating effect, i.e., they make it more difficult to control corrosion by passivating inhibitors. Thus, it is important to maintain inhibitor concentrations at a safe level in waters containing dissolved salts, particularly the chlorides.

B.1.1.3.2 Municipal drinking water can not be treated with most inhibitors because of their toxicity. Fortunately, treatment with lime to raise the pH usually affords sufficient protection to steel or cast iron water pipes. If the water is high in chlorides or sulfates, then polyphosphates are used for added inhibition. Silicates also may be used in municipal waters, but they have the disadvantage of forming precipitates with iron and calcium which scale pipes and heat transfer surfaces.

(to be continued)

APPENDIX B.1 (continued)

B.1.1.3.3 Cooling water systems may be either recirculating or once-through types. In closed recirculating systems, oxygen can be excluded, and corrosion often can be controlled by adjusting the pH to an alkaline value. Recircualting systems are more easily controlled by inhibitors since higher concentrations can be applied because the water is reused. Sodium chromate or sodium nitrite are both effective in all-steel, closed recirculating systems. Sodium nitrite may from ammonia by reduction at cathodic sites; therefore, it should not be used in systems which include brass or copper, since these materials are subject to stress corrosion cracking by ammonia.

B.1.1.3.4 Glycol-water mixtures, such as those used to cool engines and to transfer solar heat, can not be inhibited with oxidizing inhibitors such as chromate or nitrite because the glycol is oxidized. This not only consumes the inhibitor, but also forms organic acids which attack the cooling system. Such cooling systems usually are inhibited with a mixture of borax (for maintaining an alkaline pH) and mercaptobenzothiazole, which inhibits the corrosion of brass and copper. Borax alone is satisfactory for steel in contact with glycol-water mixtures, but borax and glycol attack zinc galvanizing rapidly and attack the zinc in brass due to the formation of complex zinc compounds at low temperatures.

So, the addition of mercaptobenzothiazole is necessary in mixed metal cooling systems. A soluble oil also is often added to increase protection and to lubricate moving parts in the cooling system. In some mixed metal systems, silicates and nitrates are now used. Amine phosphates have also long been used in such systems.

B.1.1.3.5 Once-through cooling systems require inexpensive corrosion inhibitors. In open systems, corrosion is more severe and good inhibition is imperative. The situation is similar to that in municipal water supplies, so comparable remedial measures, namely addition of lime or polyphosphates, are used. In waters which are very corrosive due to high chloride concentrations, chromates or nitrites may be required in addition to polyphosphates.

Waters which may contain appreciable quantities of organic matter, such as sea water and oil field injection brines, usually are not inhibited with oxidizing inhibitors such as chromate and nitrite because of the high consumption of inhibitor through oxidation of the organic. Non-oxidizing inorganic inhibitors such as sodium silicate also must be used in high concentrations due to the high chloride content of brines. Generally, organic inhibitors offer the best means for protection in organic-contaminated brines. Concentrations of only 10 to 20 ppm of inhibitors such as the fatty amines often effectively control corrosion in oil field brines.

B.1.1.4 High salt concentrations

Extremely high salt concentrations are used in aqueous solutions for heat transfer in refrigeration systems. The temperatures encountered are always low, and since the brines are recirculated, a high concentration of inhibitor can be maintained economically. Sodium chromate is effective in refrigeration brines, provided there is no limitation due to its toxidity. If physiological effects are a factor, then disodium phosphate can be used, although it is not as effective as sodium chromate in controlling corrosion.

B.1.1.5 Effects of pH

B.1.1.5.1 The pH of aqueous solutions is extremely important is determining the type of corrosion inhibitor which is most effective and most economical. Natural hard waters retain compounds of calcium, including calcium carbonate ($CaCO_3$) and calcium bicarbonate ($Ca(HCO_3)_2$), along with carbon dioxide, in solution. There is an equilibrium which occurs among these species as shown by Equation (B1.2).

$$CaCO_3 + CO_2 + H_2O \Leftrightarrow Ca(HCO_3)_2$$

insoluble   **soluble**   **(Eq. B.1.1)**

(to be continued)

APPENDIX B.1 (continued)

At high temperatures the reverse reaction occurs, and heated surfaces become coated with $CaCO_3$. A protective scale is produced also when $Ca(HCO_3)_2$ becomes alkaline in the region of a cathodic area. The scale thus deposited inhibits corrosion by reducing the cathodic area, restricting diffusion of cathodic depolarizers, and increasing ohmic resistance. This scale is often developed on cathodically protected steel surfaces in sea-water, and is often called a calcareous deposit. For this reason, some natural hard waters are less corrosive than softened waters. The addition of zinc sulfate $(ZnSO_4)$ in alkaline solutions also inhibits corrosion by precipitating insoluble zinc hydroxide $(Zn(OH)_2)$ on the cathodic area.

B.1.1.5.2 Hydrogen sulfide is a particularly troublesome problem. The dissolved gas attacks steel only slowly when first exposed due to the formation of a protective layer of iron sulfide. The iron sulfide film affords only temporary protection, however, because it becomes permeable to hydrogen sulfide, and the corrosion rate increases with time, producing blistering, high metal loss, and possibly hydrogen embrittlement. Organic corrosion inhibitors prolong the interval preceding higher corrosion rates, but the iron sulfide film eventually prevents access of the inhibitor to the steel surface and, as a result, the corrosion process can proceed uninhibited.

The most effective chemical control measures against hydrogen sulfide (sour) corrosion are removal of the hydrogen sulfide from the water by counter-current gas stripping or by cleaning the steel periodically with acid to allow access of the inhibitor to the metal surface. Steel sometimes can be cleaned sufficiently for inhibition to be effectively by the use of a powerful wetting agent.

B.1.1.6 Strong acids

High acid concentrations are encountered in pickling processes, oil well acidizing, and during the transportation of acids for use in chemical processes. Hydrochloric acid of all concentrations requires an inhibitor if steel is to be used. The use of an inhibitor in pickling processes also allows the acid to dissolve scale from steel without appreciable attack on the metal. Pickling acids are effectively inhibited by adding about 0.2% of an organic compound such as anilines, pyridines, thiourea, or sulfonated castor oil. Cathodic inhibitors such as arsenates (As_2O_3), e.g., sodium arsenate (Na_3AsO_4), are also good inhibitors for pickling acids, but are less popular than organics because they cause blistering and hydrogen embrittlement of some steels. Arsenic compounds should never be used in fluids which are to be catalytically processed because arsenic is a poison to most catalysts.

Sulfuric and phosphoric acid concentrations up to 70% can be inhibited by methods similar to those used for hydrochloric acid. Concentrations of sulfuric acid higher than 70% are strongly oxidizing, attack steel slowly, and do not require inhibition. Fertilizer grade phosphoric acid (73% black acid) attacks steel readily and usually is inhibited with potassium iodide. Organic inhibitors are not effective in concentrated phosphoric acid when used alone, but it has been reported that a lower concentration of potassium iodide is required for inhibition if a fatty amine is also added.

B.1.2 Non-aqueous systems

B.1.2.1 Corrosion in non-aqueous liquids such as fuels, lubricants, and edible oils is usually caused by the small amounts of water often present. Water is slightly soluble in petroleum products, and its solubility increases with temperature. If a non-aqueous solvent is saturated with water and the temperature is lowered, then some of the water will separate to attack steel that it contacts. Oils that have been subjected to high temperatures in air will contain organic acid that will be extracted by any water present to increase the rate of attack on steel.

B.1.2.2 Corrosion in steel systems handling wet oils can be inhibited with both organic and inorganic compounds. Effective organic compounds include various amines, lecithin, and mercaptobenzothiazole. The inorganic inhibitors include sodium nitrite and sodium nitrate. Chromates are not used because of their instability in the presence of organics.

B.1.2.3 Small amounts of water inhibit corrosion in some non-aqueous solvents. Halogenated (containing chlorides, fluorides, bromides, or iodides), non-aqueous solvents can be particularly troublesome. Organic amines are effective inhibitors for steel degreasing vessels that contain hot chlorinated solvents.

(to be continued)

APPENDIX B.1 (continued)

B.1.2.4 Inhibition of corrosion of aluminum when in contact with halogenated solvents is more difficult. Aluminum in contact with many of the one and two carbon chlorocarbons can explode after a varying incubation period if the solvent is dry. A few parts per million of water will inhibit the reaction. On the other hand, if water is added exceeding the limited solubility in the solvent, the water layer will become highly acidic from hydrolysis of the organic compound. Thus, inhibition in systems containing these materials must be approached with caution.

B.1.2.5 Water also inhibits the stress corrosion cracking of steel in ammonia and titanium in methanol, as well as the attack on titanium by "dry" chlorine.

A trace of water (0.001%) in liquid Hydrogen Fluoride (HF) behave as a passivating inhibitor for nickel. This is an extreme example of the importance of solvent-inhibitor interactions. The exact mechanism of inhibition by water in HF is unknown, but the passivating effect is similar to that observed on steel in the presence of chromates in aqueous.

B.1.2.6 Solubility is an important factor to be considered in evaluating corrosion inhibitors for non-aqueous fluids, because they do not have the tremendous solvent power range of water. Because an inhibitor must be transported through the environment to sites where corrosion occurs, it must be either soluble in the environment or sufficiently dispersed in fine droplets that settling does not occur. Also, the inhibitor must not form filter-plugging insoluble products by reaction with metals or components of the non-aqueous fluid. Some corrosion inhibitors formerly used in gasoline were found to react with zinc in galvanized fuel tanks to form a precipitate that clogged fuel filters.

B.1.2.7 Testing inhibitors in non-aqueous media is more difficult than in aqueous solutions, especially if corrosion is due to water separating to form a two-phase system. This condition is difficult to duplicate in the laboratory, and polarization curves can not be used effectively because most non-aqueous solvents are nonconductors. Furthermore, corrosion coupons placed in pipes or tanks carrying fuel or similar products may give misleading results because they may not be contacted or wetted by the water phase.

A widely accepted laboratory test for two-phase systems (called the wheel test) consists of alternately wetting a corrosion specimen by the organic and water phases by rotating a bottle containing the two phases. This test is very useful, but not always reliable because of the restricted volume of the solvents and the difficulty in duplicating velocity and stagnation effects in real systems.

B.1.3 Gaseous environments

B.1.3.1 Introduction

Gaseous environments include the open atmosphere, the vapor phase in tanks, natural gas in wells, and the empty space in packaging containers. Here again, water and oxygen are the principal corrosive agents, but the main problem in providing inhibition is to transport the inhibitor from a source to the sites where corrosion may occur.

B.1.3.2 The open atmosphere

Inhibitors for corrosion in the open atmosphere are applied directly to the metal surfaces to be protected. The most common method is the use of chromates in paints. Zinc chromate and red lead are used in primer coats. Rivet heads are coated with a slurry of micro-encapsulated zinc chromate. When the rivet is driven against another surface, the capsules rupture to provide lasting inhibition to the crevice under the rivet head. Volatile inhibitors are never used in the open atmosphere because they are impractical and can not saturate the vapor space.

(to be continued)

APPENDIX B.1 (continued)

B.1.3.3 Closed vapor spaces

B.1.3.3.1 The walls of tanks above a water line are subject to extensive corrosion because the relative humidity is always high and oxygen is plentiful if the tank is vented to the atmosphere. Where water contamination is not a factor, a layer of oil on the surface helps to maintain a low humidity and, as the level is raised and lowered, the walls are coated with a layer of oil. The oil may contain an organic inhibitor and an agent (usually an amine) to cause the oil to spread on the metal surface. An oil layer containing about 15% lanolin has been used in ship ballast tanks to control corrosion.

B.1.3.3.2 Gas wells corrode mostly in the reflux zone, which is an area of the well somewhere between the bottom and the wellhead where condensation occurs. As the gas flows up the well, its temperature drops due to expansion, and this causes condensation when the temperature reaches the dew point of the gas. Volatile inhibitors such as formaldehyde and ammonia, injected into gas well have been used successfully to inhibit corrosion. Many gas wells today are protected by injecting amine inhibitors continuously, in slugs, or by squeeze which means they coat the well when injected and also enter the gas stream partially by vaporization and partially by entrainment.

B.1.3.3.3 Packaged materials may be protected from corrosion in several ways. Packages which can be sealed and which contain parts that can not be coated with an inhibitor or exposed to volatile inhibitors (such as electronic parts) are protected by placing a desiccant, such as silica gel, in the package to maintain the humidity at a low level.

Vapor Phase Inhibitors (VPI) can be placed in a package in bulk or by wrapping an article in paper impregnated with a VPI. These compounds are volatile organics, so the package in which they are used must be fairly well sealed. The most common VPIs in use are Dicyclohexylamine Nitrite (DHN) and Cyclohexylamine Carbonate (CHC). These inhibitors are very effective for steel, but they should be tested if metals other than steel are present because they attack some nonferrous metals.

B.1.3.3.4 Inhibited coatings provide a cheap, effective method for controlling corrosion of packaged materials. Easily strippable coatings which do not harden are called soft coatings or slushing compounds. Oils and greases containing amines may be used. Steel and zinc articles can be protected with a thickened aqueous solution of sodium benzoate or sodium nitrite.

B.1.3.3.5 Metals which are very sensitive to hydrogen sulfide, such as copper and silver, are protected by enclosing them in paper impregnated with copper or zinc compounds. These materials are not corrosion inhibitors in a strict sense since they adsorb gaseous sulfur compounds to prevent reaction with the silver or copper.

B.1.4 Effect of elevated temperatures

B.1.4.1 Most effects of elevated temperatures are adverse to corrosion inhibition. High temperatures increase corrosion rates (about double for a 15°C rise at room temperature), and they decrease the tendency of inhibitors to adsorb on metal surfaces. Precipitate-forming inhibitors are less effective at elevated temperatures because of the greater solubility of the protective deposit. Thermal stability of corrosion inhibitors is an important consideration at high temperatures. Polyphosphates, for example, are hydrolyzed by hot water to form orthophosphates which have little inhibitive value. Most organic compounds are unstable above about 200°C (400°F); hence, they may provide only temporary inhibition at best.

B.1.4.2 In neutral or slightly alkaline, oxygen-free aqueous systems, corrosion of fairly clean steel occurs at a very low rate at elevated temperatures. This principle is the basis for most boiler water treatment to prevent corrosion, i.e., treatment is designed to provide alkalinity, to remove oxygen, and to prevent scale deposition. Other additives are also used to prevent foaming, but these will not be considered here.

B.1.4.3 In oxygen-free hot water, steel is protected by formation of a natural coating of magnetite (Fe_3O_4 or black rust) formed by the reaction:

$$3Fe \;+\; 4H_2O \;\rightarrow\; Fe_3O_4 \;+\; 4H_2 \qquad\qquad\qquad \textbf{(Eq. B.1.2)}$$
Iron   Water   Ironoxide Hydrogen

(to be continued)

APPENDIX B.1 (continued)

If oxygen is present, then nonprotective Fe_2O_3 (red rust) is formed. At elevated temperatures, oxygen is removed readily from boiler waters by reaction with sodium sulfite or hydrazine. Hydrazine is preferred because it does not increase the salt content of the boiler water; moreover, it reacts faster than sodium sulfate at elevated temperatures, the dosage required to react with a given amount of oxygen is lower, and it is easier to apply because it is a liquid.

B.1.4.4 Boiler waters maintained at an alkaline pH to facilitate formation and maintenance of the Fe_3O_4 protective film (Chapter 8). It is desirable to use an additive which will be carried into steam condensate lines to maintain an alkaline condition in these areas also. Volatile amines such as ammonia, morphine, cyclohexylamine, and octadecylamine are used.

Deposition of scales in boilers reduces heat transfer and produces pitting-type corrosion. Water softeners often are used to treat boiler feed to remove objectionable ions such as calcium, magnesium, and ions, but usually a scale inhibitor such as sodium phosphate also is added. The phosphates prevent scaling by increasing the supersaturation of $CaCO_3$ and $CaCO_4$ in water.

In high-pressure, high-temperature boilers, demineralized water often is used. In these cases, only oxygen removal with hydrazine is required.

High temperatures always increase the rate of attack of metals in acids because the driving force for the anodic and cathodic reactions is greater and hydrogen over-voltage is decreased. Other factors such as the greater solubility of corrosion products and the higher rate of solution of metal oxides also increase the rate of attack.

B.1.4.5 While hot acids are handled best by resistant alloys or coated steel, an exception is the acidizing of oil wells. It is impractical to coat or line oil well casing because the coating is soon destroyed by the insertion of tools, etc. Bottom-hole temperatures of oil wells are often 93 to 150°C (200 to 300°F) and sometimes as high as 230°C (450°F). Inhibitors for acids used to increase the permeability of oil-producing formations (usually HCl) are effective, but have temperature limitations. Amine-type pickling acid inhibitors are often used for oil well acidizing.

IPS

PART TWO

REQUIREMENTS

FOR

CORROSION CONTROL OF PETROLEUM

AND

PETROCHEMICAL INDUSTRIES

CONTENTS :

APPENDICES:

1. SCOPE

1.1 This Part 2 of IPS-E-TP-780 specifies corrosion problems involved in Oil, Gas and Petrochemical Industries as well as requirements for controlling corrosion by inhibitors.

2. REFERENCES

See 1 (general).

3. DEFINITIONS AND TERMINOLOGY

See 2 (general).

4. UNITS

See 3 (general).

5. CORROSION PROBLEMS IN PETROLEUM INDUSTRIES

5.1 General

The petroleum industry contains a wide variety of corrosive environments. Thus it is convenient to group all these environments together. Corrosion problems occur in the petroleum industries in at least four general areas as follows:

- Exploration (drilling and completion of oil or gas wells).
- Production.
- Transportation and storage.
- Petroleum refineries and petrochemical plants.

5.2 Exploration

5.2.1 General

Corrosion is one of the problems that must be reckoned with in the successful drilling and completing of an oil or gas well. Recognition of the causes of corrosion in this environment, as in others, has led to the development of numerous corrosion control techniques.

It is well known that environment components such as oxygen, carbon dioxide, hydrogen sulfide and dissolved salts accelerate corrosion attack. These corrosion accelerators are commonly encountered in drilling and completion fluids and in many instances all are present. To offset their corrosive effect several techniques are used, including dilution, concentration, precipitation, neutralization and chemical inhibition. Living organisms are not usually classified as corrosion contaminants, but they have the ability to produce corrosives to the extent that they, too, are an important consideration in corrosion control.

5.2.2 Factors important in corrosion attack during drilling and their control

5.2.2.1 Microorganisms

Microorganisms are common to drilling and completion fluids and can produce hydrogen sulfide, carbon dioxide or organic acids. Some bacterial species, including Desulfovibrio desulfuricans, also increase corrosion by metabolically depolarizing the cathode. Because of the prolific nature of bacteria in these environments, both biostats and biocides are often used for their control, (see Part 2, Clause 5.5) on biological influences.

5.2.2.2 Mechanical and metallurgical factors

Corrosion due to mechanical and metallurgical problems also exist. Metal tools used in drilling wells are often softer than the formation being penetrated. The abrasiveness of formation solids can easily erode protective films from drilling equipment, leaving metal exposed to corrosion-erosion attack. Mechanical and chemical separation of abrasive solids helps control this attack. It is difficult, however, to control stress concentrations in a string of drill pipe that may reach kilometers into the earth. Stress increases corrosion attack and must be controlled through proper design and use of equipment, as well as by reduction of environmental corrosives. For example, corrosion pits concentrate stress and are prime initiation points for corrosion fatigue cracks which are the major cause of drill pipe failure. It is easily understood that corrosion problems become more critical as well depth increases, because among other things, high temperature becomes one of the more critical problems faced in many deep drilling projects.

5.2.2.3 Effect of high temperature

There are two generally accepted high temperature corrosion effects in drilling and packer fluid environments. As temperature increases corrosion attack increases exponentially and high temperature degradation products of chemical additives increase environmental corrosiveness. Thermal stability is a primary prerequisite for materials involved in chemical corrosion control under high temperature conditions. Dilution, precipitation and corrosion inhibition are also used to combat this problem.

5.2.2.4 Time factors

Time also is always an important factor in corrosion control. The current trend in oil well drilling which requires probing deeper strata of the earth increases equipment exposure time under the critical conditions.

Good practice involves decreasing the area of equipment surface exposed, the exposure time and the critical conditions. Drill pipe internally plastic coated and sealed bearing bits are two examples of decreased surface equipment exposure.

Increasing penetration rates by optimizing drilling conditions has played an important role in reducing equipment exposure time. Use of temperature-stable materials, corrosion inhibitors or converting to non-corrosive oil systems also changes conditions. Not all practices can be considered beneficial even though they improve one or more of the detrimental conditions. As an example, air or mist drilling greatly increases the penetration rate and therefore decreases equipment exposure time. Although this technique is often considered economical, corrosive conditions are almost always severe and require correction.

The relationship between the chemical, mechanical and time factors involved in controlling corrosion caused by drilling and packer fluids has been recognized for many years. Early recognition of corrosion problems in the drilling industry led to the development of some of the technology used in current exploration and production practices.

5.2.3 Problems related to packer fluids

Drilling fluids are often left as packer fluids in the tubing and casing annulis. The packer of "fill-in fluid" must function in a way different from the drilling fluid, because dynamic circulating drilling conditions are changed to a static fluid column. While drilling, the fluid must remove from the bore hole tremendous quantities of formation debris, some of which is trapped in the circulating fluid and may present a corrosion problem when the mud is left as a packer fluid.

One function of the packer fluid is to stabilize and maintain the entrained materials in suspension. This fluid must be of sufficient density to contain the well pressure in the event of a pipe failure. Under long-term, static conditions, detrimental changes may take place that can not be rectified easily. Packer fluids must be conditioned to function for years, because no opportunity is afforded for correction without great expense. Corrosive contaminants, such as carbon dioxide and hydrogen sulfide are produced by bacterial action, thermal degradation or electrochemical reduction. The fluid places in the annular space of the well requires careful selection for the assurance of successful and economical completion.

5.2.4 Some problems related to water base fluids and their control

Water base drilling fluids present corrosion problems primarily because they are subject to contamination from corrosion accelerators such as oxygen, carbon dioxide, hydrogen sulfide or salts that are always present in varying quantities. The sources and effects of these contaminants have been the subjects of numerous investigations. Early investigators were primarily concerned with oxygen, which is still a major problem today.

For example, oxygen scavenger treatments are being adjusted through measurements with an oxygen meter and electrical corrosion probes. The quick response of these instruments is an important benefit in controlling corrosion during drilling. They permit measurements at pump suction and flow line.

Oxygen scavenger treatments are adjusted to keep suction readings the same as or less than those of the flow line. This procedure is based on the fact that oxygen enters the pump suction and is consumed in reactions on the drill string while circulating back through the hole to the flow line. Experience has shown that a sulfite residual in the drilling fluid is necessary to take care of oxygen pickup during "trips", chemical or water additions and mud pit cleaning.

The most effective control for oxygen corrosion is to keep oxygen out of the system. This is difficult, because the drilling fluid is exposed to the atmosphere as it circulates through the pits. However, carelessness is often the cause of excessive oxygen pickup. For example, the improper use of mud guns or mud hoppers is a common occurrence and results in added oxygen contamination. Aerated muds, oxygen contaminated make-up water and oxidizing chemicals all are sources of this environmental corrosion accelerator. In the case of air or aerated drilling, corrosion is a most serious problem.

In aerated sea water, corrosion rates of more than 11.5 mm/y (450 mpy) or (18 lb/sq-ft/yr) have been measured with downhole coupons. In drilling fluids the control of corrosion rates below 1.27 mm/y (50 mpy) or (2 lb/sq ft/yr) with uniform corrosion is considered a practical objective. Attack from oxygen in this environment is almost always in the form of pitting, which in a short time can produce irreversible damage to drilling equipment. Sharp-bottomed pits are especially damaging to drill pipe because they cause stress concentrations that increase susceptibility to fatigue failure. Pitting is one of the most deceiving forms of corrosion under drilling conditions. Severe pitting will not always result in the expected associated failures. Pits with round bottoms do not cause failures as often as do those with sharp profiles. Longer exposure and higher stresses are required to produce failures when pits have wide-angled geometry. What makes a pit around or sharp bottomed is not clearly, understood but the grade of steel, environment and stress conditions are all thought to be important factors. Proper environment control has a strong influence on both the form and rate of corrosion attack.

When pitting occurs, mitigation techniques should strive to lower the corrosion rate to less than 1.27 mm/y (50 mpy) and make the attack uniform. A rate expressed in mils per year has little meaning unless corrosion is uniform, because pits concentrate stress and lead to premature fatigue failures of drilling equipment.

In drilling fluid environments, pits which often are the result of corrosion concentration cells, affect stress and fatigue life. Concentration cells are caused by a difference in the concentration of ions on the affected metal surfaces. Conditions for this to occur in drilling fluids are most often caused by incomplete barriers such as mud solids, scale and corrosion by-product deposits on the exposed drilling equipment. Since ion concentration under-neath the barrier is different from that on clean metal, an active corrosion cell can exist. In oxygencontaminated fluid, concentration cells are serious pitting accelerators. Elimination of the barrier or difference in ion concentration is needed to control this cause of pitting.

Sand blasting has been used to clean drill pipe and remove the barriers and scale from the metal. Control methods most often used on operating equipment include frequent treatments with oil soluble, organic, amine inhibitors applied directly to the affected metal surface. Oil-soluble, organic inhibitors must penetrate and cover either the anodic or cathodic areas (or both) of the corrosion cell in order to stifle the cell.

Thick scale or corrosion by-products that prevent the inhibitor from reaching the base metal interfere with protection. Mechanical removal of the barrier is necessary under these conditions.

Controlling concentration cell corrosion by the removal of an offending ion, such as oxygen, would be impractical in aerated drilling systems. However, the reduction of oxygen is often achieved in normal drilling by additions of tannates, quebracho, or lignosulfonates. Sodium sulfite is now being used in the non-dispersed, low-solids polymer muds. These chemicals, along with organic amine treatments, can provide significant protection against oxygen corrosion (concentration cell).

5.2.4.5 How amines are used

There is some discussion under way how on the merits of amine inhibitors for controlling oxygen corrosion. Experience shows that they are ineffective at low concentrations, but work better if applied directly to the affected metal as mixtures of 5 to 20 percent inhibitor in oil or water.

Oxygen corrosion in drilling is not limited to aerated systems, however make-up water contaminated with oxygen has a strong influence on corrosion of drilling equipment. In some drilling operations, over 16 m³ (1000 barrels) of water per day are used. In one case, approximately 20 percent of the drill pipe wall was penetrated by pitting in three days' exposure. Approximately 22000 litres of fresh water were added during this period.

Corrosion by-products from the pits were identified as oxides of iron, evidence clearly pointing to oxygen as the major cause of corrosion and providing an indication of the damage that can result from simple make-up water additions. Polymer type drilling fluids are susceptible to strong oxygen corrosion attack because they normally do not contain thinners and are generally of a low pH. These fluids tend to foam and entrap air. Oxygen scavengers, organic inhibitors and defoamers are commonly required in these systems.

Oxidizing chemicals, such as chromates are often used in small quantities as a thinning agent in drilling fluids. An increase in corrosion (pitting) has frequently been experienced following chromate additions. Additions both of oxygen contaminated water and oxidizing chemicals will continue because they are useful and necessary in drilling operations. This is an important point, because corrosion is only of the factors involved in a complex mixture of mechanical and chemical considerations. The primary objective is to drill a well safely and economically, so consideration must be given to methods that permit this to be done most efficiently. If the use of materials that cause an undesirable increase in corrosion can not be avoided, then adequate inhibitor treatments shall be used to control corrosion.

5.2.5 Techniques to control corrosion in drilling operations

5.2.5.1 Acid-forming gases, carbon dioxide and hydrogen sulfide are serious environmental corrosion accelerators that must be dealt with in drilling fluids. These are often associated with the hydrocarbons of the produced crude oil or gas as well as in formation water and are a major cause of corrosion in the petroleum industry. Both general attack and stress corrosion are caused by them and they produce highly insoluble corrosion products that often are detected in pits, and fatigue cracks of drilling equipment.

5.2.5.2 Influence of gas contamination

Contamination by carbon dioxide or hydrogen sulfide from the formation can be quite serious if large volumes of gas are allowed to enter the fluid column. This is best prevented by properly controlling the hydrostatic pressure. When drilling operations are at a pressure near that of the formation or at underpressure, larger quantities of formation gas can enter the mud and more acid contamination will occur.

Contamination can occur while drilling either gas or water-bearing formations, so it is customary to provide an alkaline buffer to help neutralize them. In most cases the alkaline buffer is used to preserve drilling fluid properties as well as to reduce corrosion problems. Alkaline materials have limitations and may be insufficient to neutralize the acid gases if serious contamination is occurring. Under these conditions much of the gas may be vented to the atmosphere from the surface pits or disposed of even more efficiency by de-gassing equipment. In addition, drilling fluid properties can be adjusted to facilitate the escape of the gas.

Hydrogen sulfide in sufficient quantities is poisonous if uncontrolled and will be dangerous to rig crews. When control is necessary, metallic salts can be added to the fluid to precipitate the sulfides and reduce the danger. Compounds such as zinc oxide or zinc carbonate are used to combine with sulfide ions to form highly insoluble precipitates in strongly basic muds. This reaction reduces the harmful effects of the sulfide from a health standpoint and possibly aids in mitigating corrosion. However, the long term effects of a continuous buildup of a zinc sulfide precipitate in the drilling fluid is unknown and may become a problem. For example, if pH is lowered, hydrogen sulfide can be regenerated.

While this reaction can be controlled in drilling fluids, the pH is naturally reduced under packer fluid conditions. Some caution should be exercised in the use of a packer fluid in which a semi-stable sulfide compound is present when high-strength tubing and casing are used call for a packer fluid free of sulfide precipitate.

Zinc oxide and carbonate compounds are only sparingly water-soluble, but the solids still react with the sulfide ion. The insoluble character of the zinc materials allows for the addition to the drilling fluid as a pre-treatment and buffer against sulfide contamination.

5.2.5.3 Copper is a corrosion hazard

Copper compounds also are used as sulfide ion precipitators. The copper compounds are efficient in precipitating sulfide, but can cause accelerated corrosion of steel. Basic copper carbonate is used to combat the sulfide ion problem. Copper carbonate has very limited solubility in water and, as with zinc compounds, the solids react with sulfide ions. The limited solubility of copper carbonate in drilling fluids becomes a corrosion problem as the result of an electrochemical reaction whereby the copper ion is displaced from solution by iron going into solution, causing metallic copper to be plated on the steel equipment. For this reason, copper compounds are not generally recommended in drilling fluids.

5.2.5.4 Influence of temperature

Acid gas contamination has resulted from drilling fluid materials that have been altered by temperature, microbiological activity or electrochemical effects.

Contamination originating from thermal breakdown of drilling fluid additives is conditioned by time and temperature. Serious breakdown of many commonly used organic materials containing carbonyl or sulfur-oxygen groups into carbon dioxide or hydrogen sulfide begins at approximately 150°C (300°F). Thermally stable materials should be used when well temperatures are expected to exceed the 150°C (300°F) range for extended periods because thermal degradation tends to destroy drilling fluid properties.

Water dilution or small additions of sodium chromate are often used together with other additives to keep thermally degraded mud fluids. Both alternatives add oxygen and accelerate corrosion. During drilling operations, organic amine corrosion inhibitor treatments applied to the drill string and alkaline materials in the drilling fluid are usually effective in offsetting the corrosive effects of thermally degraded muds fluid. Both alternatives addition of drilling fluid additives is a serious problem in packer fluids.

5.2.5.5 Biological effects

Microorganisms readily attack drilling fluid additive, resulting in their chemical breakdown to carbon dioxides, hydrogen sulfide and other degradation products. The breakdown of these additives can result in detrimental changes which are significant in controlling fluid properties and corrosion.

Alkaline materials are considered biostats in drilling fluids, but for efficient microorganism kill, biocides are used. The most readily measurable effect of microorganisms in drilling fluid is their consumption of chemicals that results in the loss of desired filtration control and rheological properties. Bacterial cultures can be made from the drilling fluid to determine their presence and populations so that pH adjustments and/or biocide treatments can be regulated.

Drilling fluids also contain materials that can be biodegraded into corrosion accelerators with little effect on hydraulic properties. Plant and wood fibers are prime examples. It is reasonable to assume that corrosion probably is caused by microorganism by-products in some drilling wells and that their control is desirable.

Practical control of microorganisms can be accomplished if pH can be maintained above 10, or if the fluid is saturated with a salt such as sodium chloride. However, because of the proliferous nature of microorganisms in certain drilling fluids, biocides are needed for control. Chlorinated phenols or paraformaldehyde at concentrations up to 5.7 kg/m³ are used in drilling fluids. These treatments can vary because solids in drilling fluid usually favor the growth of microorganisms and tend to reduce biocidal efficiency.

5.2.5.6 Electrochemical factors

One form of corrosion by-product has been attributed to the flow of direct current in the corrosion cell. Electrochemical reduction of sulfur-oxygen groups results in hydrogen sulfide being formed at the cathode. This well-known corrosion cell reaction provides reactive hydrogen near the metal cathode surface. The hydrogen combines with the ever-present sulfur-containing compounds in drilling fluid to form hydrogen sulfide, which in turn may attack the steel.

5.2.5.7 Effect of hydrogen

Hydrogen embrittlement resulting from exposure of steel to a wet environment at a moderate temperature has been a problem for many years. Surface corrosion initiates the attack which is accompanied by the absorption of nascent hydrogen into the interior of the steel. This results in a reduction of strength and toughness of the structure. The rate of hydrogen absorption is influenced by such environmental factors as contaminants, pH and temperature.

Steel hardness (strength) determines the type of failure or damage to a given structure. Spontaneous brittle failure occurs in high-strength steel and blistering occurs in low-strength steels. Hydrogen embrittlement, recognized as a special problem, has resulted in limited use of high-strength steels in the petroleum industry.

5.2.5.8 Embrittlement by hydrogen

Preconditions for hydrogen embrittlement are high-strength steel, stress, exposure time and environmental factors. Steels with yield strengths greater than approximately 551.2 mpa (80,000 psi) and hardness exceeding Rc 20 are susceptible to spontaneous brittle fracture. It is common to find steels of this strength and hardness in drilling and producing equipment.

5.2.5.8.1 Influence of stress

Both residual and applied stresses increase embrittling tendencies. Continuous stress for a given time is required for this form of failure to occur and under some conditions the metal may be purged of potentially damaging hydrogen from the interior of the steel. Purging requires that hydrogen must be allowed to diffuse to the surface. Increased temperature is considered beneficial in facilitating movement of the entrained hydrogen through the steel lattice. Heat seems to have a dispersing effect and enhances hydrogen's escape from the metal matrix, a beneficial effect that may be linked to the relaxation of bonds between metal atoms as the result of increased temperature.

5.2.5.8.2 Effect of acid gases

The acid gas contaminants (carbon dioxide and in particular, hydrogen sulfide) increase environmental embrittlement tendencies. Their effect is to increase the volume of hydrogen entering the steel by causing corrosion which supplies hydrogen ions and by interfering with cathodic reactions. Chemical treatments can be utilized to overcome some of these effects.

Chemical control of hydrogen embrittlement is usually difficult because environmental alterations will affect only one of the four basic conditions leading to this form of corrosion. However, wells are currently being drilled and successfully completed under embrittling conditions.

5.2.5.8.3 Effect of alkaline additions

Alkaline materials neutralize the acid formed by the gases and thus reduce the hydrogen gradient into steel. Sodium or calcium hydroxide or sodium carbonate are the primary materials used to increase and maintain a basic pH in drilling fluid. Film-forming amine-type inhibitors also are used as inhibitors against hydrogen embrittlement. These materials are known to affect the cathodic sites and tend to offset the detrimental effects of sulfide or other cathodic poisons.

Amine-type salts that contain sulfur groups or triple-bonded components tend to be effective against embrittlement in drilling fluid environments. Oil muds (water in oil emulsion systems) are clearly recognized as a most effective defense against hydrogen embrittlement as well as other forms of corrosion attack.

5.2.5.9 Use of saturated salt solutions

Saturated salt solutions are commonly used both as drilling and as packer fluids. Unsaturated salt solutions are believed to cause more sever corrosion than saturated fluids. Increased solubility of acid gases in the dilute solutions is the basic cause. Inhibitors are recommended for these solutions because corrosion is clearly a problem in highly conductive salt environments.

5.2.5.10 Oil mud drilling fluids

Oil mud drilling fluids have been in wide use for a number of years. These fluids are composed of a continuous oil phase in which water has been emulsified. The emulsifying agents consist of organic soaps and amine-reacted compounds and are not only strong emulsifiers but also are excellent corrosion inhibitors. The water that is emulsified into the oil contains various salts, including alkaline materials. In a properly prepared oil mud, the water phase does not contact the drilling equipment. This type of drilling fluid is stable to extreme pressures and temperatures encountered. Due to their electrical non-conductive properties corrosion is not a problem.

5.2.6 Drilling fluid inhibitors

Inhibitors are used most often to remove or neutralize contaminants or to form a film with relatively high dielectric strength on the equipment. Oxygen scavengers, such as sodium sulfite are currently used in both water and oil muds. Calcium or zinc compounds are used to precipitate carbon dioxide or hydrogen sulfide. Alkaline materials are used in drilling fluids for both rhelogical control and corrosion inhibition.

Generally, pH is increased above that normally required for good fluid properties when corrosion inhibition is needed. Although this can be done with most alkaline materials, sodium hydroxide is the main chemical used for this purpose. As a rule when corrosion rates are below 9.76 kg/m²/yr (2 Ib/ft²/yr) and uniform corrosion attack is occurring, pH control is all that is needed for effective inhibition. If corrosion attack is localized or of the pitting type, then organic, film forming inhibitors such as cathodic amine salts are strongly recommended. Some judgment is required in these inhibitor treatments. For example, previous pitting damage of the drilling equipment (drill pipe) shall be taken into account.

5.2.7 How film forming inhibitors are to be used

5.2.7.1 General

Film-forming organic inhibitors are most effective when applied directly to the metal surface. Because they have the ability to displace water in surface pits and fatigue cracks, they are extremely useful in drilling fluid environments. Batch type treatments are used to deliver the organic material to the exposed metals. This avoids mixing the inhibitor with the bulk of the drilling fluid. Film forming inhibitors tend to be adsorbed on the solids in drilling fluids and thereby lose their effectiveness. For this and other obvious economic reasons, the batch method is recommended over continuous concentration type treatments. Because some organic inhibitors are compatible with certain types of drilling fluids, a fixed concentration can be established for corrosion control. Such materials are primarily long chain organic acids soaps useful as torque reducers and extreme pressure lubricants. Their dual usefulness tends to justify the extra cost of continuous concentration type treatment.

Organic inhibitors used to protect drill pipe in weighted as well as in low-solids muds are effective when proper attention is given to the application method. Every effort should be made to apply the inhibitor to the drill pipe rather than to mix in the drilling fluids. This permits better control of drilling fluid properties and avoids excessive corrosion inhibitor costs.

5.2.7.2 Steps in the procedure follow

5.2.7.2.1 Establish corrosion rate and identify type of corrosion attack with drill string corrosion coupons prior to treatment. Each well should be evaluated individually and inhibitor treatments based on evaluation of the corrosion coupons.

5.2.7.2.2 Prepare a mixture of organic inhibitor with diesel oil or sweet crude oil in a separate mixing tank. The inhibitor-oil mixture can be varied from 1 to 6 to 1 to 13.

Example:

For 378 lits. (100 gallons) of a 1 to 13 mixture: 26.5 lit. (7 gallons) of inhibitor to 351 lit. (93 gallons) of oil. Because concentration and frequency of treatment will vary, better results will be obtained by establishing the proper treatment for each well.

When the inhibitor can not be diluted with oil, it can be used in its concentrated form. Some organic materials are dispersible in water, which may be substituted for the oil.

5.2.7.2.3 Drill pipe in the hole should be filmed initially by adding 38 lit to 76 lit (1 to 2 barrels 42-84 gallons) of inhibitor-oil mixture at the pump suction and pumping the batch around.

5.2.7.2.4 For maintenance treatment, batch 19 to 95 lit (5 to 15 gallons) of inhibitor-oil mixture through the pump suction every 2 to 4 hours. If the corrosion rate is reduced and pitting or localized corrosion attack is not occurring, treatment frequency usually can be reduced.

5.2.7.2.5 After completion of the well, the drill pipe should be washed inside and out to remove all the drilling fluid and drilled solids. It should then be treated with inhibitor-oil mixture by spraying inside and out or dipping prior to storage on the rack.

5.2.7.2.6 Where corrosive conditions are severe, the inhibitor-oil mixture can be batched down the drill pipe during connections and poured into the annulas to film the drill pipe while making a trip. This type of batch treatment is usually based on the rule of thumb: 5.7 lit. (1.5 gallons) of inhibitor-oil mixture for each 304 m (1000 feet) of drill pipe in the hole. Spray equipment has been designed to treat the O.D. of the drill pipe while making trips. This technique is preferred in coating the outside of the drill string.

5.2.7.3 A weighted (high-solids) drilling fluid is more abrasive than a low-solids fluid and the solids will tend to erode the inhibitor/oil film from the drill pipe. In this case, more frequent treatments are required. In a high-solids or viscous drilling fluid, the use of a water cushion directly ahead of the inhibitor/oil mixture can be beneficial. This cushion tends to clean the drill pipe to allow the inhibitor-oil mixture to reach and adhere to the metal surface more readily.

5.2.8 Packer fluid corrosion control

For packer fluid corrosion control see "Corrosion Inhibitors" Edited by C.C. Nathan, NACE publication.

5.3 Production

5.3.1 General

Oil and gas fields consume a tremendous amount of iron and steel pipe, tubing, casings, pumps, valves, and sucker rods. Leaks cause loss of oil and gas and also permit infiltration of water and silt, thus increasing corrosion damage. Saline water and sulfides are often present in oil and gas wells. Corrosion in wells occurs inside and outside the casing. Surface equipment is subject to atmospheric corrosion. In secondary recovery operation, water may be pumped into the well to force up the oil.

5.3.2 Characteristics of oil and gas wells

While there are many other ways to categorize oil and gas wells. This Standard considers them in the following broad categories:

5.3.2.1 Oil well-that is, producing mainly liquid hydrocarbons.

5.3.2.2 Gas well-gas well is a well that produces fluids from a gas or gas condensate reservoir.

5.3.2.3 Condensate well-that is, producing significant quantities of liquid hydrocarbons along with gas at high pressures and temperatures.

5.3.3 Oil wells

5.3.3.1 Sweet oil wells

5.3.3.1.1 It appears that corrosion in high-pressure flowing wells that produce pipeline oil has become almost commonplace in many areas. Three methods are used to combat this corrosion as follows:

  a) coated tubing;
  b) inhibitors;
  c) alloys.

5.3.3.1.2 Coated tubing has found most favor. Epoxy paints and powder epoxy coatings shall be used (see IPS-E-TP-100 and IPS-E-TP-350).

5.3.3.2 Sour oil wells

5.3.3.2.1 These wells handle oil with higher sulfur contents than sweet wells and represent a more corrosive environment. In high-H_2S wells there may be severe attack on the casing in the upper part of the well where the space is filled with gas. Water vapor condenses in this area and picks up H_2S and CO_2.

5.3.3.2.2 Corrosion is reduced by inhibitors which are injected continuously or periodically depending on the well corrosivity. For selection of inhibitor see Clause 12 Part 1.

5.3.3.3 Condensate wells

5.3.3.3.1 Condensate wells handle fluids (gas containing dissolved hydrocarbons) at pressures up to 680 bars (10,000 lb/in²). Depths run up to 4570 m (15,000 ft.).

Carbon dioxide is the chief corrosive agent, with organic acids contributing to the attack. Approximately 90% of the corrosive condensate wells encounter conditions as follows:

  1) depth greater than 1500 m (5000 ft.);
  2) bottom hole temperature above 71°C (160°F) and pressure above 100 bars (1500 lb/in²);
  3) a carbon dioxide partial pressure above (1 bar); and
  4) a wellhead pH of less than 5.4.

5.3.3.3.2 Corrosion characteristics of a well are determined by:

a) inspection of surface equipment;
b) analysis for carbon dioxide, organic acid, and iron;
c) coupon exposure tests; and
d) tubing-caliper surveys.

5.3.3.3.3 Organic inhibitors available in oil-soluble, water dispersible, or water-soluble forms may be used to control corrosion. Determination of iron content and tubing-caliper surveys are used to measure the effectiveness of inhibitor treatment. Substitution of medium-carbon manganese steels by alloy steels and the use of stainless steel, monel, stellite and copper-base alloys for valves and other wellhead parts for corrosion control are subject to the technical and economical evaluation of the subject. For material selection see IPS-E-TP-740.

5.3.4 Gas wells

5.3.4.1 Sweet gas

With regard to CO_2 corrosion alleviation in flow lines, there are several choices as follows:

a) Low alloy steel with a corrosion allowance can be used.

b) Use of corrosion-resistant materials, alloy, or coating. With regard to CO_2, either type 316 stainless steel or duplex stainless steel will provide sufficient internal corrosion resistance. If H_2S is present, then NACE MR-01-75 must be followed.

c) To internally line low-alloy steel pipelines with a corrosion-resistant material.

d) To use nonmetallic pipe materials.

5.3.4.2 Sour gas

If the partial pressure of H_2S is greater than 0.34 KPa (0.05 Psia) the gas stream is sour and materials that resist sulfide stress cracking must be used. The latest revision of NACE MR-01-75 lists materials that are recognized to have acceptable resistance to sulfide stress cracking.

5.3.5 Offshore production

Offshore production presents many interesting corrosion problems. Platforms are built over the water and supported by beam piles driven into the ocean floor. Each beam is surrounded by a pipe casing for protection. Similar platforms are used far out at sea for radar towers.

A variety of corrosion prevention methods are used in such structures, some of which are beyond the scope of this engineering Standard. The corrosion prevention methods include:

5.3.5.1 Adding inhibitors to the stagnant sea-water between beams and casings.

5.3.5.2 Cathodic protection, with sacrificial anodes or impressed currents, of underwater structures (see IPS-E-TP-820).

5.3.5.3 Paints and other organic coatings to protect exposed structures above the splash zone. (see IPS-E-TP-100 and IPS-E-TP-350).

5.3.5.4 Monel sheathings at the casing splash zone. This portion of offshore structures is the most susceptible to rapid corrosion (see IPS-E-TP-740).

5.3.6 System requirements for corrosion control of oil-field by inhibitors

Before a corrosion prevention procedure using inhibitors can be implemented, the system requirements shall be clearly understood. The following problem areas and parameters will dictate the requirements and performance specifications of a particular inhibitor.

5.3.6.1 Pipelines and flowlines

5.3.6.1.1 Top of pipe

The 12 o'clock position in a line is the most difficult part to inhibit. Where the flow velocity is less than required for turbulent flow, liquids will not contact this area except in areas of slug or partial slug flow. Addition of a volatile component to the inhibitor may be required.

5.3.6.1.2 Water wet area-bottom of pipe

In most cases free liquid moves along the bottom of the pipe. Depending upon velocity, the layer may be both condensate and water, or as discrete layers of oil and water. At low velocities solids dropout can cause concentration cells and pits underneath the deposits.

5.3.6.1.3 Turbulence prone areas

Areas downstream of welds, minor buckling of the line, low spots and solids deposits can increase shear stress and turbulence which may aggravate corrosion. Low spots cause slugs of liquid at intervals.

Turbulence removes protective scale, aggravates abrasion and erosion if solids are present, and may affect inhibitor performance by removing the film. Inhibitors must be able to withstand the shear stresses.

5.3.6.2 Producing systems

5.3.6.2.1 Tubing

Protection of production tubing requires that the inhibitor be squeezed, added continuously or have film persistency so that batch treatment is feasible. Shear stresses impose the same requirements on inhibitors to withstand velocity effects. The tubing will be wetted more completely on the low side in deviated (non-vertical) wells, and in low-volume producers a separate a layer of water on the low side may be the only corrosive area.

5.3.6.2.2 Downhole pumps

In rod pumped wells, if any, abrasion of rods on tubing adds the requirement that the inhibitor film have some lubricating properties. In many wells entry of air through the annulus requires that the inhibitor function in the presence of oxygen. Downhole centrifugal pumps are susceptible to failure due to scaling, and to velocity effects.

5.3.6.2.3 Surface equipment

Problem areas include well heads, chokes, and vessels where velocity effects are substantial, and separators and other vessels where stagnant areas, scale and solids deposits can create concentration cells. Growth of bacteria may occur in these areas.

5.3.6.2.4 Injection systems

Secondary recovery (water-flooding) and tertiary recovery using CO_2 micellar fluids, and polymers introduce some specific requirements. Inhibitors must have proper solubility and wetting characteristics and be able to perform in the presence of the surfactants and polymers added to the flood. A surfactant component may be required in the inhibitor to maintain injection rates in produced water injection systems.

5.3.6.3 Gas/liquid composition and operating conditions

The major controlling factors for corrosion rates are the composition of the gases and liquids produced or transported, and conditions of flow, temperature, and pressure.

5.3.6.3.1 H_2S-CO_2 content

The acid gas content determines the type of corrosion and greatly influences the corrosion rate. Corrosion rates are directly related to the amount of CO_2 dissolved in the water which determines the amount of carbonic acid and subsequent metal dissolution. If organic acids are present corrosion rate is increased by removal of bicarbonate ion, and by dissolution of protective ion carbonate:

$$CH_3COOH + HCO_3^- \rightarrow CH_3COO^- + CO_2 + H_2O$$

$$2CH_3COOH + FeCO_3 \rightarrow Fe\,(CH_3COO)_2 + 2H^+$$
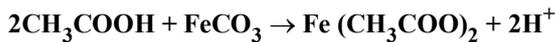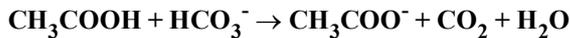
High velocity causes turbulence and increases corrosion rates. The temperature of the system, increased salinity and bicarbonate content also affect the corrosion rate and the inhibitor requirements.

Where H_2S is present line failures due to penetration underneath pits can occur in a short time. The sulfide film formed may be anodic to the metal surface, and afford some degree of corrosion protection. In many cases, however, the layer of FeS is not continuous and if so, may be porous. The net result is pit formation and growth.

Sulfide stress cracking and hydrogen embrittlement are also factors to consider in inhibition for H_2S.

In systems where H_2S and CO_2 are both present, the ratio of CO_2 to H_2S determines whether CO_2 or H_2S corrosion mechanisms will dominate.

Inhibitors shall be effective against H_2S and CO_2.

5.3.6.3.2 Liquid composition

Water composition may range from water of condensation to high salinity formation water. Inhibitor solubility and dispersibility requirements will be affected.

Water floods range from sea water to mixtures of re-injected produced water with surface and well water. In some cases fresh produced water is discharged into streams so environmental requirements are of concern.

Hydrocarbons may range from low molecular weight aliphatics to high molecular weight asphaltenes. Condensate usually does not enhance inhibitor filming, while higher molecular weight hydrocarbons and organic compounds may help the inhibitor. Paraffins and waxes form deposits and require treatment.

5.3.6.3.3 Temperature

Carbon steel corrosion by CO_2 is directly dependent upon temperature. At temperatures below 60°C scale provides little corrosion protection. In the temperature range of 60 to 100°C iron carbonate will form both remote and no the surface. The scale may result in lower than predicted corrosion rates, but severe pitting can (and usually does) occur.

At temperatures above 100°C scale is formed on the surface as a thin, dense layer of iron carbonate/magnetite, and affords good corrosion protection under most conditions.

Temperature affects the inhibitor requirements as far as stability and filming ability is concerned. No polymerization of the inhibitor can be tolerated, since plugging can take place.

5.3.6.3.4 Pressure

Pressure has a direct effect since corrosion rates are proportional to acid gas partial pressures. It will affect inhibitor solubility since at extremely high pressures methane will act like a liquid and may remove the inhibitor, leaving a thick residue.

5.3.6.3.5 Flow parameters

The flow parameters to consider are velocity, type of flow, and gas to liquids ratio.

Velocity has definite effects on the ability of inhibitors to control corrosion. The type of flow is determined by velocity, is characterized as annular, stratified, or slug flow. Flow regimes vary in different sections of lines and tubing, because of restrictions, and low places. Slug flow in producing wells increases turbulence.

Distribution of the inhibitor in all areas of a pipe line is related to flow velocities and the composition of the gas and liquids in the line. At annular flow velocities, the stream is homogeneous, and inhibitor added continuously will contact all portions of the line equally.

When flow velocities are lower, the flow is partly annular, with a higher concentration of liquids in the bottom half of the pipe-i.e. the film of liquids is thicker. Lower flow velocities allow some free liquid to collect in the bottom of the line, and slug flow predominates. As the flow rate declines stratified flow predominates and the stream is a gas phase and a liquid phase. The top portion may not be regularly contacted at all with liquid except that condensed from the gas. A vapor phase inhibitor or some means of a periodic batch that contacts the top of the line shall be considered.

In stratified flow, partitioning of the inhibitor between oil and water layers is important. Slug flow increases requirements for ability to withstand shear stress.

At velocities of less than 10 m/s it is reported that very little effect on CO_2 corrosion rates will take place. At velocities of 10 to 20 m/s, turbulence can cause local areas of higher attack, and at velocities above 20 m/s corrosion by-products will be removed. This increases corrosion rates and could affect inhibitor filming ability.

5.3.6.4 Other factors affecting corrosion inhibitor requirements

Other factors affecting corrosion include bacteria, scaling, mechanical or chemical treatment of lines prior to commissioning such as treatment of the pipe during storage, and completion methods and treating procedures. Economics of treating is important. Compatibility of the inhibitor with scale inhibitors, oxygen scavengers, and biocides imposes special requirements.

5.3.6.4.1 Bacteria

Bacteria, particularly sulfate reducers, can increase corrosion rates and may need to be controlled with organic biocides. Organisms may be introduced during hydrotesting of lines, and by contamination of producing systems from sumps and sea water flushing of vessels.

5.3.6.4.2 Scale

Scaling may need to be controlled to prevent pitting corrosion. The inhibitor may be a combination material or scale inhibitor may be used separately.

5.3.6.4.3 Mechanical and chemical pre-treatment

Pipelines may require treatment to remove mill scale and deposits prior to a successful inhibitor treatment regime, and will be hydrotested. Prevention of corrosion and bacterial growth during testing is required.

5.3.6.4.4 Completion methods and treating procedures

Completion methods dictate the treating procedures. If the well is flowing with a packed-off annulus it may be necessary to install a chemical string for continuous treatment. Side pocket mandrels with chemical injection valves or capillary strings require that inhibitors be stable in the annulus or the string for extended periods.

If a chemical string is not feasible, batch treatments using film persistent inhibitors may be used. The inhibitor is designed to form a tough film that is not too soluble in the production stream so it will last for a sufficient time between treatment. The batch may be displaced with liquids, gas, or nitrogen.

Squeeze inhibitors must be designed to be stable in the formation, and not cause severe emulsion problems in the formation. The adsorption characteristics shall be controlled for proper feed back of inhibitor.

Pumped wells, if any, can be treated by continuous addition or batching down the annulus.

5.3.7 Type of inhibitor

5.3.7.1 The most important type of inhibitor to the oil industry is the filming inhibitors. One end of the inhibitor molecule is adsorbed to the metal surface. The non-polar tail of the inhibitor molecule is oriented in a direction generally vertical to the metal surface. It is believed that the hydrocarbon (non-polar) tails mesh with each other in a sort of "zipper" effect to form a tight film which repels aqueous fluids, establishing a barrier to the chemical and electrochemical attack of the fluids on the base metal. A secondary effect is the physical adsorption of hydrocarbon molecules from the process fluids by the hydrocarbon tails of the adsorbed inhibitor molecules. This increases both the thickness and effectiveness of the hydrophobic barrier to corrosion. Based on the above explanation, it may be understood why such inhibitors are generally more effective in the presence of oil phase. In fact, it is often difficult to use filming inhibitors effectively and economically in the absence of an oil phase.

Filming inhibitors are available in a wide variety of formulations and solubility characteristics. The question of whether to use an oil soluble or a water soluble inhibitors is somewhat arbitrary. Some operators prefer to use a water soluble or water dispersible inhibitor when the water to oil ratio of the producing well is greater than one. Other operators hold an opposing view, preferring rather to build a high concentration of oil soluble inhibitor in the lessor phase. In practice, both methods have been shown to be effective, leading to the conclusion that the gross physical properties of the inhibitor is less important than getting good circulation of the inhibitor through the system. The type of inhibitor must be selected on the basis of the individual system.

5.3.7.2 Vapor phase inhibitors are added as gases or volatilize from the liquid inhibitor. In boilers, volatile basic compounds such as morpholine or ethylenediamine are transported with steam to prevent corrosion in the condenser tubes by neutralizing acidic carbon dioxide. In gas lines, the volatile inhibitor is present in the gas phase separate from any liquid in the line. Compounds of this type inhibit corrosion by making the environment alkaline.

5.3.7.3 Oxygen scavengers are added to water either alone or with a corrosion inhibitor to retard corrosion. Organic corrosion inhibitors alone in aerated brine water will slow general corrosion, but will not always prevent pitting attack. The most common oxygen scavengers used in water at ambient temperature are sodium sulfite and sulfur dioxide.

5.3.7.4 The effectiveness of film-forming inhibitors, as already stated, depends upon strong adsorption of inhibitor molecules on the metal surface to be protected. Clean up, consequently, is very important in the control of corrosion. Some corrosion inhibitors have the ability to clean by nature of their makeup or with the aid of added surfactants. These surfactants actually remove oil coated corrosion products which allows the inhibitor to attach itself to the clean metal. It shall always be in mind that without proper clean up, control of corrosion is generally unsuccessful.

5.3.8 Selection of inhibitor

5.3.8.1 A system must be carefully examined before a program of corrosion inhibition can be planned effectively. The examination must include a survey of any adverse effects an inhibitor may have on the process. The most likely adverse effects are foaming, the formation of an emulsion, and loosening of scale.

5.3.8.2 The test for foaming is to be performed in accordance with Clause 12.2.2.1.4.

5.3.8.3 Most corrosion inhibitors cease to function at a pH below 3. The normal film-forming organic inhibitors of the water-soluble type have an upper temperature limit of 140°C (300°F) while the oil-soluble have a limit of 196° of (385) when cooled, the inhibitor is active again, so it is not destroyed if the temperature is not too high. Watch for inhibitors which polymerize at the higher temperatures. Also be aware that the evaporation of solvent carrying the inhibitor can leave the inhibitor as a "gunk" in the well. In treating dry gas wells, this can be minimized by using a solvent which is considerable higher in boiling point than the consendate produced by the well.

5.3.8.4 For most applications it is desirable to use an inhibitor which is insoluble, but dispersible, at a 10 to 25% concentration in the hydrocarbon diluent, which may be distillate, aromatic solvent, crude oil etc. The inhibitor will film from the liquid onto the metal surface. Care must be taken that the inhibitor is not tied-up as the inner phase of water emulsion. The inhibitor has difficulty breaking from a dispersion of this type to film on the metal.

5.3.8.5 Remember that a corrosion inhibitor program is basically a coating treatment. The amount of in- hibitor required depends upon the amount of metal to be protected, not upon the volume of fluid produced by the well. The amount of fluid produced by well determines the frequency of treatment, although it is probable that no well should go longer than three months between corrosion treatments. Most wells are probably over-treated initially with the time to next treatment stretched out too long. For instance, a well 1.800 feet deep, making 8 m³ (50 barrels) of oil and 300 m³ of water daily may be treated every 6 months for corrosion with one drum of chemical. This is poor since 37.8 dm³ (10 gallons) of chemical would treat the well with the other 0.15 dm³ (40 gallons) wasted. The treatment, if corrosion is not too severe, will last from 30-60 days, leaving the well exposed to a corrosive environment for 4 to 5 months. A treatment using less chemical on a more frequent basis is more successful than a larger treatment stretched out too long.

5.3.8.6 When setting up a corrosion inhibitor program, it is needed to learn:

    a) Where is corrosion occurring?
    b) How can inhibitor be applied to this area?
    c) How fast is the corrosion occurring?
    d) How much oil, water, gas and condensate are produced per day?
    e) Are the fluids sweet or sour?
    f) Is oxygen present?
    g) What size tubing, how deep, bottom hole temperature, and pressure?
    h) What has been done in the past, what worked, what failed?
    i) How does the operator prefer to treat?

5.3.8.7 For final selection of inhibitor running tests shall be performed in order to choose the best inhibitor(s) (see Clause 12 Part 1).

5.3.9 Measurement

5.3.9.1 Several tools are available to determine if a well is corrosive or if a corrosion treatment is effective. Among these are:

    a) Equipment failure records.
    b) Instruments such as hydrogen probe, corrosometer, corrater, pirameter, galvanic probe, and oxygen meter.
    c) Oil and water production data.
    d) Coupon surveys.
    e) Caliper surveys.

f) Well and flow line inspections.

g) Manganese count.

h) Amine residual.

Iron count data are no better than the technique used in obtaining and analyzing the sample. Samples taken at the well-head are usually superior to all others. In addition, because of their detergent action, many inhibitors often cause an initial increase in the amount of sludge and scale going into the process stream as oil deposits are loosened by the detergent-inhibitor and slough-off equipment. This increase must be recognized for what it is and not be assumed to signify an increased corrosion rate.

5.3.9.2 Iron counts, or more precisely, the dissolved iron concentration in the water, can be one of the best methods of monitoring corrosion in sweet systems depending on system characteristics. Several precautions shall be taken to assure good results:

5.3.9.2.1 Determine if there is an "natural" iron in the water. Some formation waters naturally contain from a few to very high ppm iron even when no corrosion is occurring.

5.3.9.2.2 Of primary concern is the amount of iron dissolved in the water in systems containing little or no oxygen. This means a single speck of solid corrosion product can lead to incorrect results. It is advisable to filter the sample to remove any suspended solids. Also, exposure of the water to air will cause all of the dissolved iron to precipitate as ferric hydroxide, $Fe(OH)^3$ Therefore, good iron counts shall be run on samples immediately after sampling, or acidify the sample with hydrochloric acid to prevent precipitation.

5.3.9.2.3 Iron counts in systems which are throughly aerated or which contain H_2S are of limited value unless the pH of the water is below 4. If carbon dioxide is present, as the pH may be low enough to prevent the precipitation of iron as iron hydroxide.

5.3.9.3 Properly installed coupons are excellent for monitoring corrosion. They are not very successful in pipeline programs because the place they need to be installed is generally not easily accessible. Offshore pipelines often have coupons installed both at the bank and on the platform, at the inlet of the system. The coupons on the bank are of little benefit because most of the corrosion has occurred before the fluids reach the bank; thus, the corrosive gases are no longer present. The coupons at the inlet are at a location before water fallout nor does it create a stagnant liquid area that is constantly replenished with corrosive gases.

5.3.9.4 Manganese is sometimes found in produced water, making it difficult to use dissolved manganese as a method of monitoring corrosion except to determine change in concentration from entrance to exit of a system.

5.3.9.5 Some comment should be made about "oil and water production data". In the history of each oil field it can be observed that corrosion and the ration of produced water and oil are closely tied together. The production becomes corrosive only after passing a certain critical point in water to oil production. Although wide variations in this critical ration exist from field to field narrow limits usually apply to a single field. This "rule" does not apply to condensate wells which can be corrosive from the time of completion.

5.3.9.6 Inhibitor residuals are occasionally used to monitor corrosion control programs. By knowing at what concentration certain water soluble inhibitors give protection, we can generally tell if protection is being accomplished.

5.3.9.7 Caliper surveys are not recommended for pipe which has been protected with corrosion inhibitor. The caliper leaves marks on the pipe where the inhibitor is scraped off; these scratches then corrode. A caliper can be run while the tubing is filled with inhibitor.

5.3.10 Factors governing oilwell corrosion

5.3.10.1 Most crude oils are non-corrosive and as long as well bore and surface equipment are in an oil-wet condition the producing system is protected. This condition will persist as long as oil remains the external phase of the produced liquids. The phase relationship between the oil and water will generally invert between a cut of 25-35% so that water becomes the continuous phase. With the inversion the well bore equipment will change to a water-wet condition. The time required for equipment to become water-wet is a function of the tenacity and thickness of the oil film. However, once the phase inversion has occurred eventually the system will become water-wet.

5.3.10.2 It is suggested when the cut approaches 25% analyses be reviewed or tests be made to evaluate the potential corrosivity of the wells. In most producing areas waters from the same formation will be roughly comparable as to corrosivity. Also where the produced gas contains either hydrogen sulfide and/or carbon dioxide, it should be anticipated the produced water will be corrosive. The installation of corrcoupons at this time is highly desirable. If significant corrosion occurring, the coupon will give an indication of severity. After a corrosion program has been started a comparison "before and after" results are a measure of the treating effectiveness.

Fig. 1/2 represents a step-wise procedure that can be followed in evaluating the corrosive possibilities in a well. As shown, with the produced waters having a pH of 6 or lower, serious corrosion is inevitable once the system becomes water-wet. If the pH ranges between 6.0 and 7.0 corrosion will also occur once the water becomes the external phase and inhibiting would be desirable when the attack is of the pitting type or over 0.127 mm/y (50 mpy).

5.3.10.3 In using this approach it is imperative the pH measurements be on freshly produced samples as soon as after being withdrawn from the system as practical. The order of magnitude rather than a high degree of precision is the principal requirement of this measurement; data obtained from pH paper is quite adequate. Where samples are transported to a laboratory or stored for any significant time (1 or 2 days) the pH will not be representative. In cases where this type of measurement is the only one available and the pH is below 7.0 it would be suggested that the measurement be lowered by 1.0 in using Fig. 1/2.

5.3.10.4 Another factor frequently overlooked in corrosion inhibition programs is the changes that occur in the producing characteristics of the wells during primary depletion or in secondary recovery periods. Chemicals and treating methods that give good protection during the period when the water cuts are relatively low (25 to 40%) are frequently inadequate when large volumes of water are produced. It is highly desirable to begin a systematic monitoring program at the same time an inhibition program is started. This, in addition to establishing the success of the program, will usually indicate when a change in chemicals for application method is necessary.

5.3.10.5 One condition that is frequently overlooked in oil well corrosion programs is the possibility of air entering the system. Occasionally wells are maintained in a pumped off condition with the annulus open. In the later stages of depletion, with high water cuts and no significant gas, air can contaminate a system through the open annulus. Other sources of air are polish rod stuffing boxes, and valve packings on the well side of the flow-line check valves. In this presentation, it is presumed that the systems are air-tight and all corrosion is from the produced fluids.

5.3.10.6 These are generalities that can be used in a preliminary evaluation of the possibility of corrosion in a specific oil well or field and treating conditions that can be considered when no other information is available. Some of these "Rules of Thumb" are given below:

    a) In wells producing less than that 25% water the equipment will be oil wet and corrosion would not be anticipated.

    b) In wells producing between 25-40% water the equipment may be either oil or water-wet and the possibility of corrosion depends on the corrosivity of the water.

Notes:

Phase relationship of water-in-oil will invert between 25-40% water. After inversion, equipment will be water-wet and corrosion may occur. The following is suggested as one procedure for early detection of corrosion:

```
  pH less        pH            pH            pH
  than 6.0    6.0 to 6.5    6.5 to 7.0    Over 7.0
     |            |            |            |
  Corrosion    Corrosion    Corrosion    Corrosion
  Probable      Likely       Possible     Unlikely

            ← Install Corrosion Coupons →

         Coupon Data                    Coupon Data

 Less than   Less than   More than   Less than   Less than   More than
 0.127 mm/y  0.127 mm/y  0.127 mm/y  0.127 mm/y  0.127 mm/y  0.127 mm/y
 (5 MPY)     (5 MPY)     (5 MPY)     (5 MPY)     (5 MPY)     (5 MPY)
 No PITS     PITS (3)                No PITS     PITS (3)
    |           |           |           |           |           |
 Corrosion   Isolated    Corrosion   Corrosion   Isolated    Corrosion
 Unlikely(2) Corrosion   Occurring   Unlikely(2) Corrosion   Occurring

         Corrosion Inhibition           Corrosion Inhibition
         Program Desirable              Program probably
                                        Desirable
```

1) Corrosion occasionally occurs above a pH of 7. Where field experience indicates corrosion follow dashed line.

2) When equipment becomes water-wet corrosion will occur. Maintain a planned monitoring program.

3) Check systems for air entrainment. If air entarinment is found, eliminate and retest.

GENERAL PROCEDURE FOR OILWELL CORROSION
Fig. 1/2

c) In wells producing over 45% water the equipment will be water-wet and corrosivity will depend on the corrosivity of the water.

d) When the equipment is water-wet and the pH is between 6.5 and 7.0 mild corrosion is probable, but unless it is a pitting type attack frequent equipment failure would not be expected.

e) When the equipment is water-wet and the pH is between 6.0 and 6.5 significant corrosion is occurring and further tests are required to determine how serious the attack may be.

f) When the equipment is water-wet and the pH is below 6.0 serious corrosion is occurring and an inhibition program shall be started.

g) When equipment inspection or coupon data indicates a pitting type attack the corrosion shall be considered serious regardless of mmy (millimeters per year) and an inhibition program shall be started.

h) Where applicable an oil soluble-water dispersible inhibitor shall be used.

i) Where applicable the periodic batch treating procedure shall be preferred.

j) A treating rate of 10-15 ppm shall be used for mild corrosion.

k) A treating rate of 15-25 ppm shall be used for moderate corrosion.

l) A treating rate of 25 ppm plus shall be used for serious corrosion.

m) Initial treating shall be on a weekly basis and extended as monitoring indicates.

5.3.10.7 Frequently iron counts are used as a means of monitoring corrosion and the effectiveness of inhibitor treatments in gas wells. Interpreting iron counts without supporting data can be misleading. In order to properly assess iron counts the chloride content, rate of water production, and information as to hydrogen sulfide or carbon dioxide content of gas is necessary.

The following are the "Rules of Thumb" to use in interpreting this type of data:

5.3.10.7.1 Chloride content-ppm

<div style="margin-left: 2em;">
During this period water production is usually 56-168 liters/1000 m³.
</div>

0 - 25   Water primarily condensed from gas as pressure and temperature. Changes in tubing. Corrosion will occur principally in upper parts of tubing (0-900 m) and in wellhead. If CO_2 is present, corrosion can be quite severe in zones of high turbulence, with marked localized pitting, with H_2S, corrosion will be of a more general type.

Iron counts up to 150 usually are not of concern, providing proper metallurgy has been selected for well head.

5.3.10.7.2 Chloride content-ppm

<div style="margin-left: 2em;">
During this period water production is usually 168 to 280 liters/1000 m³.
</div>

250 - 500   Water production is now a combination of formation and condensed water with corrosion possible over the entire tubing string and wellhead. With CO_2 or H_2S, severity is approximately the same as above.

Iron counts of 50 to 150 are acceptable providing proper metallurgy has been selected for well head.

5.3.10.7.3 Chloride content-ppm

<div style="margin-left: 2em;">
During this period water production is usually 280 liters/1000 m³.
</div>

500 and up   The water is not primarily from the formation; corrosion will occur over the entire tubing string and wellhead. With only trace amounts of CO_2 and H_2S, severity will decrease with increasing water production. However, inhibition may become more difficult due to tendency of water to desorb or wash inhibitor film from equipment.

Iron counts of 50 or less are desirable with permissible count decreasing as water increases.

5.3.10.8 Whenever possible a base iron count on formation water shall be obtained. Produced water can contain significant amounts of iron in solution. This should be deducted from iron count data before applying the above criteria. Where base iron counts are not possible a number of iron counts shall be obtained prior to inhibiting the well. The reduction in count after treating can then be used as a base.

5.3.11 Application of inhibitor

Unless otherwise specified by the supplier of the inhibitor the following procedures shall be performed.

5.3.11.1 Gas condensate and flowing oil wells

Wells of these types are squeezed, displaced, batch treated, and continuously injected.

5.3.11.1.1 Squeeze (see also 8.3 Part 1)

Squeeze treatments are made by mixing the selected inhibitor in oil, aromatic solvent, or water at the proper ratio. The proper ratio is determined by inhibitor fall out. The inhibitor may not be totally soluble in the dilutent, but must be dispersible enough to be carried by the fluid into the tubing and downhole.

Pump the mix into the tubing and displace it to the bottom, followed by sufficient fluid to over-displace the mixture into the formation by 3.178 to 11.91. It is advised to shut the well for 2-4 hours after the squeeze is completed. Bring the well on-stream slowly.

Wells with low bottom hole pressure can not stand the hydrostatic head. They can be treated the same as above, however, except the inhibitor-dilutent mix is atomized with nitrogen and then displaced and over-displaced with nitrogen. The squeeze job with nitrogen is costly because of the equipment required. It may be possible to use high pressure natural gas for the squeeze instead of the expensive nitrogen.

It shall be born in mind that the squeeze treatment can damage the oil well. Loosely-consolidated sand will move and is worse when the flow is reserved. Squeezing this type of well brings the loose sand into the flow channels and into the well. The use of fresh water shall be avoided with formations which contain clay since the clay will swell in the presence of fresh water.

5.3.11.1.2 Tubing displacement

Tubing displacements are handled the same as squeezes except there is not over-displacement. Add one drum of the inhibitor mixed in the displacement fluid. Leave the well shut in about three hours after displacement is accomplished. The total volume of fluid-spearhead plus displacement-should be only sufficient to displace to the bottom of the tubing. If the fluid level tends to drop, or the well goes on vacuum, the liquid will collect in the hold beneath the tubing instead of being sucked into the formation.

Special type of inhibitor in accordance with the recommendation of supplier shall be mixed with the spearhead to minimize the possibility of formation blockage, should the treating fluid to be sucked into the formation. Also use this inhibitor in the displacement fluid to prevent the production of an emulsion when the fluid is returned.

5.3.11.1.3 Batch

Batch treatments are similar to the above two except displacement fluid is not added to the tubing. The diluted inhibitor is pumped in, leaving the well left shut in long enough for the mixture to fall to the bottom if no water is present in the tubing or to the oil-water interface if water is present. The well is then brought back slowly. In cases such as offshore where inhibitor dilution is not possible, batches have to be used "neat". This becomes a serious problem because restrictions (storm chokes, ball valves, etc.) stop the fall of the inhibitor. As the inhibitor attempts to get through the small opening, and leaches the solvent from the inhibitor. The increased viscosity causes the inhibitor to fall slowly and to leave an uneven coating on the wall of the tubing. Some of the inhibitor that stays above the restriction eventually "gunks" prediluted inhibits are being used. In some cases where the restriction is close to the surface. A batch of hydrocarbon is used to push the inhibitor through the restriction. Heavy film forms cause problems that the users can not live with.

5.3.11.1.4 Continuous injection

Continuous injection is generally the best method, if it can be applied. Inhibitor is always present to repair places where the "old" inhibitor has been removed. Some wells are completed with parallel strings, concentric strings and U-tube type strings. If the well will support the column of inhibited fluid (parallel and concentric) completions), then continuous injection can be accomplished. In most cases, the U-type completion will have a back pressure valve toward the bottom of the small string and can be loaded with the inhibited fluid. In some cases, downhole injectors are used; these are generally located in the packer. The annulus is loaded with the inhibited fluid and pumped in at the surface at the desired rate. The pump must have a sufficient output pressure to overcome the downhole pressure (taking into consideration the hydrostatic head) to open the injector.

5.3.11.1.5 General criteria

5.3.11.1.5.1 Wells that are completed in high pressure oil or gas/zones are often completed with a packer between tubing and casing so there is no communication with the surface except through the tubing. These wells may be producing oil and water plus gas or they may produce only gas. The inhibitor treatment method is dependent on what is in the tubing when the well is shut in.

5.3.11.1.5.2 If the well is a gas well making little or no fluid (5.6-11.2) liquid m³/Mm³/gas the shut in condition will leave the tubing full of gas. This well can be batch treated by pumping diluted inhibitor into the tubing. The volume of the treatment will vary from 18.926 to 37.75 litres of inhibitor in 158.9 to 749.85 litres of diluent to 1 drum of inhibitor in 0.1589 m³ to 1.589 m³ of dilluent depending on weather the corrosion is known to occur near the surface or near the bottom of the well.

Weighted inhibitors are not recommended; wells of this type are best treated by a tubing displacement or squeeze. When a gas condensate well is shut in, the water which collects in the tubing generally runs back into the formation-leaving only gas and condensate in the tubing. Trying to treat with a weighted inhibitor may not work because the water has disappeared.

Inhibitors for batch treatment or tubing displacement in gas wells are returned to the surface cut with water and distillate. The inhibitor concentration is high-and at high concentrations some inhibitors behave as good emulsifiers for water and oil. For this reason the inhibitors recommended for gas wells contain emulsion breakers to prevent emulsions that cause trouble in separators.

5.3.11.1.5.3 If a well is a flowing oil well making mostly fluid (oil and water), the shut in conditions will leave considerable fluid in the tubing. This well is best treated by a tubing displacement or squeeze if the bottom pressure is sufficient to return the injected fluids. This type of well can be treated, also, with weighted inhibitors. The weighted inhibitor should be pumped or lubricated into the tubing and allowed to fall through the oil and water in the tubing. The well shall remain shut in as long as possible after injecting the inhibitor to allow the inhibitor to fall into the rat hole; no flush shall be used.

5.3.11.2 Gas lift

Gas lift wells are treated by the four methods described above. The batch is generally accomplished with weighted inhibitor because of the high water level encountered. The weighted inhibitor should be selected on release rate.

Gas lift wells should be treated by squeeze if the corrosion occurs below the operating valves.

Some gas wells are completed with a macarone string, a kill string, or a bottom hole injector valve in a packer that permits communication from the surface to the bottom of the well. Wells completed in this manner can be treated by batch or continuous injection through the kill string.

Gas lift wells are sometimes treated by injecting the inhibitor with a chemical pump into the lift gas line. This inhibitor gives protection only from the operating valve to the surface. For this kind of application the continuous injection type inhibitors, or the batch type inhibitors are effective. It is best to inject at the well, but injecting at the compressor is also possible. The compressed gas will be distributed to a number of wells. In these cases it becomes necessary that both closest and farthest wells from the point of chemical injection be monitored closely. This shows weather good inhibitor distribution throughout the system is being obtained.

5.3.11.3 Pumping wells

5.3.11.3.1 Total production from a well is the basis for calculating the ppm of chemical to be added; do not base treatment upon oil production alone. The initial treatment shall be several times greater concentration than the periodic treatment. The batch is pumped into the annulus; it must be followed by flush, generally with well fluids from the flow-line. The amount of flush shall be 158.9 to 145.2 liters depending on the height of annulus fluid above the pump 159 liter (one barrel) of flush is adequate if the well pumps off daily; 795 litre (five barrels) is generally adequate for 30.45 m of fluid above the pump; 175.2 liters is adequate up to 152.4 m of fluid above the pump.

The height of fluid in the annulus can be determined by instruments such as the Echometer. A water-soluble dye added to the flush water can be used to determine how quickly the treating chemical reaches the bottom of the well.

5.3.11.3.2 If large flush volumes can not be used because of high annulus pressure, then batch treatment with conventional inhibitors should not be recommended. Weighted liquid inhibitors should be used. Treatment with weighted inhibitors is recommended also, for very high fluid level wells and for wells that produce out of the casing. The weighted inhibitor application is as follows: Flush 158.9 lit of well fluid down the casing. Lubricate or pump weighted liquid into the annulus. Leave the casing shut in four to twenty-four hours. Do not flush behind a weighted inhibitor.

5.3.11.3.3 Reda pumps have been treated with weighted inhibitors. The bottom portion of the Reda is generally in water. Since the impeller of the Reda is in the top section, the bottom is not protected by inhibitor treatments through the annulus. Weighted inhibitors which fall to the bottom of the rat hole will protect the pump.

Long or extended period batch treatments are occasionally performed on wells producing low water cut fluids (0 to 25% water). Oil soluble or nearly oil soluble inhibitors may be batched into the annulus. Usually half (½) to one (1) drum of chemical is used. The well fluids are circulated for two to four hours to mix the inhibitor into the annulus oil. The wells are then produced for a period of time (one month), when 37.8 to 56.7 liters (ten to fifteen gallons) are again batched and the well circulated for two to four hours. With high fluid level wells this treatment has lasted for up to three months per batch. This procedure is a general guideline and the exact procedure shall be supplied by the manufacturer.

5.3.11.4 Gas pipelines

5.3.11.4.1 Pipeline inhibition is accomplished after clean-up by mixing an oil dispersible inhibitor in hydrocarbon and batching between two pigs. Use the formula proposed by the supplier. In wet gas systems use a continuous injection type at an economical rate specified by the supplier depending on severity of the problem and the amount of water being handled. Continuous injection is used after clean-up and batch treatment has been accomplished. In dry gas systems handling condensate, the same programs apply. Condensate shall always be considered as containing some water. In dry gas systems that handle no liquids, clean-up and batch treatments are recommended. Continuous injection is not desirable because there is nothing to help carry the inhibitor down the line. Pipeline programs have to be designed for each system separately.

5.3.11.4.2 Gas gathering lines will generally have water collected on the bottom portion of the pipe on uphill slopes. Corrosion is bad at these spots. All of the surface of the pipe is probably water-wet and is subject to corrosion at a slower rate. Even those gas gathering lines which have separators and small glycol units at the well head generally contain some water. The H_2S or CO_2 produced by the gas wells is still in the gas, of course, so that the gas in a gathering system must be considered as corrosive.

5.3.11.4.3 Corrosion inhibitor should be injected downstream of the separator or glycol unit, or at the well head if neither of these is used. Most of the liquid in the lines, and the corrosion inhibitor, will be removed by the separator and the filter at the gasoline plant, but some will always come through as a mist to the sweetening towers. The sweetening towers will use MEA, DEA, sulfinol, or liquids of this type. Always test the corrosion inhibitor which is being considered with the liquid being used for sweetening to determine if foaming will occur or emulsions form.

5.3.11.4.4 Hydrogen probes shall be used in lines to monitor corrosion. These probes should be located where any liquid in the line contacts the probe; otherwise they are sensing the "corrosion" in the gas phase. Should the probe be in the gas phase, should a water mist be carried by the gas, and should the Company rely on the reading of the probe, a vapor phase inhibitor must be used.

5.3.11.5 Water-flood and water disposal

5.3.11.5.1 The main hazard encountered in shifting from primary production to secondary recovery is in the possibility that foreign materials may be introduced into the production system. From the corrosion standpoint, the most important of these materials is oxygen. Oxygen is rarely present in primary production environments below a few hundred meters. Oxygen may be present in make-up water if the water comes from sources open to the atmosphere (rivers, lakes, the ocean, or even some source shallow wells) or it may enter the system through vents in storage tanks, along the shafts of the suction side of centrifugal pumps or even through such equipment as diatomaceous earth filters.

5.3.11.5.2 Acidity in injection water is possible when produced water (water produced from the formation along with the oil) is used for flooding. This acidity is generally caused by residual acidic gases (carbon dioxide or hydrogen sulfide), but also may be due in part to low molecular weight organic acids.

If the waters handled contain hydrogen sulfide, or are acid with pH values below 6.5, or contain oxygen, they exhibits corrosive tendencies and need to be treated to reduce maintenance costs resulting from corrosion.

5.4 Transportation and Storage

5.4.1 General

5.4.1.1 Petroleum products are transported by tankers, pipelines, railway tank cars, and tank trucks. The outside submerged surfaces of tankers and the outside surface of underground and underwater pipelines are protected with coatings and by using cathodic protection. Cathodic protection is also applied to the inside of tankers to prevent corrosion by sea water used for washing or ballast. Gasoline-carrying tankers present a more severe internal corrosion problem than oil tanks because the gasoline keeps the metal too clean. Oil leaves a film that affords some protection. Tank cars and tank trucks are coated on the outside for atmospheric corrosion (see IPS-E-TP-100).

5.4.1.2 Internal corrosion of storage tanks is due chiefly to water, which settles and remains on the bottom. Coatings and cathodic protection shall be used.

5.4.1.3 Alkaline sodium chromate (or sodium nitrate) is an effective inhibitor for corrosion of domestic fuel oil tanks.

5.4.1.4 Internal corrosion of product pipelines can be controlled with linings (see IPS-E-TP-350) and inhibitors (a few parts per million) such as amines and nitrites. Ingenious methods for lining pipelines in place underground have also been developed.

For more information about corrosion protection by means of other methods rather than inhibitors see IPS-E-TP-100 (Paint), IPS-E-TP-820 (Cathodic and Anodic Protection), IPS-E-TP-270 (Coatings) and IPS-E-TP-350 (Linings).

5.4.1.5 Internal corrosion of sour gas pipelines shall be controlled by suitable inhibitors which are injected continuously or periodically depending on the type of inhibitor. For selection of inhibitor see Clauses 5.4.3 and 5.3.8.

5.4.2 Corrosion control by inhibitor

5.4.2.1 When the above referred corrosion control systems are impractical and/or uneconomical the corrosion control by inhibitor shall be implemented.

5.4.2.2 The chosen corrosion control system shall control corrosion effectively and economically with regard to this engineering Standard.

5.4.3 Selection of inhibitor

Selection of inhibitor shall be based on knowledge of the production characteristics of the system, field performance tests and laboratory confirmation of performance.

5.4.3.1 Field factors

A partial list of field factors which shall be considered in inhibitor selection are listed with brief note below:

5.4.3.1.1 Transmission lines-gas

5.4.3.1.1.1 Factors affecting inhibitor selection:

- Volume transmitted.
- Line pressure, temperatures.

- Line sizes and lengths.
- Associated liquids (water and condensate).
- Gas and water analyses.
- Use of methanol injection for hydrate control.
- Field contours.
- Location of field dehydrators and fluid residence times.
- Inlet separator facilities and retention times.
- Presence/absence of asphaltene/iron sulfide/elemental sulfur.

Flow speed in gas transmission lines is a significant factor affecting corrosion. At low flow speeds (usually 3 m/sec or less), liquid drop out, particularly water, can lead to a corrosive situation. Field contours can be critical-valleys followed by steep uphill sections of line lead to liquid accumulation. The area of gas breakout (splash zone) is particularly vulnerable to pitting corrosion leading to early line features.

Inlet separator size and fluid residence time are of importance in systems where fluid (water and condensate) volumes are significant compared to the gas volumes. If residence times are short, the corrosion inhibitor must not only protect the system but also provide quick, clean separation of condensate from water.

5.4.3.1.1.2 Recommendations for corrosion inhibition of gas gathering systems shall take into account the following:

- Flow regimes and flow speeds in the system.
- Selection of inhibitor to meet gas and liquid characteristics and separator factors.
- Economy of injection rate with full consideration of surface area protected, gas and water production levels.

5.4.3.1.2 Transmission lines-oil, oil and solution gas

Factors affecting selection include:

- Volumes transmitted.
- Line sizes and lengths.
- Gas/oil ratio and gas composition.
- Flow regimed.
- Water and solution gas analyses.
- Presence/absence of wax/asphaltene/iron sulfide.

Brine levels have considerable significance in selection of inhibitors. If a field is on water injection, breakthrough to some wells will affect water composition and corrosive properties. In such cases analytical data may be required from a number of wells in the system. Production from different zones may also give rise to different corrosion characteristics and inhibitor distribution ratios between oil and water phases.

5.4.3.1.3 Storage tanks and tankers

Inhibition of storage tanks and tankers handling crud oil and/or petroleum products shall be based on consideration of corrosion control by inhibitor (see Clause 5.4.2).

* Acquired on the amount of inhibitor necessary to provide protection in a system and the most economical rate of addition to ensure protection.

5.4.3.2 Laboratory evaluation

Laboratory evaluation of nominated inhibitor(s) shall in addition to tests described in (Part 1 Clause 12.2.2.1) be included the persistency study, distribution study and stability study of the inhibitor(s) as well as inhibitor film development and the subsequent resistance of the film to displacement and loss of protective efficiency by medium. Information shall be acquired on the amount of inhibitor necessary to provide protection in a system and the most economical rate of addition to ensure protection.

5.4.4 Application

The application method of inhibitor(s) for pipeline shall be in accordance with appropriate method of Clause 5.3.11.

5.5 Biological Control in Oil and Gas Systems

5.5.1 General

5.5.1.1 Micro-organisms (bacteria, "bugs") can produce serious effects in oil and gas systems. Bacteria can cause or contribute to:

a) Corrosion of pipelines and equipment,
b) plugging of injection lines, well bores or formation.

5.5.1.2 Bacteria are frequently classified according to their need for oxygen to grow and multiply. The three categories are:

a) Aerobic bacteria-require oxygen to grow.
b) Anaerobic bacteria-grow in the absence of oxygen.
c) Facultative bacteria-grow in the presence or absence of oxygen.

In an oil or gas system three general types are likely to be encountered.

5.5.1.2.1 Slime formers

Aerobic or facultative bacteria that produce dense slimes on solid surfaces can cause plugging and contribute to corrosion by shielding the surfaces from the protective action of corrosion inhibitors.

5.5.1.2.2 Iron bacteria

Deposit a sheath or iron oxide around them as they grow. They can cause plugging and create conditions that lead to corrosion.

5.5.1.2.3 Sulfate-reducing bacteria (SRB's)

Cause the most serious problems in systems. They can create pitting corrosion directly below a colony of bacteria, produce iron sulfide leading to plugging, and generate H_2S leading to an increase in corrosion rates and pitting and/or sulfide cracking throughout a system. Because these bacteria grow in groups or colonies on pipe walls and steel surfaces pitting occurs whenever they thrive. Furthermore, because they are normally attached to a surface a positive test on a fluid sample usually indicates a severe infestation of the system.

5.5.1.2.4 Culture and identification

Cultures of samples made in the field using septum culture bottles containing a growing medium can give information on bacteria present and the degree of contamination.

The culture bottle technique employs successive dilutions of the field water in the culture media. The more dilute the sample bottle that shows bacterial activity, the more contaminated is the field water sample. This technique is termed "extinction dilution" or "serial dilution". For schematic diagram see Fig. 2/2. With suitable culture media bottles this method can be used for either aerobic bacteria or sulfate reducing bacteria.

As a general guide:

For aerobic bacteria, counts of less than 10,000 per ml are not normally considered significant, counts of 50,000-100,000 per ml indicate a strong probability of plugging and requirement for treatment.

Any positive identification for sulfate-reducing bacteria indicates a problem.

5.5.1.2.5 Scales and deposits

As bacteria often attach themselves to pipe walls or under a scale, culture of deposits or scrapings can frequently detect bacterial contamination, when culture of water samples has provided inconclusive results but there is field evidence of bacterial problems.

5.5.2 Control

5.5.2.1 Chemical control can be classified into four types:

    a) Bactericides
    b) Bacteriostats
    c) Biocide
    d) Biostat

In oil and gas operations control of "other forms of life" other than bacteria, discussed above, frequently means control of algea. Algea form slime and grow on water surfaces exposed to air such as holding ponds or disposal pits. Subsequent injection of algea-containing water into disposal wells can cause plugging problems. Algea growth can also, in pond or pit provide a good environment for bacterial growth.

5.5.2.2 Chemicals available for bacterial and/or algea control may be inorganic or organic.

Chlorine (inorganic) is widely used for biocidal control either injected as gas or generated in the system from bleach (sodium hypo-chlorite solution-usually supplied as a 12% available-chlorine solution).

Organic formulations-a wide range of formulations are available. The general classes are amines, quaternary ammonium compounds, and aldehydes. Some specific compounds that have in recent years been found to be particularly effective against oil-field bacteria are isothiazolones and halogenated amides.

5.5.2.3 Consideration in the selection of a chemical control system shall be as follows:

5.5.2.3.1 Complete kill or control

Sulfate-reducer require a bacteriocide to obtain a total kill. A moderate number of aerobic species (bacteria or algea slime-formers) can be tolerated without serious problems, thus a bacteriostat or biostat may be sufficient for control.

5.5.2.3.2 Source of biological species and control points

It is important to determine the source of the biological problem. For example, gas producing systems are normally free of biological activity. Contamination can arise from the introduction of bacteria with well-workover or completion fluids. Once established, such downhole bacteria can continue to give problems. Treatment at the downhole source may be required and the formulation chosen shall be effective and shall not produce production problems such as emulsion blocks following treatment.

In oil systems, biological control may require batch treatment of treaters to kill established growth as well as continuous treatment of water disposal systems.

Injection points shall be selected to avoid interference problems with other chemicals in the systems.

5.5.2.3.3 Economics

Chemical control shall be selected on a cost-effective basis. The cost per liter of a formulation is less important than the total cost of achieving biological control when a selection is made. If continuous injection is required, an initially high dosage is recommended followed by a lower maintenance dosage. The cost shall then be considered on an ongoing basis over a period of several months or a year.

5.5.2.3.4 Method of application

Chemical control agents can be applied as batch treatments, at high concentrations injected over a short period, or continuously. The method shall be selected according to the characteristics of the system and the sources and degree of contamination. Addition rates shall be adjusted from monitoring the performance in the system.

5.5.2.3.5 Resistance time

Some formulations used on batch basis for control of sulfate-reducers require an adequate contact time for complete kill. If residence time of water carrying the biocide slug in a vessel is short, full kill may not be achieved. In such cases, injection using a chemical pump over a longer period may be required. On a cost-effective basis, 6 hours per week injection at high concentration may achieve a better kill compared to continuous injection at a low rate, 24 hours per day.

In selection, tests made by consulting laboratories of kill vs. time shall take into account the performance of a formulation over a period of time as some formulations take 48-72 hours to establish full control.

5.5.2.3.6 Monitoring

A biological control program shall include regular monitoring of field samples as discussed in the Clause 5.5.1.2.4.

Use of biological control products shall be supported with field monitoring programs. Injection rate adjustments shall be performed on the basis of data obtained from field tests.

5.5.2.3.7 Interferences

Performance of biological control formulations in the system can be affected by other chemical control programs (e.g. oxygen scavengers, some corrosion inhibitors). Oxygen scavengers and biocide formulations are usually incompatible. Widely separated injection points are advisable.

Hydrogen sulfide can also react with some formulations resulting in decreased activity. Manufacturer Technical Service Group should be consulted or selection of products for water containing H_2S and biological contamination.

5.5.2.3.8 Resistance

Bacteria may develop over time strains resistant to a particular formulation. Change of biological control formulation at intervals is advisable particularly if the treatment method is continuous at low addition levels.

5.5.2.4 Proper diagnosis of a field biological problem and its control is frequently a complex process. Assistance of supplier of inhibitor(s) regarding information, details of laboratory evaluation and recommendation shall usually be requested.

1 ml Water Sample		Bottle No.	Dilution Factor	Number of Bacteria in Original 1 ml Water Sample
1 ml		1	0	1 - 10
1 ml		2	1:10	10 - 100
1 ml		3	1:100	100 - 1000
1 ml		4	1:1000	1000 - 10 000
1 ml		5	1:10 000	10 000 - 100 000
1 ml		6	1:100 000	100 000 - 1 000 000
1 ml		7	1:1 000 000	1 000 000 - 10 000 000
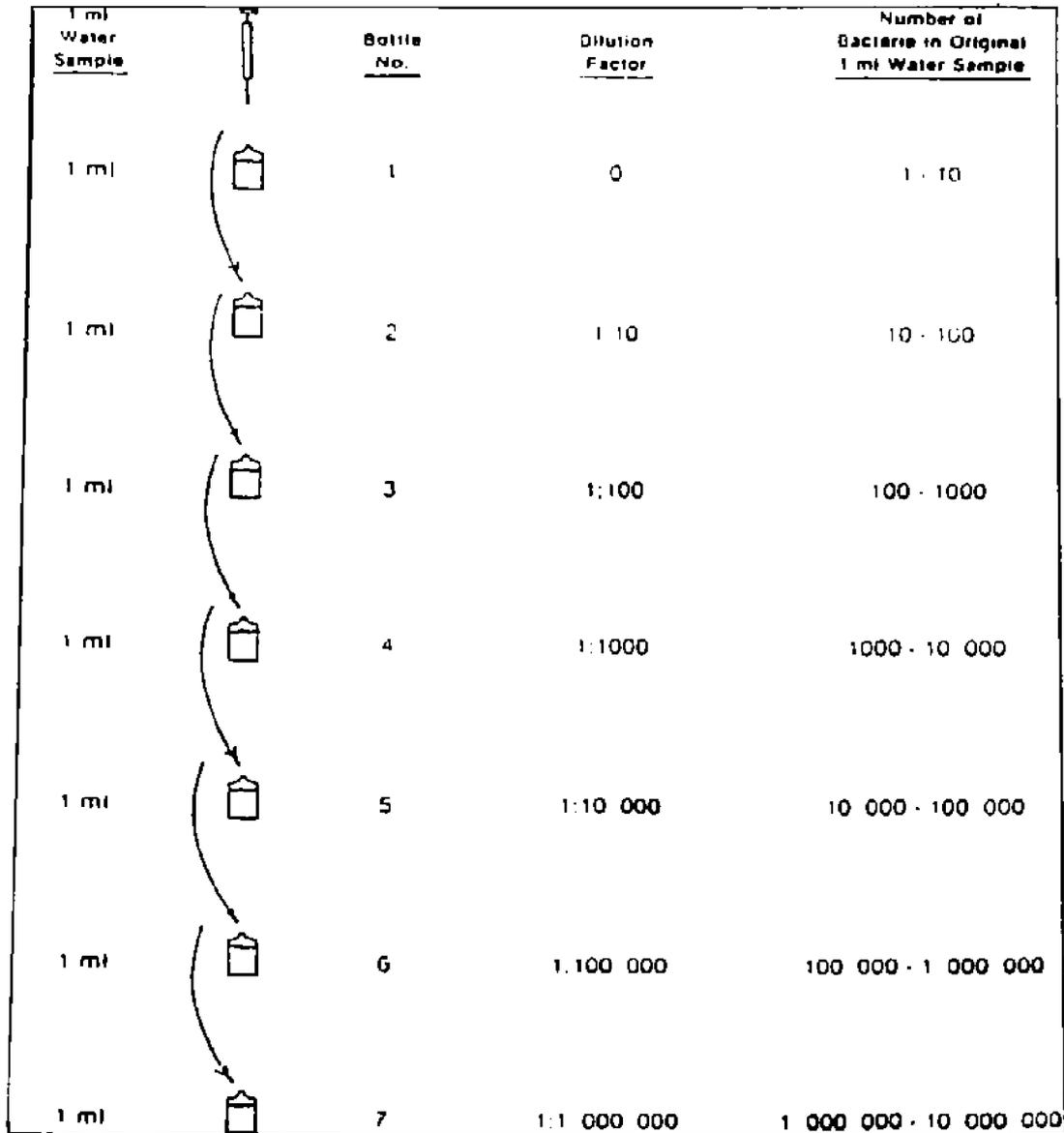
Each bottle contains 9 ml of growth medium.

SCHEMATIC DIAGRAM FOR EXTINCTION DILUTION TECHNIQUE
Fig. 2/2

5.6 Scale Control in Oil Systems

5.6.1 The formation of scale

5.6.1.1 Water has a tendency to dissolve everything it contacts. Some materials have the limit of their solubility set. Primarily, by the temperature of the water and the concentration of other materials dissolved in the water. Most materials which dissolve in water will ionize, that is, break down into ions and/or radicals. The ions may react with other ions where the resulting material has lower solubility than either of the original materials which were dissolved in the water. For example:

	Solubility	
$CaSO_4$ (dissolved in water) = Ca^{++} + $SO_4^{=}$ (Gypsum)	2,080	mg/l
$BaCl_2$ (dissolved in water) = Ba^{++} + $2Cl^-$ (Barium Chloride)	320,000	mg/l

but,

Ba^{++} + SO_4^{--} = $BaSO_4$	2.3	mg/l

Bringing together barium ions (Ba^{++}) and sulfate ions ($SO_4^{=}$) results in the formation of barium sulfate which has an extremely small solubility in water. The barium sulfate, consequently, precipitates from the water as crystals which we call scale.

5.6.1.2 The precipitation of solid materials which may form scale will occur when:

5.6.1.2.1 The temperature, composition, and pressure of the water changes to produce a solubility limit which is lower than the present concentration of the solid, and

5.6.1.2.2 When ions react with one another to form a new material which has a lower solubility than the number of ions of the new material present.

5.6.1.3 Solids that separate from water may separate as small crystals and deposit in a crevice, in a collar, or even between grains of sand in a producing formation. The small crystals may grow in size as more of the same material comes out of solution until it is recognized as a scale by covering a large surface area. The solids may separate from water without forming a scale as a micro-crystalline particles resulting in a sludge or turbidity in the water. This turbidity may settle and form a starting place for scale of another chemical type. For instance, a sludge of calcium sulfate and sand may be covered over or be cemented together with calcium carbonate. This is the usual manner for the formation of oilfield scales.

5.6.1.4 Scale frequently deposits in the oil formation near the well bore, in the perforations, or even on the face of the formation. Scale can form over the inlet ports of a rod pump or a Reda pump, starving them for fluid and possibly causing the Reda to get hot and burn out. Scale can form in the pump itself even though the velocity of fluid movement is high. Firetubes in all types of heaters fail prematurely when scale formation results in overheating. Corrosion is often more severe under a scale deposit.

5.6.1.5 Because of these problems, scale control shall be of primary concern in the production of oil and the injection of water.

5.6.2 Oilfield scales

5.6.2.1 Calcium carbonate

5.6.2.1.1 Calcium carbonate is a slightly soluble salt occurring in nature in the form of minerals such as calcite, limestone, dolomite and marble. The solubility is much greater in acids. Carbon dioxide in the air or within oil formations dissolves in water to form carbonic acid, H_2CO_3. This acid converts the carbonates in calcium carbonate to soluble bicarbonates which can be dissolved in water.

$$CO_2 + H_2O \Leftrightarrow H_2CO_3 \qquad \text{(Eq. 1/2)}$$

$$H_2CO_3 + CaCO_3 \Leftrightarrow Ca^{++} + 2HCO_3^- \qquad \text{(Eq. 2/2)}$$
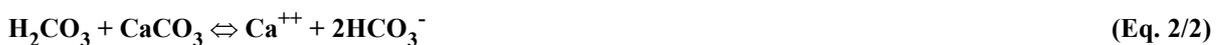
Combining these equations gives:

$$CO_2 + H_2O + CaCO_3 \Leftrightarrow Ca^{++} + 2HCO_3^- \qquad \text{(Eq. 3/2)}$$

The amount of CO_2 that will dissolve in water is proportional to the amount of CO_2 in the gas over the water and the pressure of the system. So, if either the system pressure or the percentage of CO_2 in the gas were to increase, the amount of CO_2 dissolved in the water would also increase, allowing more calcium carbonate to be dissolved.

5.6.2.1.2 The reverse is also true. It is one of the major causes of $CaCO_3$ scale deposition. At any point in the system where a pressure drop is taken, CO_2 comes out of solution, and the pH of the water rises. This shifts reaction (3) to the left and may cause $CaCO_3$ precipitation.

5.6.2.1.3 If the pH is lowered by the use of any acid, the solubility of calcium carbonate is increased: the acid does not have to be carbonic acid from the solution of carbon dioxide in water. Any increase in alkalinity, on the other hand, increases the tendency to form a precipitate.

5.6.2.1.4 The solubility of calcium carbonate is shown in Fig. 3/2. Contrary to the behavior of most materials, calcium carbonate becomes less soluble as temperature increases the hotter the water gets, the more likely $CaCO_3$ scale will form.

5.6.2.1.5 A water which cools as it flows up to the tubing will not deposit carbonate because of temperature change, although loss of CO_2 from the water can be of concern. The same water in contact with a heater tube may deposit scale readily on the firetube. The increase of temperature in water injection wells can possibly result in carbonate scale deposition.

5.6.2.1.6 Calcium carbonate solubility increases as the salt content of the water increase. The higher the total dissolved solids (not counting calcium or carbonate), the greater the solubility of $CaCO_3$ in the water.

5.6.2.1.7 The tendency for calcium carbonate scale to form increases as:

    a) Temperature increases;
    b) pH increases;
    c) Pressure drops; and
    d) Water with high salts content is diluted.

5.6.2.2 Calcium sulfate

5.6.2.2.1 Most calcium sulfate scales in oil-field work are gypsum, which has the formula $CaSO_4, 2H_2O$. The solubility of gypsum is greatest at 43°C as shown in Fig. 3/2. A temperature change can make either an increase or a decrease in solubility depending on its position on the curve.

5.6.2.2.2 Calcium sulfate may also be deposited as anhydrite ($CaSO_4$) of the temperature above approximately 43°C. Note from Fig. 3/2 that the solubility of anhydrite less than that of gypsum above that temperature. It can be expected that anhydrite might be the preferred form of $CaSO_4$ in deeper, hotter wells.

5.6.2.2.3 Dissolved salts, other than calcium or sulfate ions, increase the solubility of gypsum or anhydrite up to a salt concentration of about 150,000 mg/l. Further increases in salt content decrease $CaSO_4$ solubility. Solubility is three times greater in brine containing 150,000 ppm of salt than in distilled water. The effect of pressure is small.

5.6.2.3 Barium and strontium sulfate

5.6.2.3.1 Barium sulfate and strontium sulfate are similar, often found together and often reported as barium. The very low solubility of each makes the formation of a precipitate certain if a water containing either barium or strontium ions is mixed with one containing sulfate ($SO4^=$) ions.

5.6.2.3.2 Barium sulfate solubility increases with temperature. Because of the increase in solubility with temperature, barium sulfate usually presents no downhole scaling problems in an injection well if it is non-scaling at surface conditions. It is more commonly a problem in producing or source wells.

5.6.2.3.3 The solubility of barium sulfate in water is increased by dissolved salts just as for calcium carbonate and calcium sulfate. There is a 13-fold increase brought about by the addition of 100,000 mg/l NaCl with no change in temperature.

5.6.2.4 Iron compounds

5.6.2.4.1 Iron in water may be either naturally present or the result of corrosion. Formation waters normally contain only a few mg/l of natural iron; values up to 50 ppm are possible. Higher values are from corrosion.

5.6.2.4.2 Carbon dioxide will react with iron to form iron carbonate. Scale is likely to form if the pH is above 7. Hydrogen sulfide will form iron sulfide. It will form a thin scale, or will be suspended as small particles to give "black water".

5.6.2.4.3 Oxygen will form various compounds with iron which are generally reddish. They often become trapped in the matrix of other scale deposits, giving a reddish color to the normally brown or gray scales.

5.6.2.5 Miscellaneous

5.6.2.5.1 There are some deposits that are not scale but are cousins of scale: they are the sludges. Some sludges consist of considerable organic matter such as wax, asphaltenes, or tar. The deposits may be hard and crumbly, or soft and mushy.

5.6.2.5.2 Sand, silt, and drilling mud are often incorporated as parts of a scale, or are laid down as hard deposits which are called "scale". Corrosion products, as discussed above, are not true scales but, again, are solid products which are often called "scales".

5.6.3 Preventing scale formation

5.6.3.1 Avoid incompatible waters

One of the primary causes of scale formation is mixing two or more waters which are incompatible. This is illustrated for the formation of barium sulfate in Clause 5.6.1.1. The separate waters may be stable, but react to form a precipitate when mixed.

Mixing water produced from an oil well with water from a lake, river, or source well must be checked. Likewise, mixing a proposed injection water with the natural formation water must be evaluated.

The tendency for waters to form a precipitate when mixed can be evaluated by calculation, as discussed later, or by mixing the waters in a clear bottle, then setting aside several days for observation.

5.6.3.2 Modify the water

Water may be modified so that a precipitate of scale will not be formed by:

>   **a)** Removing the scale-forming components;
>   **b)** Lowering the pH; or
>   **c)** Blending with another water.

In practice, none of these methods find much use-primarily because of cost.

Dissolved gases such as H_2S, CO_2 and O_2 can be removed from the water. This will eliminate iron sulfide and the various iron dioxides, all of which from insoluble compounds. Removing CO_2 however, will increase calcium carbonate deposition.

Lowering pH reduces scale-forming tendency, but increases corrosion. It is practical only for small volumes of water such as boiler feed water or cooling systems.

Blending several waters must be handled with care, as discussed previously. Either diluting scale-forming components or increasing the salt concentration could be helpful.
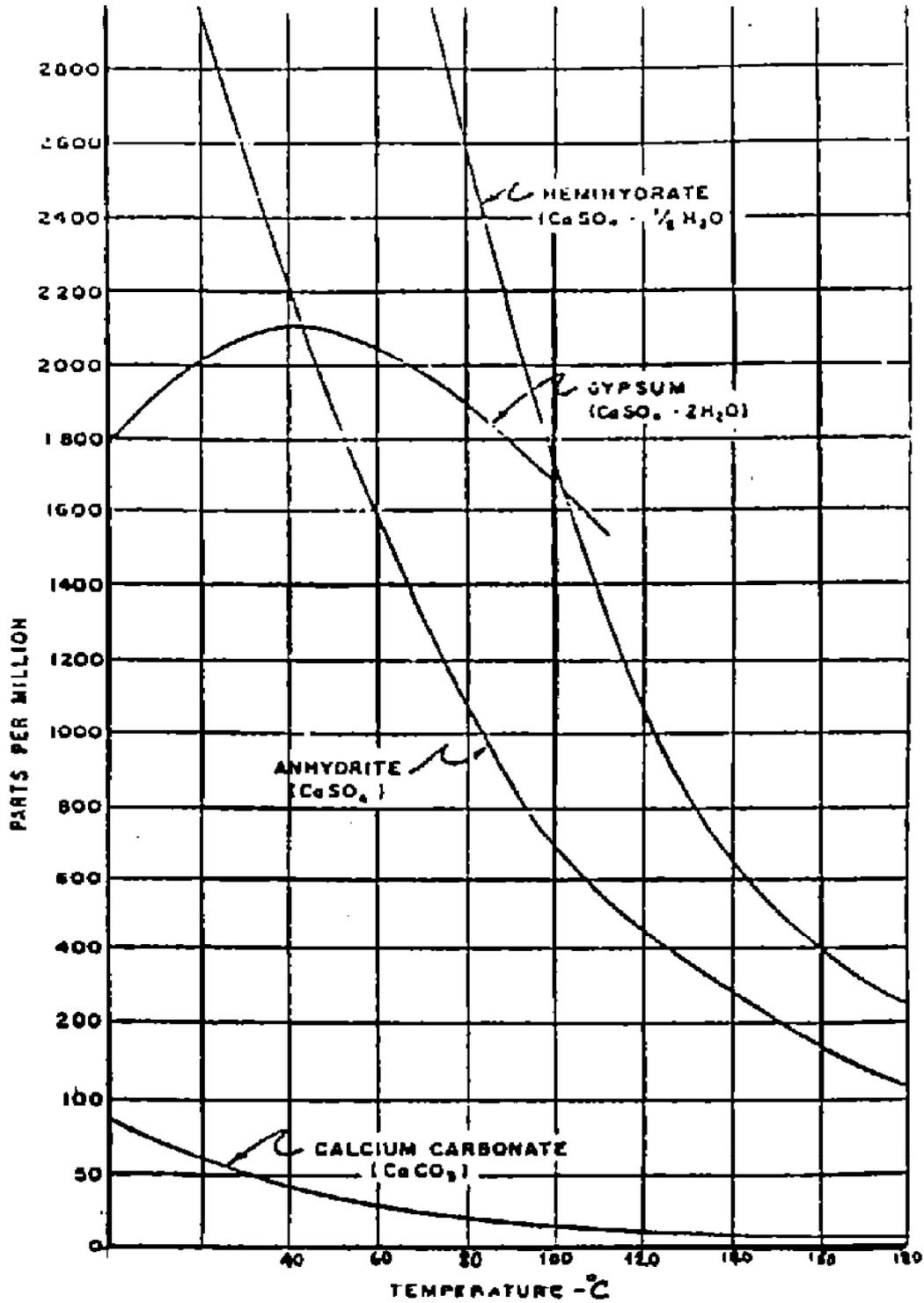
SOLUBILITY OF SCALES IN WATER
Fig. 3/2

5.6.3.3 Scale control chemicals

5.6.3.3.1 How they work

5.6.3.3.1.1 The formation of crystals from a liquid solution is felt to develop as follows:

a) Micro-crystalline particles from throughout the liquid. The crystals are extremely small, and are all similar in size and structure. The number of crystals depends primarily on temperature and concentration. This step is termed nucleation since the small crystals are nuclei upon which the larger crystals develop.

b) The crystals grown by adsorbing ions from solution onto the surface of the crystal.

c) As the size of the original particles increases they become joined together in a process called coagulation.

d) Finally, there is a competitive growth in which the larger particles grow at expense of the smaller. The smaller crystals go into solution while the larger crystals grow still larger.

5.6.3.3.1.2 Scaling and depositing of crystalline chemical compounds can be controlled in several ways:

1) An impurity can be introduced into the crystals as they form that either blocks further growth, or introduces strain into the crystalline structures;

2) Ions can be added that are adsorbed at the surface of the crystal, slowing and otherwise interfering with its further growth;

3) Chemicals can be added which form soluble compounds with the scale-forming components, and

4) The surfaces upon which the scale would deposit are made "slick".

5.6.3.3.1.3 The concentration of scale inhibitor required depends upon the temperature, the composition of the salt that precipitates, and the salt concentration. The higher the salt concentration and temperature, the greater must be the concentration of inhibitor to successfully prevent precipitation. The effectiveness of the inhibitor depends upon the tenacity of the chemisorption bond it forms with the surface of the particle.

5.6.3.3.1.4 The methods of scale control are called sequestration or chelation, film formation, or nucleation. A particular scale inhibitor may act as both a sequestration and a nucleation agent.

a) Sequestering chemicals react with certain scale-forming constituents to form new compounds which are still soluble, but which are unreactive. A well known example of this type of material is sodium hexametaphosphate, a water-softening agent. Sodium hexametaphosphate ionizes in the water solution to furnish the hexametaphosphate ion. The hexametaphosphate ion reacts with "polyvalent" ions such as calcium and magnesium. The resulting calcium or magnesium hexametaphosphate is water-soluble but does not re-ionize. The end result is to completely tie up the calcium ions in a water-soluble, unreactive form. If the calcium and magnesium ions were not so tied up, they would precipitate as calcium carbonate or magnesium hydroxide, typical scale-forming compounds.

b) Chelating agents are a special class of sequestering chemicals. They tie up the ions in non-ionizing forms, as do all the sequesterial agents, but they are distinctive because the "tying-up" is done in a very special way. That is, the chelating agents employ a special type of chemical-bonding to tie up the offending ions. The chelate-type chemical bonds are unusually strong. Most chelating agents for scale control lose efficiency as pH drops, so it is customary to formulate such materials with alkaline chemicals which will raise the pH of the system.

c) The film-formers operate through their ability to lay down thin, adherent, organic films on solid surfaces. They usually are semipolar compounds having a large, strongly polar group at one end and an oil-soluble tail at the other end. Generally accepted theory is that the polar end of the molecule is electromagnetically attracted to the solid surface while the hydrocarbon "tail" stands out from the solid surface. Theory further concludes that the filming molecules pack closely together on the surface with their hydrocarbon tails "oriented " in one direction like the hairs in a horse's coat.

Many chemists and engineers believe that, in order to have a good protective film, one must have a third component in addition to the polar "heads" attached to the surface and the "coat of hydrocarbon tails". The third component is a film of oil attracted to the hydrocarbon tails. This theory gains support from the fact that some of the semipolar film formers are not effective in 100% aqueous systems, wherein there is no oil available to form a film over the hydrocarbon "tails".

A second views as to the mechanism of operation of the films deposited on the pipe walls prevent "seeding" or "nucleation "of the depositing salts. Crystals such as those in scales need sharp edges and angles to start forming. In supersaturated solutions, it is possible to "seed-out" or "nucleate" the slats by introducing crystals of the same salts or by scratching the surface of the container to provide sharp edges and angles on which the crystals may form. Any agent which coats the container walls with a smooth film will decrease tendency to form crystals.

Support is given this theory as to the mechanism by which film formers perform through the fact that plastic pipe or plastic-coated pipe occasionally is scale free.

d) The operation of nucleating chemicals is not perfectly understood. The consensus is that they operate by furnishing many millions of tiny nuclei or seeding-centers which furnish a tremendous total surface area on which scale-forming salts will deposit preferentially. Since there are so many of these nuclei, no one of them receives a large amount of depositing salts. As a result, the system contains huge numbers of very minute scale particles rather than smaller numbers of large particles. The smaller particles have much greater tendency to be carried in the main body of the flowing fluid and are not likely to contact the pipe walls as are the large particles.

A second viewpoint as to the mechanism by which nucleating agents work renders the distinction between "nucleating agents" and "film-formers" less clear. This contention is that the chemicals act through adsorption on the salt crystals as the crystals first form. The adsorbed film on each of the crystals prevents further crystal growth and the end result is that the system contains many millions of very minute crystals.

5.6.3.3.2 Relative effectiveness of scale control chemicals

5.6.3.3.2.1 Nucleating agents can perform very well at unbelievably low dosages. This is established by the fact that polyphosphates (which are sequestering agents also) perform at dosages which are only a very small fraction of the dosages theoretically required to sequester the salts known to be present. This remarkable increase in effectiveness is attributed to nucleation.

Scale control chemicals, such as polyphosphates, which can act as nucleating agents frequently are the only chemicals which can be economically justified for use in oilwells producing large volume of water and heavy scale deposits.

5.6.3.3.2.2 Although they are not generally as reliable as the polyphosphate-type, organic filming agents frequently are able to do quite a good job at low dosages. So long as there is enough oil in the system to insure that they have adequate contacts with the metal surfaces to be protected. Their dosage requirements are virtually independent of the total amount of scale-depositing salts present. Presumably this is because a large amount of the film forming agent can be consumed in coating the very surface areas presented by a relatively small amount of minute scale crystals.

Film-forming thus can be economically attractive for use in high-water-volume oilwells, but dosage requirements may become excessive in such wells if the scale problems are severe; that is, if very large amounts of scale-forming constituents are present.

5.6.3.3.2.3 Because they involve direct chemical reaction, the sequestering agents or chelating agents can do exceptionally complete jobs in inhibiting scale formation. However, dosage requirements become prohibitive in systems wherein a large excess of scale-forming constituents is present. This occurs because the sequestering or chelating agents tie up only one or two molecules of scale-forming salt per molecule of sequestering agent.

Generally the commonly used, less expensive sequestering agents for oilwells are water-soluble. This is necessary because the ions which they must tie up are in the water phase. However, this situation means that an extremely large amount of sequestrate must be added to an oilwell producing large water volumes, in order to produce a reasonable concentration of the sequestrate in the water phase.

Thus the sequestering agents or chelating agents usually can be justified economically for use only in wells producing small or moderate water volumes and containing only small-to-moderate amounts of scale-forming constituents.

5.6.3.3.3 Type of scale inhibitors

The common inhibitors for scale control in water systems include:

- Organo-phosphonate general purpose scale inhibitor. Suitable for situations where calcium carbonate is principal component of scale formed.

- Calcium carbonate scale inhibitor.

- Calcium sulfate scale inhibitor.

- Gyp-scale converter/remover.

- Acrylate scale inhibitors for water flood applications.

- Corrosion/scale inhibitor for water disposal system.

- Phosphonate scale inhibitor for sulfate scale situations. It prevents formation of calcium, strontium and barium sulfate scale, as well as calcium carbonate.

- Phosphonate scale inhibitor, which shall be particularly designed for steam flood and other high temperature applications. It may be squeezed into the formation.

- Organic amine phosphate formulations. Suitable for producing wells severe downhole scale problems. It shall be formulated in hydrocarbon carrier solvent system.

- Corrosion inhibitors formulated with scale control components.

- Acrylate type scale inhibitors for injection systems. Scale removers.

5.6.4 Identification

There are times when the engineer in the field is called upon to identify scale samples. An operator may need to take immediate steps to remove scale from production tubing, flowlines, or other pieces of equipment, and time does not permit submitting a sample of the scale to a laboratory for analysis. The engineer must be able to determine whether the scale is calcium carbonate, iron carbonate, calcium sulfate, barium sulfate, or a combination of scales. The following procedures outline various methods that the field engineer may use to determine the type of scale in question.

Prior to subjecting any scale sample to an analytical procedure, the sample should be rinsed in a suitable solution of water and a surfactant to water wet any preferentially oil wet sample.

STEP I

Place a sample of the scale in a breaker and add enough 15% or 37% hydrochloric acid to cover the scale sample. If there is a rapid effervescence (bubbling effect) and the sample dissolves, the scale is calcium carbonate $(CaCO_3)$. If the effervescence is very slow, heat the acid to approximately 65.5°C (150°F). If the rate of effervescence increases with the addition of heat, and the acid solution turns yellow, the scale is iron carbonate $(FeCO_3)$.

If a reaction does not take place in the hydrochloric acid solution, proceed to Step II.

STEP II

Place a sample of the scale in a breaker and add enough caustic soda solution (25% by weight) to cover the scale sample. If the sample disintegrates and forms a slurry in the bottom of the breaker, the scale is calcium sulfate $(CaSO_4)$.

If a reaction does not take place, proceed to Step III.

STEP III

If the sample is dark brown or black in color, the scale could possible be iron sulfide or magnetite. Crush a portion of the scale sample and place a magnet in the crushed sample. If the magnet picks up a major portion of the sample, the scale is magnetite. If there is no attraction to the magnet, place a few drops of Iron Sulfide Detecting Solution on the sample. If a bright yellow precipitate is formed, the scale is iron sulfide.

If both test results are negative, proceed to Step IV.

STEP IV

Wash the sample in a solvent (benzene, oxylene, or etc.) to remove all hydrocarbons. Rinse the sample in distilled water to remove salt crystals. Crush the sample and mix with enough 37% hydrochloric acid to form a slurry. Dip a platinum wire into the slurry and insert the wire into the flame of a Bunsen Burner. Note the color of the flame. Calcium will emit an orange flame of short duration. Barium will emit a green flame of relatively long duration. Strontium will emit a crimson flame of relatively long duration.

5.6.5 Predicting scale formation by calculation

The values obtained from these calculation procedures should be taken only as guidelines. They indicate the likelihood of scale formation. Many assumptions had to be made in developing the method of calculation which may not apply to the specific water being evaluated.

If scale formation is indicated by calculation, it serves as an alarm. If you are looking at a possible water source, you shall avoid those which show scaling tendencies or make provision for treatment. Similarly, you shall avoid mixing waters where the blend exhibits scaling tendencies under system conditions.

For calculation procedure see Appendix A.3 (Part 3).

5.7 Corrosion Inhibitors in Refineries and Petrochemical Plants

5.7.1 General concepts

5.7.1.1 Corrosion in the hydrocarbon processing industries may be conveniently divided in to two parts: "wet" and "dry". "wet" corrosion is that which occurs in presence of liquid water. Corrosion in the absence of water is considered "dry". Wet corrosion normally implies low temperatures, i.e., below the boiling point or dew point of water. This temperature will, of course, be a function of the system pressure as well as its composition. In practice, wet corrosion is limited to about 232°C (450°F) as an upper temperature. The lower temperature is set by fluid composition. For wet corrosion to occur at any temperature there must exist either a discrete aqueous to phase or sufficient water dissolved in a liquid phase to impart electrical conducting or ironic properties to a liquid such as hydrocarbon, which does not possess these properties in the absence of water. Wet corrosion is an electrochemical process. Wet corrosion may be controlled by the use of passivating, neutralizing or adsorption type inhibitors, the use of which will be summarized bellow.

5.7.1.2 Dry corrosion is of great importance in a number of refining processes. It includes the attack of hydrogen sulfide and other sulfur compounds on steel and various alloys at elevated temperatures (as distinguished from the attack of aqueous solutions of hydrogen sulfide and mercaptans). Solutions to this type of corrosion generally depend on metallurgical approaches, such as variations in composition and/or heat treatment of the selected metal or alloy (see IPS-E-TP-740).

5.7.2 Nature of corrosive fluids

5.7.2.1 Since the discussion of refinery and petrochemical plant corrosion inhibition will be restricted to attack taking place in the presence of aqueous fluids, the composition of these fluids is of interest in sofar as their composition affects corrosion and its inhibition. Only fluids on the process side of equipment need to be considered. As an example, a heat exchanger in which naphtha vapors in the shell are being condensed by cooling water in the tubes may experience corrosion on both shell and tube side. Corrosion by cooling water and attendant scaling and fouling problems are of great importance (see Part 3)

5.7.2.2 Restricting the discussion to process streams with an aqueous phase present, such streams may be considered as being composed of:

    a) an aqueous phase;
    b) a hydrocarbon or non-aqueous liquid phase; and
    c) a gas phase.

The liquids and gas phases will be in dynamic equilibrium at all points in the system, the equilibria being determined by pressure, temperature and composition. It will be useful to examine the general concepts of equilibria and composition:

5.7.2.2.1 Gas phase

The gas phase consists of hydrocarbons vaporized by distillation processes and/or formed by cracking or other decomposition of fluids. Sulfur compounds such as hydrogen sulfide and volatile mercaptans often present in the gas phase may be components of the original feed to the unit of interest, e.g., the crude still; they may be formed by thermal degradation of disulfides, thiophenes, etc., or they may be the result of various hydrogenation processes such as hydrodesulfurizing, hydrocracking, etc.

Prevention of air-leakage or other contamination is highly desirable and is effected by proper equipment maintenance, inert gas blanketing, etc. Prevention is rarely one hundred percent effective in the practical sens. (see 5.7.13).

5.7.2.2.2 Liquid hydrocarbon phase

This phase will be in dynamic equilibrium under the conditions of temperature, pressure, etc. with the vapor phase described above as well as with the water phase contacting it. In this connection, it is of interest that the solubility of hydrogen sulfide and carbon dioxide in hydrocarbons is generally large as compared to that of oxygen and nitrogen.

5.7.2.2.3 Liquid aqueous phase

Because electrochemical corrosion reactions proceed only in a liquid aqueous phase, the chemical composition and properties determined by chemical composition of this phase are most important to consider. This phase is largely water and will be called water in the subsequent discussion. Water enters the various refinery process units in a number of ways. Of prime importance is water which is entrained and/or emulsified in the crude oil charge to the refinery, i.e., feed to the crude still. This water is produced with crude oil and remains with the crude, despite oil-field separators, liquid traps in pipelines, etc. Although the amount of water is usually small in total volume, its effect on corrosion may be large, since it usually contains a high proportion of corrosive dissolved salts, mainly chlorides of sodium, calcium, and magnesium.

5.7.3 Corrosion of steel

Steel is very unstable in acids, as might be expected from the position of iron in the electromotive force series. In the absence of inhibitors, corrosion rates increase sharply as pH falls below neutrality. At pH values above seven, steel is generally stable with increasing pH, up to values as high as 13 or great. (At higher pH's, particularly at elevated temperatures, attack results because of the weakly amphoteric properties of iron.) From the practical standpoint, neutralization of acid solutions to pH 6-8 normally is adequate to stifle direct attack on steel; however, when neutralization is augmented by inhibitors, adequate corrosion protection can be effected at pH values between 5 and 6 (The discussion above refers to reducing or oxygen free systems, which refinery process streams usually are).

5.7.4 Corrosion of copper alloys

After steel, probably the most important metal in refinery use at low (i.e. less than furnace) temperature is copper, usually in the form of such alloys as Copper Development Association alloys No. 443-445 (Admiralty) or CDA 715 (Monel) etc. In addition to higher heat conductivity, copper and its alloys are considered to be superior in corrosion resistance to steel in media such as dilute acids, saline and brackish waters and in the presence of sulfur compounds. Because copper and its alloys have lower strength and versatility and cost more than low carbon steels, substitution of steel by copper alloys must be justified in materials savings and/or process improvement. Although copper is generally more resistant to acid refinery streams than is steel, the effect of pH on corrosion of copper is more involved than on steel. Close pH control is necessary because of the dissolution of copper and its alloys at elevated pH under some conditions. At low pH, secondary factors such as presence of oxygen and fluid velocity are quite important in the corrosion of copper. At high pH, in the presence of ammonia and some amines, soluble copper complexes from which effect copper dissolution. Special precautions are required as described in Clause 5.7.5.

5.7.5 Neutralizing corrosion inhibitors

5.7.5.1 Because corrosion is known to result from acid attack on metals, the removal or neutralization of acids is an obvious solution to the corrosion problem. In theory, any material sufficiently basic to neutralize the acid and raise pH to the desired level should be satisfactory. In practice, the situation is complicated by other factors.

This is illustrated by operation of the desalter, which is usually the first processing unit in the refinery proper. Its function is to reduce the content of bottom sediment and water (B.S.&W.) from the crude charge to the crude still. As explained above, water (generally brine) causes corrosion in units downstream of the desalter as a result of decomposition of chlorides to hydrochloric acid at the elevated processing temperatures. Addition of alkali to the desalter reduce hydrolysis of calcium and magnesium chloride and consequently result in less hydrochloric acid being formed in the crude still overheads, etc.

5.7.5.2 Inexpensive neutralizers such as lime, calcium carbonate and soda ash often may cause scaling problems due to precipitation of insoluble hydroxides and/or carbonates of Mg and Ca by reaction with these ions in water entrained from the desalter. Sodium hydroxide can be used in desalting, for which it is added in amounts approximating the chloride content of the desalter water.

An attempt to establish alkalinity in the desalter by using high pH boiler blowdown as desalter feed or use of high pH effluents from sour water strippers is dangerous due to the problems of scale formation of Mg and Ca salts at high pH and foaming at high alkalinity and/or in the presence of surfactants. This foaming causes poor water drawoff from the desalter, etc.

5.7.5.3 The first operating unit in a refinery after the desalter is the crude still, which effects a rough separation by boiling range of several refinery streams such as naphtha, kerosene, diesel oil, etc. Distilled vapors are condensed at one or more points and products are taken off with desired reflux ratios, etc. The condensed liquids may contain dissolved acidic components such as hydrochloric acid and hydrogen sulfide and will be corrosive to metals contacted by the liquids. Corrosion may be expected as soon as the dew point of the water is reached, so treatment chemicals must be added at or up-stream of the points of initial condensation. For treatment of overhead streams ammonia and other low-molecular weight amines such as morpholine or cyclohexylamine which are added either as undiluted liquids or vapors or as aqueous solutions are recommended.

5.7.5.4 Ammonia is the most common material because of its high neutralizing power, low unit cost, easy availability and convenience of handling. It may be injected as a liquid under cylinder pressure and flashed into the vapor phase of the crude still. Upon condensation of the vapors, ammonia will dissolve into the condensate water to effect an increase in its pH. As additional water condenses downstream of the initial point, it will be in equilibrium with ammonia gas in the condensing hydrocarbon and water vapors.

5.7.5.5 Despite the advantages mentioned above, using ammonia has several drawbacks. Addition of ammonia beyond neutralization, i.e., pH to > 7 is a dangerous practice if copper alloys are present in the condensing system or downstream of it in the water drawoff. At pH values in excess of 7 to 8.5 (depending on the source quoted), copper forms the soluble cuprammonium complex and deterioration of such materials as CDA 443-445 (Admiralty) can be expected.

Similarly, some of the low molecular amines also can form soluble copper complexes. Control of pH shall be performed automatically with automated measuring, recording and feeding equipment or by other means. The expense of such equipment can often be justified to plant management by savings in chemicals injected and in increased efficiency of corrosion control.

The use of higher molecular weight amines, which do not form chloride deposits from either the hydrocarbon or water phase and which also have good buffering capacity compared to ammonia and morpholine is recommended. Such material permits easier pH control and largely eliminates the danger of copper corrosion at high pH (above 7.5 in presence of ammonia or amines). This is shown in Fig. 4/2.
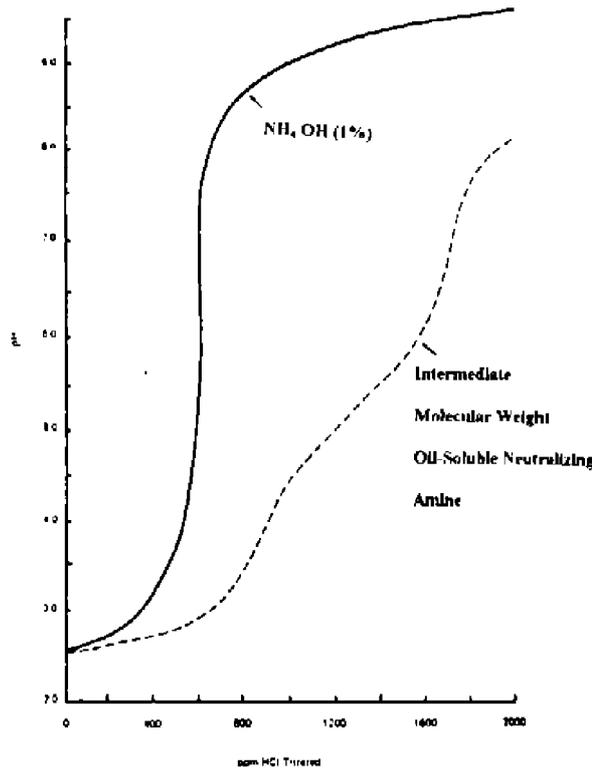
CRUDE UNIT - ATMOSPHERE TOWER OVERHEAD WATER (BETZ LABORATORIES)
Fig. 4/2

5.7.6 Filming inhibitors

Refineries and petrochemical processes employ a variety of film forming inhibitors under varying conditions. Due to the function of these type of inhibitors (see Clause 5.3.7.1) they are generally more effective in the presence of an oil phase. In fact, it is often difficult to use filming inhibitors effectively and economically in the absence of an oil phase. Inhibitors are available with a wide range of solubilities and other physical properties. The concentrations at which they are used generally is about ten parts per million (ppm) based on the hydrocarbon phase, so the economics is generally quite favorable.

The inhibitors most widely used in petroleum refining contain nitrogen bases such as amines, diamines, imadazolines, pyrimidines and their salts or complexes with fatty acids, naphthenic acids, and sulfonates. Inhibitors vary in solubility, etc., as mentioned above and also must be chosen in consonance with pH range and other fluid properties.

In general, it is more economical to reduce all or a portion of the acid content of treated stream with ammonia or other neutralizer and augment this by use of a film-forming inhibitor.

Film-forming inhibitors, as distinguished from ammonia and other volatile amines, are considered to be nonvolatile; accordingly, in any gas-liquid separation process, they remain with the liquid and so may be concentrated in the heavy fractions of a refinery process. The efficacy of an inhibitor treatment or other process changes in controlling corrosion shall be followed in refinery work by use of corrosion test coupons or spools, corrosion rate meters, corrosion resistance probes and by analysis of process streams for dissolved metal.

5.7.7 Special concepts in the use of corrosion inhibitors to refineries

Film-forming and/or neutralizing inhibitors in refineries offer no panaceas. Chemical treatment for prevention of corrosion is one of several tools used by competent engineering and management personnel as approaches to corrosion control alternative to other measures such as special resistant materials, protective coatings, design changes and the like. Before discussing the relative advantages and disadvantages of the various protective and corrective measures, some limitations, as well as pitfalls to avoid in using inhibitors will be mentioned.

5.7.7.1 Temperature limitations

Film-forming inhibitors contain organic molecules with carbon-carbon, carbon-hydrogen, carbon-nitrogen bonds and so on. In common with other organic molecules, they decompose at elevated temperatures. It was pointed out in Clause 5.7.1 that inhibitors are recommended only for "low" temperatures, by which is meant corrosion in the presence of water. Furthermore, film-forming inhibitors act through an adsorption process, which generally becomes less effective at elevated temperatures, requiring larger treatment dosage to maintain effective films on metal surfaces. This increases expenditures for the treating chemicals. Above about 230 to 260°C (450 to 500°F) it may be said that film-forming inhibitors have limited application.

Fouling reactions occurring in the range of about 150 to 370°C (300 to 700°F) present problems, many of which are amenable to use of chemical antifoulants. Above about 370 to 430°C (700 to 800°F), there is little experience to draw on in use of either film-forming or neutralizing corrosion inhibitors or use of antifoulants.

5.7.7.2 Insufficient concentration

Many corrosion inhibitors of both the passivating and the film-forming types (as explained in the chapter on inhibitors types) are classified as "dangerous", because they actually may produce increased localized corrosion and pitting compared to untreated systems if they are used in quantities insufficient to form an effective corrosion-resistant film. For this reason, it is not advisable to attempt reduction of inhibitor costs by reducing dosage below safe, effective levels.

If iron content is used to measure results of inhibitor treatment, the initial rise when treatment is begun, usually attributable to cleaning of scaled surfaces, will soon fall to a rate less than that before treatment. If it does not, then either too little inhibitor is being used, or the inhibitor is not being added in such a way that it reaches the corroding equipment.

In actual plant practice, the inhibitor is normally added at concentrations of 5 to 10 times the final desired recommended value. The high concentration reduces the time needed for sloughing of old deposits and also accelerates the attainment of a good film on the cleaned metal. The concentration is gradually reduced after this, until the desired inhibition level (as shown by coupons, resistance probes, water analysis) (see Note) is attained at an economical cost.

Note:

Start-up programs.

A- If dirty.
B- If cleaned.
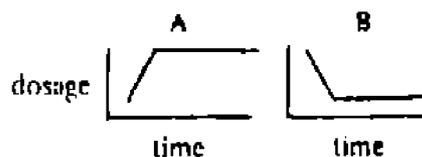
5.7.7.3 Surfactant properties of inhibitors

The effectiveness of film-forming inhibitors, as already stated, depends upon strong adsorption of inhibitor molecules at the interface between the process liquid(s) and the metal surface to be protected. It is not at all unusual for materials active at a solid-liquid interface to be active also at a liquid-liquid and/or liquid/gas interface. The former may cause emulsification problems, the latter may result in foaming. Emulsion problems are evidenced in water drawoffs in refinery equipment and in petrochemical plants, e.g., separation of oils and tars from ethylene quench water systems.

Of great importance when refining products such as jet fuels is emulsification of small quantities of water into the product. The water may enter the system because of storage tanks which "breathe" humid atmospheres or carry water bottoms or by contamination or careless handling. Water that does get into the jet fuel storage system often is difficult to remove with settlers or coalescers when surfactants are present in the system.

Because of the deleterious action of emulsified water in promoting bacterial growths in storage and in freezing and clogging of fuel injection nozzles during operation, jet fuel purchasers have strict requirements concerning such water as well as fuel response to it. This is usually determined by the ASTM method D 2550-66T (Water Separometer Index, Modified or WSIM Test). WSIM test helps to find one inhibitor among the others which is effective as corrosion inhibitor but produces minimal emolsification or which can be modified by a demulsifying agent without losing its corrosion inhibitive properties.

5.7.8 Economic aspects of chemical inhibition and other measures for corrosion prevention

In discussing various corrosion preventive measures, it is useful to consider that corrosion of the type described here, that is, attack by an aqueous liquid on a metal, has three prerequisites:

a) an aggressive or corrosive liquid,
b) an active or corrodible metal, and
c) intimate contact between the metal and the liquid.

Control measures available are altering the metal or the environment or placing a barrier between them to prevent their contact. Of course, combinations of two or more of these methods also may be applied for better results.

5.7.8.1 Altering the metal

The activity of a metal may be altered somewhat by variations in its heat treatment or slight changes in composition; however, for marked differences in corrosion resistance, a completely different metal generally will be required. Thus, carbon steel may be replaced by copper or one of its brass or bronze alloys or by one of several stainless steels or other alloys. see IPS-E-TP-740 and IPS-E-TP-760.

5.7.8.2 Corrosion preventive barriers

Various protective coatings, linings, claddings and paints, all are examples of corrosion control by means of barriers separating the aggressive environment from the corrodible metal. While the cost of such systems is high (although rarely as high as resistant alloys) their life is limited.

Protective coatings and linings are usually applied over external surfaces and to internal surfaces of vessels of such size that the condition of the coating and lining can be observed visually at intervals and defects patched or replaced. Accordingly coating and lining failures rarely result in catastrophic failure in refinery applications. Furthermore, coatings, particularly organic-based, shall not use under such extremes of temperature, pressure and chemical environment as shall refinery alloys. (see IPS-E-TP-740).

5.7.8.3 Alterations of corrosive environment

The use of neutralizing amines for acid corrosion in refinery processing is an example of alteration of environment. The use of filming amines may be thought of as a combination of environment alteration and protective barrier, for example, the absorbed inhibitor film supplemented by the sorbed oil film. Chemical treatments employing neutralizers and/or filming inhibitors screened in the laboratory and tested in the plant to verify laboratory indications. Such tests are no more error-proof than are those on metals or coatings.

In this respect, the advantage of chemical treatment that efficacy of treatment may be followed easily and cheaply in the plant and modifications quickly made if original treatment is inadequate. Because of the sensitivity, rapidity and ease of the methods used for monitoring inhibitor treatments in the field, there is a small likelihood of substantial loss of equipment, performance or of catastrophic failure. In general, all that is required is the use of a nominal volume of chemical, with appropriate feeding equipment and corrosion-measuring devices.

Probably one of the greatest economic advantages of chemical treatment over other methods is that the costs of chemicals which must be added continuously are treated for tax and accounting purposes as expensed items similar to maintenance and other operating coast. On the other hand, alloy and coatings and linings systems usually call for capital outlays of considerable magnitude. These expenses are not deducted directly from operating income and hence bear a less favorable tax position. Such generalizations, of course, may vary with individual companies and their accounting systems.

Economic evaluation shall be performed before selecting the type of corrosion preventive measure, because the success or failure of a corrosion prevention program depends on economic feasibility as well as on technical performance. The plant engineer who recommends a preventive treatment to his management shall be conversant with economic evaluation and justification (see also Clause 13 Part 1 and NACE Standard RP-02-72, 1972).

In refineries and chemical plants with highly complex and interrelated processes and equipment, down-time because of corrosion failure with concomitant loss in production and product sales and profits, may be much more important than direct costs of equipment replacement or repair and labor to effect them. Such losses can easily exceed the cost of continuous treatment by corrosion inhibitors and antifoulants.

5.7.9 Special refinery processes amenable to corrosion inhibitors

5.7.9.1 The foregoing description has purposefully been kept as general as possible in order to illustrate the basic criteria of wet refinery corrosion and its solution by chemical treatment with neutralizers and film-forming inhibitors. Use of neutralizers and inhibitors has been described in the crude still and overheads. The same concepts can be applied in other systems where there is a hydrocarbon product in contact with liquid water containing corrosive constituents, usually hydrochloric acid and hydrogen sulfide.

Corrosion by naphthenic acids can be eliminated by them with neutralizing NaOH to form oil-soluble salts and the acid number of a crude containing naphthenic acids often gives an indication of its corrosivity during processing. This problem is not a major importance in refinery operations, in these resistant alloys such as Type 316 stainless steel are used.

5.7.9.2 Hydrogen blistering problems

Hydrogen blistering problems are well known. The basic cause of hydrogen blistering is the trapping of atomic hydrogen in the interstices between grains of metal or at inclusions or laminations where the atomic hydrogen combines to form molecular hydrogen. When the molecular hydrogen can not escape through the metal surface, it causes blisters, cracking and failure, etc., due to the increased pressure resulting from its formation.

Under most conditions of acid corrosion, the equilibrium between atomic and molecular hydrogen is displaced essentially completely in the direction of molecular hydrogen. However, in the presence of a number of catalytic agents, H atoms are kept from combining at the surface. Important catalysts are cyanides and sulfur compounds, including hydrogen sulfide. High nitrogen content in the feed stock appears to increase the probability of hydrogen attack in gas plants following catalytic cracking because of CN increase brought about by hydrogenation of nitrogen compounds.

In hydrocracking system corrosion of aqueous effluents increase with the mathematical product of nitrogen and sulfur contents of the water, which can be expressed as an equivalent content of ammonium sulfide. Total water volume as well as fluid velocity are also factors determining corrosion rates. Various parameters involved in corrosion in such systems and effect of pH, sulfide content and cyanide content as competition between the formation of a protective iron sulfide film and its dissolution as soluble ferrocyanide is shown in Fig. 5/2.

This type of corrosion is becoming more common as hydrogen treating processes proliferate. It is noteworthy to point out that corrosion occurs at basic pH values, where it would be expected that iron and its alloys would be protected. A blue deposit of the ferro and ferrocyanides of iron in fouled or corroded equipment often is evidence of this sort of corrosion.

Both overall attack and hydrogen blistering may be effectively reduced by the use of "proper" film-forming amines. These amines are similar to be used for other refinery corrosion prevention services. It is very important that the "proper" inhibitor be used, as determined by preliminary laboratory and plant evaluation. This is because overall attack may be reduced, while blistering or hydrogen embrittlement is not if an "improper" inhibitor is used.

5.7.10 Corrosion in gas processing units

Acid constituents such as carbon dioxide and hydrogen sulfide shall be removed from natural gas in central field treating plants or in gas refiner before transmission of the gas for sale. Similarly, these constituents must be removed from plant gas streams, as in stream cracking of hydrocarbons for ethylene production, before the gases are subjected to low-temperature fractionation. In the production of synthesis gas for subsequent conversion to ammonia or methanol, for example, it is usually necessary to remove carbon dioxide formed either by partial combustion of hydrocarbons or by the water gas shift reactions.

Gas treating plants and gas refineries are bothered with corrosion problems. Much of these problems caused by the breakdown solvents, e.g., monoethanolamine, at the elevated temperatures of the reboiler regenerator. It is postulated that the breakdown products can chelate with iron and prevent the formation of an insoluble protective film at the high pH of operation, which pH should preclude corrosion of iron. In this respect, there is a similarity between the corrosion of iron in amine solutions in gas regeneration, for example, and that in the effluents from hydrocracking plants described earlier.

Corrosion and other operational problems can be greatly reduced by proper plant operation. It is recommended that the gas loading (ratio of moles acid gases per mole of MEA) be kept to 0.45 or less, monoethanolamine concentration be kept at 20% and that degradation products be removed by use of a side-stream reclaimer. Most of the authors quoted recommended maintaining reboiler temperatures at the lowest practical values in order to reduce solvent degradation and subsequent corrosion of equipment.

The use of sodium sulfite and hydrazine for removal of oxygen and reduction of the corrosion loading in the system is also recommended. Foaming, a common problem in many gas-liquid separation or extraction processes, may be aggravated by surfactants, particularly in MEA systems and by fine particles, such as corrosion products, which act as foam nuclei or stabilizers. Use of a side-stream filter to remove these particles often is an effective supplement to the proper corrosion inhibition in solving such foaming problems.

The use of sodium metavanadate as a successful corrosion inhibitor in an MEA system removing carbon dioxide from hydrogen streams is reported. Use of the inhibitor above 108°C (225°F) is believed to produce a highly protective film of Fe_3O_4.

Both potassium nitrate (0.5%) and potassium chromate (0.2%) are very effective in carbon dioxide systems but not with hydrogen sulfide. Use of metavanadate in hot carbonate systems can passivate steel in a carbonate solution only when bicarbonate content is low. The addition of oxygen to the system increases passivation of mild steel but increases corrosion of copper-nickel alloys.

5.7.11 Miscellaneous refinery corrosion problems

5.7.11.1 Many miscellaneous corrosion problems in refinery and petrochemical plants involve metal contact with strong acids such a sulfuric used in alkylation and acid washing, hydrofluoric in alkylation, nitric from ammonia oxidation and so on. Generally these corrosion problems are solved by means other than the use of corrosion inhibitors, e.g., by changes in process design (such as assuring water-free systems, or by maintaining sulfuric acid at sufficiently high concentrations to be non-corrosive to steel); by metallurgical approaches and selection of resistant alloys; by use of protective coatings and linings; or by anodic protection.
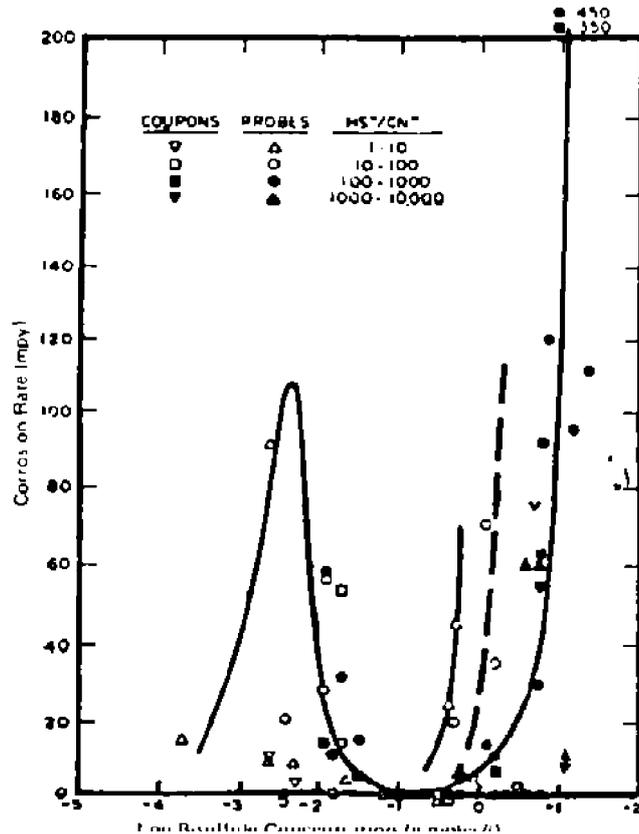
CORROSION RATES FOR TEST RUNS WITH CYANIDE PLOTTED AGAINST THE LOGARITHM OF BISULFIDE ION CONCENTRATION. THREE REGIONS OF ATTACK CAN BE IDENTIFIED: A REGION OF SULFIDE CORROSION (TYPICAL pH VALUES BELOW 8.0); A NON-CORROSIVE REGION BECAUSE OF FORMATION OF PROTECTIVE FERROUS SULFIDE SCALE (TYPICAL pH VALUES BETWEEN 8.0 AND 9.0); AND A REGION OF SULFIDE CORROSION BECAUSE OF COMPLETE DISSOLUTION OF THE PROTECTIVE SULFIDE SCALE BY CYANIDE IONS AT pH VALUES ABOVE 9.0 (EXTREME RIGHT)

Fig. 5/2

5.7.11.2 Corrosion prevention by chemicals is not ordinarily practical in refinery work for acids which are either concentrated or strong. However, diluted acid streams often may be rendered non-corrosive by use of inexpensive neutralizers and/or filming inhibitors. Examples include the mixed condensate composed of water and hydrocarbon liquids from dehydrogenation of ethyl benzene to styrene in the presence of steam, various acidic wash streams, etc.

In using inexpensive and easily available alkalis for neutralizing acidic streams, washing out vessels, etc., the chloride content of the commercially available soda ash or caustic must be carefully controlled, as also must the chloride content of the plant or source water used to make up the neutralizing and wash solutions. This is because of the deleterious effect of chloride ion in destroying passive films on normally corrosion-resistant alloys such as the various types of stainless steels, resulting in Stress Corrosion Cracking (SCC) of these materials. (A NACE publication of "L.T. overstreet). Recommendations for the use of: Neutralizing Solutions to Protect Against Stress Corrosion Cracking of Aus-

tenitic Stainless Steels in Refineries, Report of NACE Committee T-8-6, Proc. NACE 25th Conf., NACE, Houston, Tx. 578-582(1969)",which discusses this problem and gives detailed recommendations shall be followed.

With increasing use of stainless steels under a wide variety of services, the problem of stress cracking has received a great amount of deserved attention. Various parameters influencing SCC have in systems where hydrogen sulfide is a principal causative factor. Among them are strength of steel, stress level and acidity or alkalinity of the environment. Low pH is very detrimental regarding the stress corrosion cracking of high strength steel, with considerable increase in resistance to SCC as pH is raised from 2 to 5.

Hydrodesulfurizer units, etc., in refineries face presence of hydrogen sulfide and polythionic acids formed by reaction between hydrogen sulfide and sulfur dioxide. Air increases susceptibility to SCC in these systems, as it is also known to do in systems where chloride is the principal causative factor. Chemical agents can be used for prevention of stress cracking by alteration of the environment, e.g., by changing the pH or by use of antioxidants for removal of oxygen.

Although the principal means of preventing SCC are by controlling the environment as described above or by alteration of the metal, protection by barriers can be used, provided they can be kept intact. This is usually difficult with protective coatings; however, it may be effected by use of films formed by inhibitors, which are in dynamic equilibrium with liquids containing inhibitor and in contact with the metal to be protected. Hence, the film can be repaired continuously. Use of film-forming inhibitors also reduces failure by corrosion fatigue, a phenomenon similar to stress corrosion cracking. Fatigue like can increase by a factor of as much as ten, depending upon the inhibitor used and the conditions of filming. The efficacy of the various treatments described is attributed to the strength of the film and its insolubility in the filming and contacting fluids. This would appear to indicate the potential of applying film-forming inhibitors for prevention of stress cracking and corrosion fatigue in refinery as well as down-hole applications.

5.7.12 Selection of inhibitor

5.7.12.1 Selection of inhibitor(s) for refinery processes shall be according to Part 1, Clause 12 and to the requirements of this Clause 5.7.

5.7.12.2 Test methods

5.7.12.2.1 Irrespective of the method, it should be remembered that the relative corrosion rate before and after treatment is used as a basis of comparison. This is generally easier to determine and of more use than the absolute rate. It is also important to consider that the build-up, breakdown and repair of films formed by adsorption-type inhibitors are not instantaneous processes but may require times of the order of several days. Accordingly, the limitations of spot readings as determined by electrical corrosion rate meters and "grab" samples of fluids for metal ion analysis must be considered. In addition, because a corrosion rate meter gives readings only in electrically conducting media, readings are dependent on the conductivity of the medium and suitable corrections must be made for stream composition and/or conductivity.

5.7.12.2.2 Process stream analyses for dissolved metals such as Fe^{2+}, Cu^{2+} among others, can be carried out quickly and cheaply, but are of questionable value in streams containing hydrogen sulfide, because its corrosion products usually will be insoluble sulfides.

Obtaining a representative and reliable sample of the stream is difficult under such conditions. In addition, because of their detergent action, many inhibitors often cause an initial increase in the amount of sludges and scale going into the process stream as old deposits are loosened by the detergent-inhibitor and slough off equipment. This increase must be recognized for what it is and not be assumed to signify an increased corrosion rate.

5.7.12.2.3 Test coupons are the most widely used tool in monitoring refinery corrosion and its treatment because they may be easily prepared, inserted, removed and evaluated. Coupons are composed of metals similar to those of interest and exposed to conditions similar to those of interest.

Accordingly coupon exposure times are generally 2 to 4 weeks for determination of "before" and "after" conditions. Exposure time will be limited and data questionable if process changes are made during the exposure period. Such variations as changes in feed stocks, processing charge rates, temperatures and the like may affect corrosion rates sufficiently to negate the effects caused by changes in the inhibitor program under investigation (see also IPS-I-TP-802).

5.7.13 Control of fouling

5.7.13.1 Scope of fouling

Despite long use, the meaning of the word "fouling" remains nebulous. In this engineering Standard, fouling is considered to relate to the presence of solid materials, without respect to origin and nature, which are insoluble in the process streams of interest. These materials cause operating difficulties by deposition onto surfaces of equipment contacted by the process streams either in zones where the insolubles are formed and/or in downstream units. Such deposits interfere with mass and heat transfer, as evidenced by reduced heat transfer coefficients and flow rates and by increased pressure drops.

Accordingly, throughputs are reduced, while pumping costs and heating or cooling requirements are increased. In extreme cases, fouling may result in complete plugging, or burning out or rupturing of critical process units. Thus, the scope of fouling problems is seen to be quite broad.

5.7.13.2 Inorganic fouling deposits

It is sometimes useful to classify fouling deposits as to their inorganic or organic nature, because such a classification may point to the cause of the fouling and indicate possible methods of prevention or alleviation. Corrosion products such as metallic oxides and sulfides may deposit on equipment downstream of the area of corrosive attack, causing fouling problems. Use, of corrosion inhibitors to solve the corrosion problem is a possible solution to the fouling problem due to the existence of an interdependence is indicated between fouling and corrosion in process equipment.

Another common fouling problem due to inorganic deposits may occur when ammonia is used to neutralize HCl formed by hydrolysis of chlorides after crude desalting. Increasing the pH in order to reduce corrosive potential results in formation of the oil-insoluble salt, NH_4Cl. This may result in a fouling problem which can be alleviated by adding water either continuously or intermittently to affected unit. Another approach is to reduce the amount of ammonia added for neutralization and operate at a lower pH and instead use organic film-forming inhibitors to control corrosion. Frequency of this approach has increased because of the development of inhibitors active over a wider pH range than those originally used in refinery work. A third solution to the problem employs neutralizers other than ammonia, e.g., morpholine, cyclohexylamine or other high molecular weight amines, which combine with mineral acids to give salts having higher oil solubility and/or dispersibility than does NH_4Cl.

5.7.13.3 Organic fouling deposits

5.7.13.3.1 Organic fouling is much more prevalent but less well understood than inorganic fouling. Organic foulants usually are high molecular weight materials formed by oxidation, polymerization or other reactions of constituents in the process streams. These constituents may be the principal components of the streams or impurities in them. Deposits range in consistency from rubbery-like solids to "pop-corn" and coke. Deposit as well as stream analyses may be of value in determining the composition of the deposit to indicate its origin and remedy. However, such analyses are often time-consuming, expensive and do not yield a great deal of useful information. Nevertheless, some useful generalizations can be made on factors influencing fouling and possible methods of prevention. Several examples will be discussed below.

5.7.13.3.2 It should be emphasized that although the term paraffin (low affinity) implies that such materials are non-creative, this is not necessarily the case at the elevated temperatures and pressures involved in petroleum processing and in the presence of certain contaminants. Paraffins are relatively non-creative, compared to other more active components such as olefins, aromatics and heterocyclic hydrocarbons encountered in petroleum refineries and particularly in petrochemical operations. The presence of such reactive materials, even in the range of parts per million (often beyond the scope of conventional stream analyses) can lead to severe fouling. Consideration must be given to the effect of concentrations of ppm multiplied by stream volumes of thousands of barrels per day and continuous operations of months to give large quantities of deposits from streams containing only minute concentrations of foulants.

5.7.13.3.3 Operating parameters such as temperature, pressure and contact time, all of which increase fouling reaction rates, ordinarily are set by processing conditions. Additional factors are stream contamination effects, which may or may not be amenable to process changes. Many fouling reactions proceed through free-radical oxidation and polymerization routes, so that the elimination of free-radicals or their precursors is desirable. Because oxygen is effective in many free-radical reactions, prevention of air contamination in a system is desirable. This is accomplished by "tightening up" the system, minimizing transfer and storage times and/or by such procedures as inert gas blanketing of storage vessels. Many materials are so sensitive to traces of oxygen, however, that even these measures allow some fouling to occur. Consequently, antioxidants may be used to negate the effect of air.

5.7.13.3.4 Another factor which increases fouling is the presence in the process streams of trace quantities of certain active metals such as iron, nickel, vanadium and particularly copper. These metals are present because of original occurrence in the crude streams or from corrosion of process equipment constructed of the metals or their alloys. Surfaces of these metals are also active catalysts for fouling reactions. Here again, the interdependence of corrosion and fouling is illustrated, since metal contaminants resulting from corrosion in up-stream units may be reduced by use of corrosion inhibitors.

5.7.13.3.5 Oil-soluble dispersants are widely used to alleviate both organic and inorganic fouling problems. The object is not to prevent the initial formation of coke nuclei and other insoluble particles in the stream, but to reduce their tendencies to agglomerate into larger precipitates which can settle out of the process stream and deposit on and in various places in the equipment. A test for effectiveness of materials as antifoulants based on their ability to disperse carbon black in hydrocarbons can be established.

Commercial materials recommended for use as antifoulants in process industries contain combinations of dispersants, antioxidants, metal deactivators and/or corrosion inhibitors. The choice of the best material for a given application shall be determined by effectiveness and cost. Screening tests to differentiate between alternative materials will be described below. Because of the wide variety of streams requiring treatment, many commercial antifoulants have been developed for different applications. The situation is similar to that in corrosion inhibition and no universal remedy is available.

5.7.13.3.6 An additional important property of antifoulants is high temperature stability. Temperature above 200°C (400°F) are common and applications in the range of 315 to 345°C (600 to 650°F) are not unusual.

Higher temperatures also may be possible for very short contact times. Applications of antifoulants are being attempted under extreme conditions such as in ethylene stream-cracking pyrolysis units. The surface of the pyrolysis furnace tubes may be altered by the antifoulant so as to reduce the catalytic effect of the surface in promoting coke formation.

5.7.13.4 Use of antifoulants

Principal uses of antiflouants are in hydrodesulfurizers (for naphtha, gas and lubricating oils), in naphtha reformers, in crude and catalytic cracking units. Other units include cokers, visbreakers, alkylation units, ethylene units, deethanizers, solvent recovery units, etc. While fouled equipment consists primarily of heat exchangers, furnace tubes, piping and distillation towers can also be affected.

The economic justification for using an antifoulant is usually based on how it increases on-stream time, improves heat transfer efficiency, reduces fuel costs, improves fluid throughputs and the like. Costs of cleaning, repairing and replacing fouled equipment are generally of secondary importance. All direct and indirect costs must be balanced against the cost of the treatment program used for fouling prevention or alleviation.

5.7.13.5 Evaluation of antifoulants

5.7.13.5.1 Despite the effectiveness of antifoulants used in relatively small concentrations (5 to 20 ppm) and the modest unit cost of the chemicals, total costs can be appreciable because of the large volume of streams treated. It is desirable to optimize the cost versus effectiveness of the treatment by selecting the additive(s) best for the specific application under consideration. Because of the wide diversity of refinery and various petrochemical streams, no single approach or chemical may be expected to be a universal solution to all fouling problems.

Due to the cost as well as time in testing antifoulants in plant applications, some laboratory test methods has been involved to determine the fouling potential of process streams and evaluate the effects of alternative additives and treatment levels. These laboratory tests are always of relatively short duration-form several minutes to several days-and require intensification of the causative factors to increase fouling rates and thus provide measurable changes in the system parameters during the test times which are short relative to the weeks or months of actual field fouling problems. Temperatures may be higher, contact times longer, or contaminant level greater (as by blowing air into the test fluids).

Because of the more severe conditions of the tests, additive levels are usually higher than under plant conditions. Several screening tests described below illustrate these concepts. It is more important to remember that these tests are for screening rather than for prediction of additive performance under actual field conditions which may be very much different from the test conditions. Accordingly, the screening test shall be used only to obtain preliminary information on materials which appear promising on a cost-performance basis. Promising materials shall then be evaluated in the field for optimization of the antifoulant treatment.

5.7.13.5.2 Erdco CFR coker test method

This method is a modification of the Erdco jet fuel testing procedure (ASTM D-1660). In this unit, the test fuel is pumped at a controlled rate over a heated surface 204°C (400°F) which is designed to simulate feed preheat exchanger conditions. Decomposition of materials in the process stream on the hot surface causes deposition of polymers and coke, some of which adhere to the surface. However, some decomposition products also are carried in suspension by the fluid stream. The stream is then pumped through a metal filter having 20μ pores. These capture much of the suspended matter from the stream.

Because suspended matter plugs the filter, the pressure across the filter rises exponentially with time. The slope of log pressure drop versus time is used as a measure of the fouling index which the authors have correlated with plant fouling conditions for both treated and untreated conditions. In ASTM D-1660, the physical appearance of the heat transfer surface, i.e., blackening and coking, is expressed in a quantitative manner to correlate with fouling tendencies of heated jet fuels, etc. The method is developed by A.W. Frazier, J.G. Huddle and W.R. Power in Oil and Gas Journal, 117 (1965) May, 3 entitled "New Fast Approach to Reduced Preheat Exchanger".

5.7.13.5.3 JFTOT device developed

Better correlation between test results and refinery experience with antifoulants is claimed with data from the Jet Fuel Thermal Oxidation Tester (JFTOT) developed by a San Antonio, Texas firm. The device operates on the same principles as the Erdco coker developed in 1965 by Amoco and according to the Erdco Aviation Fuel Testing Procedure (ASTM D-1660). One of the main advantages of the JFTOT tester is that it uses only one quart of fuel.

Because JFTOT and Erdco produce much the same sort of data, data from JETOT can be posted on Erdco data sheets. Enjay's experience with the device is reported by Gillespie (see Note 1).

5.7.13.5.4 There are numerous variations on the above methods. The "hot wire" is a fairly simple and inexpensive test which employs heating of the test fluid by contact with a hot nichrome wire (see Note 3). The wire is heated by a current (about 5 to 10 amperes) sufficient to elevate the temperature to incipient redness. As the fluid decomposes on the hot metal surface, fouling may be observed by:

> **a)** An increase in the apparent diameter of the wire as coke covers the wire.
> **b)** Discoloration of the liquid.
> **c)** Changes in the current through the wire brought about by reduction of the wire's thermal and electrical conductivity.

Normally, several determinations are carried out simultaneously with the test wires in series electrical connection. Thus, the treated and untreated systems can be compared visually and followed with time.

5.7.13.5.5 Field methods used to follow the course of fouling and its reduction by various treatments are based on changes in operating parameters. Because fouling usually reduces fluid flows and decreases heat transfer rates, but increases pressure drops and heating (or cooling) demands, all of these or the rates of their changes in the treated and untreated systems may be used as indications of the effectiveness of the treatment. However, it should be noted that many of these parameters also can be changed by process variations independent of fouling, e.g., changes in charge rates, cracking severities, feed stocks, etc. Accordingly, tests which are carried out for extended times require careful control and data interpretation.

Other methods of rapid evaluation in laboratory and/or field are proposed from time to time because of the need for a guide and accurate screening method for antifoulants. These methods should be considered as to their ability to measure true fouling rates or fouling potentials or some other physical or chemical property purported to be related to the desired property. When extrapolating the test conditions to the field conditions, it should be remembered that the dangers in such extrapolations increase as the conditions between actual and test conditions diverge.

A summary of present day laboratory and field methods of evaluating antifoulants was presented during a round table discussion in a September, 1971 meeting of NACE T-8 (Refinery Corrosion) Committee in Chicago.

An additional concept in the evaluation of antifoulants by laboratory screening devices has been pointed out by Nathan and Dulaney (see Note 4). This concept considers the wide fluctuation in reproducibility of test data obtained at intermediate efficiency values of additive applications. At low efficiencies, such as those obtained at low treatment levels, or at high efficiencies, such as those obtained at high treatment levels, replicate tests have good reproducibility.

However, poor reproducibility at intermediate concentrations and efficiencies limits the ability to differentiate between the cost-effectiveness of alternative additives. Similar difficulties have been reported with respect to the evaluation of corrosion inhibitors in refinery processes and other applications (see Note 5) and in testing the effect of surfactants employed as corrosion inhibitors and/or antifoulants on the water tolerance of jet fuels (WSIM Test). The limitations of screening tests emphasize the inadvisability of undue reliance on them and the need for following such tests with careful plant studies to obtain reliable technical and economic data on antifoulant applications.

Notes:

1) B.G. Gillepsi. A New Process Antifoulant Test Correlates Better with refinery experience, paper 40, NCE 27 th Conference. March, 1971, see also Material Protection and Performance, 10, No. 8, 21-25 (1971) Aug.

2) A.S. Couper and F.B. Hamel. Process Side Antifoulants in Petroleum Refineries, Report of Work Group T-8-2a, Materials Protection, 9, 29-33 (1970) June.

3) Anon. Simple Device Tests for Foulants, Oil and Gas Journal, 96 (1969) February 3.

4) C.C. Nathan and C.L. Dulaney. Statistical Concepts in Testing of Dispersants, I. & E.C. Prod. Res. and Dev. (1970) December.

5) C.C. Nathan and C.L. Dulaney. Statistical Concepts Facilitate Evaluation of Corrosion Inhibitors, Materials Protection 10, 21-25 (1971) February.

APPENDICES

APPENDIX A.2
A TYPICAL EVALUATION METHOD OF OIL FIELD INHIBITORS INTERNATIONAL TEST # 2

A.2.1 General

The degree of protection afforded by a corrosion inhibitor can be determined in a dynamic environment under varying conditions of corrosivity using weight loss coupons in Wheel-test equipment.

In this study made by a manufacturer A, B, and C-type inhibitors were evaluated.

A-type inhibitors are designed for initial film deposition by batching or pigging. A persistent effective film is required on a product for this application.

B-type inhibitors are designed for annulus fill in stabilized Produced Crude Oil. Good thermal stability and effective corrosion is required of these products.

The C-type products are for film maintenance of a successful B-type product and as such were to be evaluated in conjunction with a B-type product.

The A-type inhibitor evaluation was a repeat of the previous study where dubious results were obtained and some technical problems encountered. The B-type inhibitor evaluations were undertaken on products resubmitted by vendors after the first submission had failed to reach requirements with respect to thermal stability and corrosion protection. C-type inhibitors were as originally provided by Contracting Company.

A.2.2 Procedures

All analyses were undertaken in quadruplet unless stated. Controls were included for each set of test conditions.

A.2.2.1 Test fluids

Centrifuged produced crude oil in varying proportions with synthetic formation water make up is shown in Table 4.1. A total fluid volume of 150 mls was used for all tests. Carbon dioxide was bubbled through each bottle (5 psi gage setting) for 30 seconds prior to acid/sodium sulfide addition.

A.2.2.2 Hydrogen sulfide generation

Hydrogen sulfide was generated in situ by adding 2 mls of 15% hydrochloric acid solution per 150 ml total fluids followed by varying quantities (2-10 ml) of 10% sodium sulfide solution. Analytical grade sodium sulfide varies between 32 and 38% sodium sulfide. With the latter also being hygroscopic and of indeterminate water of crystallization, it is only possible to obtain an approximate idea of the sulfide ion concentration. Hence it is essential that the same batch of sodium sulfide solution is used for each set of controls and inhibited fluids used. Approximately 1 ml of 10% (W/V) sodium sulfide solution will generate 90 mg of hydrogen sulfide per liter of total fluid which is equivalent to 59.400 (V/V)ppm H_2S in the gaseous phase were all the H_2S to be expelled from solution.

A.2.2.3 Inhibitor solution addition

B and C-type inhibitors were dosed from a 10% (V/V) solution in 90% Isopar/4% Xylene.

(to be continued)

APPENDIX A.2 (continued)

A microsyringe was used for addition to give concentrations ranging from 10 to 60 ppm (V/V). 15 microliters of 10% inhibitor solution were dosed per 10 ppm (V/V) of inhibitor required in 150 ml of total fluid. A-type inhibitors were used at 10,000 ppm (1% V/V) total fluid and added to directly to Wheel Test fluids using a calibrated micro-pipette.

A.2.2.4 Corrosion coupons

The 1018 mild steel corrosion coupons of dimensions 75 mm × 14 mm × 4 mm and grit blasted to uniform finish used in this study were from the same batch as those used in the study reported in February 1987. Again weights were determined to 0.1 mg.

A.2.2.5 Wheel test conditions

As in the previous study, the oven temperature was maintained at 65% for the duration of each test. The exposure period for each test, with the exception of one six day evalution was approximately three days (Exact time recorded in hours).

A.2.2.6 The effects of increasing sodium sulphide concentration on corrosivity

While outside the scope of work, it was considered pertinent to study the effect of increasing the sodium sulfide concentrations on corrosivity while maintaining other conditions constant. The objective was to account for apparent anomalies in baseline control corrosion rates obtained by Vendors and Oil Plus in the previous study.

A 50:50 Produced Oil/Brine mixture was treated with carbon dioxide and 2 mls of hydrochloric acid. Sulfide concentration was varied by adding 0, 2, 4, 8, and 10 mls of 10% sodium sulfide respectively and the effect on corrosivity evaluated in a three day wheel test.

A.2.2.7 A-type inhibitors (A1 to A5)

The procedure used in the last study was modified. 10,000 ppm of inhibitor (quadruplet with quadruplet control) was placed in 50:50 Isopar; brine mixtures and coupons inserted and capped. The bottles were placed on the wheel for 2 hours at 65°C. After this period, the coupons were transferred to uninhibited brine: Produced Oil (50:50) which had been pretreated with carbon dioxide, 2 mls of 15% hydrochloric acid solution and 2 mls of 10% sodium sulfide solution. The bottles were capped and reloaded onto wheel to experience 3 days exposure.

A.2.2.8 B-type inhibitors (B1 to B5)

For an evaluation of B-type inhibitors combinations of 100% brine, 80:20 brine: Produced Oil, 50:50 brine: Produced Oil and 20:80 brine: Produced Oil were used. Inhibitors were evaluated at 30 and 50 ppm with three days exposure. Fluids were treated with carbon dioxide, 2 mls of 15% hydrochloric acid solution and 2 mls of 10% sodium sulfide solution.

One 6 day wheel test was performed at a Supplier's request to determine whether increased exposure would improve inhibitor performance. For this test 50:50 and 20:80 oil:brine mixture were used using the above treatment plus an additional test at 50:50 brine:oil where the sodium sulfide dose was increased to 6 mls. A sequential test in accordance with NACE was also undertaken. This procedure is designed to simulate the actual field situation where a fresh inhibitor solution will be introduced into the system continuously from the annulus.

A.2.2.8 In this test the fluids were changed after 24 hours exposure 30 ppm of inhibitor and 50:50 and 20:80 oil brine were used . Fluids were treated with carbon dioxide. 2 mls of 15 % hydrochloric acid solution and 2 mls of 10% sodium sulfide solution. The total exposure time was 3 days.

(to be continued)

APPENDIX A.2 (continued)

A.2.2.9 B + C-type inhibitors

The combinations were selected according to manufacturer codings supplied by the Contractor. B1 was eliminated at the Contractor's request following its poor performance in thermal stability and dispensability tests. The following combinations were used:

B2 + C4
B3 + C5
B4 + C3
B5 + C1

All tests were carried out in 50:50 brine: Produced oil mixtures over three days. Concentration used were B:C 30 ppm: 10 ppm, B:C 30 ppm: and B:C 20 ppm: 10 ppm with 2 mls of 10% sodium sulfide solution added to the fluids. In addition 30 ppm: 30 ppm B:C and 20 ppm: 10 ppm B:C doses were applied to fluid containing 6 mls of 10% sodium sulfide solution.

A.2.2.10 Coupon Cleaning and inspection

After cleaning and drying, coupons were reweighted. At this time any significant corrosion features were also recorded, e.g., pitting, crevices, cracks, etching.

A.2.2.11 Data Processing

The corrosion rate was calculated using.

$$mpy = \frac{\Delta W \times 43985}{A \times T}$$

Where:

mpy	= Corrosion rate in mils per year.
ΔW	= (Weight loss) Initial weight of coupon - weight after exposure.
A	= Coupon area in mm².
T	= Exposure time in hours.
43985	= Constant.

The % protection was derived from:

$$\% \text{ Protection} = \frac{(CR_{blank} - CR_{inhib})}{CR_{blank}} \times 100$$

Where:

CR_{blank}	= Control corrosion rate, in mpy.
CR_{inhib}	= Corrosion rate with inhibitor applied, in mpy (see Note).

To facilitate easier data handling with large numbers of data points Oil Plus utilized a microprocessor.

Note:

Mil per year (mpy) $\times$ 0.02540 = millimeter per year (mm/y).

APPENDIX B.2
TEST PROTOCOL FOR HIGH TEMPERATURE HIGH PRESSURE SYSTEMS
INTERNATIONAL TEST # 1

B.2.1 Corrosion inhibitor selection and testing

The corrosion inhibitors are to be selected and tested on the basis of specification SPC-PT-36 "Corrosion Inhibitor Specification". The specification covers the following:

- Performance guarantee required of the inhibitors,
- description of the system operational aspects and design parameters which the inhibitors must meet,
- inhibitor evaluation testing.

The selection of inhibitors will be amongst inhibitors formulated for sour gas corrosion inhibition. The inhibitor testing will provide for final inhibitor selection through evaluation of the candidate inhibitors' performances. The inhibitor testing is to evaluate the following:

- Corrosion protection testing.
- Foaming tendency.
- Emulsion tendency.
- Dispersability.
- Hydrogen embrittlement.
- Temperature.

The details of the corrosion testing follow.

B.2.2 Corrosion protection testing

To evaluate corrosion protection provided by the inhibitors two types of tests shall be done-the "wheel" test and electrokinetic testing. The wheel test is an established procedure for measuring the efficiency of corrosion inhibitors in oilfield environment. The procedure is described in the NACE report 10182-"Wheel Test Procedure Used for Evaluation of Film Persistent Inhibitors for Oil-field Use". The procedure utilizes a revolving wheel to which sample bottles are attached. In each sample bottle a steel coupon in subjected to a H_2S saturated brine similar to that in the producing field. The sample bottle is only partially full so that during wheel revolution the coupon is alternately wetted. Each sample bottle has a measured amount of corrosion inhibitor. The following wheel test parameters shall be used.

- test solution - acidity and H_2S level similar to producing field,
- test temperature - 23°C and 70°C,
- inhibitor concentration - blank, 10 ppm, 100 ppm and 200 ppm.

The electrokinetic method utilizes the anodic and cathodic corrosion reactions of a corroding steel specimen in a corrosive solution to predict an instantaneous corrosion rate. The method is very useful in determining any reduction in corrosion rate from adding corrosion inhibitor to the solution. The following electrokinetic test parameters shall be used:

- Test solution - acidity and H_2S level similar to producing field.
- Test temperature - 25°C and 70°C.
- Inhibitor concentration - blank, 1 ppm, 10 ppm, 50 ppm, 100 ppm and 200 ppm.

In addition the testing laboratory shall have computerized test equipment and trained personnel.

(to be continued)

APPENDIX B.2 (continued)

B.2.3 Foaming tendency

The inhibitor's foaming tendencies when mixed with diethanolamine and water are to be determined. The test method consists of blowing compressed air into a mixture of diethanolamine, water and corrosion inhibitor and then, observing the level of foaming. The following test parameters shall be used:

- Solution Composition - Two test solutions of 20% and 30% diethanolamine in water. Inhibitor concentrations shall be blank, 1 ppm, 10 ppm, 100 ppm and 1000 ppm.

- Temperatures - 20-35°C. The level of foaming shall be reported in every solution and inhibitor concentration.

B.2.4 Emulsion tendency

The inhibitor's tendencies of producing stable emulsions shall be determined through agitating a solution of water, oil and corrosion inhibitor. The time for phase separation after agiation is measured. The parameters of the testing shall be:

- Oil type - similar to that of producing field.
- Corrosion inhibitor concentration - blank, 1 ppm, 10 ppm, 100 ppm and 1000 ppm.

B.2.5 Dispersibility testing

Testing shall be done to determine the dispersibility of each inhibitor of each inhibitor into the oil and water phases. A measured amount of inhibitor is injected into a glass containing both water and oil. The dispersibility is then visually observed. The glass container is then agitated and any change in the dispersibility is noted. The parameters of the test shall be:

- Water chemistry - similar to that of the producing field.
- Oil type - similar to that of the producing field.
- Corrosion inhibitor concentration - 10 ppm, 100 ppm, and 1000 ppm.

B.2.6 Hydrogen embrittlement

Following the wheel testing, the test coupon shall be examined for hydrogen embrittlement is accordance with the coupon folding procedure as developed by the Physico-chemical Institute of the Academy of Sciences of the previous USSR.

B.2.7 Temperature stability

The tubing/wellhead inhibitor shall be tested to determine its resistance to high bottom hole temperatures. The inhibitor shall be heated at 110°C for several time periods (4 days, 1 week, 2 weeks and 3 weeks). The corrosion inhibitor shall be mixed with methanol at 5% and 30% concentrations for the testing to simulate the producing field well annulus fluid concentrations.

PART THREE

UTILITY

(COOLING WATER AND BOILER WATER SYSTEMS)

CONTENTS :   PAGE No.

APPENDICES:

1. SCOPE

1.1 This Part Three of IPS-E-TP-780 specifies requirements for controlling corrosive environments of utility including cooling water and boiler systems.

2. REFERENCES

See general.

3. DEFINITIONS AND TERMINOLOGY

See general.

4. UNITS

See general.

5. CORROSION CONTROL OF COOLING WATER SYSTEMS

5.1 General

Evaporation is the chief source of cooling in a recirculating cooling water system. As it proceeds, the dissolved solids (e.g. the mineral salts) content of the water increases until solubility considerations necessitate its limitation (i.e., by blowdown). Intimate contact of the circulating water with the atmosphere is provided by the cooling tower or spray pond in order to facilitate the evaporation. This keeps the dissolved oxygen content of the circulating water near saturation. Both of these factors, high content of salts and high dissolved oxygen increase the corrosivity of the cooling water.

Cooling water systems usually consist of a number of dissimilar metals and nonmetals. Metal picked up from one part of the system by the water trends to deposit elsewhere in the system on contact with more anodic components. This produces galvanic couples which further aggravate the attack.

Corrosion control in cooling water systems involves good design and materials selection as well as good fabrication, installation and operation. Complete corrosion prevention by materials selection requires expensive materials such as stainless steels. Materials commonly used in a cooling water system are carbon or low alloy steel, copper alloys, stainless steels, aluminum and wood.

Substitution of carbon or low alloy steels in cooling water systems for those of more expensive materials results in a marked savings in initial costs. Use of cheap materials can increase the costs of operation including water treatment and inhibitor application. A compromise between the cost of construction, materials and operation shall be performed in the design stage.

5.2 Economics of Cooling Water Corrosion Control

Principal economic advantages for the treatment of cooling water system from two sources:

 a) It reduces frequency of maintenance and inspection shutdowns.
 b) It permits more extensive use of iron and carbon or low alloy steel instead of high alloy steel and copper alloys.

Production losses during shutdowns are the major economic concern. The frequency of periodic shutdowns for maintenance and inspection depends on the reliability of the corrosion control program. The more corrosion control applied the lesser shutdown will be occur in the system. Thus, less time is lost from scheduled shutdowns. Frequency of costly, unscheduled outages can reduce even more drastically.

5.2.1 Use of inhibitors justification

Substitution of carbon or low alloy steel tubes for those of the more expensive copper alloys in heat exchanger service results in a marked savings in the initial costs. Because Admiralty tubes are roughly 60% more expensive than carbon steel, the designer must be assured of reasonably long and trouble-free service if the additional cost of the copper alloy tubing is to be justified. The tubes must resist the buildup of corrosion products which will interfere with heat transfer and flow as well as accelerate the development of leaks.

Treatment of once-through cooling water with inhibitors is too costly for frequent use. Replacement of steel tubes because of their limited useful life in once-through systems is accepted as a necessary addition to the cost of the cooling operation. One alternative is use of more expensive alloy tubes. However, it is important to recognize the importance of growing concern with thermal contamination of the environment which indicates that once-through systems for other than perhaps sea water cooling will not be acceptable much longer.

5.2.2 Problems exist with blowdown disposal

Disposal of blowdown from recirculating cooling systems also poses environmental contamination problems. Inhibitors and process contamination are the major concerns, although excessive dissolved solids may prove objectionable in some cases. A number of the major components now used in cooling water inhibitors must be removed before blowdown is acceptable for disposal in surface supplies (i.e., lakes and streams). Cost of this removal must be included in economic evaluation of inhibitor treatment. The alternative, environmentally innocuous inhibitors, may be used for satisfactory corrosion control. Corrosion inhibitors alone probably account for 60 to 70% of the total.

In addition to NACE Standard RP-62-72 for more details of the economics of corrosion control in recirculating cooling systems see some Economic Data on Chemical Treatment of Gulf Coast Cooling, Waters, Corrosion, 11, 61-62 (1965) Nov. reported by NACE Recirculating Cooling Water Sub-committee.

5.3 Selection of Inhibitor

For treatment of cooling water systems and selection of inhibitor(s) in addition to this Engineering Standard (see 12) reference is made to NACE publication on "Corrosion Inhibitors" edited by C.C. Nathan. IPS-M-TP-675 gives a procedure for selecting and purchasing inhibitor(s) for a cooling water system.

6. CORROSION CONTROL OF BOILER SYSTEMS

6.1 General

6.1.1 Corrosion in boiler systems can not be isolated entirely from a number of other concomitant problems which have a direct effect on the type, amount and location of corrosion and the functioning of the boiler. These problems which are considered along with corrosion can be identified as scale, sludge and carryover.

6.1.2 There are a number of locations in a boiler system where various types and amounts of corrosion can occur. These locations can be grouped in three generalized locations, preboiler, boiler, and post-boiler.

6.2 Preboiler Corrosion Problems

The preboiler system is defined here to include feed water pumps and lines and auxiliary equipment through which the feed-water is pumped prior to actually reaching the boiler. If not restricted, one could include a vast variety of units in which the makeup water is conditioned but which in themselves are essentially not a part of the boiler system. This definition then includes such equipment as stage heater and economizers.

Using this definition, one finds both corrosion and deposit problems in the preboiler system which can manifest themselves as general corrosion, pitting, or erosioncorrosion. The deposit problem can result from either deposition of suspended solids which should have been removed earlier the clarifier unit or else it may be caused by formation of adherent calcium, magnesium or iron scales.

6.2.1 Corrosion effects

Corrosion can attack iron, copper or nickel. General corrosion or pitting may occur for conventional reasons, e.g., dissolved oxygen, low pH, presence of deposits, stagnant areas, stress in the metals, defects in metal composition or surface conditions. Dissolved oxygen often will cause pitting attack when coupled with certain other conditions such as deposits on the metal surfaces or metal defects. Acidic pH values will lead to general corrosion. The other factors will generally favor localized attack. Cavitation-corrosion can be encountered in the pumps or at other locations where turbulent or high velocity flow may occur. Stage heaters and economizers are designed to increase the feed-water temperature which will increase the operating efficiency of the entire system and, as the temperature is increased, susceptibility to corrosion is greatly increased also.

6.2.2 Sources of deposits

6.2.2.1 There are two major sources of deposits in the preboiler system. These are identified as (a) suspended or (b) dissolved. Suspended solids are the mud or silt commonly found in surface water such as that from lakes or streams. These suspended solids shall be removed from the water by the clarification equipment before it enters the preboiler system. However, improper operation of such equipment may result in suspended solids entering the system. The standard coagulation process may employ lime, which removes some of the hardness and changes the alkalinity balance of the water. Additionally, suspended turbidity, such as clay particles, is removed from the system. Additional coagulants, such as high molecular weight polymeric materials can be used, as are alum, ion salts or sodium aluminate.

The residence time in the clarifiers shall be sufficient and the filters function properly so that not allowing fine floc particles to be carried through to the preboiler system where can, settle out and cover the lines with deposits. The particles that do not settle out in the lines go to the boiler system and cause trouble there.

6.2.2.2 The other major source- dissolved solids - is common to practically all aqueous systems and will result in the formation of calcium, magnesium or iron scales. Tightly adherent calcium carbonate or phosphate, magnesium hydroxide or silicate or deposits of iron compounds are laid down on the metal surface, water flow, interfere with heat transfer and set the stage for localized pitting. Deposit composition varies widely and is a function of the water constituents and temperature. For prediction of scale formation see Appendix A.3.

6.2.2.3 Phosphate deposits present a real anomaly. On one hand, polyphosphates are deliberately added (as will be shown later) to prevent adherent deposits and on the other hand, their reversion product, orthophosphate, can cause undesirable deposits. For this reason, temperature and pH conditions which accelerate reversion of polyphosphates must be considered carefully.

6.2.2.4 Economizers can present additional deposit problems. These units are designed to take boiler stack gases at about 480°C (900°F) and reduce them to temperatures approaching the dew point. In most cases, temperatures are in the range of 138 to 204°C (280 to 400°F). Since relatively low temperature gases are involved, it is necessary to design the economizer with a relatively large heating surface and this usually results in low feed-water flow rates in the units. The low rate of flow combined with the increase in feed-water temperature-sometimes approaching-boiler water temperature-can lead to severe deposition problems.

6.3 Boiler Corrosion Problems

General problems in boiler are deposits, carry over and corrosion, which are common to most or all systems.

6.3.1 Deposits in boilers

6.3.1.1 Deposits in boilers can be considered in two major categories: Sludge and scale. The usual way to tell the difference between them is by the nature of their adherence. Scale is commonly thought of as being tightly adherent to the metal while sludge may be dispersed in the boiler water, can be spread on the metal surface from which it is easily removable or else it can possibly serve as a binding agent for scale.

6.3.1.2 Sludge is often created deliberately. For example, orthophosphate is added to boilers as an "internal treatment" with the objective of precipating all the calcium and magnesium in the form of easily removable sludge. An example of sludges which are not desirable, on the other hand, are organic compounds which may result from contamination of feed water during passage through planted areas.

6.3.1.3 Oil contamination of feed-water causes a sludge which adheres to the boiler walls and is difficult to remove. The formation of sludge balls can be encountered when the binder is a corrosion inhibitor, a paint residue, a fuel oil or a lubricant. These sludge balls can become very large under some turbulent conditions. Severe attack may be resulted on carbon steel and even on Monel by sludges.

A chemical analysis of the scales will only identify the chemical composition so, for positive identification of the crystalline nature of consituents, X-ray diffraction must be employed. Table 1/3 shows scale constituents of deposits of high operating pressure boiler that have been identified by X-ray diffraction.

TABLE 1/3 - CRYSTALLINE SCALE CONSTITUENTS IDENTIFIED BY X-RAY DIFFRACTION

NAME	FORMULA
Acmite	$Na_2O . Fe_2O_3 . 4SiO_2$
Analcite	$Na_2O . Al_2O_3 . 4SiO_2 . 2H_2O$
Anhydrite	$CaSO_4$
Aragonite	$CaCO_3$
Brucite	$Mg(OH)_2$
Calcite	$CaCO_3$
Cancrinite	$4Na_2O . CaO . 4Al_2O_3 . 2CO_2 . 9SiO_2 . 3H_2O$
Hematite	Fe_2O_3
Hydroxyapatite	$Ca_{10}(OH)_2(PO_4)_6$
Magnetite	Fe_3O_4
Noselite	$4Na_2O . 3Al_2O_3 . 6SiO_2 . SO_4$
pectolite	$Na_2O . 4CaO . 6SiO_2 . H_2O$
Quartz	SiO_2
Serpentine	$3MgO . 2SiO_2 . 2H_2O$
Thenardite	Na_2SO_4
Wallastonite	$CaSiO_3$
Xonotlite	$5CaO . 5SiO_2 . H_2O$

6.3.2 Problems from carryover

Carryover from boilers can be defined as the presence of water in the steam leaving the boiler. This water contains solids which cause deposit and corrosion problems in the postboiler system, one of the more serious of which is the rapid build-up of silica deposits on turbine blades. The silica concentrations are so critical that saturated steam is not safe for turbine vanes unless it contains less than 10 to 15 ppb $SiO_3^=$. The problem of silica deposits on turbine blades is primarily present under high pressure conditions, whereas at lower pressures a considerable amount of SiO_2 can be tolerated in the boiler water. At pressures over about 27 to 41 bars (400 to 600 psig), boiler water silica will vaporize and contaminate the steam. As pressure is reduced as steam passes through the turbine, the silica begins to deposit, causing reduced turbine efficiency.

If salt mixtures such as sodium chloride, sodium sulfate or sodium hydroxide are carried out and form deposits, then corrosion occurs, especially if the melting point of the mixture is lower than the steam temperature. Copper and its oxides deposits also can cause corrosion. The American Boiler Manufacturers Association has established standards for boiler water balances in its standard steam purity guarantees. These are identified as "ABMA Limits" and are listed in Table 2/3.

The carryover can occur as a result of mechanical or chemical causes. Carryover is generally classified as foaming, priming or general entrainment in the steam. Some of the mechanical factors that influence boiler water carryover are:

a) Boiler design.
b) Severe steam load swings.
c) High water level.

The foaming problem is the most difficult to control and can be caused by a number of factors. Some of the major ones follow:

- oil contamination;
- other organic or collodial contamination;
- high total dissolved solids content;
- high alkalinities; and
- suspended solids.

Maximum limits for oil in boilers shall be of 7 ppm or less than 1% of the suspended solids. At constant loading of a boiler the height of the foam rises with the salt content of the boiler water. The nature of the salt is important: Na_2CO_3 has a greater effect than NaCl or Na_2SO_4. Foam can be caused by solid carbonates which are present due to evaporation of feed-water or dislodged incrustants.

TABLE 2/3 - STEAM PURITY

OPERATING BOILER PRESSURE BAR (psi)	TOTAL ppm		SUSPENDED SOLIDS
	Solids	Alkalinity	
0 - 20 (0-300)	3500	700	300
20 - 30 (301-450)	3000	600	250
30 - 40 (451-600)	2500	500	150
40 - 50 (601-750)	2000	400	100
50 - 60 (751-900)	1500	300	60
60 - 100 (901-1000)	1250	250	40
100 - 136 (1001-1500)	1000	200	20
136 - (1501-2000)	750	150	10
136 - (2001 and higher)	500	100	5

6.3.3 Corrosion problems

The corrosive factors in a boiler vary, but in a broad sense they can include dissolved oxygen, high temperatures and pressures, high salt concentrations, high-heat transfer conditions, stresses, localized concentrations of caustic (boilers are purposely operated at high pH values), erosion, peculiar localized flow conditions, deposits of salts, metals and metallic oxides and scales and sludges with localized overheating. The materials of construction are invariably carbon steel or low-alloy iron and steel except in nuclear boilers where alloys may be used. Various types of corrosion which can be encountered include pitting, concentration corrosion, caustic embrittlement, stress corrosion, erosion-corrosion and in nuclear installations, mass transfer.

This list shows that major corrosion problems in the boiler are local in nature. General corrosion of boiler tubes is not of much concern as a rule. Failure occur at specific sites and are associated with unique factors, such as deposits, crevices and stagnation. A brief survey of some of the more common types follows.

6.3.3.1 Pitting of boiler materials

Pitting is frequently associated with attack by dissolved oxygen and is manifested throughout the boiler system. The oxygen causes the formation of Fe_2O_3 instead of the desired Fe_3O_4 and causes rapid tube failure.

Deposits, such as those caused by scale, sludge or mill scale, promote pitting. The deposits are cathodic to iron and intensify local attack, while at the same time they contributed to overheating the deposit zones due to their heat insulating properties.

Metal precipitation, especially of copper, is generally believed to accelerate pitting. The copper originates from copper or its alloys used in the preboiler and postboiler systems.

Stresses or solid impurities in the steel promote pitting. Anodic areas are formed and the pits are found to be aligned with the stress, such as in fin tubes at the point where the fin has cracked and in the expanded zones of boiler tubes.

6.3.3.2 Concentration corrosion

A number of forms of localized corrosion problems can be grouped under the general term concentration corrosion. This corrosion is essentially the result of high concentrations of chemicals in specific locations, brought about by deposits and/or stagnant flow conditions, crevices and localized overheating. The most common causative agent is a high sodium hydroxide concentration.

Attack on steel in boiler is a function of pH and that maximum protection is achieved at pH 11 to 12. As the concentration of NaOH rises to give pH values above 12, the attack becomes rapidly aggravated by the formation of soluble Na_2FeO_2 instead of the protective Fe_3O_4. Corrosion rates also increase as the pH drops below 11, but the NaOH attack is by far the more common occurrence. Attack by concentrated NaOH proceeds more intensively in high-pressure boilers than in medium-pressure boilers.

Excess NaOH concentration is caused primarily by concentration of boiler water. Bubbles of steam formed at the surface of a boiler tube results in a localized temperature increase, with in turn, concentrates the boiler water at the interface between the bubble and the heat transfer surface. The result is a rapid increase in caustic content at that point.

6.3.3.3 Caustic embrittlement

Caustic embrittlement can be considered a special manifestation of the caustic-concentration problem. The major corrosive factor here is an abnormally high concentration of caustic in contact with steel under relatively high tensile-stress. Crevices in the system, especially at rivet holes, present ideal conditions for embrittlement and the bulk of cracking of this type has been associated with the presence of rivets.

The mechanism of embrittlement cracking is generally believed to be dependent on happenings at grain boundary atoms.

6.3.3.4 Stress corrosion

Caustic embrittlement is actually only one type of stress corrosion cracking. It is the one most frequently found in boilers and for that reason merits special consideration.

The most likely place for cracking to occur is in a stainless steel tubed steam generator where high chloride concentrations and steam-blanketed areas develop. In addition, considerable free oxygen is likely to be present. Oxygen has adverse effect on chloride stress corrosion and oxygen and chloride both must be present for stress corrosion to occur.

The problem of stress corrosion cracking becomes especially severe for those stainless steel parts which are intermittently exposed to boiler water. This exposure represents a much more severe condition for inhibition than in the case of the parts that are submerged in water continually. The cracking in the parts that are in the vapor phase does not occur if the water which contains chloride does not come in contact with them by splashing or by some other mechanism.

6.3.3.5 Erosion-corrosion

On occasion, failures which occur in boiler tubes can be attributed to an erosion mechanism.

They generally occur at areas in the tubes where the normal direction of flow has been altered abruptly, a condition of turbulence created and a new flow path followed. The resultant corrosion is similar to that found in some feed line systems. Here again a situation exists where the primary cause of the failure is physical one, i.e. the flow pattern while the resultant chemical corrosion causes the damage.

An example of this type of attack is erosion-corrosion of brass tubes in a reheater of boilers. The attack takes place where the direction of flow changes. Overheating and local boiling takes place with a disruptive effect on protective films, particularly at the exit and the entry where turbulence is the greatest.

6.4 Postboiler Corrosion Phenomena

The postboiler system is broken down into two areas:

> **a)** The superheater.
> **b)** The condensation and return system. Each will be considered separately.

6.4.1 Superheater

The allocation of the superheater to the postboiler group rather than to the boiler itself is purely arbitrary. Problems in the superheater are somewhat similar to both those of the boiler and those of the return and condensate system. For that reason it serves as an effective transition problem between the two.

The attack on superheater tubes can be attributed to three corrosive factors:

6.4.1.1 The reaction between steam and metal at high temperatures.

6.4.1.2 The carryover by steam of salts which are then deposited on the metal surfaces.

6.4.1.3 Condensation that occurs when the system is banked or is temporarily out of service.

Corrosion of metal by steam at very high temperatures is a serious problem but it is not amenable to solution by use of corrosion inhibitors, so it is beyond the scope of this engineering Standard. It must be minimized by the choice of suitable alloying materials (see IPS-E-TP-740 for material selection).

6.4.2 Steam condensate and return systems

Corrosion of steam condensate and return systems presents a two-fold problem to power-generating and steam-heating plants. Equipment damage and frequent replacement of lines, valve and traps result in a serious maintenance problem. In addition, corrosion products frequently formed are carried back into the steam-generating equipment and deposits there. The result is plugging of lines, localized overheating and promotion of corrosion in the boiler system itself.

Corrosion in the condensate system manifests itself in certain typical forms, depending upon the corrosive factors involved. These factors are basically oxygen, carbon dioxide and condensed water. The attack due to dissolved oxygen is characterized by tuberculation, pitting and build-up of iron oxide deposits.

6.4.2.1 Oxygen concentrations below 0.5 ppm cause negligible corrosion when the temperature is less than 70°C and the pH of the condensate is 6 or higher.

6.4.2.2 In the pH range 6 to 8 and at oxygen concentrations of 0.5 to 4 ppm, the rate of attack for general corrosion is given by the equation:

$$R = 24 (C-0.4)^{0.9}$$

Where:

R   is the average rate of penetration in mdd.

C   is the oxygen concentration in ppm.

This equation is not valid for pitting corrosion and does not take into account the accelerating effect of temperature. An increase in temperature from 60 to 90°C will double the rate of oxygen corrosion. Normally, one would expect a dual effect due to oxygen as a function of increasing temperature. On one hand, the corrosion rate should increase rapidly with temperature in accordance with normal kinetic considerations while on the other hand, the decreasing solubility of oxygen with temperature should decrease the attack. In this particular closed system, however, the oxygen can not escape and consequently the normal increase in reaction rate with temperature is to be expected and does in fact occur.

Carbon dioxide attack manifests itself by thinning and grooving the metal walls with failure occurring most readily at threaded connections. The walls are relatively clean, in contrast to the masses of corrosion products which cover the areas of oxygen attack. The corrosion rate of carbon dioxide is given by the equation.

$$R = 5.7W^{0.6}$$

Where:

R   is the rate in mdd.

W   is the concentration of carbon dioxide in condensate in ppm multiplied by 0.1.

An increase in temperature from 60 to 90°C raised the rate of attack of carbonic acid on low carbon steel by a factor of 2.6. The absolute magnitude of the corrosion will, of course, vary from system to system. There may be found a system where the corrosion rate of steel panels in the desuperheating condensate system be as high as 1285 mdd prior to treatment.

6.5 Corrosion Control of Boiler Systems

Corrosion of boiler systems will be controlled by water treatment either externally or internally or both as required. The term external treatment (pre-treatment) is usually applied to clarification, softening or de-mineralizing equipment, whereas the term internal treatment usually refers to treatment injected into the deaerator, feedlines, boiler or steam-condensate systems.

6.5.1 Preboiler treatment

Pretreatment (external treatment) is generally intended to solve both corrosion and scale problems in preboiler and boiler systems.

6.5.1.1 Pre-treatment

Pre-treatment of feed-water is designed to render it as non-corrosive or nonscale-forming as possible. Corrosion-control methods include various ion-exchange techniques designed to remove dissolved ionized solids from raw water which is blended with the condensate makeup to compose the feed-water. The ion-exchange materials most commonly used now for this purpose are synthetic organic exchangers, rather than the naturally occurring zeolites or their synthetic analogues which at one time were in wide use.

Cation-exchange resins can be used to soften water by removing the hardness ions, i.e., Ca^{++} or Mg^{++} and replacing them with sodium. Similarly, use of a cation resin in the hydrogen form produces an acid. Passage of the produced acid through an anion-resin bed in the hydroxide form results in pure demineralized water. This process can be carried out either by having one resin bed immediately after the other or by mixing the two resin types in one column. Similarly, alkalinity content and type of feed-water can be controlled by a suitable exchange of ions.

Deaeration to remove oxygen from feed-water must be provided if oxygen corrosion is to be avoided. Deaeration is generally accomplished through a combination of mechanical and chemical means, a combination which is the most effective and economical available. A number of different mechanical systems, wherein water is heated to drive out dissolved gases, have been devised for this purpose. Oxygen removal down to 0.03 cc/l (21 ppb) is common when the unit is operated at saturated conditions although some units are designed to remove more oxygen.

6.5.1.2 Corrosion control practices

General corrosion is frequently prevented by pH control. Maintenance of 9.0 pH reduces general corrosion appreciably. There are two approaches to raising feed-water pH to this value. The earlier one consisted of either adding NaOH or recirculating alkaline boiler water and aimed at the protection of all metals generally found in these systems.

The mechanism of inhibition is as follows:

As the (OH^-) activity is raised, the solubility of all oxides and hydroxides is reduced and the degree of supersaturation set up in the liquid very close to the metal is raised. This situation favors production of closely spaced nuclei of ferrous hydroxide, ferrous oxide or magnetite and promotes the formation of a protective film. Ferrous oxide or hydroxide are formed initially and their transformation to magnetite can take place readily if nickel or copper are present as catalysts. There are some inherent disadvantages to this approach, however. Sufficient recirculation of the alkaline boiler water may be impractical or may lead to deposit problems as precipitate formation proceeds with the lowering of temperature. Use of NaOH can cause increased blowdown requirements in the boiler system. Two points in this regard to be noted are as follows:

6.5.1.2.1 Alkalinity arising from massive dissolution of iron is no substitute for the addition of alkali, and;

6.5.1.2.2 In view of the temperature involved, measurement of pH would be of more value than measurement of pH since the former is much less temperature-dependent. A more recent approach to pH control in preboiler systems involves the use of ammonia or other amines. This is necessary in systems operating above the 61 to 82 bars (900 to 1200 psig) range with high purity water. These weak bases permit a more closely controlled regulation of pH. Following values in ppm for the amount of material are necessary to give pure water a pH of 9.0:

   a) Ammonia-less than   0.5.
   b) Cyclohexylamine   2.0.
   c) Morpholine   4.0.

The use of ammonia or amines for pH control is satisfactory provided the O_2 and CO_2 content to be kept at a minimum.

The primary problem appears to be oxygen and it is generally believed that use of ammonia or amines for pH control is satisfactory provided the oxygen content is carefully controlled also.

Control of dissolved oxygen in the boiler water is accomplished chemically by the use of either sodium sulfite (preferably catalyzed) or hydrazine.

The level to which it is necessary to remove the dissolved oxygen to prevent corrosion varies as a function of temperature. Followings are the recommended levels cites 0.30 ppm of oxygen in cold water, 0.10 ppm in hot water (70°C), 0.03 ppm in low-pressure boilers under 17 bars (250 psi) without economizers and less than 0.005 ppm in high-pressure boilers or when economizer are used. It is emphasized to keep oxygen concentration at zero regardless of the system.

Sodium sulfite is used alone or as a catalyzed formulation. The catalysts ordinarily used are very small amounts of copper or cobalt. At very high temperatures sulfite alone is effective in removing oxygen from water rapidly. Varying amounts are recommended. Usually about 8 kg of sodium sulfate is required to remove 2.2 kg of oxygen. An excess of about 30 ppm of Na_2CO_3 is needed to insure complete oxygen removal. Typical dosage values recommended by suppliers for scavenging oxygen are 20 to 40 ppm excess. Tash and Klein 100 to 140 ppm Na_2SO_3 for their high-pressure boiler-water composition is recommended. In the case of 115 bars (1700 psi) boiler, both vacuum and pressure dederative is needed to reduce dissolved oxygen in the feed-water to 0.005 ppm.

Catalyzed sulfite is used in the same range as uncatalyzed sulfite but is more rapid and more effective. Activated carbon, as an additive to sulfite, functions by adsorption and concentration of the oxygen. An increase in temperature is advantageous.

Certain disadvantages are implicit in the use of sodium sulfite. One is that it can decompose to form SO_2 or H_2S in high-pressure, steam-generating equipment, thus appreciably increasing corrosion rates in the steam-fed water cycle. It is believed that limiting concentration of 10 ppm, sulfite decomposition occur in 61 bars (900 psi) boilers. Another disadvantage is increased total dissolved solids in the boiler water which requires more blowdown. The catalysts can plate out in boiler tubes and promote pitting. For these reasons, there has been a considerable interest in another chemical additive for deoxygenation: Hydrazine (Na_2H_4). The reaction is as follows:

$$N_2H_4 + O_2 \rightarrow N_2 + 2H_2O$$
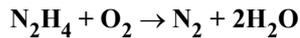
Reaction rate of hydrazine with oxygen increases rapidly with temperature to the extent that all oxygen can be substantially removed at 200°C (400°F) with reasonable values of reaction times and N_2H_4 concentration. At feed-water temperatures normally encountered in most industrial boiler systems 105 to 115°C (220 to 235°F), the reaction rate of hydrazine is considerably slower than the sulfite-dissolved oxygen reaction rate.

A competing reaction which can cause the formation of undesirable products is the catalytic of thermal decomposition of hydrazine. The resulting ammonia may attack nonferrous metals. Decomposition reaction of hydrazine is as follows:

$$2N_2H_4 \rightarrow H_2 + N_2 + 2NH_3$$
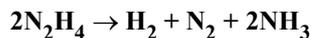
and at pH 8 the reaction is the:

$$3N_2H_4 \rightarrow 4NH_3 + N_2$$
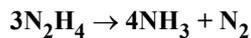
If the residual hydrazine content of the boiler is kept below 0.2 ppm, the NH_3 content of the steam will not be greater than 0.3 to 0.5 ppm. In actual plant operation feeding hydrazine at three to five times the theoretical amount is required to react with the dissolved oxygen left a residue in the boiler water and produced NH_3 content in the feed-water of 0.05 to 0.15 ppm. Addition of hydrazine to 100% in excess of the oxygen requirement results in a rapid rise in NH_3 and pH values with a resultant corrosion of copper-nickel and brass tubes.

If the concentration of hydrazine is regarded carefully to prevent breakdown of the excess to ammonia, its use instead of sodium sulfite has a number of advantages. Salt content does not increase as it does when sulfite is added. Another advantage is that alkalinity can be controlled with proper excess of hydrazine. Maintenance of a hydrazine residual in the water protects the boiler against occasional increases in dissolved oxygen content which result from variations in operating, conditions. Finally, much smaller dosage levels are required.

Although sodium sulfate is more reactive than hydrazine, the latter is advantageous when air is admitted accidentally. Vapor pH is less than 7 with sodium sulfate compared to a desirable value of 9 for hydrazine. The amount of dissolved Fe decreased with hydrazine, but the amount of Cu in solution is unaffected. Hydrazine is superior economically despite higher initial chemical cost. Hydrazine is more efficient than sodium sulfate, it is also effective in high pressure boilers.

Hydrazine is now being used in boilers with a wide spectrum of pressures ranging from 27 to 134 bars. It is easy to apply and can be controlled readily.

6.5.1.3 Deposits

6.5.1.3.1 As indicated earlier, deposit problems in preboiler systems can be divided into two categories based upon their origin. The first is deposition of suspended solids which may be carried into the system with the makeup water, while the second is from dissolved solids such as calcium, magnesium or iron.

6.5.1.3.2 The first problem, deposition of suspended solids, is attacked by filtration and/or clarification of the makeup. Filters can be of either the gravity or pressure type. Pressure filters are usually favored in industrial plants because of their relatively small space requirements. Filtration without clarification (coagulation and sedimentation) will commonly remove only the largest particles of the suspended solids and, therefore, often will prove unsatisfactory.

6.5.1.3.3 Coagulation for suspended solids removal is not practiced alone as a rule because floc can be carried over from time to time. Therefore, coagulation equipment is almost always followed by filtration. The problem of flock carryover frequently can be resolved by closer attention to operating practices, redesign of the clarification system so that more residence time is provided for the floc to settle out, or changing the chemical coagulation procedure.

6.5.1.3.4 Efficient operation of the coagulation and/or softening process is essential for proper feed-water maintenance. There are some high molecular weight polymeric materials which markedly improve clarification procedures.

Polymers used in the clarification process are generally required at low feed rates, usually in the range of 1 to 20 ppm. Their function is to agglomerate particles which otherwise would remain small (and become floc carryover) into larger particles heavy enough to settle out of the water. The three broad classes of these polymers are:

a) cationic;
b) anionic; and
c) nonionic.

Effectiveness of each varies, depending upon the charge on the suspended solids and molecular weight of the polymer. Further, some of the polymers may be used as a primary or secondary coagulation. Some are of such high efficiency that they may be used just prior to a filter without the installation of clarification equipment. This latter application is referred to as "in-line" clarification.

6.5.1.3.5 Polyphosphates added to feedlines for deposit control also function as corrosion inhibitors. The mechanism of protection is described elsewhere in this Engineering Standard in connection with cooling-water corrosion control. Polyphosphates also can prevent precipitation of hydrous ferric oxide if the water contains soluble iron.

The injection of ortho or polyphosphate into feed-water in a preboiler system which contains an economizer will invariably lead to serious economizer deposits when calcium is present. The physical condition of flow rates and water-metal interface temperature combined with the usual chemical environment will result in deposits which will be predominately tricalcium phosphate. Economizer deposits are commonly composed of tricalcium phosphate, magnesium silicate and iron oxide. Until recent years, the preferred method to reduce deposits was to eliminate phosphates from the preboiler system and add organic dispersants. These dispersants include tannins and lignins as well as synthetic polymers.

While the use of organic dispersants reduces economizer deposit problems considerably, they are not the preferred treatment method. Chelant applications to boiler systems, true deposit control in economizer (and preboiler systems in general) can be achieved by application of chelant. Chelants solubilize polyvalent metallic ions such as calcium, magnesium, iron etc. In the chelated form, such ions will not drop out of solution.

6.5.2 Treatment of boilers

6.5.2.1 Deposits

The term internal treatment is used for the direct addition of chemicals to the boiler, in contrast to external treatment which refers to mechanical processes (coagulation, softening, etc.) treating makeup water prior to the makeup water's entrance into the preboiler system. Internal treatment for prevention of deposits can be divided into two techniques:

a) precipitating treatment and;
b) solubilizing treatment. Each control method will be reviewed separately.

6.5.2.1.1 Precipitation treatments shall be used for boiler pressures up to the range of 61 to 68 bars (900 to 1000 psig). The two common techniques use phosphates control or carbonate control. These treatments involve the formation principally of calcium phosphates or carbonate sludges, their dispersion by various organic chemicals and finally, their removal by blowdown.

Sufficient alkalinity must be used with phosphate control because at low alkalinity values calcium phosphate becomes more soluble and tends to form a sticky adherent sludge. Adequate alkalinity for complete reaction with calcium requires a minimum pH of 9.6 in a steaming boiler, a figure comparable to 10.5 at room temperature. The "phenolphthalein alkalinity" must be greater than one half of the "methyl orange alkalinity" and the latter value shall be at least 200

ppm. A pH of 11.0 to 11.5 is favor for scale prevention and can be maintenanced by use of NaOH or Na_3PO_4. It must be recognized, however, that while this is a very desirable range, all makeup water do not have the same characteristics.

Frequently, where external treatment has not been provided, it is necessary or desirable because of economics to operate with much higher phenolphthalein and methyl orange alkalinities, resulting in much higher boiler water pH values.

6.5.2.1.2 Since the mechanism involved here is one of actually reacting with the calcium on a stoichiometric basis, it is apparent that an excess of phosphate must be maintained. This excess will vary from 10 to 100 ppm of phosphate, depending on the plant operating conditions and the efficiency of the feed-water hardness control.

Because many feed-waters contain magnesium in addition to calcium, it is necessary to consider the proper internal treatment of this feed-water component. The upper limit of 100 ppm for phosphate excess is used because above this value magnesium phosphate can begin to precipitate. Magnesium phosphate deposition has been encountered even at lower phosphate values. This is an undesirable precipitate since it is very adherent to boiler surfaces. Additionally, it will tend to cause greater volumes of hydroxyapatite and other precipitates to deposit on the boiler surfaces because of its adherent characteristics. Therefore, precipitation of magnesium in this form is to be avoided. This can be accomplished by maintaining the proper silica and hydroxide concentrations. Many feed-waters do not contain sufficient silica to react with most or all of the magnesium to form the magnesium silicate precipitate identified as serpentine (3MgO, $2SiO_2$, $2H_2O$) and some will precipitate as the hydroxide. While both are desirable, internal conditions frequently can be dramatically improved by adding sufficient silica as internal treatment to precipitate the magnesium as serpentine.

Carbonate control is not practiced as widely as phosphate control. Not only is the calcium carbonate precipitate more difficult to control (i.e., remove from the boiler) but an excessive amount of soda ash must be fed to maintain an adequate amount of carbonate.

Iron or copper may be present in the feed-water in an ionic form or may be present as a metal oxide. With precipitating type treatments, regardless of the original state, iron and copper will end up as a precipitate to increase the amount of sludge.

After formation of the above described precipitates, whether they be phosphates, carbonates, silicates, hydroxides or metal oxides, they must be conditioned so that they remain suspended in the boiler water as free-flowing sludge. Unconditioned or improperly conditioned sludges tend to collect in locations where circulation rates are low and form packed layers of deposit on metal surfaces which can interfere with circulation and heat transfer. Use of organic dispersants can help to keep this sludge in the free-flowing state.

Organic dispersing agents function not only by dispersing the sludge, but also by adsorption and crystal distortion. Crystal distortion is very important because it lessens the possibility that large crystals will form during the precipitation process and thus limits the potential for the development of a dense sludge deposit. Further, adsorption of the precipitates provides for a fluid sludge which is less adherent to boiler internal surfaces. And, finally, their dispersing characteristics tend to keep the precipitates in a finely divided state, in which form they are readily removed from the boiler by blowdown. The materials commonly used do not promote foaming and are not corrosive.

The organic materials usually used for this purpose are alkaline tennin extracts, vegetable derivatives, polymeric compounds containing adjacent carboxy groups such as a methylstyrene-maleic anhydride copolymer, carboxy methyl cellulose, polyacrylates, o-nitrophenol dimers, collodial peat and a wood-fat-molasses-coal mixture.

Control of magnetic iron oxide deposits can be achieved by using sodium nitrite or an organic nitrite derivative to convert it to ferric oxide. water-soluble lignins are more efficient in preventing Fe precipitation from water supplies than are molecularly dehydrated phosphates.

6.5.2.1.3 Solubilizing treatments

Many problems still exist with the precipitating type treatment programs previously outlined, even where the guidlines set forth are closely followed. Some boilers are very demanding with respect to feed-water quality and the amount of suspended solids that they will tolerate. steaming rates per square meter of space occupied are very high in these boilers. This then correctly implies that heat transfer rates are also high, which in turn, requires improved treatment programs. This leads to the common use of solubilizing treatments employing chelants.

The word chelate is coined from the Greek word "chela" which means the nipper-like organ or claw terminating the limbs of certain crustaceans such as the lobster. Thus, the word chelate is used to describe the grip of a class of amines and organic acids on metal ions, while the word chelation describes the reaction between these materials and the metal ions.

Deposit control with chelants involves the use of this class of chemicals to react with metallic ions in the feed-water or boiler water. The resultant chelant-metal ion complex is soluble.

Many chelating agents are available commercially. The two which have come into common use for boiler deposit control are Ethylenediaminetetraaceticacid (EDTA) and Nitrilotriaceticacid (NTA). In practice, the tetra-sodium salt of EDTA and the trisodium salt of NTA are used, rather than the acid. Both of these materials chelate bivalent and trivalent metallic ions on a moll for basis. The reaction rates for technical grades of EDTA and NTA are listed in Table 3/3.

The choice between these two chelants will depend upon many factors, such as concentration of the various metallic ions to be chelated, the concentration of the chelant which can be employed economically, the degree of reactivity required in the particular application and the chemical characteristics of the boiler water. The chelation reaction, while very energetic, is reversible under some conditions. Where high alkalinities are encountered or the feed-water contains phosphate, there is competition between the dyhydroxide and/or phosphate and the chelant for the metal ion. This may cause some precipitation in the boiler which might not be expected otherwise. A case in point is the chelation of ion. If boiler alkalinities are allowed to over-concentrate, the high hydroxide levels may cause the iron to precipitate. This can result in iron deposits. Since EDTA is a stronger chelant than NTA, this problem is more likely to occur in an NTA treated system.

Because chelants are organic compounds, consideration must be given to temperature or pressure stability of these treatment materials. It has been reported that NTA should not be used in excess of 61 bars (900 psig), while the upper Pressure level for EDTA is about 82 bars (1200 psig). Corrosivity of both EDTA and NTA treated boiler water have been investigated, with the conclusion that both materials are no more corrosive than phosphates in properly controlled boiler applications.

The solubilization characteristics of both EDTA and NTA, particularly the former, have been used to remove boiler deposits. The chelant is fed to the system at a concentration in excess of that required to chelate the metal ions in the feed-water. The excess chelant will enter the boiler and react with deposits such as tricalcium phosphates and magnesium hydroxide. The calcium and magnesium will be chelated or solubilized. The sodium phosphate and sodium hydroxide, also formed, are soluble and all may then be removed by boiler blowdown.

As is the case with precipitating type treatments, dispersants and polymeric materials are employed with the chelants. As previously pointed out, competing ions such as hydroxides and phosphates may cause precipitation to occur to some degree in the presence of the chelant. In such cases, the polymer is used to insure that precipitate deposition will be held to a minimum.

TABLE 3/3 - REACTION RATES OF TECHNICAL GRADES OF TWO CHELATES

METAL IONS	PPM/PPM METAL ION	
	EDTA	NTA
Calcium	4.67	2.75
Magnesium	4.67	2.75
Iron	8.35	4.90
Copper	7.35	4.30
Aluminum	17.30	10.00

6.5.2.2 Treatment for carryover

6.5.2.2.1 Carryover of boiler water with steam be first minimized by proper boiler design. Close attention to operating practices including restricting load swings, carrying proper water level, etc. shall be the second approach to reduce sus-

ceptibility to carryover problems. The last approach to be considered, will be the use of anti-foams. When the application of anti-foams is the only solution to problem attention is drown to the synthetic products. There are two major classes of anti-foams used in boiler waters-polyamides and polyoxy anti-foam.

6.5.2.2.2 A number of excellent polyamides are made from polyamines and carboxylic acids. For any given amine there will be a limited range of carbon atoms in the carboxylic acid for maximum effectiveness. Similarly, for a given acid the range of amines is limited. The most effective diamides can be made from ethylenediamine of diethylenetriamine and the most effective triamides from diethylenetriamine and the distearoyl amides of dibasic acids and of alkylenediamines.

6.5.2.2.3 Selective ion vaporization or carryover also can be a severe problem. Silica deposits on turbine blades are a frequent problem because of this selective characteristic. Severe problems also have been experienced with aluminum deposits. Such selective carryover is attacked by removing the ions from the makeup or feed-water, or in some cases, by limiting concentrations in the boiler water. Boiler water silica concentration is usually regulated to assure less than 0.02 ppm silica in the steam.

6.5.2.3 Corrosion reactions in the boiler

6.5.2.3.1 The way to prevent corrosion in boilers is to keep oxygen out, maintain proper alkalinity and keep the surfaces clean.

The problem of pitting is directly associated with the presence of dissolved oxygen and the development of deposits. The use of hydrazine or sodium sulfite together with the prevention of scaling are optimum means of minimizing this type of attack. The other corrosive agent, copper deposition, must be prevented by proper treatment of the feedlines and return lines. It should be noted that oxygen can enter the system by leakage, so it is essential to insure that an excess of sodium sulfite or hydrazine is present in the boiler. One method of insuring this excess is to add some of the oxygen scavenger directly to the boiler on a continuous basis.

6.5.2.3.2 The problem of corrosion, because of high localized NaOH concentrations, is generally attacked by one of a number of methods, all of which rely on proper ratios of various salts and alkalinity in the boiler-water. Thus, the need for close control of boiler-water composition and frequent analysis to verify the control becomes apparent.

The pH control situation is very complicated because while the hydroxyl ion will passive the surface, too much will cause cracking. The problem then is to use a system which substitutes something else for most or all of the NaOH as a source of alkalinity. The coordinated pH approach rests upon the premise that the alkaline pH should come from trisodium phosphates as much as possible rather than from NaOH.

6.5.2.3.3 Corrosion and scale formation in low-pressure boilers can be held to a minimum by maintaining the boiler water at a hydroxide alkalinity of 100 to 350 ppm and a total alkalinity of 300 to 500 ppm, both expressed as $CaCO_3$. Addition of silicates, carbonates, phosphates and chromates can make up the non-hydroxide alkalinities. In this case alkalinities up to 1000 ppm does no harm. Corrosion of boilers operating below 14 bars (200 psi) can be controlled by keeping total alkalinity at 10 to 15% of the total dissolved solids. When the boilers go over this pressure, deoxygenation of water is helpful. Alkaline phosphates can protect boiler steels subjected to a substantial amount of stress and the combined action of caustic soda and silica providing ratio of Na_3PO_4 to NaOH be equal to or greater than one to prevent caustic cracking. In drum-type boilers without stages of evaporation, the excess $PO_4^{\equiv}$ concentration should be maintained below 40 ppm and NaOH alkalinity at 9 ppm minimum. For boilers with stages of evaporation, the last stage should show a maximum of 100 ppm $PO_4^{\equiv}$ and a minimum in the boiler of 5 to 7 ppm, with the water tinged by phenolphthalein.

6.5.2.3.4 A ratio of Na_3PO_4 to NaOH equal to or greater than one is necessary to prevent cracking. Phosphated waters which produce cracking may invariably have more NaOH than $PO_4^{\equiv}$. It shall be noted that the use of an Na_3PO_4 to NaOH ratio is not certain and Na_3PO_4 functions well in the absence of hydroxide ions, a situation which occurs only infrequently in boilers.

Fig. 1/3 gives the relationship between pH and phosphate concentration and shows the areas in which caustic or phosphate will occur on evaporating surfaces. When pH and phosphate values intersect below the curve, the residue will be phosphate. Above the curve, free caustic will be present. Boiler water conditioned so its characteristics are represented in the area below the curve can be concentrated without raising the hydroxyl ion concentration appreciably.

6.5.2.3.5 Another approach to the prevention of caustic cracking involves the maintenance above a certain value of the ratio of sodium sulfate to alkalinity in the boiler water.

If chemically treated water is used along with condensate as the feed-water, then the ratio of (Cl^-) plus ($SO_4^=$) to NaOH should be no less than 5. Excessive alkalinity may be reduced by neutralizing with H_2SO_4 and then using an ion-exchange resin to free the water of excess alkalinity by replacing Na ion with H ion.

The most widely accepted chemicals for the prevention of caustic embrittlement are the nitrate ion and quebracho extract.

The amount of nitrate used is critical and must be 35 to 40% of the total alkalinity calculated as NaOH.
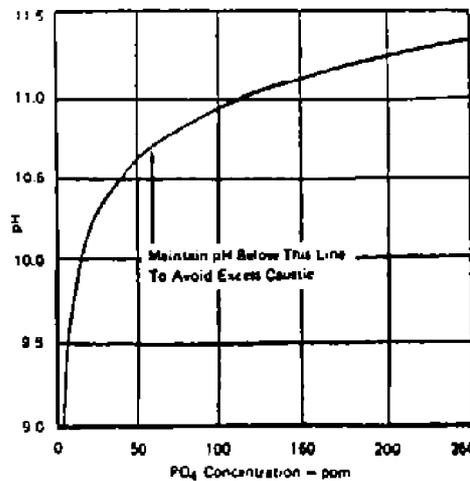
RELATIONSHIP BETWEEN pH AND $PO_4^=$ CONCENTRATION IN TERMS OF PREVENTION OF EXCESS CAUSTIC. (FIGURE COURTESY OF S.F. WHIRL. TRANS. ASME, (1942)
Fig. 1/3

The U.S. Bureau of Mines recommends using ratios depending on boiler operating pressure as given in Table 4/3. Potassium nitrate functions as well as the sodium salt and waste sulfite liquors containing $NaNO_3$ are also effective. Tannins and butyric acid (in the amounts of 0.5% of the amount of alkali present) are also effective in preventing caustic embrittlement.

TABLE 4/3 - U.S. BUREAU OF MINES RATIOS OF SODIUM NITRATE/SODIUM HYDROXIDE TO BOILER PRESSURE

UP TO BAR	RATIO $NaNO_3$/NaOH
17	0.20
27	0.25
48	0.40

6.5.2.3.6 For preventing chloride stress-corrosion attack of austenitic stainless-steel-tubed steam generators nitrate and sodium sulfite are effective inhibitors. The combination of the two is superior to either inhibitor alone or to any other inhibitor or combination. These inhibitors are effective in alkaline phosphate boiler water containing up to 500 ppm chloride.

6.5.2.3.7 The erosion-corrosion problem in boiler tubes is attacked by:

- Redesigning the system to avoid turbulent flow,
- eliminating deposits and keeping the tubes clean,
- preventing corrosion of the copper in the preboiler and post boiler systems, and,
- maintaining proper dosage of the corrosion inhibitors previously mentioned, especially the oxygen scavengers.

The solution thus becomes a combination physical and chemical approach.

6.5.3 Control of post boiler corrosion

6.5.3.1 Superheater

It was pointed out earlier that the corrosion of metal by steam at very high temperatures is not readily prevented by the use of corrosion inhibitors. The most satisfactory preventive technique involves the choice of suitable alloys, a procedure beyond the scope of this Engineering Standard (see IPS-E-TP-740).

Carryover of salts by steam is best attacked by preventing carryover. This is usually accomplished in the boiler by using properly designed steam separators and anti-foam agents (see Clause 6.5.2.2).

Corrosion due to condensation of steam in superheaters is treated in the same manner as corrosion of steam condensate and return systems (see Clause 6.5.3.1.1).

6.5.3.1.1 Steam condensate and return systems

6.5.3.1.1.1 The causes of corrosion in the steam condensate and return systems are oxygen and carbon dioxide. The development of corrosion inhibitors for these systems should therefore bear these two factors in mind. The first problem, corrosion due to oxygen, is generally attacked by techniques described for eliminating the oxygen content of boiler water (see Clause 6.5.1.2). This method usually insures that oxygen present in condensate will be derived essentially from leaks in the return systems. When oxygen leakage into the return system becomes sufficient to promote corrosion, then the preferred solution is a mechanical one designed to eliminate the leaks or else a metallurgical one calling for using proper alloys. Sodium sulfite can be added to the condensate system when oxygen can not be eliminated in any other manner. A preferred approach is to increase condensate pH with volatile amines. Raising the pH of the condensate will minimize oxygen attack.

6.5.3.1.1.2 A very successful approach to the problem of acidic corrosion caused by carbon dioxide cells for using volatile amines. They are added to the boiler water, volatilize along with the steam, condense with it, neutralize the carbon dioxide and produce a condensate having a neutral or alkaline pH. Alternately, they can be added to the steam lines. In either event, they stay with the steam and condensate with it, thus providing alkaline material at the places it is needed.

A number of amines have been employed for this purpose. The most obvious one is ammonia. The material is generally added as ammonium hydroxide or ammonium sulfate to the boiler feed-water with the resultant liberation of ammonia in the boiler. The major use of ammonia is in central stations with low percentage makeup and low carbon dioxide concentrations in the steam. When carbon dioxide concentrations are quite high, as they tend to be in industrial plants, the required ammonia level for neutralization becomes high and this treatment runs into the disadvantage of serious corrosion of copper and zinc-bearing metals. For this reason, other neutralizing amines have been developed which are not corrosive to copper at the dosages required for carbon dioxide neutralization.

The two neutralizing amines used most frequently are morpholine (C_4H_9NO) and cyclohexylamine ($C_6H_{11}NH_2$). Both chemicals are being sold in considerable quantities under different trade names by inhibitor manufacturers.

At 25°C, the pH at which carbonic acid is completely converted to morpholine bicarbonate is slightly higher than 7.3, but it shall be noted that contamination of the condensate by 1% of a synthetic boiler water raised the pH from 7.3 to 8.0 and lowered the untreated corrosion rate. Due to this phenomenon plants having trouble with boiler-water carryover in the steam usually do not have condensate corrosion problems as serious as those where there is no carryover. Morpho-

line is stable at high temperatures and pressures and is evenly distributed. For effective corrosion control, a pH of 8.8 to 9.0 and a morpholine residual of 3 to 4 ppm are maintained. Morpholine is stable up to a boiler pressure of 170 bars (2500 psi) and to 650°C (1200°F) in superheated steam.

Cyclohexylamine and dicyclohexylamine as inhibitors can prevent the corrosion of iron by steam condensate containing oxygen and carbon dioxide. Several other volatile amines such as benzylamine, 2-diethylamineothanol, ethylene di-amine, and amine alcohols are also effective.

6.5.3.1.1.3 The concentration of an amine at any location in a steam-condensate system is dependent on the distribution ratio. This ratio is a comparison of the amount of amine in the steam versus the amount present in the condensate. The ratio for cyclohexylamine is 3 whereas that for morpholine is only 0.4. This would indicate that the greater concentration of morpholine will be found in the condensate. This characteristic makes it well suited for applications in central stations where protection is required in the wet end of high pressure turbines. The relatively high distribution ratio of cyclohexylamine makes it more applicable in extensive steam-condensate systems found in refineries and petrochemical plants.

The differing distribution ratios of the volatile amines have been used in commercial return line corrosion inhibitors. These inhibitors are generally combinations of morpholine and cyclohexylamine so blended as to obtain the benefits of the differing distribution ratios. Amine requirements are approximately 3.6 ppm morpholine (40%) or 3.0 ppm cyclo-hexylamine (40%) per ppm of carbon dioxide to elevate condensate pH to 7.0.

The volatile amines can be added to the steam condensate system by addition to the feed-water, boiler, or return lines, but there are some advantages and disadvantages for each approach. Some prefer direct addition to the boiler or else the feed-water. One objection to this method is that it becomes necessary to treat the entire system to obtain adequate protection in a desired localized section. In the latter case, the preferred method is direct injection of the inhibitor into the steam or condensate lines by means of a chemical feed pump.

6.5.3.1.1.4 Another approach to prevention of steam condensate and return line corrosion is that of using "film-forming" chemicals to lay down a protective film on surfaces. This approach has come into widespread use with development for this purpose of suitable long-chain nitrogenous materials. It is specially effective in systems where high concentrations of carbon dioxide make the use of neutralizing amines uneconomical.

One approach to this method is inhibition by film forming techniques involved materials such as sodium silicate, oils or polyphosphates. Sodium silicate reduces corrosion but can not prevent it entirely. A very successful approach is the use of long-chain nitrogenous compounds as film-formers for condensate and return lines. They do not normally accumulate in the boiler because they either are eliminated at the vent of the deaerating heater or steam distill from the boiler water. While a number of materials are now being employed, octadecylamine ($C_{18}H_{37}NH_2$) and its salts are most frequently used and typify this class.

The film-forming inhibitors, as well as the emulsifying or dispersing materials that may be used with them, have strong surface active properties. Consequently, their introduction into the system can result in the loosening of previously formed deposits and clogging of the lines by these materials. For that reason it may be better to clean the lines before starting to use the inhibitor or alternately to clean out the system after the loosened deposits have begun to accumulate. This cleaning will improve heat transfer as well as corrosion inhibition.

The use of film-forming inhibitors becomes economical when the carbon dioxide content of the steam is so high that the cost of using sufficient neutralizing amine is excessive. By contrast, the dosage of filming amines is independent of dissolved gas concentration. Typical dosage is 0.5 to 10 ppm with 2 ppm as the recommended level. On the other hand, levels of 15 to 30 ppm of a commercially dispersed filming amine to establish and maintain the desired corrosion resistant film on the metal surfaces is recommended. By using a treatment level of 3 to 4 ppm of octadecylamine, can achieve satisfactory inhibition of the distribution system of a large process steam plant caused by 2 ppm oxygen and 4 to 5 ppm carbon dioxide in the condensate and makeup. Interruption of treatment for a few hours can be tolerated because of the film that had been built up.

The rate at which the protective film builds up is quite important. The effectiveness of inhibitor is also a function of time and the corrosion rate decreases gradually if sufficient amount of inhibitor is not used. For this reason the film-forming inhibitors can be classified as "dangerous". If enough inhibitor to form a continuous film is not used, then anodic action leading to severe local attack can occur. It is desirable to start treatment at a high dosage level to lay down the protective film rapidly and then to reduce the treatment level to that necessary to maintain and repair the film.

There is some disagreement as to the desirable feeding point for film-forming inhibitors. All inhibitor suppliers say that the materials can be fed directly to the steam and condensate systems. Some suppliers recommend adding the inhibitor to the feed-water or directly to the boiler and say that the inhibitor will evaporate with the steam and condensate in a thin, continuous film. However, most of the commercially available filming inhibitors are formulated products, each component having a somewhat different volatility (and solubility) and, therefore, the preferred point of addition should be the steam header.

In some cases, the use of filming amines has led to deposit formation, particularly following the use of the first developed inhibitor, octadecylamine acetate. These deposits were polymerized amine and oil-oxide combinations. It was originally thought that overfeed of the inhibitor was the only cause of these accumulations, but investigation led to the conclusion that the octadecylamine acetate had polymerized with iron oxide and/or oxygen. Improved formulations were developed to eliminate this problem. Current commercial inhibitors have stabilizing agents which inhibit polymerization and thus deposit formation.

6.5.4 High temperature hot water systems

A high temperature hot water system is usually defined as a system operating above 149°C (300°F). The corrosion problems associated with such systems are summarized below:

6.5.4.1 Acidity (low pH due to carbon dioxide and/or decomposition of organic matter).

6.5.4.2 Dissolved gases (primarily oxygen).

6.5.4.3 Galvanic action (due to contacts among dissimilar metals).

In a properly designed system there is little opportunity for scale formation, because there is no evaporation within the system and thus little makeup water is needed. Therefore, solids in makeup water do not concentrate and saturation values are not exceeded. However, when designing such a system, it is a good practice to include the use of pretreatment such as zeolite softening. Demineralized water also may be used sometimes as makeup.

Characteristics of makeup water are important with respect to corrosion in high temperature hot water systems. If the circulating water pH is properly adjusted, much of the corrosion potential can be minimized. In all-steel systems, the pH can be adjusted to 11.0 to minimize corrosion. However, in bimetallic systems, pH values shall not be allowed to reach this level because of possible reaction of the alkalinity with brass, bronze, copper and/or aluminum.

Before a new hot water system is put into operation, it shall be cleaned of all pipe dope, grease or cutting oils, dirt, sand and soldering flux. If these substances are not removed, they may result in the formation of concentration cells and greatly increase the corrosion load. Phosphates are most commonly used for cleaning. A satisfactory cleaning solution is a 2% solution of sodium hexametaphosphate or sodium tripolyphosphate.

Chromates, nitrates, nitrites, borates and silicates have been employed as corrosion inhibitors in hot water circulating systems. However, their use must be carefully controlled because they can cause problem in mechanical or patent circulating pump seals. Evaporation can occur, resulting in crystallization of the inhibitor with resulting wear on moving parts. Buffered chromates at 150 to 250 ppm concentration have been employed successfully.

6.6 Selection of Inhibitors

Regarding to this Engineering Standard, when the situation dictates the use of inhibitor(s) for treatment of the boiler systems reference shall be made to the provisions of Section 13 as well as to this Section (6).

7. TREATMENT OF ACID SYSTEMS

7.1 Industrial Exposures of Metals to Acids

Metals are exposed to the action of acids in many different ways and for many different reasons. The exposures can be most severe but in many cases, the corrosion can and shall be controlled by means of inhibitors. Processes in which acids play a very important part are:

7.1.1 Acid pickling (see IPS-C-TP-101)

In these processes, undesirable oxide coatings are removed from metals-usually ferrous metals-and the surface is prepared for further operations, such as phosphate coating, enameling, electroplating, painting, etc. The acid of choice has for many years been sulfuric acid.

7.1.2 Industrial acid cleaning

This very important procedure is applied chiefly to the removal of scale and other unwanted deposits from steam generating equipment and from chemical and petrochemical reaction vessels as well as cooling system. Hydrochloric acid is widely used, frequently with an important assist from hydrofluoric acid or fluorides.

Tests, reported by NACE, showed that at 74°C, concentrations of inhibitor at 0.03% reduced corrosion rates in 5, 10 and 20% acid from 0.1 to a little more than 0.001 mg/cm²/day, rates at all three concentrations clustered about the same point. At 95°C, under the same conditions, results were more scattered, the rate for 10% acid being reduced from 0.1 mg/cm²/day for the uninhibited control to a little less than 0.01 mg/cm²/day in 5% acid; with slightly increased corrosion rates for the 10 to 20% concentrations. Rates of all three at 95°C were less than 0.01% for 0.03% inhibitor concentration.

7.1.2.1 Cleaning of oil refinery equipment

7.1.2.1.1 Maximum temperature for inhibited hydrochloric acid used for cleaning cast iron in petroleum refinery equipment is 51°C (125°F), while other metals can be cleaned safely at 77°C (170°F). Using 7.5% acid at 77°C (170°F) causes graphitization of some cast irons, particularly those with combined carbon.

7.1.2.1.2 In cleaning systems that include stainless steel, extreme care must be used to assure that all the acid is thoroughly flushed from the system because retained chloride ions will cause disastrous stress corrosion cracking. Copper, plating out on steel surfaces from ions dissolved from copper tubing in heat exchangers, is another hazard of circulating cleaning procedures. Copper ions react with the iron in an oxidation reduction against which most inhibitors are ineffective.

7.1.2.1.3 Production of explosive and poisonous gases is a hazard in acid cleaning. Hydrogen gas must be vented and precautions taken against fire and sparks. Hydrogen sulfide, hydrogen cyanide, arsine and phosphine have been found in vessels being cleaned. Neutralization of these gases by caustic or burning or venting to the atmosphere is necessary.

7.1.2.1.4 Because ferric ions accelerate corrosion by cleaning solutions, a limit of 0.4% by weight usually is the "accepted" maximum. A 1% solution of ferric ions has been known to increase the corrosion rate by a factor of nine.

7.1.2.1.5 Table 5/3, test reported by NACE, shows some of the results achieved with various inhibitors in reducing corrosion rates of refinery equipment from acid cleaning solutions.

Stannous chloride, lead nitrate and lead acetate have been tested in efforts to reduce accelerated carrosion that sometimes occurs in crevices; however, they are ineffective in the presence of hydrogen sulfide. Accelerated attack also may occur because of galvanic couples between metals differing in their solution potentials. Low carbon steel was 0.031 mv positive to Type 304 steel in one test.

TABLE 5/3 - INFLUENCE OF INHIBITORS IN 5% HYDROCHLORIC ACID ON RATES OF DISSOLUTION OF IRON OXIDES AND SULFIDES[1]

	% INHIBITION IN DISSOLUTION OF:					
INHIBITOR	LOW C STEEL	FREE MACHINING STEEL	FeS	FeS_2	FeO	Fe_3O_4
C	66	71	5	(-)	13	170
B	98.2	99.7	50	(-)	38	12
A	99	99.9	23	(-)	62	(-)
D	98.5	—	15	(-)	75	10

Note:

(-): Sign indicates slight acceleration of dissolution. In the case of Fe_3O_4 in inhibitor C, acceleration of dissolution as compared with plain 5% HCl was by 170%.

1) All tests at 66°C (150°F) in 5% acid for 2 hours.

7.1.2.1.6 Spent acid from one cleaning operation should not be used in another cleaning operation because of possible bad effects from concentrations of cupric or ferric ions in the used solutions. All stainless steel systems can be cleaned effectively using sulfuric or nitric acid solutions. Stainless steels that have reached their sensitization temperature are likely to suffer inter-granular attack.

7.1.2.2 Heat exchangers

By injecting hydrochloric acid solutions of 1-2N concentration and containing a commercial inhibitor directly into cooling water immediately before it enters an operating heat exchanger, the exchanger can be cleaned on-stream. This procedure, exposes the copper tubing to the acid for several minutes with no apparent bad effect. Scale removes by the treatment along with residual acid is recirculated in the system with no apparent bad effect. Inhibitors are very important in chemical cleaning and their selection and use are important ingredients in a successful job.

7.1.2.3 Oil well acidizing

For oil well stimulation, large quantities of acid-usually hydrochloric are pumped at high rates of flow through the oil well tubing into the producing formation. The primary objects is to act on the formation in such a way as to stimulate the oil flow. If the nature of the formation requires it, hydrofluoric acid is added to the hydrochloric acid.

Oil well acidizing represents a severe test for inhibitors. The acid concentrations are high -usually 10 to 15% HCl by weight and at the times 28%. Temperatures at the bottom the hole can be as high as 177°C (350°F).

Effects of agitation, exposure, time, acid type and concentration and inhibitor concentration at 38 to 177°C (100 to 350°F) are reported.

7.1.2.4 Manufacturing processes

In this very broad field, very little that is specific can be said. Usually it is the intent of the manufacturer to select reaction vessels from alloys that will be resistant to reactants and products in his process. If this is not feasible, other means must be used for protection, one of which could be the use of inhibitors.

It is usually desirable to select alloys that are resistant to acid to be stored. When this is not possible, it is necessary to protect the metal (usually mild steel) by means of a suitable inhibitor.

7.1.2.4 Vapor-liquid systems: condensing vapors

One of the most important examples of corrosion from condensing acid vapors is that of combustion gases, where SO_2 is converted to SO_3, which forms sulfuric acid by reacting with water condensed in the cooler zones of the combustion equipment. Attempts shall be made to protect such zones by means of inhibitors.

7.2 Selection of Inhibitors

Selection of inhibitor for a particular application shall be in accordance with the provisions of this engineering Standard. In addition selected inhibitor shall be capable of maintaining the corrosion rates to as minimum as possible. For treatments of acid environments in addition to this Section 7 reference is also made to Appendix B.3 and NACE Publication ISBN 0-915567-67-9 Section "Inhibitors in Acid Systems".

APPENDICES

APPENDIX A.3
PREDICTING SCALE FORMATION

A.3.1 Value of calculations

The values obtained from these calculation procedures should be taken only as guidelines. They indicate the likelihood of scale formation. Many assumptions had to be made in developing the method of calculation which may not apply to the specific water being evaluated.

If scale formation is indicated by calculation, it serves as an alarm. If you are looking at a possible water source, you should avoid those which show scaling tendencies or make provision for treatment. Similarly, one should avoid mixing waters where the blend exhibits scaling tendencies under system conditions.

Scale

Some of the critical properties of water change very quickly after sampling. These properties shall be determined in the field immediately after the sample is taken in order to determine an acceptable scaling tendency. Two properties which shall be determined in this manner to have any value are pH and bicarbonate (HCO_3^-). The instant that the pressure is reduced, any dissolved "acid gases" (H_2S and (CO_2) will begin to escape from the water and the pH will begin to rise. The loss of dissolved CO_2 will have a direct effect on the bicarbonate and carbonate concentrations. Generally only the bicarbonate determination is needed; carbonate concentration is small.

A.3.2 Calcium carbonate

A.3.2.1 Calcium carbonate precipitation is caused by a shift toward carbonates in the carbonate-bicarbonate-carbon dioxide equilibrium. When the equilibrium shifts in the other direction, the precipitate goes back into solution. Since there is usually considerable delay between the establishment of an equilibrium and the precipitation or solution of calcium carbonate, unstable conditions exist in which a water will precipitate or dissolve calcium carbonate on standing.

A.3.2.2 Langelier developed an equation setting forth the conditions of carbonate equilibrium. By the use of this equation the pH of a water at equilibrium can be calculated. If the pH is higher than the calculated pH, the water has a tendency to form scale. If it is lower, the water has a tendency to be corrosive. Langelier's equation can be expressed in a single form as follows:

SI = pH - pCa - pAlk - K

Where:

SI is the stability index. A positive index indicates scale formation. A negative index indicates corrosion. This equation was derived with many assumptions which do not apply in all cases. Because of this, do not apply the results too adamantly. If SI is +0.5 or above, consider the system as having a tendency to scale. Any value between 0.5 and 2.5 will indicate a probable scaling problem; the higher the value, the more likely the formation of scale.

pH is the pH of the water sample as actually determined. The value must be determined in the field immediately after the sample is taken to be reliable. Record the pH value on the bottle label or on the Lab Request sheet.

pCa is the negative logarithm of the calcium concentration.

pAlk is the negative logarithm of the total alkalinity. Bicarbonate $(HCO_3)^-$ must be determined in the field, and handled in the same manner as pH. If bicarbonate and pH are not determined accurately on the fresh water sample the calculated SI loses most of its value.

K is a constant, the value of which depends on the total salt concentration and the temperature.

Scale

A.3.3 Calculation

A water analysis plus Tables A.1 and A.2 are used to calculate SI. The bicarbonate $(HCO_3)^-$ and pH values are those determined in the field on the fresh sample. Factors used in the calculation of ionic strength (μ) are given in Table A.2. The procedure for calculating SI is shown in Tables A.1 and A.2.

TABLE A.3.1 - FORM FOR CALCULATING SCALING INDEX

ppm		eq gr epm	Factor
HCO_3^-	—	61.1	5×10^{-4}
Cl^-	—	35.5	5×10^{-4}
SO_4^{--}	—	48	1×10^{-3}
Ca	—	20	1×10^{-3}
Mg^{++}	—	12	1×10^{-3}
Na^+	—	—	5×10^{-4}

pH
* pCa
* pAlk

$$SI = pH - (pCa + pAlk) - K$$

* K = at 15.6°C	**SI at 15.6°C**
37.8°C	**37.8°C**
49°C	**49°C**
71°C	**71°C**

* Get values from the respective graphs.

TABLE A.3.2 - SI CALCULATION

	ppm[1]				epm		Factor		
HCO_3^-	878	-[2]	61.1	=	14.37	×	5×10^{-4}	=	0.007
Cl^-	47.000	-	35.5	=	1,322	×	5×10^{-4}	=	0.661
SO_4^{--}	3,910	-	48	=	81.5	×	1×10^{-3}	=	0.081
					1,417,9				
Ca^{++}	2,560	-	20	=	128.0	×	1×10^{-3}	=	0.128
Mg^{++}	826	-	12	=	68.9	×	1×10^{-3}	=	0.070
Na^+				=	1,221.0[3]	×	3×10^{-4}	=	0.611
					1,417,9			=	1.558[6]

pH$^{(2)}$ = 6.9

pCa$^{(4)}$ = 1.20   SI   = pH - (pCa + pAlk) - K

pAlk$^{(5)}$ = 1.84 = $\dfrac{3.04}{3.69}$(subtract)

K$^{(6)}$ = 3.53 at 20°C.   SI   = +0.33 at 20°C$^{(7)}$

              = 3.14 at 40°C.   = +0.72 at 40°C$^{(8)}$

Notes:

1) From lab. water analysis (see Table A.3.3).

2) Determined in the field immediately after the sample is taken.

3) Determine emp of Na to make total emp of the cations equal the emp of the anoins.

4) From Fig. A.3.1.

5) From Fig. A.3.1 using ppm of (HCO_3^-).

6) Use æ to calculate K at specific temperature from Fig. A.3.2.

7) Shows a tendency to scale.

8) More likely to scale as temperature goes up.

TABLE A.3.3 - WATER ANALYSIS FIELD, LEASE OR WELL

CHEMICAL COMPONENT	ppm
Chloride (Cl)	47,000
Iron (Fe)	
Total Hardness ($CaCO_3$)	9,800
Calcium (Ca)	2,560
Magnesium (Mg)	826
Bicarbonate (HCO_3)	878
Carbonate (CO_3)	0.0
Sulfate (SO_4)	3,910
Hydrogen Sulfide (H_2S)	strong
Specific Gravity	1,047
Density, kg/m³ (lb/gal)	
pH-Beckman ( ) Strip ( )	6.9
SI at 15.6°C	35
SI at 37°C	60
SI at 49°C	95
SI at 71°C	1.70

From a gypsum solubility curve based on the brine content, this water would be positive for scaling calcium sulfate.

By Stiff and Davis method a positive index indicates calcium carbonate is likely to precipitate; a negative index shows corrosive tendencies.
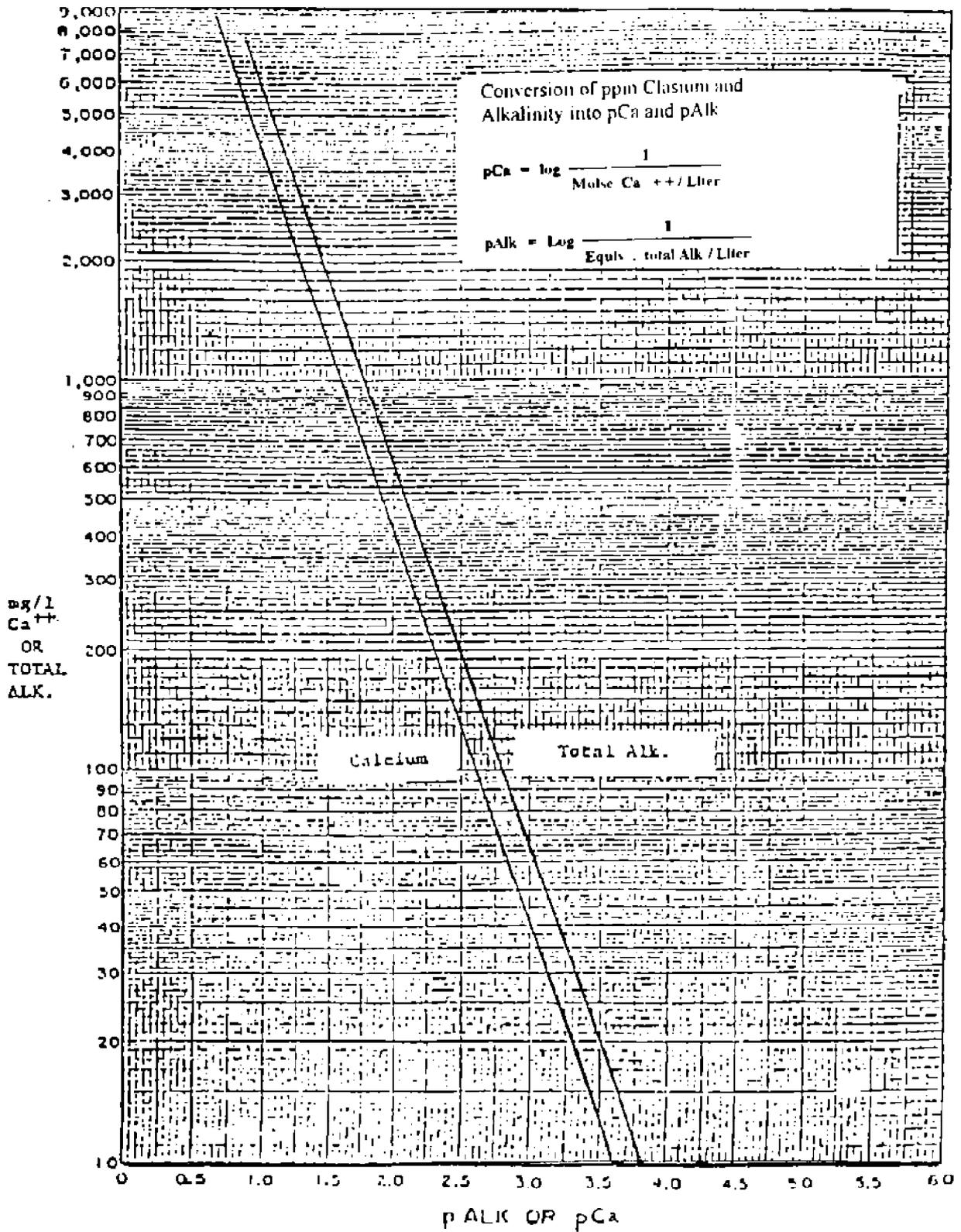
**GRAPH FOR CONVERTING PARTS PER MILLION OF CALCIUM AND ALKALINITY
INTO pCa AND pAlk
Fig. A.3.1**

(The total ionic strength is the sum of the ionic strength or the individual ions).

ION	FACTOR ppm	FACTOR epm
Na^+	2.2×10^{-5}	5×10^{-4}
Ca^{++}	5.5×10^{-5}	1×10^{-3}
Mg^{++}	8.2×10^{-5}	1×10^{-3}
Cl^-	1.4×10^{-5}	5×10^{-4}
HCO_3^-	0.3×10^{-5}	5×10^{-4}
SO_4^{--}	2.1×10^{-5}	1×10^{-3}
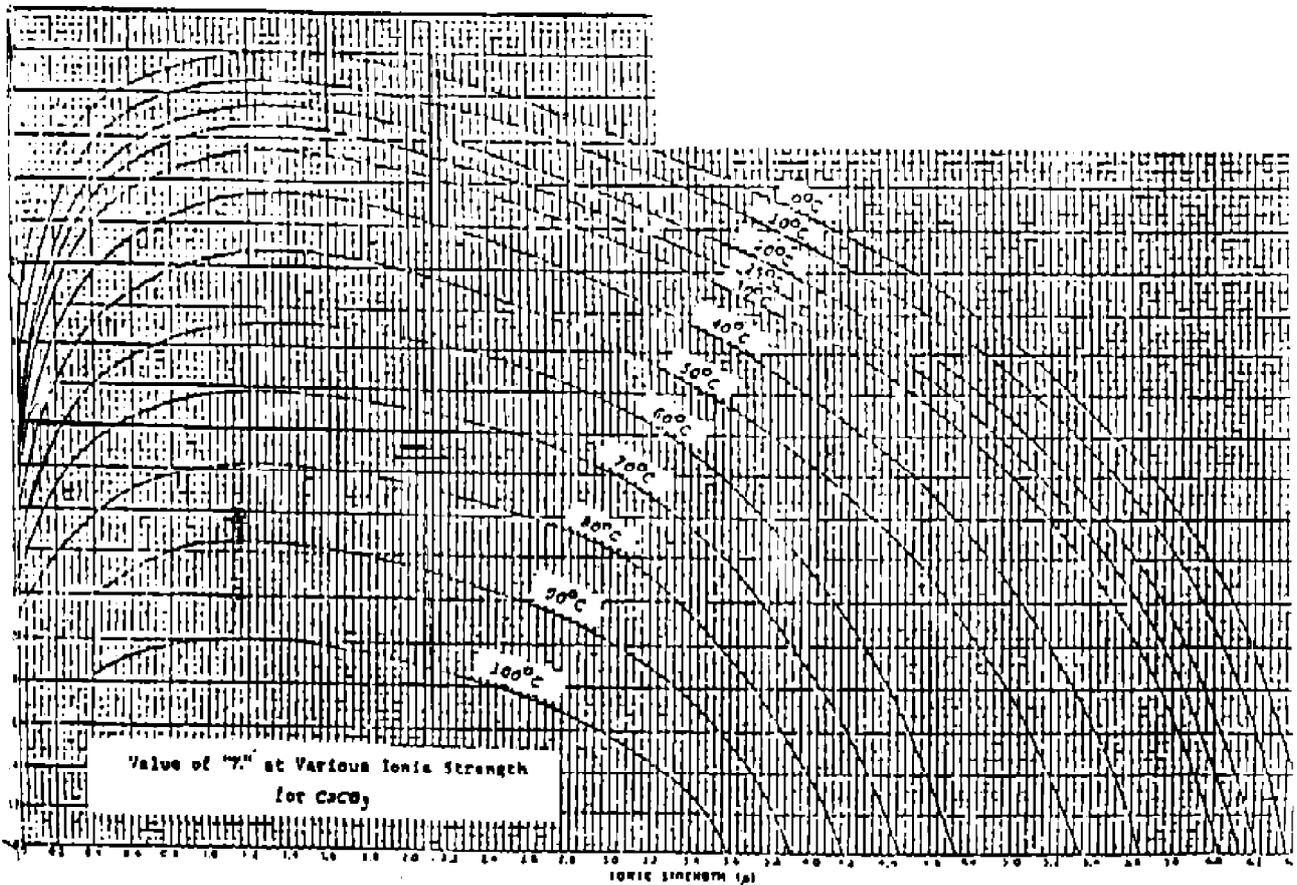
VALUES OF K AT VARIOUS IONIC STRENGTHS
Fig. A.3.2

A.3.3 Calcium sulfate

Fig. F.3 illustrates the increase of gypsum solubility with increased chloride content. This chart is drawn for relative values of $SO_4^=$ and Ca^{++} against chloride content. The chart may be used with assurance when the points fall well to the left and below the NaCl lines, indicating negative gypsum formation, or to the right and above indicating positive gypsum formation.

THEORETICAL MAXIMUM CONCENTRATION

Na_2SO_4 as $SO_4^=$ vs. $CaCO_3$ as Ca^{++} 29.4°C
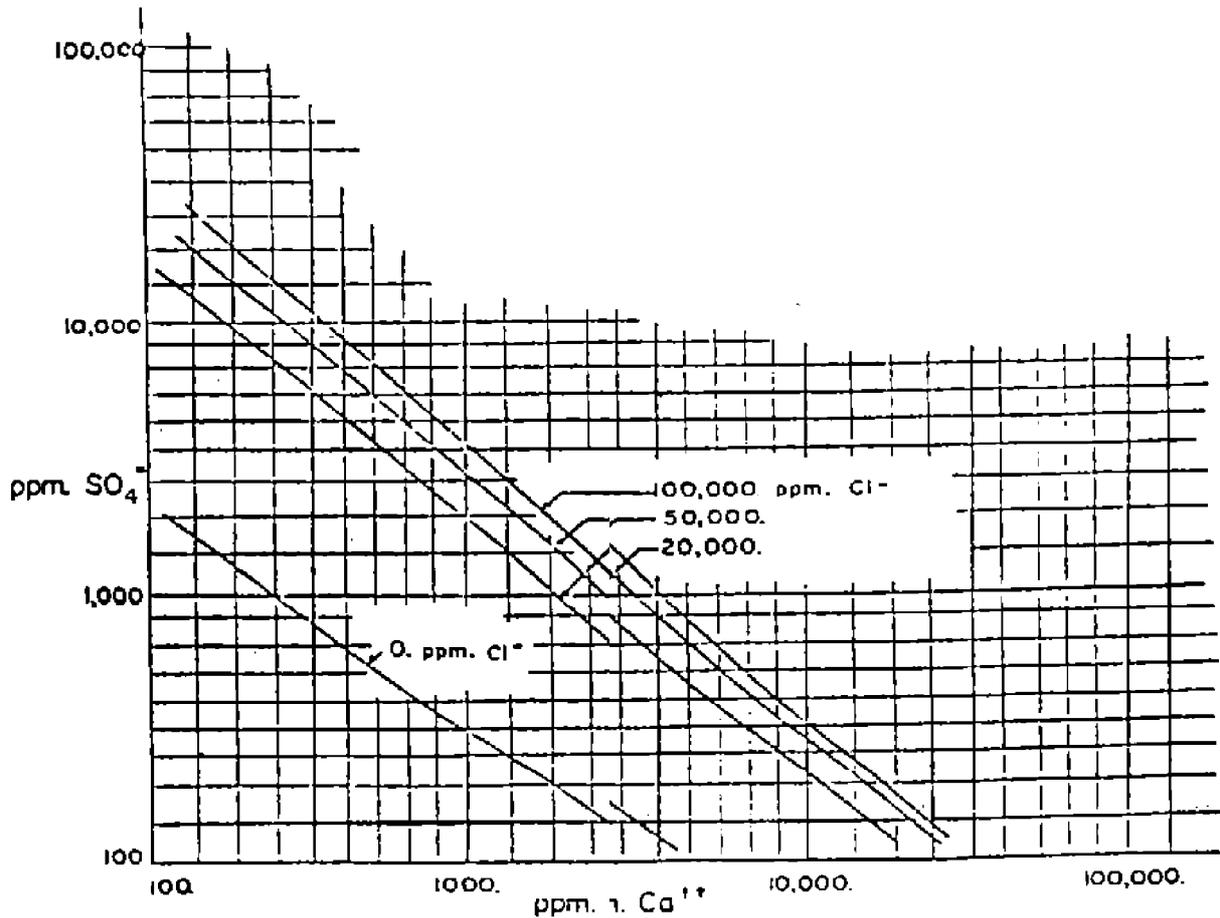
GYPSUM SOLUBILITY CURVE
Fig. A.3.3

A.3.4 Barium sulfate

Because $BaSO_4$ has such limited solubility, the appearance Ba^{++} and $SO_4^=$ ions in any water indicates a strong possibility of scale formation. The data of Templeton giving the solubility of barium sulfate in brine at various temperatures is given in Fig. A.3.4. It can be used to determine the approximate conditions under which barium sulfate scale will form as shown in the following examples:

Examples:

1) A mixture of equal parts of a brine containing 40 mg/l of a barium and 20.000 mg/l of chlorides was made with a brine containing over 100 mg/l of sulfates and 1,000 mg/l of chlorides. Would barium sulfate scale form?

Answer:

Mixing the two brines would provide a water that contained 20 mg/l of barium and 10.500 mg/l of chloride. Consulting the graph would show that 20 mg/l of barium would be soluble only when the following chloride concentrations and temperatures were provided.

CHLORIDES mg/l	TEMPERATURE
19,000	80°C
25,000	65°C
48,000	50°C
60,000	25°C

Barium sulfate scale would form by equal mixtures of the two waters described above.

2) Would barium sulfate deposit from a mix containing 35 mg/l of barium and 100,000 mg/l of chlorides at 65°C if it were allowed to cool to 25°C?

Answer:

Yes, the solubility of barium is at its maximum at 65°C. Any cooling of the water would lower the solubility and precipitate barium sulfate.

Testing

Table E.5 offers a guide to the field identification of scales and probable causes. The use of this abbreviated chart is often complicated by appreciable amounts of oil and corrosion products being in the deposit. It is seldom possible to make a satisfactory examination of a scale which is oil soaked. After removal of most of the oil from compact scales, the criteria for tentative identification are usually made apparent by viewing with a hand lens and testing acid solubility.

The procedure to be followed in a complete laboratory analysis of the scale sample is given in Table A.3.4. A Scale Analysis Report is shown in Table A.3.5.
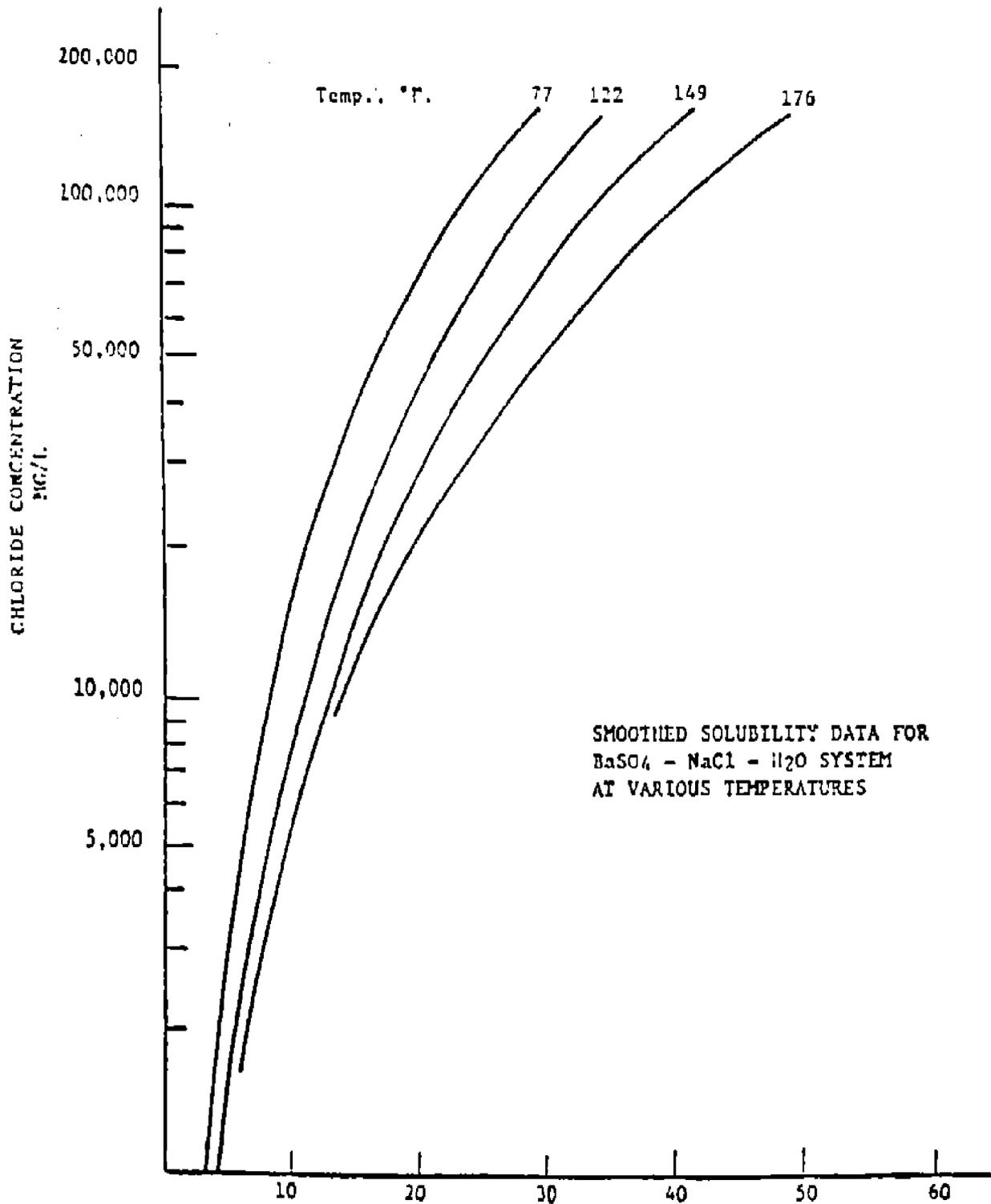
BARIUM SULFATE SOLUBILITY AS mg/l BARIUM
Fig. A.3.4

TABLE A.3.4 - GUIDE TO IDENTIFICATION OF SCALES AND PROBABLE CAUSES

Reference: Case, L.C. Water Problems in Oil Production, pp. 23-25

PHYSICAL APPEARANCE	ACID SOLUBILITY etc. (15% HCl)	INDICATED COMPOSITION AND ORIGIN
1. White or Light-colored: 1.1 Hard, compact, fine granular	Insoluble	$BaSO_4$, $SrSO_4$, $CaSO_4$. Incompatible waters.
1.2 Compact, with long, pearly crystals	Powder dissolved slowly with no gas bubbles Solution gives $SO_4^=$ test with $BaCl_2$	Gypsum - $CaSO_4 . 2H_2O$. Incompatible waters or supersaturation.
1.3 Compact, fine grain or crystals which break into rhombohedrons	Easily sol. in HCl with gas bubbles	$CaCO_3$ or mixture of $CaCO_3$ and $MgCO_3$ if more slowly dissolved. Supersaturation, rarely incompatible waters.
2. Dark Colored, Brown to Black:		
2.1 Compact, brown	Essentially insol. brown color dissolved on heating. Acid turns yellow. White insol. residue.	See 1.1 and 1.2 above for white residue. Brown, iron oxide is corrosion product or precipitate due to oxygen.
2.2 Compact, black	Black mtl. dissolves slowly with evolution of H_2S, white insol, residue.	See 1.1 and 1.2 above for residue. Black color is iron sulfide corrosion product, in-compact, waters, or both.
2.3 Compact, brown or black	Easily sol. in 4% HCl (Dilute 15% 1:4) with gas bubbles. Brown or black color remains.	$CaCO_3$ with iron oxide or iron sulfide coloring matter.
2.4 Soft muck, usually brown or black:		
2.41	Insoluble	See 1.1 above
2.42	Dissolved, no bubbles	See 1.2 above
2.43	Dissolved, gas bubbles	See 1.3 above
2.44	Insoluble, except brown mtl., yellow solution	Iron oxide, see 2.1 above
2.45	Black material dissolves evolution of H_2S	Iron sulfide, see 2.2 above

Discussion of inert residue and organic slime is omitted from the above outline. it should be emphasized that acid-insoluble residue occurs in all scale deposits, sometimes being the major ingredient. Also "soft muck" deposits may contain all the others, in finely-divided state, and their recognition difficult due to more or less organic slime.

TABLE A.3.5 - SCALE ANALYSIS
USUAL REACTION OF COMPOUNDS, IN SOLUTION IN WATER, TO FORM SOLID DEPOSITS

1) $BaCl_2 + Na_2SO_4 = BaSO_4 + 2NaCl$	Barium Sulfate, in compact, waters.
2) $SrCl_2 + MgSO_4 = SrSO_4 + MgCl_2$	Strontium sulfate, as above.
3) $CaCl_2 + Na_2SO_4 = CaSO_4 + 2NaCl$	Gypsum, carbonate, by incompact. waters or supersat.
4) $2NaHCO_3 + CaCl_2 = CaCO_3 + 2NaCl + CO_2 + H_2O$	Calcium carbonate, by incompat. waters.
5) $Ca(HCO_3)_2 = CaCO_3 + CO_2 + H_2O$	Calcium carbonate, by supersat., due to pressure decrease, heat agiation.
6) $Fe + H_2S = FeS + H_2$	Corrosion. Iron sulfide may deposit or cause "black water".
7) $2Fe_2O_3 + 6H_2S = 2Fe_2S_3 + 6H_2O$	Inherent H_2S, or that from corrosive bacteria, combines with iron oxide in solution or suspension.

Weigh 2 gms. of scale sample into a 100 ml. breaker. If the scale is white, you can proceed to test for $CaCO_3$ and then $CaSO_4$. If it neither dissolves in 1:1 HCl nor T-306, run a $NaCO_3$ fusion and test for Ba. and Sr.

I) Paraffins

    a) Boil the sample with benzene and decant.

    b) Repeat step A. until the benzene remains light in color.

    c) Decant, dry and weigh.

Calculation:

$$\frac{100 \ (\text{Initial wt.} - \text{final wt.})}{\text{Initial wt.}} = \% \text{ wt. paraffin}$$

II) Acid Solubles

    a) Total Acid Soluble:

        1) Crush the dried residue and boil with 25 ml. of 1:1 HCl. (At this point place a piece of moist lead acetate paper above the beaker. If it turns dark, FeS is present).

        2) Allow the residue to settle and decant the acid into a graduated 250 ml. beaker.

        3) Repeat to assure the $CaCO_3$, FeS or Fe_2O_3 has dissolved.

        4) Wash with 25 ml. hot water and decant the water into the same 250 ml.

        5) Dry and weigh.

Calculation:

$$\frac{100 \ (\text{ wt. of benzene insol. residue} - \text{wt. of acid washed residue})}{\text{wt. of original sample}}$$

    b) Iron Oxide and Calcium Acid Phosphate.
(Fe_2O_3 is usually brown, red, or black in color).

        1) Dilute acid solution to 100 ml.

        2) If a white precipitate flocculates when the acid solution is diluted, dissolve about 2 grams of the original samples in 50 ml of conc. HCl and filter. Dilute the resultant filtrate to 100 ml., boil 30 minutes, and 5 ml. of 5% sodium molybdate solution and 5 ml. of amino solution while hot. Reheat to a boil and cool. A resultant blue color indicates the scale is calcium acid phosphate.

        3) If the white precipitate does not appear titrate this solution with 40% stannous chloride in hydrochloric acid, using a 2 ml. pipette until the yellow color disappears. (If it changes after one or two drops, then it can be assumed there is no iron dioxide).

Calculation:

$$\frac{100 \ (\text{ ml. } SnCl_2) \ (0.28)}{\text{wt. of original sample}} = \% \text{ iron oxide}$$

    c) Total Iron and Iron Sulfide

(FeS is magnetic, black and stickly and gives a positive test with lead acetate paper).

1) After adding the $SnCl_2$ solution to the end point in Part II, B, add one drop in excess.

2) Cool the solution and add 15 ml. of saturated $HgCl_2$ solution.

3) Two minutes later add 50 ml. of 50% phosphoric acid and 6 drops of diphenylamine sulfonic acid.

4) Titrate with standard $K_2Cr_2O_7$, 0.1913 M.

5) Calculation:

$$\frac{(100)\ (0.1)\ (ml.\ K_2CR_2O_7)}{\textbf{Total wt. of sample}} = \%\ \textbf{Total Iron as Iron Sulfide}$$

6) % Iron sulfide = Total Iron - % Iron Oxide

(This can be done because the percent of iron in iron oxide is nearly the same as it is in iron sulfide).

III) Asphaltense or Sulfur

a) If the residue from the acid washing is black, ignite a portion of the original sample.
b) If SO_2 (From the acid odor) is formed, the residue is sulfur.
c) Otherwise it is an asphaltene.
d) Estimate % by subtracting benzene and acid solubles and the weight of the residue after burning.

IV) Calcium Sulfate

(If the scale consists of shiny white crystals, a qualitative test for $CaSO_4$ should probably be run first).

a) If asphaltenes or sulfur are present, burn the original sample and dissolve in hydrochloride acid to remove the acid solubles.

b) Place either this residue or the light residue from the acid treatment in boil hydrogen peroxide. If the solid dissolves, $CaSO_4$ is present.

c) Also dissolves calcium sulfate with the evaluation of gas.

Calculation:

$$\frac{100\ (\textbf{wt. of soild dissolved in }H_2O_2\textbf{ or C - 31})}{\textbf{wt. of total sample}} = CaSO_4$$

V) Barium Sulfate and Strontium Sulfate

a) If the sample does not react in any of the above tests, then the scale is probably either barium sulfate or strontium sulfate, and a sodium carbonate fusion is necessary. Usually these samples are white.

b) Place the sample in a mortar with three times as much sodium carbonate by weight and 0.5 gm. KNO_3. Mix well with grinding, then transfer completely to a Coors crucible.

c) Place the crucible in a clay triangle and heat with a Meeker burner until the solids melt and the melt stops bubbling.

d) Cool the crucible and place in a beaker so that crucible is immersed in a small amount of distilled water, boil until the sample becomes soft. (Tested by prodding with a glass rod).

e) Add 4 or 5 drops of HNO_3.

f) Place 6 ml. portions of the liquid into two test tubes and acidity with a few drops of acetic acid.

g) To one test tube add 5 drops of potassium chromate solution. If a yellow precipitate forms, the scale is barium sulfate.

h) If a precipitate does not form, add 5 drops of dilute ammonium hydroxide, 3 drops of potassium chromate and heat it in a boiling water bath.

i) When hot, add dropwise with stirring, 40 drops of 95% ethyl alcohol.

j) Remove the tube, cool in a beaker of cold water and stir occasionally. A yellow precipitate means the scale is strontium sulfate. (The yellow precipitate can be tested by a flame test. A red flame is a check for strontium).

k) Theoretically the specific gravities of these substances are different but these determinations are unreliable because the densities are dependent on the way the scales are deposited.
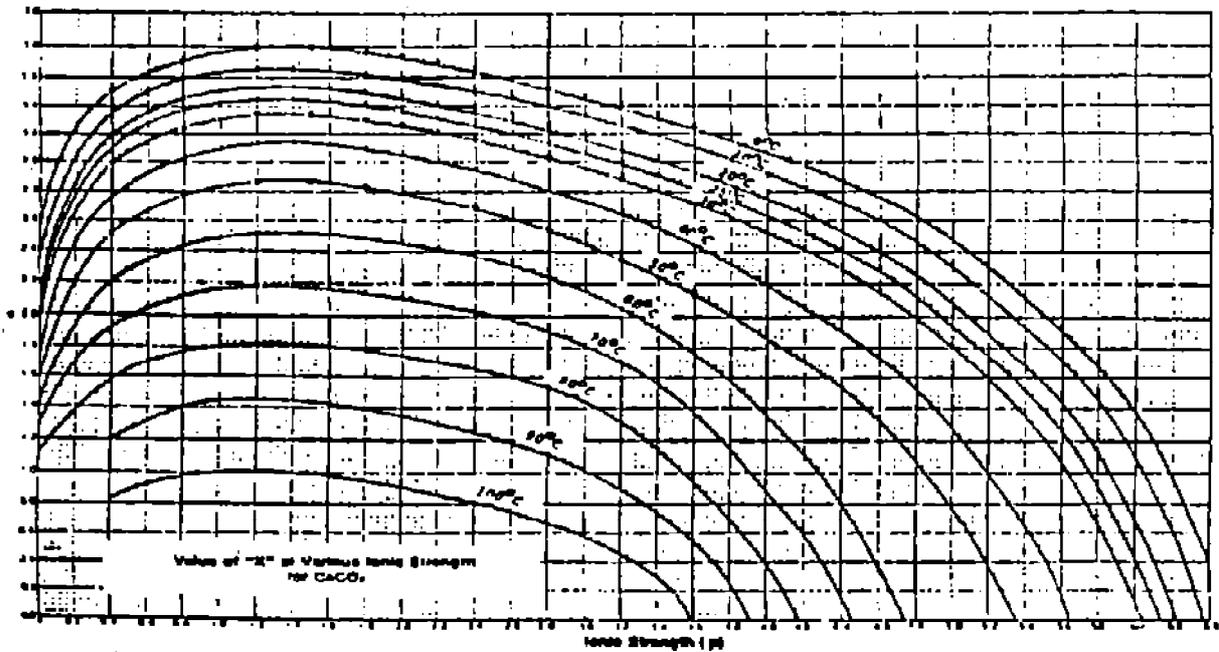
Fig. A.3.5
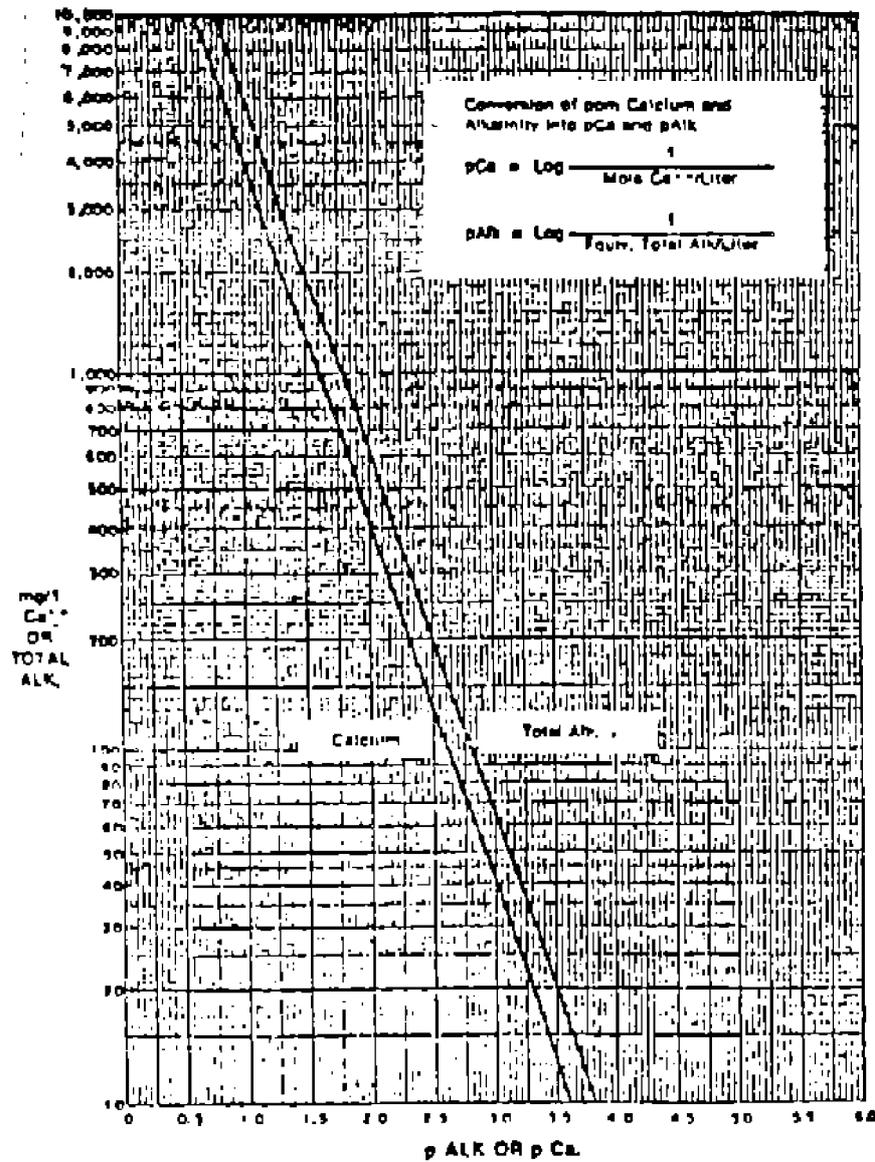
Fig. A.3.6
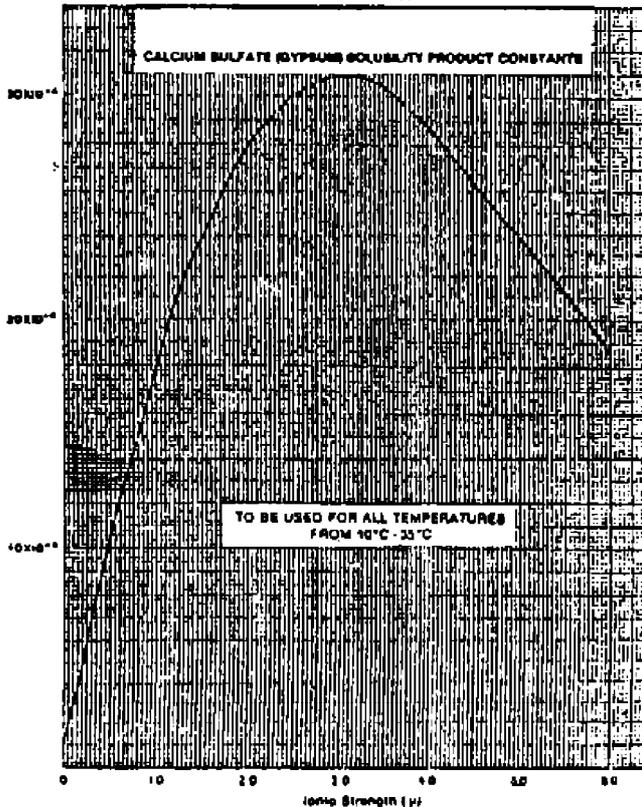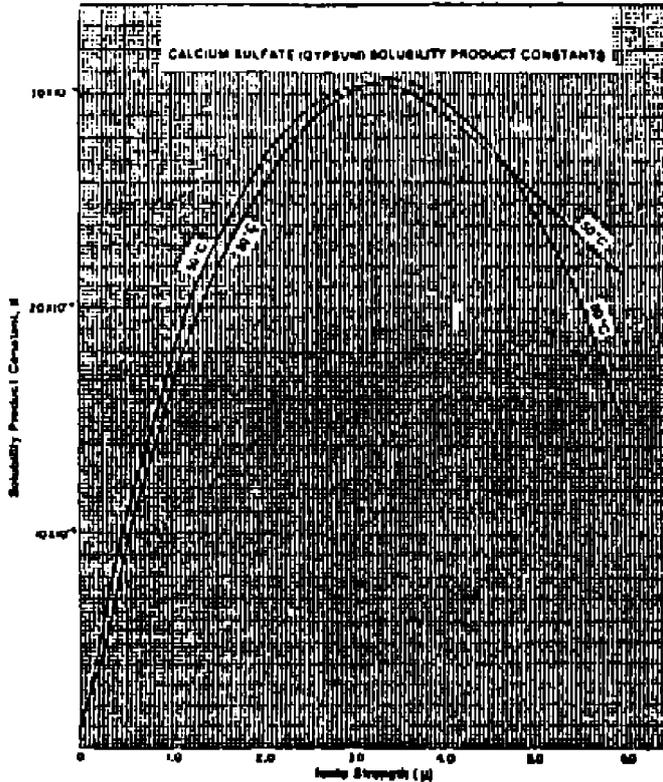
EXAMPLE CALCULATIONS

Ionic Strength, CaCO₃ Scaling Index and CaSO₄ Solubility

Water Analysis		Ionic Strength Calculation	
Ion	Concentration (mg/l)		Conversion Factor
Na⁺	7,550	2.2 x 10⁻⁵ =	16,630 x 10⁻⁵
Ca⁺⁺	877	5.0 x 10⁻⁵ =	4,385
Mg⁺⁺	238	8.2 x 10⁻⁵ =	1,980
Cl⁻	12,294	1.4 x 10⁻⁵ =	17,212
CO₃⁻	0	3.3 x 10⁻⁵ =	0
HCO₃	556	0.82 x 10⁻⁵ =	456
SO₄⁻	1,740	2.1 x 10⁻⁵ =	3,654
	Total Ionic Strength = μ =		44,297 x 10⁻⁵
		μ =	0.44

Temperature = 80°C; pH = 7.04

Calcium Carbonate Scaling Index Calculation

$$K = 2.24$$
$$pCa = 1.67$$
$$pAlK = 2.05$$
$$SI = pH - (K + pCa + pAlK)$$
$$= 7.04 - (2.24 + 1.67 + 2.05)$$
$$SI = +1.08$$
$$SI > 0, \text{ so } CaCO_3 \text{ scale is likely}$$

Calcium Sulfate Solubility Calculation

$$K = 9.2 \times 10^{-4}$$
$$4k = 36.8 \times 10^{-4}$$

Ion	Conc (mg/l)	Conv Factor	M (moles/l)
Ca⁺⁺	877	2.5 x 10⁻⁵	2192.5 x 10⁻⁵
SO₄⁻	1,740	1.04 x 10⁻⁵	1809.6 x 10⁻⁵

$$X = \Delta M = 382.9 \times 10^{-5}$$

$$S = 1000 \left[\sqrt{(0.147 + 36.8 \times 10^{-4}} - 382.9 \times 10^{-5} \right]$$

$$S = 57 \text{ meq/l}$$

Ion	Conc (mg/l)	Equiv. Wt	Conc (meq/l)
Ca⁺⁺	877	20	43.9
SO₄⁻	1,740	48	36.3

Actual CaSO₄ Conc. = 36.3 meq/l

$S >$ Actual, so CaSO₄ scale is unlikely.

Fig. A.3.7

Fig. A.3.7

APPENDIX B.3
CHEMICAL CLEANING OF PROCESS EQUIPMENT

B.3.1 General

Process equipment and piping shall be cleaned to prevent contamination of a process or product, to improve the operation of a process, to reduce the opportunity for premature failure, and to prepare equipment for inspection. However, equipment should be cleaned only for good reason. In addition to the cost of unnecessary cleaning, problems may be introduced. For example, most chemical cleaning processes cause some metal loss. In other cases, washing before cleaning may cause accelerated corrosion, such as during the preparation of a concentrated H_2SO_4 storage tank for inspection. Other potential problems are:

- Difficulties associated with pumping hot corrosive through temporary connections.
- Difficulties associated with a crowded work space, for example, during a turnaround.
- The need to dispose of wastes.
- The possibility of generating toxic or flammable by-products during cleaning.

There are four types of equipment cleaning: preoperational, chemical, mechanical, and on-line. These must be evaluated for each job in order to select the most cost-effective. To make a sound evaluation, the deposit to be removed shall be thoroughly characterized.

B.3.2 Fouling of equipment

Deposits that cause fouling accumulate in equipment and piping and impede heat transfer or fluid flow or cause product contamination. Deposits may be organic, inorganic, or a mixture of the two. Scales are crystalline deposits that precipitate in a system (see Table B.3.1). There are four principal sources of deposits: water-side, fire-side, process-side, and preoperational.

B.3.2.1 Water-side deposits

Water-side deposits are of many types. Hardness (calcium and magnesium) based deposits and iron oxide are the most common water-side deposits and often affect boilers and cooling systems. Process and oil leaks can foul boilers and cooling systems. Biofouling, mud, and debris are often found in cooling systems. Treatment chemicals, if not properly controlled, can add to deposits and scales. Silica can form hard, adherent deposits in boilers, steam turbines, and cooling systems. Corrosion products can add to deposits.

TABLE B.3.1 - SUMMARY OF COMMON TYPES OF SCALE - FORMING MINERALS

Scale	Chemical formuls
General	
Sodium iron silicate	$NaFe(SiO_3)_2$
Barium sulfate	$BaSO_4$
Sodium aluminum silicate	$NaAl\ Si_2O_6.H_2O$
Aragonite (rhombic crystals)	$CaCO_3$
Calcium carbonate — (hexagonal crystal)	$CaCO_3$
Calcium sulfate	$CaSO_4$
Magnesium carbonate and hydroxide	$3MgCO_3.Mg(OH)_2.3H_2O$
Calcium phosphate	$Ca_{10}(OH)_2(PO_4)_6$
Iron oxide	$Alpha\ FeO(OH)$
Iron oxide — magnetite	Fe_3O_4
Iron oxide — red	Fe_2O_3
Iron chrome spinels	$CrFe_2O_4$
Iron sulfide	FeS
Magnesium hydroxide	$Mg(OH)_2$
Magnesium oxide	MgO
Manganese dioxide	MnO_2
Aluminum silicate	$Al_2O_3.4SiO_2.4H_2O$
Sodium aluminum silicate	$Na_8Al_6Si_6O_{24}.SO_4$
Calcium sodium silicate	$4CaO.Na_2O.6SiO_2.H_2O$
Magnesium silicate	$Mg_3Si_2O_7.2H_2O$
Silica	SiO_2
Sodium aluminum silicate	$Na_8Al_6Si_6O_{24}.Cl_2$
Magnesium iron aluminum silicate	$(Mg,Fe)_3(Si,Al)_4O_{10}(OH)_2.4H_2O$
Calcium silicate	$5CaO.5SiO_2.H_2O$
Copper or copper alloy equipment	
Copper iron sulfide	$CuFeS$
Copper sulfide	CuS and Cu_2S
Basic copper chloride	$CuCl_2.3Cu(OH)_2$
Copper oxide	Cu_2O
Chalcopyrite	$CuFeS_2$
Beta zinc sulfide	ZnS
Green basic carbonate	$CuCO_3Cu(OH)_2$

B.3.2.2 Fire-side deposits

Fire-side deposits can be extremely corrosive. Slags from burning oil and wastes can corrode boiler equipment if they become moist. Fly ash deposits can accumulate in coal-fired boilers. Gas-fired boilers are generally clean. Some compounds that are burned in incinerators or waste heat boilers can seriously corrode or erode boiler tubes.

B.3.2.3 Process-side deposits

There are many types of process-side deposits. Organic residues, tars, and coke are common in the petroleum and petrochemical industries. Iron oxide and sulfides are often present in these organic deposits. Sulfate deposits are common in H_2SO_4 plants. Iron-, copper-, and nickel-containing deposits often occur in HF plants.

Organic deposits may develop through the polymerization of leaking gases or from the decomposition of process constituents. In some cases, organics help to bond inorganic deposits, such as iron oxides or sulfides.

Some process-side deposits are pyrophoric when exposed to air or oxygen. The most common is iron sulfide, which is likely to be found in natural-gas and petroleum-refining processes or when aqueous solutions of hydrogen sulfide (H_2S) are dried in the absence of air.

B.3.2.4 Preoperational deposits

Preoperational deposits are formed during the fabrication and erection of process equipment and piping. In addition to mill scale residues, metal surfaces become coated with dirt, oil, grease, weld spatter, pipe-threading compound, protective shop coatings, and corrosion products.

Highly alloyed materials, such as stainless steels, nickel-base alloys, reactive metals, or high-temperature alloys, may become contaminated with iron from tooling; zinc, cadium, and aluminum from scaffolding; and zinc, sulfur, and chlorine in certain making materials. These elements can cause corrosion or embrittlement.

B.3.3 Critical Equipment Areas

Requirements for cleaning will vary with the type of equipment. The operating characteristics and design shall be assessed before selecting a cleaning method.

B.3.3.1 Columns

The two critical areas for deposit formation in a column are at the trays, where vapor passes through a valve, sieve, flapper, or riser, and in the flash zone, where vapor condenses. Operating history sometimes indicates which areas require cleaning; for example, the vapor line is suspect if the column vapor rate becomes limiting. Inspection is necessary to determine the extent and location of fouling.

B.3.3.2 Glass-lined vessels

Glass-lined vessels require special attention when their water jackets are chemically cleaned. The recommendations of the manufacturer must be followed. The most commonly recommend cleaning solution is dilute alkaline sodium hypochlorite (NaClO). If strong acids are used, atomic (nascent) hydrogen formed by corrosion diffuses into the shell and recombines as hydrogen molecules at the glass/metal interface, which causes spalling of the glass.

B.3.3.3 Oxygen, chlorine, and fluorine piping systems

Oxygen, chlorine, and fluorine piping systems must be free of organic contaminants. Organic materials, particularly hydrocarbon greases and oils, react violently with these chemicals. Preoperational cleaning is mandatory in such cases. After cleaning, the lines should be blown dry, using oil-free nitrogen or air.

B.3.4 Identification of deposits

To select an effective cleaning procedure, the deposit must be characterized, or identified. The sample should represent the deposit in the most critical fouling area. For exchangers and boiler, this is the highest heat transfer section. Expediency should not dictate the location of the sample. A cleaning procedure should not be based on a sample of loose deposit from a non-critical area, because the sample at this location may not be representative. Table B.3.2 lists some common components of boiler deposits.

When removed by scraping, the samples should be as intact as possible. They should be removed to the base metal, taking care not to introduce any metallic chips from the blade or substrate. Thickness, density, porosity, type (homogeneous or layered), and color should be noted.

When only a limited amount of deposit is available, replication tape is a useful method of removing it. Polyvinyl Chloride (PVC) or other chloride-containing tapes should not be used on stainless steels, which are susceptible to chloride pitting and stress cracking.

Many analytical techniques are used to characterized deposit samples. Typical methods include x-ray diffraction, optical emission spectroscopy, and x-ray spectrometry. Most chemical cleaning contractors, water treatment supplies, and analytical laboratories have the facilities to characterize deposits.

TABLE B.3.2 - COMPONENTS OF BOILER DEPOSITS

Mineral	Formula	Nature of deposit	Usual location and form
Acmite	$Na_2O.Fe_2O_3.4SiO_2$	Hard, adherent	Tube scale under hydroxyapatite or serpentine
Alpha quartz	SiO_2	Hard, adherent	Turbine blades, mud drum, tube scale
Amphibole	$MgO.SiO_2$	Adherent binder	Tube scale and sludge
Analcite	$Na_2O.Al_2O_3.4SiO_2.2H_2O$	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	$CaSO_4.2H_2O$	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	$4Na_2O.3Al_2O_3.6SiO_2.SO_4$	Hard, adherent	Tube scale
Pectolite	$Na_2O.4CaO.6SiO_2.H_2O$	Hard, adherent	Tube scale
Serpentine	$3MgO.2SiO_2.H_2O$	Flocculent	Sludge
Sodalite	$3Na_2O.3Al_2O_3.6SiO_2.2NaCl$	Hard, adherent	Tube scale
Xonotlite	$5CaO.5SiO_2.H_2O$	Hard, adherent	Tube scale

B.3.5 Preoperational cleaning

Unlike process-or water-side deposits, the types of deposits in original equipment are easily categorized. Preoperational cleaning shall include consideration of the degree of cleanliness required and the material of construction. Areas where preoperational cleaning is used include:

- Process equipment start-up, boilers, and steam-generating and compression systems.
- Lubricating oil systems before oil systems.
- Critical services, such as oxygen, chlorine, or flouring piping.
- Water treatment and inhibition programs.

B.3.5.1 Boilers

Boilers are cleaned to remove oils, grease, and mill scale. When boilers are coated with heavy protective greases, two-stage cleaning (for organic and inorganic deposit removal) should be used. A degreasing step using alkaline boilout solutions or emulsions is first used. Common second-step solvents include chelants, organic acids, or HF.

B.3.5.2 Columns

Columns contain similar contaminants. They are cleaned by fill and soak, cascade, or foam methods, using solvents similar to those used for boilers. The design of the column may eliminate certain methods, such as cascade cleaning for a packed column.

B.3.5.3 Shell and tube heat exchangers

The most serious fouling is found on the interior (tube side) or exterior (shell side) of the tubes. Other locations are on the shell side at baffles or drain nozzles.

The head should be removed for inspection if tube-side fouling of the tubes is suspected. The shell is more difficult to inspect, unless the tube bundle is removable, but limited information may be gained through nozzles.

Heat-exchanger tubes may be cleaned mechanically or chemically. Mechanical cleaning may damage tubes. Individual tubes should not be steam blown, because this may damage rolled tube joints. Tubes should not be hammered with any metallic tool, and scraping or rodding should be done with care because any scoring or gouging can lead to premature failure. High-pressure and ultrahigh-pressure water cleaning are preferred.

Chemical cleaning methods use circulation, fill and soak, or foam. However, severely blocked tubes may resist the entry of the cleaning agent or may retain it beyond the neutralization step of the cleaning process, leading to corrosion during shutdown or in service.

Heat-exchanger shells are normally chemically cleaned using the circulation or the fill and soak method. If the tube bundle is removable, mechanical cleaning with high-pressure of ultrahigh-pressure water is good technique.

B.3.6 Cleaning of boilers

B.3.6.1 Typical water-side deposits found in boilers are listed in Table B.3.2. Deposits vary depending on raw water composition, feed-water treatment, and operating pressure.

The heaviest deposition occurs in tubes with the highest heat input, an area that may be physically impossible to inspect. A tube section can be taken from the area where deposition is known to be heaviest in order to characterize the deposit. Although various (ingrams of scale per square foot) have been proposed for determining the need to clean, each case should be individually evaluated. Factors to be considered are the degree of fouling, the type of service, the reliability required, the operating history, and future operation.

Chemical cleaning of the water side is generally more effective than mechanical cleaning, particularly in designs with heavily swaged tubes and tight bends. Preoperational cleaning of boilers must be conducted to allow the steel surface to develop a protective film of magnetite (Fe_3O_4), when the boiler is put into service and to remove mill scale.

B.3.7 Cleaning of furnaces

The external fouling of furnace tubes depends on the nature of the fuel. Oil-burning furnaces usually have significantly more deposit formation and corrosion problems than coal-burning types, while natural-gas-burning furnaces have very few problems.

Slag accumulates when metallic salts and oxides are vaporized and condense in various parts of the furnace. Because its melting point is relatively low, the slag forms a sticky corrosive deposit of various salts, primarily sodium and vanadium. These slags should be mechanically removed by chipping or dry sandblasting. Wet cleaning methods may cause acid formation. For internally cocked tubes, steam-air decoking or mechanical cleaning is preferred.

B.3.8 Cleaning of pumps and compressors

Cooling water jackets are often chemically cleaned to remove iron oxide, water-formed scale, and possible oil infiltration. All loose material is first removed by opening the clean-out plates and flushing. A two-stage chemical cleaning process is then used, first to dissolve any organic deposits and then to remove inorganic scales. The acidic cleaner selected for inorganic scales should be compatible with the materials of construction.

B.3.9 Cleaning of piping

Piping may contain various contaminants, including dirt, loose paint, sand and grit, varnish, grease and oils, weld spatter, mill scale, and rust. Piping should first be inspected and all construction debris removed. Dirt, loose paint, sand, and grit are removed by flushing with clean water or blowing with dry compressed air or steam. Varnish, grease, and oils are removed by steam blasting with detergent or hot water containing an alkaline degreasing agent. Mechanical cleaning may be required, depending on the amount of weld spatter, mill scale, and rust. The piping may then be chemically cleaned if necessary, using organic acids and chelants, followed by neutralizing and passivating.

Moisture removal may be required for such specific applications as compressor or refrigeration piping. When all traces of moisture must be removed, the system can be filled with alcohol, evacuated to evaporate the alcohol, then flushed with an inert gas.

Piping carrying oxygen, chlorine, and fluoride requires stringent cleaning to remove organic contamination. No organic-containing residues can be permitted.

B.3.10 Chemical Cleaning

Chemical cleaning is the use of chemicals to dissolve or loosen deposits from process equipment and piping. It offers several advantages over mechanical cleaning, including more uniform removal, no need to dismantle equipment, lower overall cost (generally), and longer intervals between cleanings. In some cases, chemical cleaning is the only practical method.

The primary disadvantages of chemical cleaning are the possibility of excessive equipment corrosion and solvent disposal. Chemical cleaning solvents must be assessed in a corrosion test program before their field acceptance.

Chemical cleaning is performed by a contractor who specializes in this work. Some cleaning procedures are protected by patents.

B.3.11 Chemical cleaning methods

There are six major chemical cleaning methods: circulation, fill and soak, cascade, foam, vapor phase organic, and steam-injected cleaning. A seventh variation is discussed in the section "On-line Cleaning" in this consideration.

B.3.11.1 Circulation. The most common method, is applied to columns, heat exchangers, cooling water jackets, and so on, where the total volume required to fill the equipment is not excessive. The equipment is arranged such that it can be filled with the cleaning solution and circulated by a pump to maintain flow through the system. Movement of solution through the equipment greatly assists the cleaning action. As cleaning progresses, temperature and concentration are measured in order to monitor the progress. The cleaner may be replenished (sweetened) occasionally to maintain efficiency. Corrosion coupons or on-line monitoring determines the effect of the cleaning chemicals on the equipment materials.

With circulation cleaning, the rate of flow through the equipment is critical. Large-diameter connections are preferred, and a high-capacity pump may be necessary to produce the required circulation. After cleaning, the equipment is drained, neutralized, flushed, and passivated.

B.3.11.2 Fill and soak cleaning, involves filling the equipment with the cleaner and draining it after a set period of time. This may be repeated several times. The equipment is then water flushed to remove loose insolubles and residual chemicals.

Fill and soak cleaning offers limited circulation. The poor access of fresh cleaning solution to the metal, together with the inability to maintain solution temperature, may cause the cleaning action to cease.

The method is limited to relatively small equipment containing light amounts of highly soluble fouling and to equipment in which circulation can not be properly controlled. Because good agitation is achieved only during the flushing stage, flushing should be as thorough as possible. Circulation and fill and soak cleaning are sometimes used alternately.

B.3.11.3 Cascade cleaning, a modification of the circulation method, is usually applied to columns with trays. The column is partially filled, and the liquid is continuously drawn from the reservoir and pumped to the highest point. The liquid then cascade down through the column, cleaning surfaces as it passes over them. The liquid draw-off point must be suitably located to avoid recirculation of loosed foulants. High-capacity pumps and large-diameter piping are required to achieve the necessary transfer of liquid to produce a flow pattern that will contact all fouled surfaces within the column.

The cascade method is primarily used in large columns and is suitable for most types, except for packed columns. Cleaning is not effective in inaccessible areas, such as the underside of trays, due to poor contact with the cleaning solution. Contact may be improved by injecting air or nitrogen at the base of the column. If steam is used to heat the chemicals, the location of the steam injection point should not lead to localized overheating. High temperature can also increase corrosion in the vapor space.

B.3.11.4 Foam cleaning, uses a static foam generator that employs air or nitrogen to produce a foamed solvent. Foam stabilizers are required to prolong foam life and increase the effectiveness of the cleaning chemicals. Foam cleaning is used on the equipment that can not support full or partial filling with liquid. Foam cleaning results in significantly less liquid volume for disposal compared with other methods.

B.3.11.5 Vapor phase organic cleaning is used in equipment that is difficult to clean with liquids. For example, vaporized organic solvents are used to remove organic deposits from columns. The organic solvent is vaporized, injected into the top of the column, condensed, collected in a circulation tank, and revaporized. The principal concerns are the handling and disposal of the solvent and its flammability (when applicable). The recirculating tank should be purged and blanketed with nitrogen, fitted with an adequate venting and condensing system, and grounded to prevent accumulation of an electrical charge.

B.3.11.6 Steam-injected cleaning involves the injection of a concentrated mixture of cleaning chemicals into a stream of fast-moving steam. The steam is injected at one end of the system and condensed at the other. The steam atomizes the chemicals, increasing their effectiveness, and ensures good contact with the metal surface.

Steam-injected cleaning is very effective for critical piping systems. As with foam cleaning, the method produces a relatively low amount of liquid for disposal.

B.3.12 Chemical cleaning solutions

A wide variety of standard chemical cleaning solutions are available (Table B.3.3). Many proprietary solutions are based on these chemicals. Some are patented or involve patented equipment. Chemical cleaning contractors are the best source of information on standard or patented techniques, (see also industrial cleaning manual, TPC-8 NACE.

Most chemical cleaning contractors calculate the concentration of chemicals in weight percent, but some use volume percent. The user must be aware of this. For example, a 10 wt% solution of HCl is equivalent to 25 vol% of the normal 30% concentrated HCl.

Chemical cleaning solutions include mineral acids, organic acids, bases, complexing agents, oxidizing agents, reducing agents, and organic solvents. Inhibitors and surfactants are added to reduce corrosion and to improve cleaning efficiency. Following the cleaning cycle, a passivating agent can be introduced to prevent further corrosion or to remove trace ion contamination.

Mineral acids are strong scale dissolvers. They include HCl, hydrochloric/ammonium bifluoride (HCl/ NH_4HF_2), sulfamic acid (NH_2SO_3H), HNO_3, phosphoric acid (H_3PO_4), and H_2SO_4.

Organic acids are much weaker. They are often used in combination with other chemicals to complex scales. An advantage of organic acids is that they can be disposed of by incineration. They include formic (HCOOH), hydroxyacetic-formic, acetic (CH_3COOH), and citric acid.

Bases are principally used to remove grease or organic deposits. They include alkaline boilout solutions and emulsions.

Complexing agents are chemicals that combine with metallic ions to form complex ions, which are ions having two or more radicals capable of independent existence. Ferricyanide [$Fe(CN_6)]^{4-}$ is an example of a complex ion. Complexing agents are of two types: chelants and sequestrants. Chelants complex the metallic ion into a ring structure that is difficult to ionize, and sequestrants complex the metallic ion into a structure that is water soluble.

Oxidizing agents are used to oxidize compounds present in deposits to make them suitable for dissolution. They include chromic acid (H_2CrO_4), potassium permanganate ($KMnO_4$), and sodium nitrite ($NaNO_2$).

Reducing agents are used to reduce compounds in deposits to a foam that makes them suitable for dissolution and to prevent the formation of hazardous by-products. They include sodium hydrosulfite ($NaHSO_2$) and oxalic acid.

Inhibitors are specific compounds that are added to cleaning chemicals to diminish their corrosive effect on metals. Most inhibitors are proprietary, and recommendations for their use are available from the supplier.

Surfactants are added to chemical cleaning solutions to improve their wetting characteristics. They are also used to improve the performance of inhibitors, emulsify oils, improve the characteristics of foaming solvents, and act as detergents in acid and alkali solutions. As with inhibitors, most surfactants are proprietary products.

TABLE B.3.3 - SCALES AND SOLVENTS

Scale component	Solvent(a)	Testing conditions
Iron oxide	5 to 15% HCl	65-80°C (150-175°F)
Fe_3O_4 (Magnetite or mill scale)	2% hydroxyacetic/l formic	65-80°C (150-175°F) Circulating
Fe_2O_3 (red iron oxide or red rust)	Monoammoniated citric acid	85-105°C (185-220°F) Circulating
	Ammonium EDTA	75-150°C (170-300°F) Circulating
	EDTA organic acid mixtures	40-65°C (100-150°F) Circulating
Copper, oxides	Copper complexor in HCl	65°C (150°F)
	Ammoniacal bromate	50-85°C (120-185°F)
	Monoammoniated citric acid	60-85°C (140-185°F), pH 9 to 11
	Ammonium persulfate	Below 40°C (100°F)
	Ammonium DETA	65-80°C (150-185°F), pH 9 to 11
Calcium carbonate	5 to 15% HCl	Preferably not above 65°C (150°F)
	7 to 10% sulfamic acid	Do not exceed 60°C (140°F)
	Sodium EDTA	Circulate at 60-150°C (150-300°F)
Calcium sulfate	Sodium EDTA	Circulate at 60-150°C (150-300°F)
	1% NaOH-5% HCl	Circulate at 50-65°C (120-150°F)
	EDTA organic acid mixtures	40-65°C (100-150°F) Circulating
Hydroxyapatite of phosphate compounds ($Ca_{10}(OH)_2.(PO_4)_6$)	5 to 10% HCl	Preferably above 65°C (150°F)
	Sodium EDTA	Undesirable to add fluoric Circulate at 65-150°C (150-300°F)
	Sulfamic acid 7 to 10%	Do not exceed 60°C (140°F)
Silicate compounds, for example, acmite ($NaFe(SiO_3)_2$) and analcite ($NaAlSi_2O_6.H_2O$)	Prolonged treatment with 0.5 to 1% soda ash at 345 kPa (50 psi), follow with HCl containing fluoride	Alkaline preboil at 345-690 kPa (50-100 psi) for 12 to 16 h
Pedtolite ($4Ca.Na_2O.6SiO_2.H_2O$)	HCl containing ammonium bifluoride	65-80°C (150-175°F)
Serpentine ($Mg_3Si_2O_7.2H_2O$)		
Sulfides ferrous: troilite (FeS) and pyrrhotite (FeS)	HCl, inhibited	Heat slowly to avoid sudden release of H_2S toxic gas
Disulfides: FeS_2, marcasite and FeS_2, pyrite	Chromic acid, followed by HCl	Boiling 7 to 10% chromic acid, followed by inhibited HCl
Organic residues	Potassium permanganate, followed by HCl containing oxalic acid	Circulate at 100°C (210°F), add 1 to 2% $KMnO_4$ solution. Oxalic acid added to HCl controls release of chlorine toxic gas
Organo lignins		
Algae		
Sume polymeric residues		

(a) The chemicals listed are to be considered possible solvents only. There are many alternative solvents for each deposit listed.