CHAPTER I

INTRODUCTION

(a) General

'Corrosion', though natural, is phenomenally the very antithesis of 'production'. Recognised for its devilish accomplishment by the ancient metallurgists, corrosion has the unique character of 'continuity' through scores of centuries, despite the wonders of modern technology. Rare examples of non-corrosive pieces such as the iron pillar of Delhi (1), which symbolises excellence in metallurgical achievements of the ancient peoples, are mere exceptions. Corrosion is so widespread and so dangerous that it can relish the metaphor of being called the cancer of metals which can take the 'life' out of anything composed of metals and cause irrepairable damage to both life and property.

There is no field that is not affected by 'corrosion'. Of the three destructive terms - 'erosion', 'abrasion' and 'corrosion', the last one is more chemical than the other two. Being 'chemical', it is more devastating in its impact than the destructiveness of the other two. Metallurgy is the technological miracle of 'producing' and 'refining' metals and 'corrosion' is the system inducting their return to nature. Be it a house, a bridge, a factory or war fields, transportation systems, scientific instruments, energy generating sources, sports fields, negotiating tables, conference halls etc. etc., if 'metal' is involved anywhere, 'corrosion' must be omnipresent with it.

Corrosion of metals in general is one such problem whose potential of affecting any growing technology that depends upon metals, in such adverse a manner as to nullify all the gains put together, is simply enormous. Wars may be won or lost on this factor alone, though strange it may look. Truth is stranger than fiction, and so goes the story of damage done by the natural phenomenon known as 'corrosion'.

(b) Corrosion and its economic aspects:

Being wide in its range of effect and almost inseparable from the technological activity, corrosion can have much wider impact on the economics of technology and may even be directly or indirectly responsible for the economic dwindling of technology in general. Chemical plants as systems or sources of production are no exceptions to this overwhelming rule since the advancing tentacles of corrosion simply work to establish their governance over the metals.

In modern chemical process plants, the economics are governed by an 'on-stream efficiency' (2). Corrosion is one of the main causes of breakdowns in machinery and materials leading to loss of man power, material and money (3). This has been a matter of great concern both to the industrialists and state. Two pioneers in the field working on the cost of corrosion control and cost of corrosion mitigation, placed an estimate, which is some what speculative. It was Hapfield (4) in U.K. who showed the cost of corrosion all the world over to be around £ 600 millions and Hudson (4) who suggested that cost of corrosion control for U.K. alone could be around £ 200 million. Thorough studies made later indicated that in U.K. about 2 to 3 tons of steel is lost every minute due to corrosion, thus wasting away 3-5% of national production (5). This amounted to £ 1365 million in 1971. Of this, it has been estimated that atleast £ 310 million could have been saved if proper corrosion control measures were adopted.

The NBS study (6) revealed that metallic corrosion annually costs the US $ 70 billion of which atleast US $ 10 billion is avoidable by better choice of materials and corrosion control measures. This annual corrosion loss represented about 4 % of the US gross national product in 1975 (6). Though no such systematic studies have been conducted in India, it is, however, assumed that the annual corrosion loss may be any where around Rs.100-500 crores, requiring greater attention to reduce the effect of corrosion.

Several authoritative monographs (7, 8, 9) on conservation of materials and energy, economy of our society and the safety and reliability of our industrial processes and some reviews (10, 11) on corrosion and selection of materials of construction for the process industries covering a wide range of metals, plastics and other materials under different service conditions, have been published recently.

Surveys have shown that corrosion is now costing the economy of the Federal Republic of Germany annual losses of about 19000 million D.M. Of this sum, approximately 4300 million D.M. could have been saved if full advantage were taken of the modern technology. Another investigation (12) has shown that about 80 % of the losses are caused by atmospheric corrosion. For this estimate, data from 800 industries and several government departments were obtained. These are shown in the Table 1.

Table 1

Cost of Corrosion Estimated in U.K. in 1971

No.	Name of organisation	Estimated cost in million £	Estimated amount of avoidable expenses million £
1	Transport	350	100
2	Marine	280	55
3	Building and construction	250	50
4	Oil and Chemical	180	15

Table 1 (continued)

No.	Name of Organisation	Estimated cost in million £	Estimated amount of avoidable expenses million £
5	General Engineering	110	35
6	Power	60	25
7	Government department	55	20
8	Food	40	4
9	Water	25	4
10	Metal refinery and semi-fabrication	15	2
	Total	1365	310

In India a similar report published in the year 1961 (13) estimated the cost of corrosion at Rs. 150 crores and by the end of fifth five year plan about Rs. 600 crores. A recent report (14) talks of loss worth Rs. 1000 crores due to corrosion in industries. This comparison can throw light on the amount of money lost year after year by way of wasteful corrosion. Table 2 depicts the comparative picture.

Table 2

Loss due to Corrosion

Item	Loss in million Rs. (approx.)
Indian Railway	210
American Railways	2037

Table 2 (continued)

Item	Loss in million Rs (apporx.)
American automobile components	5455
U.K.Transport	1800
U. S. Marines	1170
U.K. Marines	900
Indian Marines	100 (15)

These are only some representative figures to show that for our gross national product this loss is really of high proportion. Several countries are taking effective steps to cut down the losses due to corrosion and work out the economics of control measures. A very interesting account about the amount spent on coating alone by some countries is given (16) in Table 3.

Table 3

Cost of Coating

Year	Country	Investment on corrosion control (million Rs)	Amount spent for coating %
1961	India	1530	27
1955	U.K.	7200	40
1975	U.S.A.	76000	30
1974	Australia	9000	40

Consideration of losses due to breakdown, failure and corrosion of equipment and piping in fertilizer industry is of basic significance; the data are given in Table 4.

Table 4

Corrosion failure in metallic piping and equipment

Type of corrosion	1968 %	1969 %	1970 %	1971 %	Cumulative %
General	18.1	18.1	15.2	9.2	15.2
Cracking and stress	13.1	11.5	11.5	15.5	13.1
Pitting	10.1	8.6	8.8	4.2	7.9
Erosion type corrosion	6.1	3.3	3.2	4.2	3.8
Intergranular	7.1	5.3	2.7	9.2	5.6
Galvanic	0.0	0.0	1.4	0.0	0.4
Others	45.5	53.2	57.2	57.7	54.0

(c) Definition and forms of Corrosion:

Corrosion may be defined as deterioration of metals to their natural state of existence through interaction with its environment which may be chemical or electrochemical.

The chemical nature of corrosion can be presented in a simple manner as follow:

$4Fe + 4H_2O \rightarrow 4Fe(OH)_2$

whitish green precipitate

$4Fe(OH)_2 + O_2 \rightarrow 2Fe_2O_3.H_2O + 2H_2O$

red brown rust

The electrochemical picturization can be :

Cathodic reaction

(a) Hydrogen evolution reaction

$H_3O^+ + e \rightarrow 1/2\ H_2 + H_2O$

$H_2O + e \rightarrow 1/2\ H_2 + OH^-$

(b) Oxygen reduction reaction

$O_2 + H_2O + e \rightarrow 2O\bar{H}$

Anodic reaction

$M \rightarrow M^{Z+}_{(aq.)} + Ze$ Metal cation

$M + ZH_2O \rightarrow MOZ^{Z-} + 2ZH^+ + Ze$ Metal anion

$M + ZH_2O \rightarrow M(OH)_Z + ZH^+ + Z_e$ Metal oxide or solid compound

where Z is the number.

Flow of electrons : from anode to cathode through external circuit

Corrosion is generally oxidation of metals. Since oxidation will be accompanied by reduction of the agent responsible for the oxidation, it can be viewed as an oxidation-reduction process. The area over which metal is oxidized is called anode; that at which the oxidizing agent is reduced is called the cathode. These areas are separated but usually not far apart, and as corrosion proceeds electrons flow through the metal between these areas. In aqueous systems cations migrate towards the cathode, while anions move towards anode. This picture is reminescent of an electrochemical cell, analogous to a short-circuited battery. The flow of electrons through the metal (the external circuit) is the corrosion current, which is limited by the rate at which electrons are accepted by the oxidizing agent at the cathode.

Corrosion is variously classified. It is broadly but conveniently classified as gaseous, atmospheric and immersed or under ground, depending on the environment. There are no clear cut divisions between the last three since they all require the presence of water. In atmospheric corrosion the supply of oxygen from air is unlimited and attack depends on the presence of water and impurities dissolved in it. In immersed corrosion in natural waters, on the other hand, attack is usually controlled by the amount of dissolved oxygen which can vary considerably. In underground corrosion all the three factors, namely water, salt content and oxygen, vary, as well as, the nature of the soil aggregate.

Corrosion may occur in different ways and forms. Depending upon the characteristics, the following forms of corrosion are universely acknowledged as the standard forms:

Forms of Corrosion

1) General or uniform corrosion
2) Pitting
3) Galvanic
4) Crevice
5) Fretting
6) Stress Corrosion-cracking
7) Intergranular corrosion
8) Corrosion fatigue
9) Differential aeration corrosion
10) Impingement corrosion attack
11) Filliform corrosion
12) Graphitic corrosion
13) Dezincification
14) Tuberculation
15) Weld decay

1) General or uniform corrosion:

In this type, surface layers of metals are converted to corrosion products in such a way that the thickness of the section is uniformly decreased.

2) Pitting corrosion:

The metal, though not corroded uniformly, is primarily corroded at distinct spots where deep pits are produced. The bottom of the pits are anodes in small corrosion cells with the surrounding surface acting as cathodes. Metals that develop very thin protective oxide films on their surfaces are particularly succeptible to this form of corrosion.

3) Galvanic corrosion:

Two dissimilar metals in the presence of small amounts of moisture form a small battery or 'corrosion cell'(galvanic effect), with the less positive metal corroding at the exposed interface between two metals.

4) Intergranular corrosion:

Where segregation of some of the components or impurities of an alloy occurs in grain or crystal boundary, a potential difference may develop between the grain boundary material and the grain, which will produce corrosion of the material that is less positive. This corrosion follows at grain boundaries and acts like cracks in material.

5) Stress Corrosion cracking:

Alloys under high tensile stress are succeptible to corrosion starting on the surface that may propagate through the lattice structure of the metal as cracks and lead to catastrophic failure. The stress may be residual, as from cold working and forming, or may result from external loading.

6) Crevice corrosion:

Corrosion of a metal at an area where contact is made with a material usually non-metallic, is known as crevice corrosion.

7) Fretting corrosion:

Corrosion at the interface between two contacting surfaces accelerated by relative vibration between them, of amplitude high enough to produce slip, is known as fretting corrosion.

8) Corrosion fatigue:

There is decrease in fatigue resistance of a metal under cyclic stress. Any corrosion of metal under fatigue producing stress will cause reduced fatigue life. A hypothesis is that corrosion produces pits, notches, or similar other points on the metal surface which function as starting points for the concentration of stress and the intiation of fatigue cracks.

9) Differential aeration corrosion:

Formation of an electrolytic cell the emf of which is due to difference in air (oxygen) concentration at one electrode as compared with that at another electrode of the same material can be the cause of corrosion at the oxygen difficient electrode.

10) Impingement corrosion attack:

Corrosion associated with turbulent flow of liquid is known as impingement attack. For some metals the action is considerably accelerated by entrained bubbles in the liquid.

11) Filliform (under film) corrosion:

Corrosion that occurs under lacquers and similar organic films in the form of randomly distributed hair lines (most common) or spots is known as filliform corrosion.

12) Graphitic corrosion:

It is a type of corrosion of gray cast iron in which the metallic iron constituent is converted into corrosion products, leaving the graphite intact.

13) Dezincification:

Corrosion of a zinc alloy, usually brass, involving loss of zinc, and a residue or deposit insitu of one or more less active constituents, usually copper, has been termed as dezincification.

14) Tuberculation:

The formation of localized corrosion products scattered over the surface in the form of knob like mounds is known as tuberculation.

15) Weld decay:

Corrosion notably of austenitic chromium steels at specific zones away from a weld is defined as weld decay.

d. Corrosion in industry:

It has been noticed with alarm that corrosion has great impact on industry and its economics. Material damage could hardly be appreciated; the cost of this damage is bound to be included in the cost of production. Therefore the cost of production would shoot proportionately. If the compulsion would be such as not to leave any option to employing costlier but corrosion resisting materials, then this too would be working in the direction of enhancing the cost of production. Several quality conscious manufacturers would go in the use of steel and rubber lined products that resist the effect of atmospheric corrosion.

Most of the deteriorations of materials by air pollution goes unnoticed because it cannot be distinguished from what might be called normal or natural deterioration. However, material damage has been evaluated at $ 65 per person per year (17). This includes cleaning costs, repair and replacement costs, over design, reduced property value and unaesthic appearance of damage materials.

As for example, in the complex of Gujarat State Fertilizer Company Limited, the pollutants which can be responsible for corrosion damage are sulphur dioxide and dust particulate of ammonium sulphate. The corrosion damage due to pollutants are shown below:

Average (static) corrosion rate - location wise (17)

Ammonia plant	: 0.0443	mmpy
D.A.P. plant	: 0.0712	mmpy
Open stores yard	: 0.0686	mmpy

This means that an unpainted carbon steel plate (17) having the surface area of 1 M^2 will loose the material, by rusting, as follow:

(i)	Material near Ammonia plant	: 0.354 Kg/year
(ii)	Material near D.A.P. plant	: 0.570 Kg/year
(iii)	Material near stores	: 0.550 Kg/year

In industrial environment, corrosion would be due to the air pollutants which are the waste products of the industries.

Quite interesting studies have been made in the various regions of our country.

The monthly rates of atmospheric corrosion due to air pollutants for mild steel, zinc and aluminium under moving exposure conditions on the Ahmedabad - Bombay railway line are found to be in the range of 582-2431, 76-383, 5-14 mg/dm^2 respectively, whereas the yearly rates are of 8,333-10,408, 1026-1,168 and 53-66 mg/dm^2 (18) respectively. It clearly signifies the variation of corrosion rates according to seasons, otherwise the annual rate would have been just a summation of the monthly rates. The rates are higher than those observed in static exposure tests at Ahmedabad or Bombay. Although pollution is maximum along the railway line (45-60 mg $SO_3/dm^2/Mo$) in April and May, the corrosion rates are maximum during the rainy season (June-August/September) when the SO_2 content of the atmosphere is at a minimum (15-20 mg $SO_3/dm^2/Mo$). This lays emphasis on the impact of humidity against the concentration of the pollutants in the atmosphere. Copper-bearing alloys show more resistance to atmospheric corrosion than the non copper alloy.

Specimens covered with various paint systems suffered a coating weight loss 2-17 $mg/dm^2/Mo$ (18), but the metal beneath did not show any signs of corrosion. During yearly exposures, the loss in weight of the coating ranged from

24 to 47 mg/dm^2, whereas the loss in weight of the base metal ranged from 6 to 29 mg/dm^2 for mild steel and 8 to 37 mg/dm^2 for zinc (18).

Protection costs and corrosion damage (19) are important burdens on the economic life of the industry and society. Approximately half of the total cost of corrosion protection in the USA in 1949 (over $ US 2.8 M) was spent on measures against atmospheric corrosion effects. The cost of paint which protects against corrosion under most atmospheric conditions, was 37.67%. Phosphating (0.38 %), galvanizing (2.52 %), and parts of the use of nickel (approximately 2.5 %) and cadmium plating (0.39 %) also belong to this category. The sum of these measures against atmospheric corrosion exceeds 43 %. There must also be taken into account a certain part of the use of non-rusting steels and other corrosion - resistant alloys and metals (e.g. alloys of copper and aluminium). Thus it seems reasonable to assume that about 50% of the total cost of corrosion protection is spent on measures against atmospheric corrosion.

Daeves and Trapp (20) calculated in 1937 that the annual conversion of iron into rust during atmospheric corrosion accounted for approximately 2% of the then German steel production. Since these calculations were based on reliable estimates of total unprotected iron surface and average corrosion rates, they should be still valid to day, when the corrosion rate will be even higher due to increased air pollution. Direct conversion to rust thus accounts for a loss of 20,000 tons from each million ton of steel produced annually.

By 1980 the nationalized road transport sector in India had about 65,000 buses on roads throughout the length and breadth of the country. In varied climatic conditions of India, the corrosion impact would also be varied. Where the climate is dry and temperature varies from 20 to 40°C, the corrosion of bus bodies is not that acute. However, in coastal areas, humidity, dust, heat and heavy rains do affect the bodies considerably. The average life of a mild steel bus body is reported to be only about two years in coastal areas as compared to the seven to eight years in climatic areas (21).

In coastal areas aluminium body is preferred due to their lightness and resistance to corrosion. In the case of steel body construction, it is the experience of users that rolled sections corrode less than do the formed ones. Although all aluminium body construction reduces corrosion of bus bodies, the availability of aluminium sometimes poses problems. Therefore, bodies operating even in coastal areas are constructed with mild steel material. Surveys show that vehicles operating in coastal areas are corroded upto 75 % whereas the extent of corrosion approaches 25 % in regions with moderate rains and 10 % in low-rain regions and dry climatic conditions (21). Economic loss due to premature destruction of automotive bodies is well documented:

(1) The U.S. department of commerce (22) states that corrosion loss in U.S. costs $ 11 billion annually, of which approximately half is in transportation field.

(2) The British automobile association estimate that the U.K. corrosion cost for auto only is $ 250,000 or $ 48 per vehicle (23).

One larger fleet owner (24) operating in Michigan, reports 90 brakeline failure a year due to corrosion. Brake line failure is most prevalent at support or clamp areas due to crevice corrosion. The corrosion site is created by oxygen deficiency versus oxygen plenty areas electrically connected by electrolyte such as water, The Canadian government research has shown that the corrosion rate in crevice site is 900 % higher than on plane surface (25).

The chemical nature and composition of fertilizer determine its corrosion characteristics. Fertilizer may be acidic, basic or neutral; their pH and hygroscopicity affect their corrosiveness in the presence of moisture (25).

Broadly speaking corrosion problem can occur in fertilizer industry in three areas:

i. production
ii. storage
iii. field application

The chemicals generally used in production of fertilizer are highly corrosive to steel and under certain conditions, even to stainless steels. Therefore special stainless steels, and high cost nickel alloys or titanium may be required to avoid shutdowns resulting from corrosion problem. In the manufacture and handling of nitrogen fertilizer solutions, chromium-nickel stainless steel and aluminium alloys provide working resistance, but copper alloys and zinc are severely corroded. Corrosion in fertilizer plants may lead to contamination of products, loss of material and equipment and operating time. It may increase maintenance expenses.

Agricultural machinery used for application of fertilizer in fields is usually made out of carbon steel. Protection against corrosion is provided by special coatings. But the coatings may deteriorate by acidic and basic characteristics of the fertilizers. This may lead to further corrosion of the unprotected areas of steel equipments.

Concentrated sulphuric acid (even upto 97.5 %) attack steel and iron with the evolution of hydrogen and a little of SO_2 gas. Corrosion gets intensified on increasing temperature (26).

At the stage of formation of phosphoric acid for manufacturing a phosphate base fertilizer, a sort of erosion type corrosion (26) problem arises due to the formation of acid slurry and fluosilicic acid. In modern ammonia plants, corrosion failures in the reformer tubes (HK-40) arise due to internal carburization followed by oxidation and stress corrosion cracking.

In urea plant, while urea is not corrosive to stainless steel, the carbamate solutions are corrosive (26). Corrosion problems with carbamate solution at high temperature and concentration is severe. Titanium and Zirconium have good resistance in carbamate service (26), but introduce great fabrication problems and are very expensive. However, in absence of any other suitable material for construction, the preference is still with titanium cladded vessels.

Catastrophic failures of all the stainless steel tubes by stress corrosion cracking were reported (27) in a polymer drier made of carbon steel shell internally cladded with austenitic stainless steel 316L.

Corrosion problems in refineries arise due to the presence of salts in the crude, as they evolve acidic substances like hydrogen sulphides, mercaptans (sulphur), hydrochlorides and napthanic acids; these cause severe corrosion of plant equipments. Different crudes cause different types of corrosion and it is necessary to identify them and eliminate their effect as far as possible. The first plant to be carefully looked into to combat corrosion due to crudes is the distillation unit in any refinery; corrosion to be tackled at hotter and cooler zones of the distillation unit also varies.

In the Gujarat refinery, Baroda, napthanic corrosion, due to North Gujarat crude, is severe and varies from 9 mmpy to 13 mmpy (28). The iron napthanate corrosion product is oil soluble and is swept away by the process stream and leaves behind sharp edged pits and holes.

Corrosion of underground pipeline has been and continues to be a serious economic problem. Assessment of economic losses in USA on account of pipeline corrosion has been reported to be several billion dollars. Similar estimate in India has not been made so far, but it can be assumed that with thousands of miles of pipe line, maintenance and repair cost, because of corrosion, should be quite enormous.

The significant factors that promote soil corrosion include low soil resistivity, potential difference (galvanic effect), presence of bacteria, low pH and structural properties which contribute to formation of differential aeration cell. For considering effective protection of the pipeline from soil corrosion it is essential to have an idea about the corrosion characteristics of the soil.

Instances of frequent failures of large diameter water mains (steel pipes) in a metropolitan city have been reported (29). The water mains are bare pipes and can give about 30-40 years of service before corrosion can render them useless. Corrosion failure of newly laid cast iron pipes in rural areas have also been cited (29).

The chloride ion is known to initiate corrosion of steel in concrete. Introduction of chloride ion from several sources (sodium chloride from deicing salt, sea salts and calcium chloride added to concrete during mixing and acceleration) disrupts the passive film and as a result causes a severe corrosion problem for steel in concrete (30). The corrosion product builds up tensile stresses of sufficient magnitude to crack the concrete. This will cause the reinforcing steel to be directly exposed to the corrosive environments which intensifies the corrosion.

It has been reported that the cost of repairing bridge deck in the U.S. in 1975 was $ 200 million (31). This cost increased to $ 600 million in 1979 (32). Much of this repair was due to corrosion.

One of the factors which provide for an uninterrupted operation of telecommunication cables is their timely and reliable protection against corrosion. The importance of this factor strongly increases in connection with the use of steel for cable sheaths because steel, as far as its corrosion resistance in soil environment is concerned, is considerably inferior to lead and sometimes inferior to aluminium due to design peculiarities of telecommunication cable sheaths. The result of investigations on the protection of corrugated sheaths against soil corrosion and stray current corrosion by means of insulating sheath is of great practical interest (33).

Materials used in nuclear reactor core are exposed to a corrosive environment which is characterised by the presence of intense radiation fields in addition to severe thermal and mechanical conditions. Many corrosion problems observed in the core materials are caused primarily by the presence of nuclear radiations and their consequent effect in the reactor core environment. The most important component in a reactor core is the fuel element. The cladding material of the fuel elements in a nuclear reactor suffers corrosive attack on the external surface (by coolant) as well as on the internal surface (by fuel). In water cooled reactor fuel elements using Zircalloy-2 cladding, the main corrosion problems are accelerated corrosion (e.g. nodular corrosion, fretting, weld contamination by nitrogen), internal hydriding of sunburst type and stress corrosion cracking of Zircalloy reduced by fission product iodine (34). Most of these problems have been solved by appropriate control of water chemistry, material improvement and control of harmful impurities in the components during fabrication.

In liquid metal cooled fast breeder reactor, the stainless steel cladding of the fuel element is exposed to high temperature sodium on external surface and to the corrosive attack of high temperature fuel on the cladding inner surface. Sodium corrosion is exhibited as selective leaching of alloying elements from stainless steel and clad wall thinning due to general corrosion (34).

In tropical harbours of India, the sea water characteristics have been found out by Naval Chemical and Metallurgical Laboratory, Bombay. It is predicted that the average corrosion penetration over ten years' period can be 71 mils for mild steel in Indian tropical waters (35). However, the data generated indicated that mild steel, stainless steel and aluminium suffer from localised corrosion.

In Indian waters the rate of generating fouling debris have been of the order of 8 to 9 Kg. per square meter per year (35). The biofouling deposit also is conducive to the growth of aerobic bacertia producing harmful sulphides. The presence of anaerobic bacteria under fouling deposits leads to severe pitting on ferrous and non-ferrous metals.

(e) Principle of open recirculating cooling water system:

Water is one of the most essential commodity of life as well as of industries. No activity the humans indulge in could be imagined to be fruitful without the existence of water. Besides the well known traditional uses of water, such as for drinking, washing, irrigation, navigation etc., the industrial uses of water are many and varied.

Three-fourth of our earth's surface is covered with water. Water thus seems to be plenty. However, excepting the navigational use, the usable water on this planet is approximately 0.03 %.

The chemical industries consume water in as a large amount as about 33 % of the total annual consumption of industrial waters. The next only to the chemical industries are the metal producing industries in their consumption of water, say, to the tune of about 32 %. This creates a very dismal picture as far as the availability of water is concerned, since with technological advancement and industrial growth, the industrial share of water is bound to go up while the sources of water do not seem to multiply.

Of the chemical industries' share of water, about 66 % is used for cooling purposes. Cooling water is used for removing unusable heat from process streams; this water flows back with the energy it has stored and unable to shirk off. Obviously, most industries return their used waters in contaminated condition to the source. In order to be able to recirculate the once used water, a lot has to be done to make it suitable for the purpose.

Cooling tower:

In Fig.1 is given a schematic diagram describing a counter flow evaporative cooling tower with induced draft provided by one or more fans.

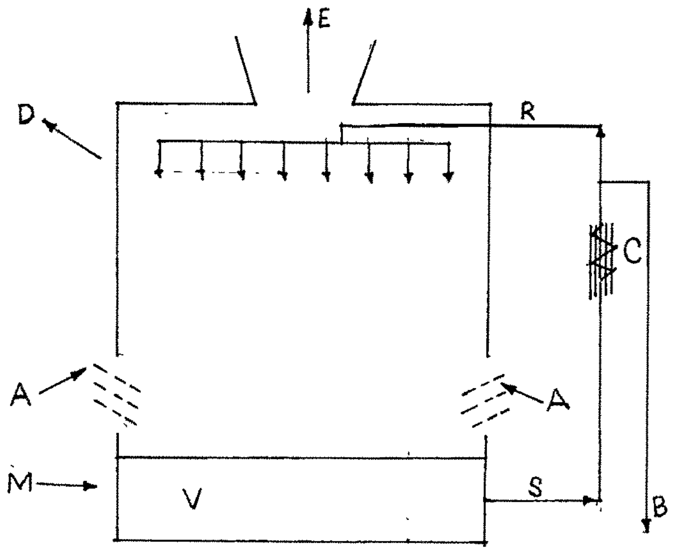


Fig. 1 : A counter flow evaporative cooling tower

(A) Air (B) Blow down (C) Heat exchanger (D) Driftor windage loss (E) Evaporation (M) Makeup water (R) Return water (S) Supply water (V) Volume of the system

The system is put into operation by filling it with V gallons of fresh water. A supply of water S is pumped from the basin through a heat exchanger C cooling some process, itself being warmed. The warm water return R is pumped to the plenum at the top of the cooling tower and distributed uniformly over the cross-sectional area through an assembly of nozzles.

The interior of the structure contains splash packing, or fill material, constructed of slats stacked in decks and spaced in staggered rows. Water splashes from row to row, breaking into droplets, at the rate of 2-4 gpm/ft^2. This rate is called the "water loading" of the tower. Film packing is also used, which exposes water to air in thin films over the surface of the fill. Fill is made of wood, cellulose, sheets, moulded polystyrene or asbestos sheets. It is essential that the fill material wets well, otherwise water splashes in rivulets instead of droplets.

The most efficient and economical cooling tower is one with mechanical draft as depicted in Fig.1, in which air A is drawn in through louvers just above the basin, and then upward counterflow to the descending rain of water. The velocity of the air is 300-700 ft. per minute.

Two kinds of heat transfer occurs within the tower between warm water and air. Some of the liquid changes to vapour with the absorption of heat. This energy, called the latent heat of vaporization, is necessary to overcome the attractive forces between molecules in liquid state. This heat, about 100 Btu/lb, is abstracted from the remaining liquid water and lowers its temperature. Absorption of latent heat accounts for 75-80 percent of the heat transferred in cooling towers. As long as the wet bulb temperature which is a measure of heat content of the atmospheric air, is lower than the water temperature, heat is transferred from the water to the air, raising its temperature and lowering that of water. This is called sensible heat; it accounts for the remaining 20-25 percent of heat transferred.

The stream of air and water vapour containing entrained droplets, is drawn upward through the tower by the fans, and passes through a 'drift eliminator' - an arrangement of baffles that produces sudden changes of direction of stream. Water droplets are thus separated from the vapour stream, and fall with the bulk of water into the basin. Water vapour E and air pass out through the fan stack to the atmosphere. A small amount of liquid water D is blown out of the tower by wind. This is called drift or windage loss; in a well designed tower it amounts to 0.1-0.2 percent of circulation rate.

A volume of water B is continuously withdrawn from the system, and another volume of fresh water M is added to the basin to maintain the total volume of water V constant:

$$M = E + B + D$$

The rate at which heat transfers in a cooling tower depends upon four factors:

1) The area of the water surface in contact with air
2) The relative velocity of air and water
3) The time of contact between air and water
4) The difference between the wet-bulb temperature of the inlet air A and the temperature of the returned water R.

Item (1) depends upon construction of fill, (2) can be controlled within limits by regulating the speed of the fans (3) is a function of (2) and the height of tower and (4) is fixed by climate.

(f) Cooling Waters:

Sources and utilization

Water is most abundant and widely distributed and used naturally occuring chemical compound. 75 % of surface of the earth is covered with water to an average depth of over two miles. In the summer the air above each square mile of land or sea may contain as much as 100,000 tons of water vapour (36).

Water furnishes steam, electricity and navigation facility and is a solvent for cleaning and washing in industries. A U.S.A. report (37) says that industries are prime users of water (160 billion gallons per day), irrigation, being the second largest user (141 billion gallons per day), while municipalities use about 22 billion gallons per day.

Much of the water used by industries for washing or cooling purposes or for irrigation, is simply a sort of 'borrowed' water and may be returned in practically uncontaminated condition for reuse at the site or at lower level.

Most places of the world with dense population have sufficient water for atleast limited domestic use. In exceptional places supplemental measures for providing better water facility may be taken, such as saline water recovery, sewage reclamation, reservoir evaporation control, besides the usual restrictive usage system.

It should be clear from Table 5 that the usable fresh water is of meagre amount.

Table 5

Estimated relative quantities of water available in earth's hydrosphere (38)

Source	Million acre-feet	index of amount relative to soil index	Total estimated fresh water present %
Oceans	1,060,000,000	51,960	
Atmosphere earth's crust[a] fresh water bodies	33,016,084	1,618	100
Polar ice and glaciers	24,668,000	1,209	74.72
Hydrated earth minerals	336	0.16	0.001
Lakes	101,000	5	0.31
Rivers	933	0.046	0.003
Soil moisture	20,400	1	0.01
Ground waters: Fissuers to 2500 ft	3,648.00	179	11.05
Fissures 2500 to 12500 ft	4,565,000	224	13.83
Plants and animals	915	0.045	0.003
Atmosphere	11,500	0.56	0.035
Hydrological cycle, annual:			
Precipitation on land	89,000	4.4	
Stream run off	28,460	1.4	

a=to 12,5000 ft. depth only

The above stated figures of large quantities of water availability and the contradictory figure of meagre amount of fresh water available, project a gloomy picture of the water availability by the turn of century. One can have a glimpse of the extent of industrial utilization of water by knowing the amount consumed in an advanced industrialized civilization. In the United States of America, the projected consumption of water upto 1980 for conventional industrial utilization was of about 600 billion gallons (39) as shown in fig.2.

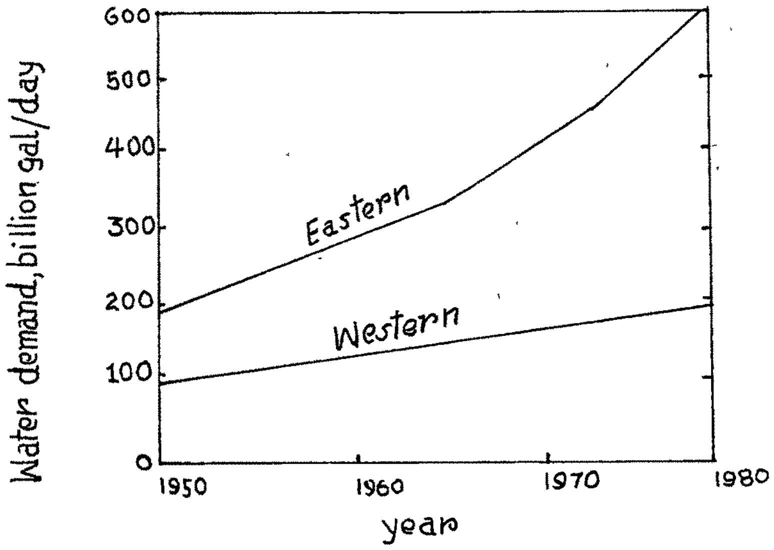


Fig.2 : Overall U.S. water demand projected to 1980

As is well known in many of the process industries, water is used for suspending, washing and condensing or cooling operations. Water requirements may be from 20,000 to 2,000,000 gal/ton of finished product. The aluminium companies report that 320,000 gal. is required for each ton of metal produced (40). It takes 770 gal. to refine a barrel of petroleum 200,000 gal. to make a ton of viscose rayon and 600,000 gal. to make a ton of synthetic rubber.

One of the potential uses of water in large amounts is for cooling water in chemical industry and for nuclear reactors. An estimate for water consumption for chemical process industries for the span 1969-1974 was of $ 1.8 billion (41). Some 50 trillion (1 trillion = 10^{12} gallons) were used for cooling in 1964, and probably 60 trillion in 1969. However, this would have caused thermal pollution, with the discharge of waste heat into natural waters with deterous effects on aquatic life. Cooling ponds and evaporative cooling towers are the most widely used methods of dissipating heat.

One aspect of water recovery that is interesting is that of treatment and utilization of sewage water. Sewage effluent (treated), with or without further industrial treatment, is used as industrial coolant or for long-distance transporting of solids, such as powdered coal.

There is wide variation in water usage from one industry to another. Table 6 summarizes the annual water use by selected industries (42).

Table 6

Annual water use by Industries

Types of Industry	Annual use (gallons)	approximate % of total industrial use
Primary metal manufacture	4.5×10^2	32
Chemicals and Allied products	3.2×10^{12}	23
Paper industry	2×10^2	14
Petroleum and coal products	1.3×10^{12}	9
Food industry	750×10^9	5
Stone and Vitreous products	248×10^9	2
Transportation equipment	247×10^9	2
Rubber and plastics	163×10^9	1
Non-electrical machinery	103×10^9	
Fabricated metals	57×10^9	
Instruments and related products	30×10^9	
Leather	16×10^9	
Miscellaneous	13×10^9	
Tobacco	3×10^9	
Furniture	3×10^9	

Several industrial groups use more than one trillion of water annually, with the aggregate industrial water use estimated to be in excess of 15 trillion gallons annually.

The use of water in an industry varies with the type of industry. For example the major use of water in a power plant is for cooling, whereas the major use of water in textile industry is for product preparation. In a typical cannery 34 percent of water is used for raw product preparation (including peeling), 6 percent for syrup or brine, 14 percent for cooling, 8 percent for clean up and 3 percent for miscellaneous uses (43).

It is estimated that 66 percent of the total water in industry is used for cooling.

As estimate for water requirements for principal water using industries for the span 1954-2000 is summarised in Table 7 (44 a).

Table 7

Water requirements of the principal industries, 1954-2000 (billions of gallon)

Industry	Year 1954 %	1959 %	1980 %	2000 %
Iron and steel	36.6	35.7	26.8	20.8
Chemical	30.9	32.7	40.7	48.2
Pulp and paper	20.9	21.8	26.0	26.3

Table 7 (contd)

Industry	Year 1954 %	 1959 %	 1980 %	 2000 %
Food	7.7	6.4	3.8	2.4
Aluminium	3.4	2.9	2.3	1.9
Copper	0.5	0.5	0.4	0.4
Total	100	100	100	100

Environmental problems associated with water use

Two fundamental problems associated with the use of large quantities of water include depletion and deterioration of its quality. Water depletion requires improved water conservation practices, whereas water quality is maintained with waste treatment techniques. These two problems are interrelated because the volume of waste water is related to the volume of water withdrawals. Reduced withdrawals imply less waste water and therefore cleaner water. The supply of usable water is also augmented through waste treatment practices. Consequently, a national water policy must recognise the interdependence of water supply and pollution control and stress both conservation and waste treatment.

Water quality changes by industrial use

Water is utilized by, and waste water generated from, more than 300,000 industrial plants in United States (44 b). Industrial production that gives rise to industrial wastes is increasing at about 4.5 percent each year, or three time faster than the population. As the intake water is used for various purposes in plant, including heat transfer, product transport, product washing and preparation and product composition and plant house keeping, its quality is altered. Water quality can be considered in terms of physical, chemical, bacteriological and radiological parameters.

Lastly, the abundant quantities of sea waters, though available to coastal industry, poses a specific type of corrosion, water treatment and related problems. Most industries return their used water in contaminated condition to rivers, lakes, etc. Due to poisonous cations and anions, not only the water becomes impotable but leads to a variety of cooling water problems, which lowers the productivity of process plants. Modern civilization and unchecked population explosion have resulted into myriad industries. Accordingly the thirst for water has increased enormously.

It will not be out of place to stress the frequent examples of acid rain water fall near and miles away of an industrial complex. This unwanted addition in lakes or rivers deteriorate the conditions of freshwater.

All this leads to the solemn thought of conserving by way of reutilization of this 'life blood' of process industry. But conservation by reutilization may give rise to problems such as corrosion, scaling, fouling, algae and micro organisms to be tackled before putting such waters to industrial reuse.

(g) Associated problems

The users of cooling water in chemical process industries face serious corrosion and scaling problems in condensers/coolers and other associated equipment, leading to failure of condensers/coolers due to leakage of tubes, unscheduled shutdowns and consequent loss of production. The bad quality of make-up waters and operating parameters of cooling water give rise to a variety of problems. Corrosion, scaling, deposition and fouling of heat transfer surfaces of cooling water side and reduction in flow of water through the condensers etc. are the usual problems. These adversely affect the heat transfer resulting into reduction of production. Hence, proper care during the operation of cooling water treatment is necessary to monitor and maintain the cooling water parameters to control cooling water side corrosion, scaling and fouling problems and reduce unscheduled shutdowns. The care during pre-commissioning, commissioning and idle periods is also necessary to avoid early corrosion failures on cooling water side. The equipment and piping on cooling water side are required to be passivated during pre-commissioning prior to regular treatment. Generally, there are three cooling water systems:

I open recirculating system
II closed recirculating system
III once through system

(i) Open recirculating system

This is the most widely used industrial cooling design. It consists of cooling tower, pumps and heat exchangers. The pumps keep the water recirculating through heat exchangers where it picks up heat on to the cooling tower where heat is released from the water through evaporation. Thus the heated water gets cooled in cooling towers with natural or mechanical draft provided in tower. Because of evaporation, the water in open recirculating systems undergoes changes in its basic chemistry, or in simpler term, it gets concentrated.

(i) This system permits great economy in make-up water requirement
(ii) Average temperature change is 10°-30°F
(iii) Examples: spray ponds, cooling tower, evaporative condensers.

(ii) Closed recirculating system

These systems use the same cooling water repeatedly in a continuous cycle. First the water absorbs heat from process fluids, then releases it in another heat exchanger and then the steps are repeated.

(i) In this system, amount of water used is negligible
(ii) Average temperature change is 10°-15°F
(iii) Examples: Diesel Engine jackets, Automobile radiators and chilled water system

(iii) Once through systems

In this system, the cooling water passes through the heat exchange equipment only once. The mineral content of the cooling water remains practically unchanged as it passes through the system.

(i) Amount of water is extremely large
(ii) Temperature change is 5°-10°F
(iii) Examples: Potable water systems, process water, general services etc.

Most industries use open recirculating cooling water system. In this process, water absorbs the heat from hot streams and is reused after cooling the same in cooling tower.

In open recirculating cooling water system, the concentration of dissolved solids builds up due to the evaporation and an equal amount of raw water is added to make up for evaporation, windage (drift) and blow-down losses. The deposition of salts and microbiological slime may promote under deposit corrosion. Accumulation of sediments, corrosion products, scale and slime may reduce the flow of water in the condensers/coolers and other equipment, as well as reduce heat transfer efficiency. Heavy growth of algae and bacteria in the cooling water system and its carry over can contribute to formation of slime and tubercles in water boxes and pipelines etc. Most of the operating plants have problems with the cooling water such as -

(a) Corrosion and pitting of condensers/coolers and other equipments using cooling water and

(b) scaling and fouling of the heat transfer surfaces.

Cooling water is given corrosion inhibiting treatment in order to achieve maximum efficiency in heat transfer at optimum cost. It should be treated for :

(a) corrosion of metal surface in contact with recirculating water,

(b) scaling of cooling surfaces,

(c) biological growth and subsequent fouling of cooling surfaces,

(d) deterioration of cooling tower timber,

(e) conservation of water,

(f) reduction of suspended solids, and

(g) increasing the life of exchangers/condensers/coolers and reducing the unscheduled shutdowns.

(a) Corrosion:

Most research is devoted to preventing corrosion in open recirculating water system. Effective anticorrosion measures have been developed which can be applied in most instances at reasonable cost. Today, the expense of corrosion prevention is minor compared to the cost of equipment replacement, downtime and production losses. Corrosion damage can require complete replacement of heat exchangers, pumps, lines and equipment. Corrosivity of recirculating water increases due to air saturation and contaminations. Various factors controlling the corrosion are given as follows:

I. Chemical factors

A. pH : acid soluble metal oxides become more soluble as pH decreases resulting into increased corrosion

B. Dissolved salts:
Chlorides and sulphates can penetrate passive metal oxide films and promote local attack.

Alkalinity may induce Ca-Mg salts to precipitate to form protective barrier.

C. Dissolved gases

i. CO_2 : reduces pH and promotes acid attack
ii. O_2 : depolarizes corrosion reaction at cathode, oxygen deficient areas become anodic (differential aeration cells)
iii. N_2 : aggravates cavitation corrosion
iv. NH_3 : Selectively corrosive to copper based metals
v. H_2S : promotes acid attack

D. Suspended solids:

Mud, sand, silt, clay, dirt etc. settle to form deposits promoting differential aeration cells.

E. Micro organisms:

Promote acid attack, differential aeration cell corrosion, cathodic depolarization, galvanic corrosion.

II. Physical factors

A. Relative Areas:

In a galvanic couple, as ratio of cathodic to anodic area increases, corrosion increases.

B. Temperature:

Increased temperature favours oxygen depolarization, lowers hydrogen over voltage, increases corrosion.

C. **Velocity :**

High velocity promotes erosion-corrosion, remove certain passivating corrosion products.

Low velocity increases sedimentation and differential aeration cell corrosion, decreases amount of corrosion inhibitor reaching passivating metal surfaces.

D. Heat Transfer:

Favours oxygen depolarization by "hotwall effect", favours differential aeration cell formation by increase of precipitation and sedimentation of solids.

E. Metallurgical Impact:

(a) Surface flows: cuts, nicks, scratches etc.
favour anodic site formation
(b) Internal stresses: promote anodic site formation
(c) Micro structure: metal inclusions, precipitation at grain boundaries, differing adjacent grains etc. promote galvanic corrosion.

Corrosion occurring in cooling water may be said to be largely electrochemical in nature. It has been demonstrated that the primary process in dissolution of metals in water is electrochemical in nature. The attack is basically chemical accompanied by the passage of an electric current. It occurs due to a potential difference existing between one part of the structure and another.

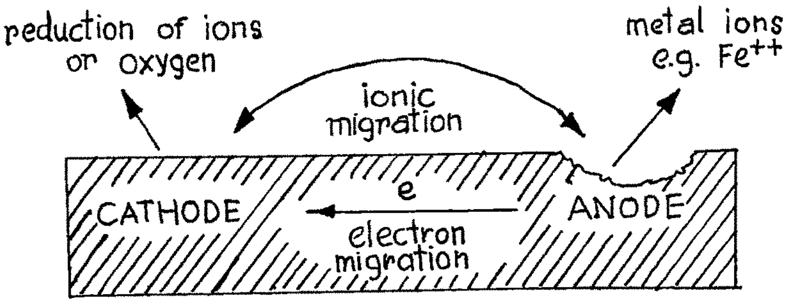


Fig. 3 : Electrochemical nature of corrosion

The primary reaction in the region of lower potential, the anode, is the dissolution of metal in the form of ions, e.g.

$$Fe \rightarrow Fe^{++} + 2e \text{ (electrons)}$$

The electrons liberated migrate through the metal part toward higher potential, the cathode, where they are utilised in the reduction of either ions or oxygen. The overall effect is the passage of a current through the circuit formed by metal and solution, the current carriers being electrons in the metal and dissolved ions in solution. Positively charged cations as H^+ and Na^+ migrate to the cathode and anions such as OH^-, Cl^- and SO_4^{--} to the anode.

A number of reactions is possible at the cathode (Fig.4) including:

1. Reduction of hydrogen

   $2H^+ + 2e \rightarrow 2H \rightarrow H_2$

2. Reduction of oxygen

   $O_2 + 2H_2O + 4e \rightarrow 4OH^-$

3. Reduction of sulphate (with the aid of bacteria)

   $4H_2 + SO_4^{--} \rightarrow S^{--} + 4H_2O$

4. Reduction of metal ions

   $Fe^{+++} + e \rightarrow Fe^{++}$

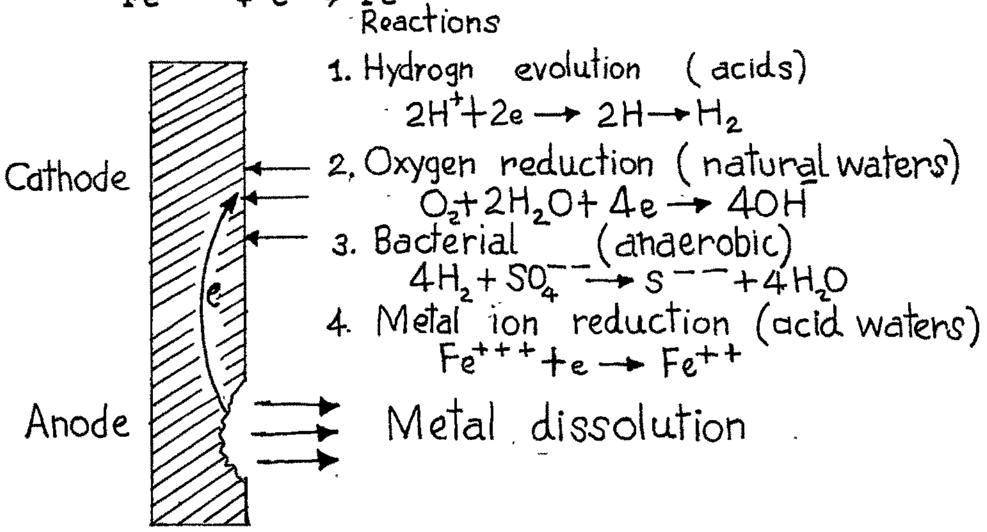


Fig.4 : Reactions on the metal surface in a simple corrosion cell

Hydrogen reduction is the main cathodic process in acid solutions where the metal dissolves with the simultaneous evolution of hydrogen gas. The accumulation of metal ions in the solution can lead to active participation of these ions in the corrosion process giving rise to the alternative cathodic process (reaction 4). This can occur with metals which have two valencies such as copper and iron and which can exist in solution as cupric and cuprous or ferric and ferrous ions respectively. This type of cathodic reaction is usually considered to be the cause of the corrosion of iron in acid mine water, the ferrous iron formed at the cathode by reaction 4 being subsequently oxidized back to the ferric form by dissolved oxygen. The reaction 2, oxygen reduction, is mostly responsible for the corrosion of metals in natural waters which have an approximately neutral reaction, i.e. are only slightly acidic or alkaline. Corrosion in such a medium is accompanied by the formation of solid product by interaction between the anodic and cathodic products, e.g.

$$Fe^{++} + 2OH^{-} \rightarrow Fe\ (OH)_2$$

When the optimum solubility of ferrous hydroxide has reached, a white product will start to precipitate from solution. In oxygenated conditions this will be rapidly oxidized to form, firstly, ferric hydroxide

$$4\ Fe\ (OH)_2 + O_2 + 2H_2O \longrightarrow 4Fe(OH)_3$$

This is unstable and subsequently loses water to form hydrated ferric oxide, FeO.OH or $Fe_2O_3.xH_2O$ (red rust),

$$Fe(OH)_3 \longrightarrow FeO.OH + H_2O$$

One of the two forms of hydrated ferric oxide is normally found in the corrosion product of iron in water, α — FeO.OH, similar in structure to the mineral goethite, and γ-FeO.OH, similar in structure to the mineral lepidocrocite or limonite. Magnetite, Fe_3O_4, haematite, α- Fe_2O_3 and maghaemite, γ-Fe_2O_3 are also formed.

In the absence of oxygen, e.g. in water from which the air has been removed, corrosion of iron can still proceed by the reaction 3 in the presence of adequate dissolved sulphate, it being usually present in sufficient concentration, in most natural waters. The bacteria, disulpho-vibrio-disulphuricans, are able to use cathodic hydrogen in their living process and bring about the reduction of sulphate to form sulphide. This type of cathodic process can also occur in aerated solutions beneath any impervious corrosion product which prevents access of oxygen to the surface of the metal. In any given circumstance more than one of the four possible reactions cited may participate in the overall cathodic process and the latter may vary with time. Thus, in acid solutions reduction of metal ions and hydrogen ions can occur, while in only slightly acidic or alkaline solutions a certain amount of hydrogen is evolved even when oxygen is present. Again in a closed vessel, corrosion can proceed by oxygen reduction until all the oxygen has been removed when sulphate-reducing bacteria can take over.

Different types of corrosion associated with cooling water systems are :

(i) pitting or localised attack
(ii) uniform general attack
(iii) stress corrosion cracking and
(iv) tuberculation

Pitting is usually caused by the concentration of electric current resulting from potential differences on the metal surface. The contact of dissimilar materials, the relative size of anodic and cathodic areas and stain have more or less the tendency to cause pitting. Pitting in turn causes failure of equipments even though other parts of equipments may remain in good condition.

Uniform corrosion over the whole surface is due to uniform general attack. A surface with a uniform deposit exhibits a reasonably uniform corrosion.

Cracking results from the combined effect of corrosion and stress. It is called stress corrosion cracking. It is mainly due to high chloride content of the cooling water.

Tuberculation is the formation of localised corrosion products distributed over the surface in the form of knoblike mounds. Pitting of the interior of iron and steel is mainly due to tuberculation.

The main objection of the tuberculation is the increase in friction and reduction in flow which in the case of small water pipes sometimes result in complete clogging of piping system.

(b) Scaling and fouling (Deposits):

The primary goal of cooling water treatment is to maintain deposit free system at a minimum cost. Otherwise deposits can cause the following problems on heat transfer surfaces:

(a) Reduced or uneven heat transfer
(b) Hot spots causing equipment failure
(c) Poor corrosion inhibition
(d) Reduced output
(e) Increased pumping cost
(f) Necessity of frequent cleaning

Deposit consists of scale and fouling.

Scaling:

Hard and dense deposits are termed scale and formed by precipitation and crystallization of inorganic solids in suspension. Scale forming substances are calcium carbonate, calcium sulphate, calcium phosphate, silica, magnesium compounds, iron and manganese.

(i) Calcium carbonate scale formation

Almost all naturally occurring water contains quantities of calcium bicarbonate which decomposes within the cooling system by action of heat in the following manner:

$$Ca(HCO_3)_2 = CaCO_3 + H_2O + CO_2$$

Calcium carbonate scaling can be predicted qualitatively by the Langelier saturation index and Ryznar stability index.

$$\text{Saturation index} = pH - pH_s$$
$$\text{Stability index} = 2\,pH_s - pH$$

where pH is the system water pH. The value of pHs is a function of total solids, temperature, calcium and alkalinity. If the saturation index is positive, it indicates calcium carbonate deposition. The stability index shows the same tendency when a value of 6 or less is obtained. The value of pH_s can be calculated from Table 8.

Table 8

Data for rapid calculation of Langlier saturation index and **Ryzner** stability index.

A Total solids (p.p.m.)		A	C Calcium hardness (p.p.m. $CaCO_3$)	C	D M.O. alkalinity (p.p.m. $CaCO_3$)	D
50-300		0.1	10.11	0.6	10-11	1.0
400-1000		0.2	12-13	0.7	12-13	1.1
B			14-17	0.8	14-17	1.2
Temperature			18-22	0.9	18-22	1.3
(°F)	(°C)	B	23-27	1.0	23-27	1.4
32-34	0-1	2.6	28-34	1.1	28-35	1.5
36-42	2-6	2.5	35-43	1.2	36-44	1.6
44-48	7-9	2.4	44-55	1.3	45-55	1.7
50-56	10-13	2.3	56-69	1.4	56-69	1.8
58-60	14-17	2.2	88-110	1.6	89-110	2.0
64-70	18-21	2.1	111-138	1.7	111-139	2.1
72-80	22-27	2.0	139-174	1.8	140-176	2.2
82-88	28-31	1.9	175-220	1.9	177-220	2.3
90-98	32-37	1.8	230-270	2.0	23 -270	2.4
100-110	38-43	1.7	280-340	2.1	280-350	2.5
112-122	44-49	1.6	350-430	2.2	360-440	2.6
124-132	50-55	1.5	440-550	2.3	450-550	2.7
134-140	56-60	1.4	560-690	2.4	560-690	2.8
148-160	61-71	1.3	700-870	2.5	700-800	2.9
162-178	72-82	1.2	880-1000	2.6	890-1000	3.0
			1020-1140	2.7		
			1150-1270	2.8		

$$pH_s = (9.3 + A + B) - (C + D)$$

The values of A, B, C and D are taken from Table 8.

Mayenkar (45) has tabulated the corrosive and scaling tendency of water (Table 9).

Table 9

Corrosive and Scaling tendency of Water

Actual pH - pH_s	Water quality
0 to 0.5	Little or no scaling
0.5 to 1.0	Little or light scaling
1 to 2.0	Little to significant scaling
Greater than 2	Significant to heavy scaling
0 to - 0.5	Little or no corrosion
-0.5 to -1.0	Little or light corrosion
-1.0 to -2.0	Light to significant corrosion
Less than -2.0	Significant to heavy corrosion

(ii) Calcium sulphate scale formation:

Calcium sulphate is fairly soluble and usually does not pose a problem in cooling system with proper blowdown. To avoid scaling, the sum of calcium and sulphate (both expressed as mg/l $CaCO_3$) should be below 1500 and their product should be less than 400,000-500,000. This corresponds to gypsum concentration of about 1200 mg/l. It is to be noted that calcium sulphate scale formation increases with increase in acidity.

(iii) Calcium phosphate scale formation:

The phosphate content of circulating water seldom exceeds 50 ppm. Precipitation can be avoided by regulating the hardness and pH.

(iv) Silica scale formation:

In cooling system, silica may deposit as a scale on heat transfer surfaces and may therefore be a limiting parameter. Dissolved silica in natural water exists in the form of $Si(OH)_4$ as ortho silicic acid. Silica may deposit if the evaporation rate is such that concentration in the circulating water exceeds its solubility. This value is not known, but towers have operated satisfactorily at pH 6.5 with 150 ppm SiO_2 and at pH of 8.0 with 225 ppm SiO_2.

(v) Magnesium compounds scale formation:

Deposits such as magnesium carbonate or magnesium silicate usually are not found in large quantities in cooling water systems. The conditions under which deposits form normally are not encountered. Usually pH readings above 9.0 and high quantities of magnesium salts in the system water are needed for scaling.

(vi) Iron and Manganese scale formation:

Iron and manganese deposits are common and pose a serious problem to users of water having a high iron or manganese content. Iron usually in ferrous form does not cause problem in itself. When water is aerated or chlorinated, or when any other oxidizing material is added, the soluble iron is converted into insoluble ferric iron which produces the precipitation of iron and manganese. These deposits adhere to metal surface or combine with other minerals to form deposits in line or heat exchanger equipment.

Factors that influence scaling:

(i) Temperature
(ii) pH or alkalinity
(iii) Solubility

Fouling:

Fouling of heat exchanger tubes is usually defined as deposition of non scale forming materials such as:

(i) Silt or iron suspended in makeup water
(ii) Naturally occurring organics in makeup water
(iii) Particulate matter scrubbed from the atmosphere and deposition of chemical additives due to poor control
(iv) Organic contamination from process leaks

(v) Migrating corrosion products

Extent of fouling depends on

(i) Water characteristics
(ii) Temperature
(iii) Velocity
(iv) Microbiological growth
(v) Corrosion product
(vi) Oil

c. Microbiological growth:

One of the primary problems affecting efficient operation of a recirculating cooling water system is the excessive growth of microscopic organisms which can cause following problems:

(i) Reduce heat transfer or restrict circulation in heat exchangers
(ii) plug tubes in heat exchangers causing emergency shutdown and loss of production
(iii) Deteriorate metal via under deposit corrosion
(iv) Destory cooling tower timber

In cooling system, three basic types of organism, namely algae, fungi, and bacteria are found. Algae are primitive plants and can vary in size from microscopic to growths several feet in length. Light and water are essential for the growth of algae and as such, they only grow on parts of the cooling tower exposed to day light and which are subjected to constant wetting. Algae can block the distribution system and screens. Alexopoulos and Bold (46) have published a thorough study of algae and fungi in relation to the cooling water problems.

Fungi refers to all simple plants which do not contain chlorophyll and which can therefore grow in dark. Fungal attack on the wooden structure of a cooling tower has been known to cause complete collapse of the tower. Two outstanding contributions to the subject of wood deterioration by fungi have been published by Duncan (47, 48).

Bacterias are unicellular organisms which can grow and reproduce rapidly under favourable conditions. Generally speaking, bacteria are responsible for the most severe problems found in cooling system. Slime forming bacteria are most commonly found and create slime which results in bio-fouling. Sulphate reducing bacteria thrive under anaerobic conditions and reduce sulphates into sulphides (49). Corrosion attributed to sulphate reducer is virtually always localized pitting. The pits are generally filled with block corrosion product which when treated with hydrochloric acid, liberates hydrogen sulphide gas which promotes acid attack. The iron depositing groups are responsible for the formation of hydrated iron oxide deposits in cooling water system piping. These organisms utilize soluble iron in water and deposit insoluble iron oxide in slurry sheath around their cells. Iron bacteria are troublesome because of deposition of iron oxide in piping (50). This type of bacteria are responsible for tubercular type of corrosion.

(h) <u>Systems of Control</u>: <u>Inhibition</u>:

The elimination of corrosion is an unattainable goal. However, for practical purposes, one attempts to keep the wastage at some acceptable level. What is acceptable in one unit may be catastrophic in another. It can be agreed in a general way that probably less than 5 mpy is negligible, 10-20 mpy is moderate, and more than 20 mpy is excessive corrosion.

Inhibiting agents that control corrosion can be classified according to the mechanism of their action as anodic or cathodic inhibitors. In practice, inhibitors are used in combinations.

A. Inhibition mechanism

I. Anodic inhibitor interferes with the anodic process while bringing about inhibition :

$$Fe \rightarrow Fe^{2+} + 2\bar{e}$$

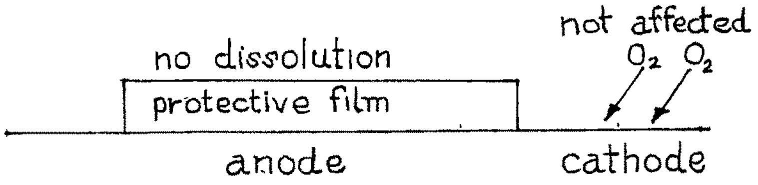


Fig. 5 High concentrations - anodic inhibitor

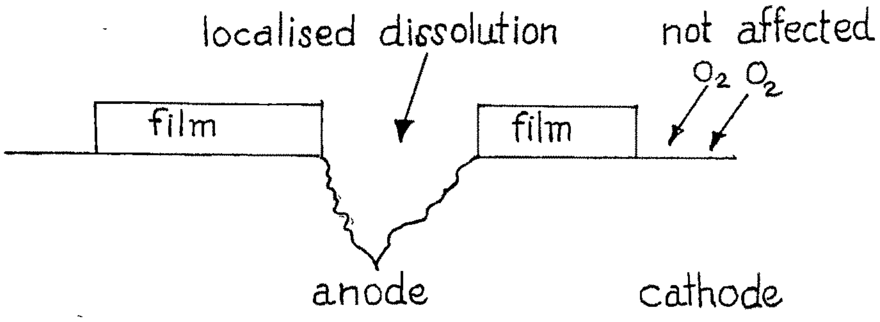


Fig.6 Low concentrations - anodic inhibitor

There are, however, certain dangers involved. Low concentrations cause pitting corrosion and therefore proper concentrations should be maintained.

II. Cathodic inhibitors suppress cathodic reaction:

$$O_2 + 2H_2O + 4e \longrightarrow 4OH$$

Often achieved by precipitating an insoluble species on to cathodic sites

$$Zn^{2+} + 2\ OH \longrightarrow Zn\ (OH)_2 \downarrow$$

forms a barrier preventing a further O_2 reduction

(vi) Chromate-phosphate-Zinc

The use of zinc with phosphate-chromate treatments overcome some of the minor limitations encountered with the dianodic method and provides excellent corrosion protection with lower concentrations of both chromate and phosphate. The use of zinc with dianodic treatments was so successful that a family of treatment was developed, known as 'the zinc dianodics'.

Typical chemical concentrations of a zinc dianodic program are as follows:

1. 15 to 25 ppm chromate
2. 2 to 5 ppm zinc
3. 2 to 5 ppm total phosphate

The pH of such a program is normally maintained in the range of 6 to 7.

(vii) Ultra-low chromate

Regulations limiting chromate discharge forced the evolution of still another chromate-based treatment program, say, ultra low chromate. These programs maintain chromate from 5 to 10 ppm at a pH of 7.5 to 8.5.

Ultra-low chromate programs have been successful only because deposit control agents, such as phosphonates, have allowed operation at pH levels that would normally result into undesirable scaling. Actually, deposits control agents make it possible to use the cathodic inhibiting properties of calcium. The controlled deposition of calcium carbonate at cathodic sites serves the same functions as the precipitation of zinc hydroxide or zinc phosphate in zinc dianodic programs.

Ultra-low chromate programs also take advantage of the reduced corrosion rate as pH of a cooling water is increased. This reduction in corrosivity attributed to increased pH allows operation at lower chromate concentrations while maintaining satisfactory corrosion inhibition.

(viii) Phosphate-phosphonate Treatments

Many early applications in cooling tower systems used polyphosphate at relatively high ranges and resulted in fouling from calcium orthophosphate. Polyphosphate when applied to water undergoes a process of hydrolysis referred to as "reversion" in that it changes back to the natural orthophosphate state.

More recently many successful applications of phosphate treatments have emphasized the lower ranges of phosphate in conjunction with the use of phosphonates. The combination can produce satisfactory corrosion control and virtually no deposition problems, if conscientious control is maintained at all times. The treatment is not as "forgiving" as chromate and requires consistant maintenance of water conditions within recommended control ranges. Some of the control ranges that define this category include:

orthophosphate : 2-10 ppm, polyphosphate : 2-10 ppm
phosphonate : 2-10 ppm, pH 6.5 - 8.5

Many investigators (59) have clearly demonstrated that pretreatment or rapid passivation or repassivation is required with orthophosphate-polyphosphate-phosphonate program when new systems are started up, and after acid cleaning or low pH excursions.

(ix) Zinc-phosphate-phosphonate

If the calcium hardness in the recirculating water is low, consideration should also be given to supplementing the polyphosphate-orthophosphate-phosphonate treatment with zinc. Table 10 provides an example indicating the need for minimum concentration of calcium hardness in water before effective corrosion inhibition can be maintained with a phosphate treatment program.

Table 10

Effect of hardness of phosphate/phosphonate treatment

Phosphate, ppm	pH	Total hardness as $CaCO_3$, ppm	Ca as $CaCO_3$, ppm	Corrosion rate mpy
6.0	8.0	0	0	50
6.0	8.0	110	0	50
6.0	8.0	195	85	0-5
6.0	8.0	381	170	0-5
6.0	8.0	450	340	0-5

(x) Copper inhibitor

When copper or copper alloys are present in the cooling water system, copper corrosion inhibitors, such as one of the azoles, (60-73) should be included in the treatment program.

(xi) Mini-chrome

Another category of chromate-based treatment used at a minimum concentration of chromate is termed 'mini-chrome'. This is essentially a combination of zinc chromate and effective phosphate-phosphonate treatment. Chromate is in the range of 2 to 5 ppm with the other active inhibitors at levels depending on the specific requirements of the system. A copper inhibitor is included when copper or its alloys are present.

pH is maintained negative with respect to the Langelier index and is usually in the range of 6.5 to 7.5.

(xii) Dianodic II^{TM}

The most recent development in nonchromate, environmentally acceptable treatment used a high phosphate level to promote the formation of gamma iron oxide (Fe_2O_3) on steel surfaces with resulting excellent protection. This significant advancement in technology is made possible by using a highly efficient organic agent that inhibits the deposition of calcium phosphate. The system of treatment, combining organic scale inhibitors, ortho and polyphosphates, is identified as dianodic II.

Typical control ranges are as follows:
Total Inorganic phosphate 14-18 ppm
Calcium as $CaCO_3$ - 400-600 ppm
pH 6.8 - 7.2

An organic corrosion inhibitor tolytriazole or benzotriazole, is included for the protection of copper and its alloys.

In many industrial applications, dianodic II has demonstrated corrosion control capabilities equal to or better than those of the earlier chromate phosphate zinc (Zinc dianodic) treatments. Efficient heat exchange is promoted because of the adherent oxide film. The role of the cathodic inhibitor, calcium phosphate, in corrosion protection is minimized with dianodic II in contrast to earlier developments, cleaner surfaces are therefore produced and the cooling system is more resistant to attacks.

(xiii) Nitrite

Sodium nitrite can also be used as a corrosion inhibitor in open recirculating cooling water systems. Nitrite will render metal surfaces passive to corrosive attack by promoting the formation of gamma iron oxide film similar to chromate.

Establishing a protective iron oxide film usually requires feeding sodium nitrite at a very high initial concentration. The feed rate can be reduced to lower levels, 200 to 500 ppm as nitrite, once the protective film is established. Sodium nitrite must be fed continuously for best results.

Oxidizing agents and certain bacteria will attack nitrite. If nitrite concentrations can be held at a constant effective level, satisfactory protection for ferrous metals is realized. Nitrite is not a good corrosion inhibitor for copper or copper alloys. To protect these metals in a nitrite-treated system, it is necessary to use a specific copper inhibitor such as an azole or maintain circulating water conditions in such a way that the self-protective copper oxide film is not removed from the metal surface.

(xiv) Silicates

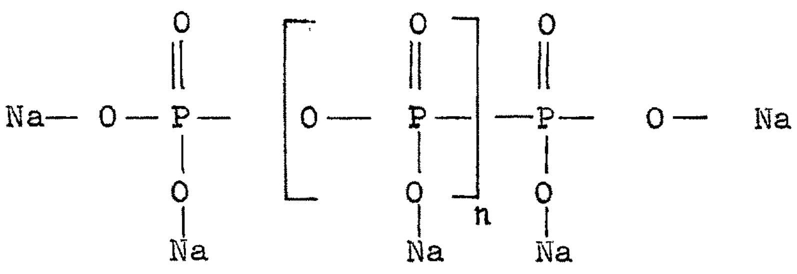
Sodium silicates have been used with some success for corrosion control. Generally, they are applied when chromate, phosphate or nitrite-based treatments cannot be used. Some polymeric species of silicates have produced better results than sodium silicate itself.

To provide protection, silicates require initial iron oxide formation. The silicates appear to function by interacting with the oxide rather than with the metal itself.

(B) Inhibitors (II) (Scaling)

(i) Polyphosphate

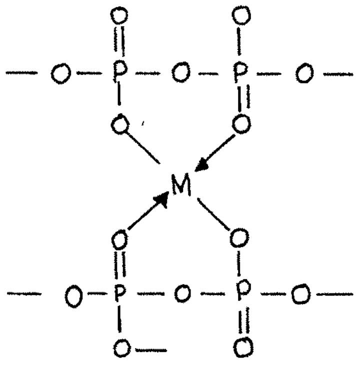
The use of polyphosphates for preventing scale was disclosed many years ago by Rosenstein (74) and since that time their use has spread throughout the world. Phosphurus is pentavalent in these compounds with phosphate groups tetrahedrally co-ordinated to share oxygen atoms.



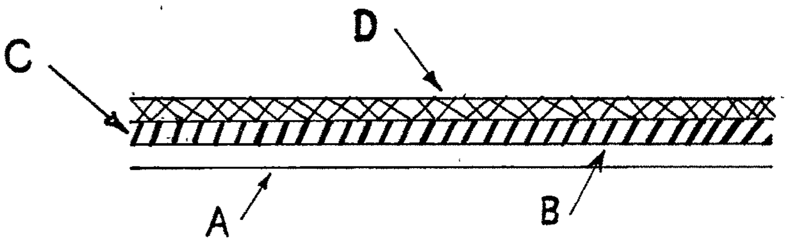
$$\mathrm{Na{-}O{-}\underset{\underset{Na}{|}{O}}{\overset{O}{\overset{\|}{P}}}{-}\left[O{-}\underset{\underset{Na}{|}{O}}{\overset{O}{\overset{\|}{P}}}{-}\right]_{n}{-}\underset{\underset{Na}{|}{O}}{\overset{O}{\overset{\|}{P}}}{-}O{-}Na}$$

Vanwazer (75-79) has published a thorough study of structure and properties of condensed phosphates. Glasses between $Na_2O.P_2O_5$ and $5Na_2O.P_2O_5$ are most used in water treatment. Graham's salt also called sodium hexametaphosphate, has been used for the purpose for many years in industry. It forms an extremely stable complex with calcium which has been formulated as $Na_2Ca_2P_6O_{18}$, although the actual molecular weight is much higher than that indicated by the formula.

The polyphosphates have been variously called condensed, molecularly dehydrated, polymerized and meta phosphates. They are ionized polymers capable of forming chelate rings between any two adjacent phosphate tetrahedra with divalent cations. The chelate structure is :



Polyphosphate is applied at a rate of 0.5 to 5 ppm in circulation water. The treatment utilizes polyphosphate below stoichiometric values required for complexing calcium hardness and is termed threshold treatment. At these concentrations polyphosphate inhibits the crystallization of calcium carbonate from saturation solution. The mechanism of scale inhibition by polyphosphate as scale inhibitor includes (1) threshold effect and (2) protective action.

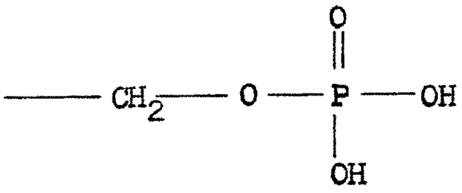


(A) Surface of metal (B) "Eggshell" layer of $CaCO_3$
(C) Adsorbed layer of polyphosphate (D) Deformed crystals of $CaCO_3$

Fig. 10 Mechanism of protective action

Conditions are so arranged that the water is unstable with respect to the deposition of $CaCO_3$, so that a thin layer is deposited on the surface of the metal. A protective film of polyphosphate is adsorbed on the layer of $CaCO_3$ crystals and superimposed on the film is a layer of deformed crystal of calcium carbonate that prevents the growth of normal calcite crystals which lead to scaling. Polyphosphates have little effect on the precipitation of calcium sulphates.

for controlling deposition of calcium scales. Typically, they contain the group in which the carbon-oxygen bond cleaves readily



$$—CH_2—O—\overset{\overset{\large O}{\|}}{\underset{\underset{\large OH}{|}}{P}}—OH$$

forming orthophosphate. In general, phosphate esters give good results with calcium sulphate, but are mediocre inhibitors for calcium carbonate deposition. Their effect, such as it is, is the threshold type i.e. they disturb the kinetics of crystal growth. Hydrolysis to orthophosphate is rapid, otherwise they are similar to sodium polyphosphates, over which they have no discernible advantage.

(iv) Polyphosphate + organics

The polyphosphates and organic combination has been used quite widely as scale preventing treatment. Usually 3 to 5 ppm polyphosphates and 10 to 100 ppm organic combination works better. The organics have the ability of clogging the crystals or scaling material to make the crystals non adherent; consequently, scaling is not produced but sludge trimmed through the normal blow down.

The effectiveness of new organic phosphate scale inhibitors such as polyesters and phosphonates etc. have been amply demonstrated over the years and these products are now well established (85-89). With the use of these antiscalents, the recirculating waters could be maintained in the alkaline range, eliminating thereby the use of acid.

(v) Polymers

Low molecular weight polymers less than 100,000 molecular weight have also been used as scale inhibitors. The polymers adsorb on the crystal structure of scale forming materials and thus limit crystal growth and ultimate scale formation. The most common polymers used in cooling water systems are polyacrylates. These materials are more frequently considered dispersants and retard formation of scale by maintaining small particles crystalline material in suspension.

Polyacrylate with molecular weight less than 10,000 is sometimes described as anti-precipitant, because of complex (not a chelate) formation between calcium ion and the carboxyl groups (90). At higher temperatures, however, it is not effective in preventing the deposition of calcium sulphate or carbonate. Scales of calcium polyacrylates can form from polymers having molecular weights around five million and over; treatment with polymers of high molecular weight (5-10 million) also causes calcium scaling. The dosage is critical.

B. Inhibitors (III) (Fouling)

(i) Dispersants: natural and synthetic types of organics such as lignosulphonates, polyacrylates, polyacrylanilines, are used at continuous low dosage to keep foulants suspended until they clear up the system. Level of treatment depends greatly on the type of foulants entering or already in the system. O'Melia (90) has given a comprehensive review of the theory and use of polymers for such purpose. For any dispersive polymer to be effective as fouling preventive material, linear water velocity should be of two to three feet per second. Neither non-ionic polyacrylamide or cationic polymer such as polyethyleneimine is particularly efficient in removing sediments. Cationic polymers, however, are said to perform well (91,92).

(ii) Flocculants: Another approach to controlling deposition is to apply high molecular weight polymers which will promote the formation of light fluffy floc (93). The floc is removed through blow down and/or side stream filters. One of the hazards of using this approach is subsidence in low flow equipment such as shell side heat exchanger. The floculant approach has some merit when flows of 5 to 7 ft/sec or greater are encountered.

(iii) Surfactants: Surface active or wetting agents have been used in petrochemical cooling systems to emulsifying hydrocarbon contaminants, preventing them from causing or aggravating deposition problems (93). More recently it has been observed that wetting agents aid dispersants in maintaining materials in suspension and allowing them to remove old deposits.

B. Inhibitors (IV) (Microbiological growth)

Toxicants used for biological control normally fall into two groups - oxidizing and nonoxidizing biocides. Chlorine is the most important oxidizing biocide. Sufficient chlorine must be added to the water to satisfy all the reactions, which are measured as "Chlorine demands" (94). A free residual of 0.2 to 1 ppm usually destroys most microorganisms. It reaches even if contact is for only short period. Chlorine upon entering water, hydrolyses into hypochlorous acid and hydrochloric acid.

$$Cl_2 + H_2O \longrightarrow HOCl + HCl$$

The pH of water governs the amount of hypochlorous acid and hypochlorite ion present in circulation water. Hypochlorus acid is about 80 times more effective than hypochlorite ions. At pH 6, 1 ppm of free chlorine in water will produce 1 ppm of HOCl, at pH 8.0, 5 ppm of chlorine is required to produce 1 ppm of HOCl and at pH 9.0 about 50 ppm of chlorine is required. However, the following should be borne in mind:

(i) Chlorine will not penetrate and disperse slime masses

(ii) Chlorine is not effective in highly alkaline system as they are at lower pH ranges

In many cases, chlorine require complimentary treatment which can provide:

(a) Dispersancy to remove existing slime masses and to prevent organism from settling on heat transfer surfaces.

(b) Penetration to permeate organic masses and to expose and kill subsurface organisms.

(c) Control of organisms in systems contaminated with H_2S, NH_3 and other reducing agents.

Non-oxidizing biocides can not only meet the complementary requirements, but can also

(a) provide activity independent of pH

(b) work persistently

(c) break down to less toxic substances or breakdown biologically

(d) control specific type of organism like fungi, bacteria, algae etc.

Oxidizing biocides kill microorganism quickly but they have limitations to react with contaminants other than microbiological growth such as H_2S, NH_3, organics, hydrocarbons etc. This causes free residuals to disappear quickly or prevent their occurances in the first place. This effect increases the amount of biocide required to control the microbiological contamination.

Walko, et al (95) advocate use of acrolein. Shult's (96) advocate the use of dispersive microbiocide with chlorination. Roffman (97) advocate the use of combination of Cl_2 and other biocidal treatment. Table 11 summarises the materials used in preventing microbiological growth.

Table 11

General Treatment preventing microbiological growth

Chemical	Organism controlled	Comments
Chlorine	Algae	Good overall microbiocide
	Bacteria	Overfeeding causes delighification of wood
Chlorophenols (Trichloro and Pentachlorophenol)	Algae Fungi	Good overall microbiocide, generally high concentrations are required
Quaternary amine	Algae	Good bactericide; some foaming at high concentration; organic matter reduces effectiveness
Thiocyanates	Algae	Good overall microbiocide. Organic matter and oils do not reduce effectiveness

Table 11 (contd)

Chemical	Organism controlled	Comments
Organo-sulphur compounds such as Methylene Bisthiocyanate	Bacteria	Good bactericide and Fungicide, generally high concentration are required
Organo tin compounds	Algae	Good overall microbiocide
	Bacteria	Synergistic with quaternary ammonium compounds
	Fungi	
Rosin amine salts	Algae	Good overall microbiocide
	Bacteria	Low concentration effective in controlling
	Fungi	
Coppersalts	Algae	Cannot be used at high pH corrosive to iron and steel

(i) Monitoring of Corrosion:

Several methods are used to measure the corrosiveness of cooling water. None of them is of much practical value for judging the state of affairs within cooling systems, but they enjoy wide currency; therefore they deserve a brief discussion.

(a) Weight loss method by coupons

Coupons are strips of metals that are suspended in a suitable rack or holder in a flowing stream of cooling water.

To obtain consistent results, the strips must be prepared in some standardized way. The American society for testing materials (98) has published a standard procedure giving exhaustive details for cutting, polishing and passivating coupons of various metals. Bregman and Newman (99) have described the preparation and use of rotating rods for laboratory corrosion tests.

After the coupon is prepared, it is suspended in the center of a pipe through which cooling water to be tested is flowing. Initially the corrosion rate is high, but then falls off steadily, finally stabilizing at some constant value. Coupons should be exposed for one to three months to obtain consistent rates. The coupon is weighed before and after exposure. Pits are measured with a dial depth gauge, and their number, size, shape and distribution are described. The average corrosion rate in mils per year is calculated from the loss in weight of the coupon.

$$\text{Average penetration, mpy} = \frac{W \times 534}{A \times D \times T}$$

Where W = weight loss in milligram

A = surface area of coupon in square inches

D = density of metal in grams/cubic centimeter

T = time of exposure in hours

Sometimes a "pitting factor" is calculated; this is the ratio of the depth of the deepest pit to the average penetration calculated from the weight loss. If the corrosive attack is uniform the pitting factor is one.

While judging the results of coupon tests, it is important to remember that no heat is transferred through the metal specimen, avoiding thus any potential for scaling. Also, conditions in the centre of pipe carrying cooling water are significantly different from those at the wall. All that a coupon test shows is the rate at which the coupon corrodes.

(b) Electrical Measurements

Several years ago Freedman, et al. (100) described a device for measuring electrical resistance, which they used to monitor corrosion rates. The principle of the measurement is that the resistance of an electrical conductor is inversely proportional to its cross sectional area. A metallic sensor is inserted into a stream of cooling water, then as corrosion proceeds, the cross-section of the metal specimen decreases, and its resistance increases; the change in resistance is correlated with the corrosiveness of the water. A standard procedure (101) is now available for measuring corrosiveness by electrical methods.

Electrical devices have the same limitations as the metal coupons, the values obtained represent the rate of corrosion of the sensor at the point of insertion, although comparative rate may be of some use. Generally, results by electrical measurements are a little higher than those obtained by weighing coupons.

(c) Test heat exchangers

A steam-jacketed metal tube with cooling water flowing through it is often used in an attempt to simulate process heat exchangers, and to predict corrosion and scaling caused by faulty water treatment. A flow meter is provided to indicate the rate of water flow and a steam pressure regulator is included to adjust the temperature of the outlet water. Steam at 5 psig is the usual heat source. Water flows through the tube at three to five gallons per minute with the steam pressure adjusted to give a temperature difference between water in and out of 2°-4°F. Constant checking is necessary to be sure that rates do not change. Tubes should be exposed at least for 30 days, after which they are removed and inspected for corrosion and scaling.

Test heat exchangers, more often than not, are operated at a excessive heat flux (Btu/hr.ft^2). A rise in temperature of 6-10°F in a 30 x 1/2-inch tube represents an enormously heavier heat load than is required of a four pass heat exchanger twenty feet long. Tubes in an actual heat exchanger operate relatively cold. As for example, when cooling an oil initially at 200°F with cooling water flowing at 3-5 fps at 100°F, the heat transfer coefficient on the oil side might be about 100, while that on the water side would be around 1000 Btu/ft^2-hr-°F. The temperature of the tubewall on the water side would then be about 110°F as distinguished from the bulk water temperature of 100°F. In a steam-jacketed tube, on the other hand, the temperature of the wall is essentially that of steam, say 225°F. If the steam is adjusted so that the temperature rise in the bulk of water is 12°F, the heat transferred by a tube 30 x 1/2 inches (0.33 ft^2) could easily be as much as 25,000 Btu/hr, which is a heat flux of 76,000 Btu/hr-ft^2, or four to six times the duty on a furnace tube.

The unheated entry length of the tube in a test heat exchanger is often found to be corroded on account of the differential temperature effect. Results obtained with this unit depend much more upon physical operating conditions than upon the chemistry of the cooling water.

(d) Water quality

Methods have been proposed for predicting the corrosiveness or "aggressiveness" of water from chemical analysis. One of the most popular of these is based on the chemistry of carbonic acid and its salts. If untreated water containing calcium and bicarbonate ions is heated, the reaction,

$$Ca^{++} + 2HCO_3^- = CaCO_3 + CO_2 + H_2O \qquad (1)$$

is shifted to the right by the increase in temperature, and the sparingly soluble calcium carbonate crystallizes on the surface where heat is transferred. Langelier (102) first introduced the concept of the saturation pH value of water. This is the pH produced when carbon dioxide is added or removed from the solution bringing the water into equilibrium with solid calcium carbonate. The pH of saturation is calculated from the expression;

$$pH_s = (pK_2' - pK_{sp}') + pCa + pAlK \qquad (2)$$

Where K_2' is the apparent second dissociation constant of carbonic acid, K'_{sp} is the apparent solubility product of calcium carbonate, $pCa = -\log_{10}(Ca^{++})$ in moles per liter, and $pAlK = -\log_{10}(M.Alkalinity)$ in equivalents per liter. The "Calcium carbonate saturation index" or Langelier's index, is then

$$\mathrm{Isat} = \mathrm{pH} - \mathrm{pH}_s \qquad (3)$$

where pH is the actual measured value at the highest temperature water reaches in a particular system.

Larson and Buswell (103) subsequently proposed the expression

$$\mathrm{pH}_s = \log_{10}(\mathrm{Ksp}/K_2) - \log_{10}(\mathrm{Ca}^{++}) - \log_{10} (\mathrm{AlK}) + 9.30 + 2.5\sqrt{\mu} \,/\, (1 + 5.3\sqrt{\mu} + 5.5) \qquad (4)$$

where $\log_{10}$ (Ca^{++}) is in terms of ppm Ca^{++}, $\log_{10}$ (AlK) is in terms of ppm CaCO_3, and μ is the ionic strength of the solution. If Isat is zero, the water is said to be in balance, that is, there is no tendency for calcium carbonate to precipitate. If Isat is greater than zero, calcium carbonate scale may deposit, while if it is less than zero the water dissolves solid calcium carbonate.

Still later, Ryznar (104) proposed an empirical expression which he called the "stability index".

$$I_{sat} = 2pH_s - pH \qquad (5)$$

This value is always positive. Values less than 6.0 indicate scale-forming tendency, at 7.0 the water is balanced and at 7.5 - 8.5, the water is corrosive.

Over the years limitations imposed by Langelier's original assumptions have been neglected, but recently Kemp (105) has recalculated the saturation pH value using the rigorous methods and notations of Ricci (106) and has emphasized that this applies only to the equilibirum between carbon dioxide and calcium carbonate. "Corrosiveness" as measured by the pH of saturation can refer to the tendency of concrete pipes to dissolve in carbonic acid, but should not be used as an indication of corrosiveness of treated water to metals. Obviously, no valid conclusions can be drawn with respect to scaling or corrosiveness from an expression derived for entirely different equilibria from those that prevail in treated cooling water. Neither the pH of saturation nor values derived from it are significant in industrial cooling systems.

Larson and Skold (107) have studied the effects of chloride and sulphate ions on the corrosiveness of great lakes water to steel and cast iron. They found that bicarbonate ion mildly inhibits the corrosion of steel, and that the general corrosion rate increases as pH rises. The following ratio correlates with corrosiveness when applied to untreated water.

$R = \text{ePm}\ (Cl^{-} + SO_4^{-2})\ /\ \text{epm}\ (\text{M. alkalinity})$
where $\text{epm}\ Cl^{-} = \text{ppm} \times 0.0282$
$\text{epm}\ SO_4^{-2} = \text{ppm}\ SO_4^{-2} \times 0.208$
$\text{epm M} = \text{ppm}\ CaCO_3\ (\text{M.alkalinity}) \times 0.0200$

If the pH is around 7 or 8, and R is less than 0.1 in an untreated water, there is relative freedom from corrosion.

The flow of anions, in particular chloride ions, to an anode disrupts passivating oxide films; chloride ions cause pitting by penetrating through pores. The stability of co-ordination complexes such as $FeCl_6^{-3}$, $CuCl_2^{-}$, and $ZnCl_4^{-2}$ may also play a role in corrosion by chloride ions. Sulphate ions are competitively adsorbed on positively polarized passive films, which are thus depolarized, and then reduced by local action (108).

(j) Case histories - Typical failures due to cooling waters:

(1) A water cooled ammonia condenser used for condensing ammonia from converted gas in modern ammonia plant shows

critical failure within 6 years of service due to cooling water corrosion problem (109).

(1) Name of equipment : Water cooled ammonia condenser
(2) Service : To condense ammonia from converted gas
(3) Total number of tubes : 620, Tube outer diameter 20 mm,
thickness 4.0 mm, length 8700 mm
(4) Fluid in tube : converted gas $(N_2 + H_2 + NH_3)$
Temperature of fluid : Inlet 93°C
outlet 38°C
(5) Shell side : Fluid cooling water
Fluid Temperature : inlet 33°C
outlet 45°C
(6) Water side problem : Microbiological and chemical fouling
Tuberculation, pitting corrosion
(7) Corrosion failures of Tubes : 34 numbers
(8) Material : Carbon steel

(2) Due to bad quality of cooling water in ammonia plant methanator effluent cooler (syngas compressor suction cooler) at IFFCO, Kalol, has shown time loss in hours as given in Table 12 (110).

Table 12

Time loss in hours due to tube leakage

Period	Description	Time loss in hours
February 1976	Tube leakage, two numbers tubes plugged	38
May 1976	Tube leakage, one number tube plugged	24

(3) Problem with no Treatment: This is a typical case representing the lack of awareness among the designers and equipment users that different waters can be differently corrosive and that certain waters can be extremely corrosive. A carbon steel cooler in an organic chemical plant (111) using fresh river water as the coolant on the tube side was found to be excessively corroding on the tube side with brownish corrosion products and unevenness of the surface. This has resulted in long shut down of the plant, only after about six months of operation. The tubes made of the same material being in service elsewhere, using different waters, were said to be in good condition. The excessive corrosion was attributed to the particular water under consideration. The complete chemical analysis of the source river water is shown in Table 13.

Table 13

River water Analysis (111)

pH	7.2	Sulphate	21 p.p.m.
Conductivity	132 mho	Chloride	10 p.p.m.
TS	120 p.p.m.	Phosphate	1 p.p.m.
Ca and Mg hardness	19 p.p.m.	Iron	1 p.p.m.
P.Alk	Nil	Saturation Index	-1.82
M.Alk	26 p.p.m.		

It is seen that the river water under reference is a soft water and is quite conductive. The contents of total solids and sulphate are quite high. The saturation index is also highly negative. All the above factors are responsible for the high corrosivity of the water. The soft water does not lead to protective film formation, thus keeping the base metal exposed and freely corroding. The presence of sulphate not only increases the conductivity of water, thereby increasing corrosion but also helps in growth of sulphate-reducing bacteria which in turn assists localised corrosion. During the six months of operation when the excessive corrosion was noted, the water was used without treatment.

(4) Problem with hard waters: This is a typical case wherein it has been demonstrated how the dangerous acid dosing adopted in hard water systems can be eliminated by resorting to organic antiscalent and organic dispersant treatments. A petrochemical plant using a nearby well water for cooling purposes has experienced initially heavy scaling problem and later severe corrosion problem after resorting to acid dosing. A typical analysis of the raw well water and that of the cooling water are shown in Table 14.

Table 14

Chemical Analysis of Raw Water and Cooling Water in a Petrochemical Plant (111)

Characteristics		Raw Water	Cooling Water
pH		7.7	7.9
P.Alk	p.p.m.	nil	nil
M.Alk	p.p.m.	546	315
Sodium	p.p.m.	343	50
Total hardness	p.p.m.	203	263
Ca-hardness	p.p.m.	65	85
Mg hardness	p.p.m.	138	178
T.D.S.	p.p.m.	740	1200
Chloride	p.p.m.	134	193
Silica	p.p.m.	35	40
Sulphate	p.p.m.	-	500
Free Chlorine	p.p.m.	-	0.1
Saturation Index		+0.4	-0.3

It is seen that the water is on the alkaline side brakish and hard. The natural tendency of the water to deposit scales was so excessive that choking of the tubes occurred during early stages. To bring down the scale forming tendency acid dosing was carried out. This has made the water corrosive leading to high corrosion rates of about 30 mils/year (0.75 mm/year). In the presence of acid, the protective carbonate scale is not uniformly formed, instead, the non protective brownish ferric oxide is formed (111).

(5) Corrosion Product Fouling: this is a typical case wherein it was experienced that excessive corrosion product fouling from an improperly treated water led to under deposit corrosion and perforation leading to a long shut down of the plant. The plant concerned is a large single stream fertilizer plant (111) in which the synthesis gas coolers in the ammonia plant showed the problems. The cooling water enters the shell side of the exchanger. After a few months of operation, the outer diameter of the tubes was found to be covered with white sludgy type fouling deposit partly adherent and partly removable. A typical analysis of this deposit is shown in Table 15.

Table 15

Analysis of the outer diameter deposit in the fertilizer (111) plant

Loss on Ignition	19 %
Acid Insoluble	27 %
Silica	26 %
Iron as Fe_2O_3	29 %
Zn as ZnO	7 %
Mg as MgO	7 %
Ca as $CaCO_3$	4 %
Phosphate as PO_4	3 %
Aluminium as Al_2O_3	3 %
Ammonia	0.4 %
Chloride	0.2 %

In addition, several tubes were found to be leaking as a result of under deposit corrosion underneath such deposits. The corrosion rate in such localized places has been much higher than 2.6 mm/year, a highly unacceptable value. The problem is traceable to the "crystallization and corrosion fouling" by the cooling water.

Table 16

Analysis of the filtered raw water and the cooling water in the Fertilizer Plant (111)

	Filtered Raw water	Cooling water
pH	7.5	7.8
Conductivity	294 micromho	1440 micromho
Turbidity	1.6 p.p.m.	14.5 p.p.m.
Ca Hardness	58 p.p.m.	248 p.p.m.
Mg Hardness	54 p.p.m.	232 p.p.m.
Chloride	24 p.p.m.	218 p.p.m.
Silica	22 p.p.m.	96 p.p.m.
Free chlorine	-	1.0 p.p.m.
Proprietary Chemical	-	70 p.p.m.

Table 16 shows the analysis of both the raw filtered water and the cooling water. The raw water is not very much scale forming (S.I. = -0.41), while the cooling water is having the scale forming tendency (S.I. = + 1.01) at the operating conditions. Once the initial corrosion products are formed, the water deposits these also in addition to the water-borne salts instead of keeping them in suspension inspite of the presence of proprietary chemicals. These are borne out by the deposit analysis shown earlier in Table 15.

(6) Problems with full Polyphosphate treatment: this is a typical case where it was experienced that conventional polyphosphate treatment with acid addition to reduce pH leads to high corrosion rate, pitting, hard scales, under scale corrosion etc. The plant concerned is a large size fertilizer plant (112) with the cooling tower make-up water of the typical analysis shown in Table 17.

Table 17

Makeup water analysis

pH	7.8	Total hardness	122 p.p.m.
Conductivity	240 mho/cm	Methyl orange alkalinity	68 p.p.m.
TDS	144 p.p.m.	Chlorides	4.6 p.p.m.

The initial treatment adopted was as follows:

Polyphosphate (sodium hexametaphosphate) - 20-25 ppm as PO_4
Zinc sulphate : 3 - 5 ppm as Zinc
pH : 6.3 - 6.8
Cycle of concentration : 1.67

The following problems were encountered:

(i) Reversion of polyphosphate to orthophosphate causes hard scales

(ii) Acid dosing to maintain pH results in formation of sulphate and due to sulphate reducing bacteria pitting corrosion results

(iii) Scale formed is non-protective and results in high general corrosion rate (5.3 mpy).

Later on, this treatment was replaced by a judicious blend or organophosphonate, inorganic phosphate, cathodic inhibitor and dispersant, namely - Aquat - NPT, which has given good results:

(i) Corrosion rate - 0.6 mpy

(ii) No scaling/deposits on coupons and heat exchanger surfaces

(iii) Cycle of concentration - 3.5

(iv) No acid dosing

(v) Lesser operating cost