ACCELERATED CORROSION OF MARINE ALLOYS IN POLLUTED SEAWATER

C. P. DE

Naval Chemical & Metallurgical Laboratory, Naval Dockyard, Bombay-400 023, India

Polluted sea water is characterised by the presence of soluble sulphide, free hydrogen sulphide and free ammonia caused by the discharge of domestic sewage, industrial effluents etc. and also by the presence of various species of bacteria. Such polluted sea water causes unpredictable and premature failure of metallic materials.

The pollutants act in many ways such as by formation of differential aeration cells, by depolarising the cathodes or by formation of metal complexes. Corrosion is mostly manifested in the form of pitting which is more dangerous than the uniform type of attack.

Ship hulls, heat exchangers and sheet pilings are some of the areas where the severity of the accelerated corrosion is experienced. Copper base alloys like brasses bronze and kunifer show accelerated corrosion particularly, in sea water polluted with sulphur. The attack on galvanic anodes like magnesium is also of serious concern since polluted sea water causes very low current output rendering the cathodic protection systems ineffective.

Mechanism by which the various pollutants cause accelerated corrosion are discussed.

Keywords: Corrosion—Accelerated; Marine Alloys; Seawater

INTRODUCTION

THROUGH the centuries past, an accepted practice all the world over is not utilise rivers and seabeds as garbage grounds for waste disposals including sewage and industrial effluents. Pollution created by this age old practice has now turned out to be a health hazard particularly through consumption of fish, a most desirable source of animal proteins. It is mainly because of this reason that pollution is being feared as one of the most serious problems confronting the family of man. As a matter of fact pollution studies such as *"Pollution in the Mediterranean'* sponsored by UNEP/FAO are mostly concerned with the toxicity to marine life and its impact on human health. There is, however, another aspect of water pollution which is equally important from the view point of our national economy and defence efforts. The problem here is that of unpredictable and premature corrosion failure of metallic materials exposed to polluted waters.

Pollution has been identified as one of the major causes of accelerated metallic corrosion. The severity of this problem can be gauged by an alarming increase in

failures of metallic components on board ships berthed in tidal basins. Penalties inflicted by way of such corrosion failures could be quite heavy. In the United States, loss estimated only as a result of bacterial corrosion (Iverson, 1968a, b) is about 500 to 2,000 million dollars. The problem of metallic corrosion under the influence of pollutants, originated from organic sewage and industrial wastes, is a very complex one. Corrosion aspects of pollution, unlike biological implications, have been inadequately treated in literature.

NATURE OF EFFLUENT DISCHARGE IN HARBOUR WATERS

The pollution in harbour waters is mainly caused by domestic sewage, industrial effluents, accidental oil spills, transportation and other maritime activities. It may be of interest to note that even permissible level of inorganic contaminants carried away as effluents can be of consequence to electrochemical reactions leading to corrosion in the enclosed areas like tidal basins and breakwaters.

Effluents containing organic matter harbour various species of bacteria. Metabolic activities of these microorganisms initiate and support the decomposition of organic matter and thereby reduce the dissolved oxygen content. This results in reduction of pH value, production of ionic species having lower redox potentials and formation of corrosive sulphur compounds like cystine and hydrogen sulphide. These changes are aggressive enough to accelerate the corrosion attack on metals. Increase in the organic pollution is indicated by biochemical oxygen demand which is equivalent to the amount of oxygen required to decompose completely the organic matter during specified period. Polluted seawater is characterised by the presence of soluble sulphide and to some extent free hydrogen sulphide. In some cases, free ammonia which cannot enter the nitrification process due to low oxygen content can also be noted.

The nature of the industrial inorganic effluents is rather difficult to define, since different kinds of inorganic species in varying quantities are discharged from various industrial units. The inorganic matter when mixed with organic effluents inhibit the natural self cleaning process of effluents by their specific action such as consumption of combined oxygen. The contaminants which originate from metal finishing, fertilizer, electroplating, and chemical process industries are generally composed of metal cations like copper, cadmium, zinc, nickel, mercury, iron, cobalt and anions like chromates, chlorates, chlorides, sulphates, phosphates, cyanides and also certain metal complexes. These contaminants bring about changes in the local environments, intrinsically a highly corrosive one, and adversely affect the electrochemical corrosion reactions even at low concentrations.

EFFECT OF POLLUTION SPECIES ON CORROSION BEHAVIOUR

Metals exposed to corrosive environments gradually build up surface films. Each metal or alloy forms corrosion product having a distinct corrosion/time function in a given environment. A long term exposure studies (Southwell & Alexander, 1969; and De et al., 1969) of various metals and alloys have established that this function

is curvilinear during first few years but after an adequate film build up, equilibrium conditions are set in and a practically constant corrosion rate is established. Today's protective methods are based on such practical corrosion data. The pollution species like dissolved sulphides, ammonia and also other cationic, anionic contaminants alter the corrosion potential in different areas of metal components or structures by way of forming differential concentration cells. This condition often results into a localised attack. In addition, such effects introduce serious anomalies in the functioning of protective technologies like cathodic protection.

Organisms in polluted waters stimulate corrosion by production of oxidising or depolarising agents. The microorganisms produce these agents as a consequence of their own metabolic activity. This biological activity interferes with the formation of protective films and thus contributes to the process of accelerated corrosion.

Some of the microorganisms identified as pollution species can thrive in aerobic and anaerobic media. These are sulphur oxidising *Thiobacillus thioparins*, iron bacteria, sulphate reducing bacteria and nitrate reducing bacteria. The well-known organism is the sulphate reducing bacteria (*Desulphovibrio*) which thrive in anaerobic media. These bacteria, acting as depolarising agents, remove hydrogen from the surface of metal. Thus an oxidising reaction is brought about. The bacteria utilize hydrogen for the reduction of sulphate ions to sulphides which ultimately produce hydrogen sulphide.

The effect of contaminants like inorganic cations and anions on metal surface is of varying nature. An important feature of ionic contamination is the formation of metal complexes, particularly with copper and nickel base alloys which may alter the electrochemical corrosion process.

The type of corrosion pattern observed in polluted seawater is of pitting type which leads to perforations. The pitting of ship hulls, buoys, steel sheet pillings, other harbour installations and subsea pipelines, if permitted to proceed, is obviously more critical than the loss brought about by general corrosion. It is reported that in sulphide bearing seawater, active/passive metals like stainless steels and copper based alloys suffer from severe pitting (Lockhart, 1964; Rowlands, 1965; Sato, 1970; and De *et al.*, 1978). The pitting caused by conjoint action of both corrosion and erosion, on condenser tube materials in sulphide bearing polluted seawater has also been found to be severe. Premature failures of copper base alloy components held in polluted seawater have been extensively studied and a good deal of information is generated to date (Syrett, 1976; and Vreeland, 1976).

It must be emphasised that the general principles of corrosion reaction hold good under polluted conditions also. It is, however, the introduction of the aggravating species through effluents that brings about the severity of corrosion. In view of the fact that these species are randomly introduced from various sources in the environment of the sea, they remain ill defined and undescribed. This is, therefore, the major constraint in achieving the effective corrosion control in polluted waters.

In the recent years, the Indian Navy is facing the problems of accelerated corrosion at some of its berthing facilities. Ship hulls, heat exchangers, condensers

and steel sheet pilings are some of the areas where the severity of the accelerated corrosion is experienced. Corrosion losses, like these, are of serious concern to us since even with well proven anticorrosive technology, it has become difficult to prevent these failures.
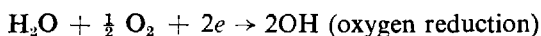
In case of ferrous metals which come in contact with unpolluted seawater, the metal dissolves through anodic reaction :

$$Fe \rightarrow Fe + 2e^-$$
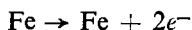
which inacidic media is sustained by conjugate cathodic reaction :

$$2H^+ + 2e^- \rightarrow 2H \text{ (hydrogen evolution)}$$
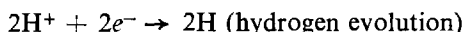
and in neutral alkaline media by

$$H_2O + \tfrac{1}{2} O_2 + 2e \rightarrow 2OH \text{ (oxygen reduction)}$$

Under polluted conditions, the rates of cathodic reactions are accelerated by intermediate metabolic reaction products. Aerobic microorganisms produce various inorganic and organic acids which accelerate corrosion (Iverson, 1968a, b). The production of sulphuric acid by a species of the genus *Thiobacillus* generates most corrosive conditions which are not only detrimental to steel but also to other non-metallic materials like rubber (Thaysen *et al.*, 1965). Production of hydrogen sulphide by sulphate reducing microorganisms brings about extensive corrosion in the following manner.

The soluble sulphides react with steel, forming iron sulphide film which is cathodic in nature compared to the iron base substrate. The breaks and discontinuities in ferrous sulphide films produce galvanic cells with large area cathodes and small area anodes which are the centres of pit formation. It is interesting to note that the growth of the sulphate reducing organisms is supported by fresh nutrients which are made available to them as a result of increased decomposition of organic matter by aerobic organisms (Harris, 1960).

The more basic metals such as magnesium used as galvanic anodes for cathodic protection of steel also suffers from similar deterioration. Under polluted conditions of sea water parasitic localised corrosion of galvanic magnesium anodes was reported to produce very low current output rendering the cathodic protection system ineffective. Fig. 1a & b bring out the difference vividly in the behaviour of galvanic magnesium anodes in polluted seawater and clean seawater respectively.

Another group of alloys which suffers accelerated corrosion damage in polluted seawater is based on copper. These copper base alloys, particularly brasses, bronzes and kunifer alloys are widely used in ships' seawater systems. Polluted seawater which comes in contact with ships' seawater system is generally from the fitting out tidal basins. Most of the effluents released in the sea are likely to be retained in confined areas like the tidal basins. Most common pollutants that are deterimental to these alloys are dissolved sulphides and dissolved ammonia which owe their origin to the bacterial reactions in seawater. Dissolved sulphides cause accelerated pitting and ammonia cause stress corrosion cracking in copper base
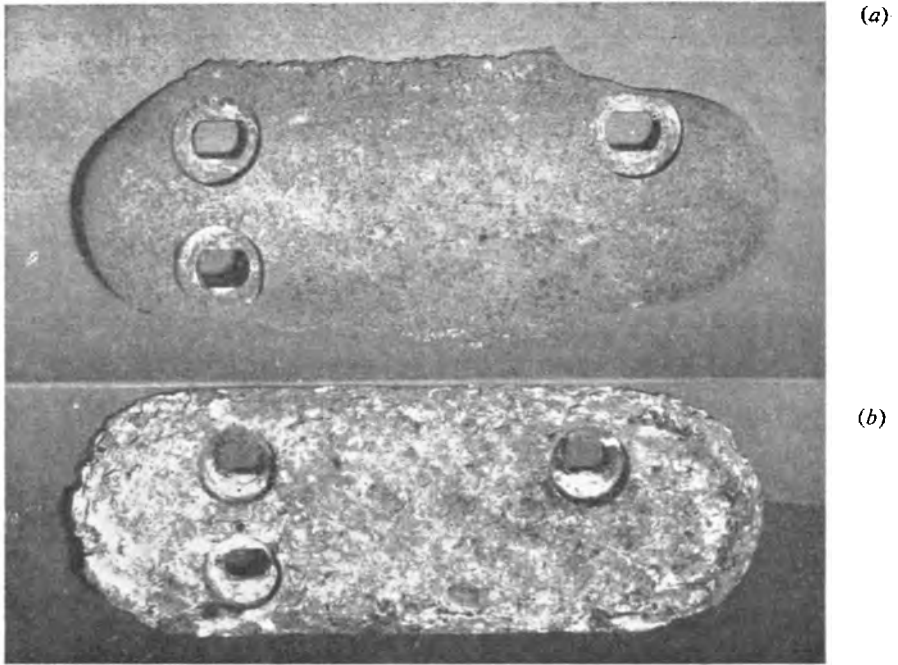
(a)

(b)

FIG. 1.   (a) Magnesium anode exposed to seawater contaminated with sewage effluents.
           (b) Magnesium anode exposed to seawater without any sewage contaminants.

alloys.   Other cationic species like mercury also can inflict heavy damage by way of cracking of brass components.

Almost all copper alloys owe their corrosion resistance in aereated seawater to the cuprous oxide protective film.   This film once formed can withstand the rigours of seawater except under most adverse erosive attack.   Under polluted conditions, initiation of the aggressive attack is mainly attributed to sulphur compounds namely cystine and hydrogen sulphide.   Both industrial and sewage effluents are the source of the sulphur and ammonium compounds.   Sulphide at the minimum level of 0.5ppm and ammonia at the level of 10ppm was found to cause severe corrosion in aluminium brass and copper nickel alloys (Sato, 1964; and Sato, 1970a, b).

A detailed survey of the service failures in respect of condenser tubes revealed that the depth of the pitting attack (t) was proportional to the product of time of total operation (T), average water velocity (v) and sequare of the amount of protrusion causing turbulence (e^3).

$$t = KTV e^2 \text{ where } K = \text{Proportionality constant}$$

Thus, the time for total penetration would be

$$T = \frac{k't}{ve^2} \ (t = \text{wall thickness})$$

and $k' = \dfrac{1}{k}$

In unpolluted seawater the value of k' in the above empirical formula was found to be approximately 0.35 for 95/5 kunifer, 0.5 for 90/10 kunifer, 0.6 for 70/30 kunifer.

In the polluted waters, however, these values are not constant and are considerably decreased in respect of all these alloys. Lower values of k' indicate early failure by pit perforation. A 70/30 kunifer tube which is supposed to give life of 30 years has been observed to perforate within 2 years of service. The heat exchangers and condensers are of critical importance in power plants and ships. The premature failures of tube plates and tubes in contact with polluted waters introduce a factor of unreliability which deserves special attention.

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