

## CORROSION PHENOMENA IN THE COASTAL AREAS OF THE PERSIAN GULF\*

T. G. TEMPERLEY

Ministry of Electricity and Water, P.O. Box 62, Kuwait, Arabian Gulf.

### INTRODUCTION

THE Persian or Arabian Gulf is an arm of the Indian Ocean. Entry is made through the Arabian Sea, the Gulf of Oman, and the Straits of Ormuz. The Gulf extends 500 miles in a north-westerly direction with an average width of 120 miles between Iran in the east and the Arabian Peninsula in the west, covering an area of 92,201 square miles.

The transverse peninsula of Kalhat rising to a height of 3,500 feet almost separates it from the Gulf of Oman. The Persian Gulf is shallower towards the north where the delta of the Shatt Al Arab builds and spreads south, and towards the Arabian shore as compared to the Persian side. On the latter coast which is mountainous, deep water lies close inshore, whereas the Arabian coastal waters are shallow and complicated by many reefs, banks and shallows. The deeper areas are usually floored with foul black mud. White clay occurs frequently along this coastal strip, but the pearl banks which stretch parallel to the shore are commonly composed of hard cemented sand, rock or coral. The average depth of the water is 85 feet.

Currents are irregular and uncertain, and are probably the result of the semidiurnal tide flows which themselves show marked irregularities.

As the Gulf receives little fresh water other than the outflow of the Shatt Al Arab in the north, and as its climate is one of the hottest in the world, it is not surprising that the lack of dilution by low salinity waters together with the high evaporation rate at the surface have resulted in the waters of the Gulf having a much higher salinity than the open ocean.

The chemical constituents of sea-water differ in concentration in the various geographical areas of the world. Usually the polar seas have a lower salinity than the seas in tropical coastal areas. On average the total dissolved solids content of sea-water is 36,000 ppm, but there is a wide range of salinities from area to area (Table 1).

TABLE 1. SALINITY OF SEA WATERS

Body of water	Total dissolved solids ppm
Baltic Sea	8,000
Black Sea	22,000
Atlantic Ocean	37,000
Mediterranean Sea	41,000
Caspian Sea	130,000
Dead Sea	260,000
Irish Sea	32,500

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The total dissolved solids content of the waters of the Persian Gulf varies from 39,000 ppm in the open sea thirty miles from the coast, to 42,000 ppm at the Arabian coast line.

Kuwait Bay, situated on the north-western coast of the Gulf, is an area of relatively shallow water approximately twenty miles from east to west, and ten miles from north to south with a narrow entrance only four miles across. Large areas of evil-smelling black mud are exposed at low water. These shallow waters and the huge areas of wet mud result in a high evaporation rate from this restricted body of water which tends to be even more concentrated than the rest of the Gulf water. The salinity of Kuwait Bay sea-water shows a seasonal variation between 44,000 ppm and 48,000 ppm with the higher concentration being in evidence towards the end of the hot season. The waters of both the Gulf and Kuwait Bay are susceptible to the influence of the local weather to the extent that the water temperature may drop 5°C within a period of two days when a brisk northerly breeze blows, while the suspended solids may rise from the normal 5 ppm to over 50 ppm within a few hours. A typical analysis of Kuwait Bay sea-water is given in Table 2.

TABLE 2. KUWAIT BAY SEA-WATER

Conductivity, $\mu$ mho at 20°C	72,000
Total dissolved solids, ppm	46,000
pH	8.8
Total alkalinity, ppm $\text{CaCO}_3$	150
Chlorides, ppm $\text{Cl}^-$	24,000
Sulphates, ppm $\text{SO}_4^{2-}$	3,400
Total hardness, ppm $\text{CaCO}_3$	7,950
Permanent hardness, ppm $\text{CaCO}_3$	7,850
Temporary hardness, ppm $\text{CaCO}_3$	100
Free Carbon Dioxide, ppm $\text{CO}_2$	Nil
Calcium, ppm $\text{Ca}^{2+}$	400
Magnesium, ppm $\text{Mg}^{2+}$	1,690
Total suspended matter, ppm	25
Bromine, ppm $\text{Br}^-$	80
Silica, ppm $\text{SiO}_2$	5

Conditions in the waters of the Gulf and Kuwait Bay favour proliferation of marine life. In the months of March, April and May the waters teem with a profusion of small fish and other life forms. Molluscs grow and multiply rapidly in the warm waters, which have a seasonal range between 8°C and 35°C in Kuwait Bay, and slightly higher minimum and lower maximum temperatures in the open Gulf.

The sea is the only source of easily obtainable water in Kuwait and along the Arabian Coast line, in sufficient quantity to be used for cooling purposes in power stations, oil refineries, etc. It also lends itself more readily to desalinization processes than do the brackish soil waters found along the Arabian coastline.

The development of Kuwait and other states on the Arabian coast of the Persian Gulf during the past fifteen years has resulted in the installation of sea-water distillation plants, power stations, oil refineries and air conditioning plants utilizing sea-water as a process or cooling media. This brought to light many unforeseen corrosion and fouling problems.

## BACTERIAL CORROSION

Shortly after the Kuwait Distillation and Power Plant was commissioned in 1953, inspections indicated that cast iron and steel objects in the sea-water handling system were suffering severe corrosion at an alarming rate. Cast iron separation plates in condenser water boxes and rotary strainers were found to be completely "graphitized" within a period of 1,000 h in service, and could be perforated by scraping with a knife. Pump suction legs, foot-valves, bolts, and unprotected pipework in contact with the sea-water all suffered from this pernicious attack.

The products of corrosion in all cases contained oxides of iron and varying amounts of iron sulphide (Table 3).

TABLE 3. CORROSION DEPOSIT FROM A CONDENSER WATER BOX

	per cent
Iron as $\text{Fe}_3\text{O}_4$	75.0
Iron as $\text{Fe}_2\text{O}_3$	10.0
Iron Sulphide as FeS	1.5
Chloride as NaCl	4.0
Calcium Sulphate as $\text{CaSO}_4$	3.5
Silica as $\text{SiO}_2$	2.0
Organic matter (loss on combustion)	4.0

Samples of a black, evil-smelling silt-like deposit that was collecting in the sea-water culvert systems were taken and analysed. The addition of acid to samples of this mud resulted in the liberation of hydrogen sulphide in appreciable quantities. The high percentage of the lower oxides of iron in the corrosion products and the presence of sulphides in both the silt-like deposit and the corrosion products indicated that the corrosion conditions were reducing and possibly anaerobic.

TABLE 4. DEPOSIT FROM SEA-WATER CULVERT SYSTEM

	per cent
Organic matter (loss on combustion)	22.2
Silica as $\text{SiO}_2$	40.3
Chlorides as NaCl	5.2
Sulphate as $\text{CaSO}_4$	1.5
Sulphide as FeS	8.2
Magnesium carbonate as $\text{MgCO}_3$	4.2
Calcium Carbonate as $\text{CaCO}_3$	18.4

The sulphide in both deposits suggested that hydrogen sulphide was the culprit in this particularly severe corrosion. As sulphides are not normally found in the sea-water, the indications were of bacterial attack involving sulphate-reducing bacteria, forming sulphides and lower oxides of iron.

Bacteriological cultures were made using samples of the corrosion products, deposits from the sea-water culverts, beach sand, mud from below the low water mark, and sea-water. The culture medium used was a modification of Beckwith's formula, of the following composition:

Culture medium	
$K_2HPO_4$	g/l. 0.5
$NH_4Cl$	1.0
Gelatin	6.0
$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$	0.1
$MgSO_4 \cdot 7H_2O$	2.5
$CaCl_2 \cdot 2H_2O$	0.1

This was made up with distilled water, taking care to maintain aseptic conditions.

In all cases except for the reference sample, bacterial growth occurred, resulting in a black to grey flocculent precipitate within a period of three days incubation. The bacteria were subsequently identified as *Sporovibrio desulphuricans*. Microscopic examination by means of a wet mount and dark-field illumination showed the bacteria to be in the form of short curved rods.

The study of specific sulphate-reducing bacteria started when research was carried out on the micro-organisms in the mud of the Black Sea. An organism, *Bacterium Hydrosulphureum*, was discovered existing at depths between 96–7,240 feet. The bacterium was found to be capable of reducing sulphate to sulphide in both aerobic and anaerobic conditions. Subsequent classification of the organism showed it to be a strain of *Vibrio desulphuricans*.

It was observed that although the optimum conditions for growth of the sulphate-reducing bacteria were anaerobic fresh-water environs at an optimum temperature of 30°C, aerobic strains of the bacteria can apparently develop. Further strains can develop in brines of high concentration, 3–20 per cent sodium chloride, and at temperatures up to 60°C.

From observations in Kuwait, I am of the opinion that an aerobic strain does *not* develop, but that the bacterium manufactures its own local anaerobic conditions in what superficially appears to be an aerobic environment. Corrosion products in the form of lower oxides of iron, and decaying organic matter, form a barrier to oxidation under which the bacteria can thrive and maintain their required anaerobic conditions.

Sulphate-reducing bacteria are common throughout the world, being most active in media where general anaerobic conditions exist, where adequate quantities of sulphates and organic matter are available for nourishment, and where the ambient temperature is in the region of 30°C. These conditions are usually found in tropical and sub-tropical bays, estuaries and harbours where the mud usually has a characteristic grey/black colour and smells strongly of hydrogen sulphide. Sometimes these conditions are met with in colder climates; the estuarial mud of the River Thames and the bottom mud of the Great Lakes Canal in Canada are examples.

Von Wolzogen Kuhr found evidence of these bacteria at depths of up to thirty-five metres in the earth, and Bosting and his collaborators isolated sulphate-reducing bacteria in a number of oil-well brines from depths of over 3,000 feet. Investigations in the California oil fields showed the bacteria to be present in a large number of samples of oil-well brines. Stewart goes so far as to claim that petroleum is actually a product of the anaerobic conditions generated by these bacteria. Bunker has analysed soil samples from all over the world; he found sulphate-reducing bacteria to be present in all his samples.

In certain parts of the world the bacteria exist in such numbers that whole areas of

seas are made anaerobic by the products of their metabolism. In the Sea of Azov there are two definite layers, the bottom one anaerobic. At certain times, due possibly to increased activity of the bacteria, this layer may rise, resulting in the wholesale destruction of fish and other aerobic forms of marine life. An area in which the existence of aerobic forms of life appears to be impossible extends from the eastern part of the Arabian coast in the neighbourhood of the Ras Al Hodd, through the Gulf of Oman, and along the Balukhistan coast to a depth of nine-tenths of a mile. In this area the bottom is covered with a soft green/black mud which smells strongly of hydrogen sulphide. Similar conditions exist in many basins and bays along the Arabian coast of the Gulf.

In Kuwait Bay there are large areas of this black evil-smelling mud, but the anaerobic conditions which obviously exist in the mud do not appear to spread to the waters of the bay, which abound with marine life. In recent years, though, there appears to be a tendency for the mud to extend, and whereas ten years ago many beaches along the coast of the bay were coated with fine yellow sand, many now have a layer of black mud visible at low water.

The bacteria, unable to utilize the free oxygen present in the atmosphere, make use of the oxygen in the sulphate radical for their metabolic processes, while free hydrogen sulphide is released to atmosphere. If the bacteria are able to generate the hydrogen sulphide below a layer of slime and corrosion products upon an iron surface, there will be a tendency for the gas to be trapped, resulting in an anaerobic atmosphere favouring the development of further colonies of bacteria, and severe attack upon the iron by the hydrogen sulphide. Gradually the metal surface becomes coated with a layer of magnetic iron oxide and iron sulphide, which progressively increases in depth. The porous corrosion deposits allow water containing dissolved sulphates to pass into the bacteria while reacting with dissolved oxygen and other oxidizing agents which could destroy the bacteria.

#### *Deterioration of concrete piling*

During the erection of the New Port of Kuwait a further example of bacterial corrosion was noted. Concrete piling in certain cases was found to deteriorate rapidly, whereas in other cases concrete made with the same cement and water was found to be up to standard in all respects.

The deterioration took the form of a sulphate attack on the outer surface of the concrete, which developed a white powdery deposit, followed by a progressive deterioration of the material.

It was discovered that the trouble was experienced only when beach sand from a particular area was used. At the site in question, the sides of the excavation contained areas that were black in colour as opposed to the usual sand colour. Cultures of the sand from both the normal coloured and black area of the pit gave positive reactions for the presence of sulphate-reducing bacteria.

It was concluded that the bacteria colonies from the sand were growing in the concrete in question, and the hydrogen sulphide generated was oxidizing at the surface of the concrete to form sulphuric acid, which of course attacked the cement and subsequently destroyed the concrete.

In the case of the sand of normal colour, protection could be obtained when a

concrete mix was made with water containing 5 ppm free chlorine. Similar success was achieved when sufficient acriflavine dye was added to the water to give it a yellow colour. (In all cases the cement used was of a supersulphate type.) In the case of concrete where samples of the black coloured sand had been used, satisfactory protection was not obtained.

### *Sea-water pumps*

The axial flow sea-water pumps situated on jetty type structures, supplying the Power and Water Producing Plants of Kuwait with process and cooling water, have their intakes set at a depth of twelve feet below the tide datum level. The pump casings are of Ni-cast iron and the shafts of stainless steel. Although the pump casing and bell mouth are initially coated with bituminous enamel, turbulence and cavitation soon destroy this protective coating on the bell mouth and fair-water. Exposure of the metal to the corrosive environment led to the failure of the fair-water and adjacent parts within a period of a year. Arrangements are now being made to replace these vulnerable sections with others of either Monel metal or 317 stainless steel.

The stainless steel pump shafts showed signs of pitting after a very short period in service. Traces of hydrogen sulphide could be detected in the atmosphere inside the pump casing and pipework when the particular pump had been off load for periods of two or three days. It would appear that the oxidizing power of the atmosphere within the pump during these shut-down periods was not sufficient to maintain a stable oxide film on the stainless steel.

The trouble has only been partially overcome by venting the pump case and pipework during off-load periods. A more resistant stainless steel containing molybdenum would possibly prevent further attack.

### *Prevention of sea-water attack*

The prevention of corrosion in the general sea-water handling systems composed of pipework, water boxes of condensers and heat exchangers, and jetty structures and piling can be discussed under three separate sections:

1. *Protective coatings.* Many types of coatings have been tested over the years in the Kuwait installations, and although testing continues three types of coatings accepted as standard application for specific sections of the plant.

Pump suction legs, discharge mains, and large sea-water piping systems are coated with hot-applied bituminous enamel. The sea-water mains in the Kuwait plant are in excellent condition after eleven years of service, and the original coating shows little deterioration.

The most suitable coating for condenser water-boxes has proved to be a self-vulcanizing synthetic rubber coating applied at works. However, in cases where such a coating has failed, or perhaps was not originally applied, the use of a zinc-rich primer followed by three heavy coats of a suitable chlorinated rubber paint has proved very satisfactory. This paint system has also been successfully used for the protection of tank interiors and the coating of jetty structures in the tidal area and spray zones.

In the case of severely corroded areas the following procedure has proved successful. The corrosion products are first removed by sand blasting or in some cases by acid

cleaning. The resulting surface is then washed down with a 1 per cent solution of acriflavine to destroy any sulphate-reducing bacteria that may be present on the metal surface. Immediately after drying, the zinc-rich primer is applied, followed by the three coats of the appropriate type of chlorinated rubber paint.

2. *Cathodic protection.* Two systems of cathodic protection are used in the Kuwait plants, impressed voltage, and sacrificial anodes. The impressed voltage system is used to protect the jetties and marine structures. In this system a *D.C. E.M.F.* is supplied from a rectifier to give a current density of between 10 and 15 mA/ft<sup>2</sup> of protected surface.

Sacrificial anodes are used to protect the various condenser water-boxes of the turbines and evaporators. In the early operational days of the plant, zinc anodes were used throughout the water boxes, but trials with other materials soon indicated the superiority of magnesium as an anode material under Kuwait conditions.

It has been shown many times in the Gulf area that cathodic protection alone is not sufficient to prevent corrosion in sea-water handling systems. However, a combination of protective coating as previously described with the two cathodic protection systems gives excellent results.

3. *Chlorination.* Unfortunately, there are certain sections of the sea-water handling system in the various plants to which access cannot be gained unless the plant is out of commission for an appreciable period and the system drained. Consequently the protective coating system on equipment in these sections cannot be renewed or repaired as often as the coatings in more accessible sections of the plant, and as cathodic protection alone is not sufficient to prevent attack in these highly corrosive conditions, it is only a matter of time until failure of the equipment results.

With this problem in view, tests were carried out to determine a means by which the sulphate-reducing bacteria in the system could be destroyed, and thus reduce the corrosive nature of the Gulf sea-water to a nominal level. Chlorine, acriflavine, and a number of other oxidizing agents and dyestuffs were found to be effective in destroying the bacteria. However, chlorination of the water was the only method that proved practical in the light of operational costs and quantities of materials required to treat the huge volume of sea-water handled by the system. In addition, this chemical was the most suitable for suppressing marine fouling.

Sterilization of the water with a continuous injection of 2 ppm of chlorine completely changed the character of the water in the system. The smell of the deposits in the condenser water-boxes disappeared, and the odour of the silt from the bottom of the sea-water culverts was reduced. The corrosion rate of ferrous materials in the water fell to a remarkably low level in the case of a clean specimen. However, a badly corroded water-box with a surface encrusted with corrosion products showed little improvement: the deposits, consisting of the lower oxides of iron and ferrous sulphide, protect the organisms from the chlorine by reacting with it before it can penetrate the corrosion product crust and reach the bacteria. After periods of chlorination, the upper layers of the corrosion crusts become oxidized to higher oxide, but the lower layers of deposit remain in the lower oxide state.

Bacteriological cultures carried out on various samples of sea-water previously treated with varying concentrations of chlorine down to 0.5 ppm showed the absence of active sulphate-reducing bacteria. Consequently, a continuous injection of chlorine

in sufficient quantity to give a minimum concentration of 0.5 ppm free chlorine in the discharge from the condensers was thought to be sufficient to ensure sterilization of the water with regard to sulphate-reducing bacteria. In the extensive culvert system of the Kuwait plants, an initial dosage of 2 ppm chlorine was required to give such a concentration at the condenser discharges.

This continuous injection of chlorine, at an approximate cost of four shillings per million gallons, also prevents marine fouling. A particular power station in the southern area of the Gulf operated for a period without chlorination. During this period each turbine had an average monthly outage time of three days for condenser cleaning, and the whole plant had to be shut down for periods while the culverts, etc. were cleared of shell growth. This station is now installing chlorination equipment.

Experience has proved that the severe bacterial corrosion found in systems handling the waters of the Persian or Arabian Gulf can be prevented or at least brought within acceptable limits by the choice of suitable resistant materials of construction combined with cathodic protection and suitable coating systems, while maintaining a continuous injection of chlorine into the sea-water intakes of the various plants in order to destroy sulphate-reducing bacteria and to prevent the growth of marine organisms.

#### ATMOSPHERIC CORROSION

During the late summer and early autumn, periods of extremely high humidity are experienced in the coastal areas of the Gulf. The dew-point is often exceeded and condensation occurs on all surfaces whose temperature approaches the ambient temperature.

In European coastal areas rain usually falls before the air at ground level becomes saturated with moisture to an extent where the dew-point is exceeded. Consequently it is possible to protect equipment by installing it inside a simple shelter. The conditions experienced in the area of the Gulf are more severe, especially in close proximity to the sea where the air contains traces of salt. Equipment cannot be protected by installation inside a building. When the dew-point is exceeded during these periods of high humidity, condensation occurs on all surfaces of similar temperature to the ambient, be they external as in the case of structural steel-work and walls, or internal as in the case of the windings of idle motors, starters, busbar connections, etc.

Under European conditions, a period of approximately five years is required for the development of a green patina on copper sheeting. A similar patina develops within a few months in the Gulf after exposure to the humid conditions at the latter end of the summer. The humidity during the winter and spring periods is low and atmospheric corrosion proceeds at a low rate during these periods of the year.

In Kuwait failure of the copper sheathing of Pyrotex cables on marine installations after periods of from six to eighteen months in service, and overheating of switchgear due to the formation of a patina on the busbar connections, were two manifestations of the troubles resulting from the corrosive effects of the Gulf atmosphere.

Analysis of the green patina formed under these conditions showed it to be composed of atacamite,  $\text{CuCl}_2 \cdot 3 \text{Cu}(\text{OH})_2$ , and malachite,  $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ , typical of patinas formed under marine conditions. The patinas formed under industrial



conditions usually contain a high proportion of a basic copper sulphate,  $\text{CuSO}_4 \cdot 3 \text{Cu}(\text{OH})_2$ , a substance not found in the Kuwait deposits.

A measure of control over these corrosive atmospheric conditions can be maintained by the use of suitable coatings for steelwork, and plastic sheathing for Pyrotenax cabling; also, regular cleaning of busbar spouts and connections prevents overheating of switchgear under normal load conditions. Coating the connections with an inert material such as petroleum jelly or silicone grease, to exclude air from the copper, has proved beneficial. Heating the air in the switch room has also been found to reduce the patina formation on the connections; an air temperature of only a few degrees above the dew-point is sufficient to prevent patina formation.

#### CONCLUSION

It has been shown that it is possible to overcome the corrosion problems particular to the Persian Gulf coastal area by choice of construction materials and by employing certain specialized protection techniques. Similar solutions to the various problems would probably be suitable in other parts of the world where similar conditions exist.