SYNOPSIS

The thesis deals with the corrosion of different metals in sea brines and its concentrates between the density of 3.5°Be' to 24.0° Be' and bittern between the density of 28.0° Be' to 36° Be' and in marine atmosphere.

The thesis is divided into two parts. Part I deals with the corrosion of metals in sea brines and bittern and part II deals with the corrosion of metals in marine and marine-cum-industrial atmospheres.

(I) Corrosion in sea brines and bitterns

Exhaustive literature is published on corrosion for different metals in sea water. Non-ferrous metals like aluminium, copper, nickel and their alloys find considerable application in marine chemical process industries, marine engineering and as materials of construction in desalination plant. Very little published data are available for the corrosion of different metals and alloys in concentrated brines and bitterns obtained by solar evaporation during the manufacture of common salt, mixed salts etc.

The present work deals with the corrosion study of different ferrous metals like mild steel (carbon steel) and stainless steel and non-ferrous metals e.g. aluminium, brass, bronze, copper, monel and zinc in sea brines and bitterns by loss in weight method and electrochemical method. The corrosion tests of these metals and alloys are carried out for complete immersion in different density of brines e.g. 3° Be, 10° Be, 13° Be, 18° Be'
24° Be, 28° Be, 32° Be and 36° Be for different intervals of time at room temperature.

The study has been also carried out at temperatures of 75°C and 96°C for the above metals and alloys for the duration of 7 days under complete immersion and half immersion in static conditions.

The corrosion rates for mild steel in 3° Be sea brine for complete immersion and half immersion for the duration of 30 days are 282.0 mg/sq.dm/month and 642.6 mg/sq.dm/month whereas in 36° Be bittern rates observed under above conditions are 43.72 mg/sq.dm/month and 78.40 mg/sq.dm/month. Similar pattern of corrosion rates is observed in case of other metals studied at room temperature as well as at high temperature.

It has been found from the corrosion rate as determined by loss in weight method that corrosion of metals first increases, but after a particular brine concentration is reached it is found to decrease with further increase in salt concentration. The initial increase is due to concentration of salt in presence of dissolved oxygen and high corrosive power of chloride ions. Secondly the increase in salt concentration decreases the solubility of oxygen in salt solutions which reduces the corrosion rate due to increase in cathode reaction. Decrease in solubility of oxygen is further supported by the fact that in
bittern, rust, in completely immersed mild steel has been found to be green in color whereas in low density of brines solutions the rust of the same mild steel piece has shown dark brown colour. This clearly shows that presence of oxygen in brines is enough to convert corrosion product to ferric state whereas green corrosion product in bittern shows the lack of oxygen in which rust does not oxidise to ferric state. Our results fairly agree with the dissolved oxygen in various densities of sea brines and bittern as determined.

In case of brass, the dezincification has been reduced in high concentrated salt solution with the decrease in corrosion rate.

This is true for most of the metals and alloys studied at room temperature and at high temperature, exception being zinc. The corrosion rate of zinc is increased as the concentration of brine is increased which may be due to the fact that high chloride concentrations along with other salts and acidic nature of the bittern also seem to be responsible of corrosion of zinc. The corrosivity of the bittern is further increased due to decomposition of magnesium chloride mostly present in it which liberates free acid.

The general corrosion rates of the metals and alloys are classified as

1) Mild steel and zinc are most corroded metals
2) Stainless steel, monel and aluminium are least corroded whereas

3) Copper, brass, bronze, nickel stand in between the above two

Moreover, in absence of oxygen and with increase in temperature, concentration and duration of exposures have effect on the corrosion of copper and its alloys, in such a way that corrosion rate is decreased considerably in high concentrated salt solutions.

It is observed that although mild steel is not able to combat corrosion by itself, it can be used (being cheap and available easily for replacement) if corrosion is prevented by some means. Two methods that are commonly used are use of inhibitor which is handy to use and surface coatings.

Inhibitors which are commonly used for sea water or in neutral salt solutions have been studied in high density sea brines and bitterns. Among them are (1) potassium chromate (2) sodium hexameta phosphate (3) agar-agar (4) gelatine (5) cutting oil (6) sodium silicates (7) sodium nitrate (8) sodium benzoate (9) E.D.T.A. (10) thiourea (11) tributalamine (12) sodium diethyl dithiocarbamate.

Commercial protective coatings are also studied. Among them are (1) epoxy paint (2) chlorinated rubber paint (3) chemical resistance paint based on bituminous coal tar paint and (4) aluminium paint.
Potassium chromate (0.4 to 0.5%) has been found to be good inhibitor for mild steel and aluminium in 10° Be' sea brine and 36° Be' bittern which give efficiency in range of 70 per cent to 90 per cent at room temperature as well as at high temperature. Chromate is oxidising inhibitor and its success in bittern to protect the metals may be due to its oxidising character which reacts directly with the metal to form protective oxide film. Epoxy base paints have been found satisfactory in bittern at high temperature.

The corrosion rate of mild steel in 36° Be bittern without inhibitor is 43.72 mg/sq.dm/month in complete immersion and for half immersion 78.40 mg/sq.dm/month, at room temperature. The corresponding rates in presence of 0.4% potassium chromate are 6.25 and 12.52 mg/sq.dm/month, with 85.5 and 84.0 per cent efficiency of the inhibitor respectively.

In this way efficiency of cutting oil in 10° Be' sea brine and 36° Be' bittern comes out to be fairly well comparable with potassium chromate. In addition, corrosion rate in half immersion test at room temperature is less corresponding to potassium chromate inhibitor which indicates the oil film protects the metal from the atmospheric oxygen, but not at higher temperature due to disturbance in the solution. Sodium diethyl dithiocarbamate is found good as on inhibitor for aluminium
whereas efficiency of this inhibitor is low in case of mild steel. Other inhibitors give low efficiency for mild steel and aluminium in both density of sea brines and bitterns.

Steady state potentials of these metals have been determined with respect to time indicating the corrosion tendency of the metals.

Anode and cathode polarization of aluminium and mild steel in 10° Be' sea brine and 36° Be bittern with and without inhibitor are studied at different current density.

The steady state potentials of metals and alloys in different density of sea brine and bitterns have indicated that as the concentration of brine increases the passivity of the metals decreases; but no direct relationship has been observed between the study state potentials and loss in weight.

Polarization of aluminium and mild steel has indicated that as the current density is increased, cathodic polarization is also increased whereas anodic polarization is not so much increased. This suggests that cathodic areas influence the corrosion velocity indicating the system is under cathodic control. With the addition of potassium chromate, the polarization is further increased; which indicates that the inhibitor is perhaps adsorbed on the cathode regions of the metal surface.
The Tafel equation is obeyed for the cathodic polarization curves when potentials are plotted against the log of current density. From the values of exchange current density, the inhibitor efficiency is calculated which is in fair agreement with the values obtained by loss in weight method.

(II) Atmospheric corrosion

Corrosion of mild steel, zinc, copper and aluminium has been studied at two sites at Bhavnagar (Latitude 21° 45' N and Longitude 72° 12' E); one in the city, 3 to 4 miles away from the sea and another at Experimental Salt Farm near the sea. Other two places are Rajkot city quite away from the sea (Latitude 22° 15' N and Longitude 70° 50' E) and Porbandar (Latitude 21° 38' N and Longitude 69° 37' E) which is industrial-cum-marine city with the pollution of ammonia.

The yearly corrosion rates of metal in Bhavnagar city observed for mild steel, zinc, copper and aluminium are 90.50, 9.70, 6.40, 1.35 mg/sq.dm/month. The study reveals that even though Bhavnagar is a coastal city, the corrosion rate has been observed less as compared to other coastal cities of India (at Bombay, 280 mg/sq. dm/month for mild steel). This is due to the fact that for the most of the period the direction of the wind at Bhavnagar is from land to sea.
At Bhavnagar mild steel corrodes 9.3 times more than zinc and zinc corrodes 1.5 times more than copper and copper corrodes 4.7 times more than aluminium.

Corrosion rate of metals studied at Experimental Salt Farm, Bhavnagar is considerable which may be due to high salinity and high relative humidity. The corrosion rate of aluminium, copper and mild steel from January to October shows the gradual increase with increase in salinity. The maximum rate is observed in month of July that is 824.0 mg/m²/month against salinity 6442 mg/m²/day. Due to nearness of the sea high salinity exists at that place, as the large volume of sea brine on vast areas are subjected to solar evaporation and fine salt dusts are blown over in the wind during the lifting and storage operation of salts. These factors contribute very high salinity in the atmosphere. The yearly corrosion rates for mild steel, zinc, copper and aluminium are 122.70, 28.20, 29.30, 3.6 mg/sq.dm/month. Same pattern of corrosion has been reported in most of the Indian sea coast, only differing in the rate of corrosion. Although aluminium has shown weight loss less, pitting has been observed at some places on the surface on long exposure. Hence aluminium metal may not be suitable choice, but aluminium coating as paint and metal spray are likely to be more beneficial near the sea coast. Mild steel corrodes 4.3 times more than zinc. Copper and zinc behave in similar way. Copper corrodes 7.9 times more
than aluminium.

At Rajkot, the yearly corrosion rates for mild steel, zinc, copper and aluminium are 97.40, 14.10, 7.35, 0.26 mg/sq.dm/month. The rate of corrosion is increased in month of June, July and August and September during which months rainfall and high relative humidity have been observed. Mild steel corrodes 5.48 times more than zinc and zinc is 1.9 times than copper and copper is 28.0 times more than aluminium.

At Porbandar, the corrosion behaviour of these metals is quite different than that at Bhavnagar, Experimental Salt Farm, Bhavnagar and Rajkot. This is due to industrial pollutions specially ammonia. The method has been evolved for the determination of ammonia pollution in the atmosphere which is based on Ambler's wet candle method with little modification. The method is satisfactory and give approximate indication of the amount of ammonia or its salt deposited on the metal surface for corrosion study.

The yearly corrosion rates for zinc, copper and aluminium are 150.40, 85.60, 1.54 mg/sq.dm/month. Mild steel panel has corroded completely losing its strength within 6 to 8 months. The high rates of corrosion from April to September are due to high rainfall and relative humidity remaining above 70% during these months. High rates of corrosion from March, April and
May are shown in spite of no rainfall and relatively low humidity which may be due to high sulphur dioxide and ammonia pollutions in the atmosphere. The corrosion of copper is attributed mainly due to high ammonia content in atmosphere polluted from nearby ammonia soda ash plant.

Good resistance has been observed with epoxy paint. As the epoxy paint is costly next preference is chemical resistant based paint and cashewnut based anticorrosive paint as these paints have shown fair performance except little pealing off the paint coating at one or two places. Asphalt based paint and cashewnut shell oil based paint are recommended for painting iron structures exposed to saline atmosphere. Surface life will be more than one year whereas they are less effective at Porbandar which requires constant repainting at every six months.