INVESTIGATIONS ON DEZINCIFICATION OF BRASS AND EPOXY COATED BRASS

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By

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DECLARATION

I hereby declare that the work presented in this thesis entitled **"Investigations on Dezincification of Brass and Epoxy Coated Brass"** is based on the original research work carried out by me under the guidance and supervision of Dr. Rani Joseph, Department of Polymer Science & Rubber Technology and co-guidance of Dr. K.P. Narayanan, Department of Ship Technology, Cochin University of Science and Technology, Kochi-22 and no part of the work reported in this thesis has been presented for the award of any degree from any other institution.

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A. Mathiazhagan

ABSTRACT

Brasses are widely used as constructional materials in marine environment due to their anticorrosive, antifouling and mechanical properties. However, its resistance to corrosion and fouling may vary according to local marine environmental condition and the seasons.

The dezincification of brass is one of the forms of selective corrosion which has attracted the attention of researchers for the last two decades. Many of the dezincification mechanistic studies have been performed in noncomplex media and hence their conclusions cannot be extended to estuarine water, which is of great significance since brass is extensively used in marine environment.

Inhibited α brasses are largely immune to dezincification and the effect of tin and arsenic addition to α / β brasses is not so reliable in controlling the dezincification. There have been many cases of dezincification in duplex brasses in both freshwater and seawater. Though there is some protection methods such as inhibitors, electro deposition and electro polymerization, there is no reliable method of inhibiting the dezincification of two-phase brass. Organic coatings are effectively used for the protection of metals due to their capacity to act as a physical barrier between the metal surface and corrosive environment. Hence, pure epoxy coating is selected for this study as it has anti-corrosion effect on brass. This thesis is addressed in seven Chapters. **Chapter 1** deals with introduction on corrosion, review of literature, objectives and scope of the work. **Chapter 2** focuses on sample preparation and experimental work.

Chapter 3 deals with dezincification of brass. The dezincification behaviour of brass of the present study has been highlighted in terms of corrosion rate, weight gain / loss, corrosion current and polarization resistance, open circuit potential, dezincification factor. The marine fouling as biomass on brass was assessed and presented in this study. The

physicochemical properties of estuarine water were correlated with corrosion behaviour of brass. The deterioration of the brass subjected to the effect of estuarine water was also investigated as a measure of loss in mechanical properties such as tensile strength, yield strength, percentage elongation and percentage reduction in area.

Chapter 4 focuses on surface characterization of brass in estuarine water. To validate dezincification data, visual observation, spot analysis, surface morphology before and after removal of corrosion products and corrosion product analysis were performed. **Chapter 5** concerns with dezincification of epoxy coated brass**.** The dezincification behavior of epoxy coated brass of the present study has been highlighted in terms of corrosion rate, weight gain/loss, corrosion current and polarization resistance, open circuit potential, dezincification factor. The marine fouling as biomass on epoxy coated brass was assessed and presented in this study. The deterioration of the epoxy-coated brass subjected to the effect of estuarine water was also investigated as a measure of loss in mechanical properties such as tensile strength, yield strength, percentage elongation and percentage reduction in area.

Chapter 6 deals with surface characterization of epoxy coated brass in estuarine water. To validate dezincification data, visual observation, spot analysis, surface morphology before and after removal of corrosion products and corrosion product analysis were performed. The results of dezincification behavior of brass and epoxy coated brass in Cochin estuary water has been presented and discussed. Attempt has been made to correlate the dezincification behavior of brass with epoxy coated brass.

Chapter 7 deals with general conclusion. The findings drawn from this study indicates that the epoxy coating could be used for brass against dezincification.

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LIST OF ABBREVIATION

V	Electrode potential
Mdd	Metal loss per decimeter square area per day
I_{corr}	Corrosion current
E_{corr}	Corrosion potential
Z_f	Dezincification factor
SEM	Scanning electron microscopy
EDS	Energy dispersive spectroscopy
XRD	X-ray diffraction
OCP	Open circuit potential
SCE	Saturated calomel electrode
R_p	Polarization resistance
b_a	Tafel slope for anode
b_c	Tafel slope for cathode
Redox	Reduction and oxidation
SRB	Sulfate reducing bacteria
SCC	Stress corrosion cracking
ASTM	American standard for testing and materials
W	Weight
T	Time
A	Area
Pvc	Poly vinyl chloride
Mpa	Mega pascal
MIC	Microbiologically induced corrosion
SCC	Stress corrosion cracking
CRP	Crack propagation rate
IG	Inter granular

EIS	Electrochemical impedance spectroscopy
Eb	Break down potential
NaCl	Sodium chloride
AES	Augar electron spectroscopy
FT	IR-Fourier transform infrared spectroscopy
Cps	Count per second

LIST OF PUBLICATIONS FROM THIS Ph.D WORK

1. Mathiazhagan, A., Rani Joseph, Narayanan, K.P., "Corrosion Behaviour of brass in Vembanad Estuary", **Journal of Marine Science and Technology,** Vol. 18, No. 5, pp. 719-722 (2010).
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CURRICULUM VITAE

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Chapter 1

INTRODUCTION

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Man's endeavors to exploit the ocean have gained considerable momentum in recent years. Offshore drilling, ocean mining, desalination, alternative food and energy resources are some of the areas of ocean engineering. The increased utilization of seawater as a medium of transportation and energy generation, oil and mineral exploration have a direct impact on problems associated with the maintenance of marine structure and machinery. The factors which have been taken into account for consideration of merit before a material is recommended for ocean service, are the structural strength, predicted life expectancy, a knowledge of uncertainty` and a thorough understanding of marine corrosion and marine fouling. Marine corrosion and fouling are interrelated which in turn depend upon the interaction of metals with biotic and natural aquatic environment. Marine fouling is an economically important problem facing all the maritime nations of the world. Fouling affects propulsion and thereby the economic operation of boats and ships.

The factors which affect the amount and rate of seawater corrosion are divided into chemical, physical and biological such as oxygen content, velocity, temperature, biological activities, salinity and pH of seawater (Pierre et al., 2000). The concentration of dissolved oxygen in sea varies greatly with location and time because rivers dilute seawater and seawater can be concentrated by evaporation. The corrosion attack by polluted seawater such as those near the industrial areas is more severe due to the presence of pollutants.

Many different types of corrosion attack can occur to the structure, ships and equipments that made up of copper based alloys since they are exposed to seawater which is a good electrolyte that can cause corrosion. Several distinctive attacks are impingement attack, dezincification of brasses and pitting (Shreir et al., 1994). Some of the most corrosive conditions are encountered in power stations and ships that draw their cooling water from estuaries and harbours. These waters are polluted to varying extents depending on location and the time of year. Corrosion initiated by polluted water may often continue even after changing to clean water (Ijsseling, 1989).

Impingement attack occurs when moving water flows over copper or copper based alloys, the turbulence cause breakdown of the surface film. The air bubbles entrained in the water break as air bubbles hit the metal surface. Dezincification of brasses occurs when regions of brass become replaced by a porous mass of copper. High chloride content of seawater and low water speed increase the rate of dezincification. As water speeds are low and deposits settle on the surface, pitting of copper and copper alloys is liable to occur (Shreir et al., 1994).

1.1 Corrosion

Corrosion can be defined as "degradation of a material due to environmental exposure". For the purposes of this work the definition of corrosion is "degradation of engineering materials by exposure to a wet environment". This definition includes corrosion of metallic materials by a wide range of processes (Trethewey, 1996).

1.1.2 The Corrosion process

The corrosion can be treated as a process, which cannot occur without the presence of water and oxygen and therefore excludes other types of attack, such as those associated with high temperature oxidation or sulphidation.

Corrosion is an electrochemical process in which a metal reacts with its environment to form an oxide or other compound. The electrochemical cell (Fig. 1.1), which causes this corrosion process, has three essential constituents:

- An anode: the anode is the site at which the metal is corroded;
- A cathode: the cathode (part of the same metal surface or of another metal surface in contact with it) forms the other electrode in the cell and is not consumed in the corrosion process.
- An electrolyte (electrically conducting solution): the electrolyte is the corrosive medium.

At the anode the corroding metal passes into the electrolyte as positively charged ions, releasing electrons, which participate in the cathodic reaction.

Hence the corrosion current between anode and the cathode consists of electrons flowing within the metal and ions flowing within the electrolyte.

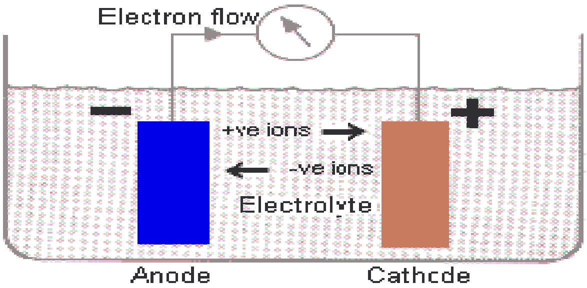


Fig. 1.1 Electrochemical cell

The surface of one component may become the anode and the surface of another component in contact with it the cathode. Usually, corrosion cells will be much smaller and more numerous, occurring at different points on the surface of the same component (Fig. 1.2). Anodes and cathodes may arise from differences in the constituent phases of the metal itself, from variations in surface deposits or coatings on the metal, or from variations in the electrolyte.

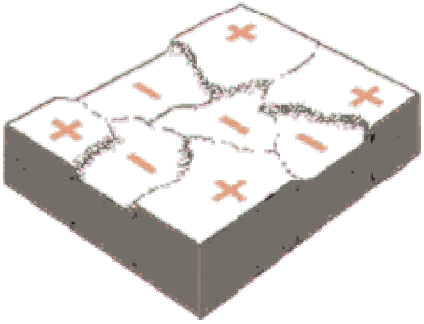


Fig. 1.2 Micro cell in metals

The metal may be immersed in an electrolyte or the electrolyte may be present only as a thin condensed or adsorbed film on the metal surface. The rate of corrosion is influenced considerably by the electrical conductivity of the electrolyte. Pure water has poor electrical conductivity and the corrosion rate will be much lower than an acid solution of high conductivity.

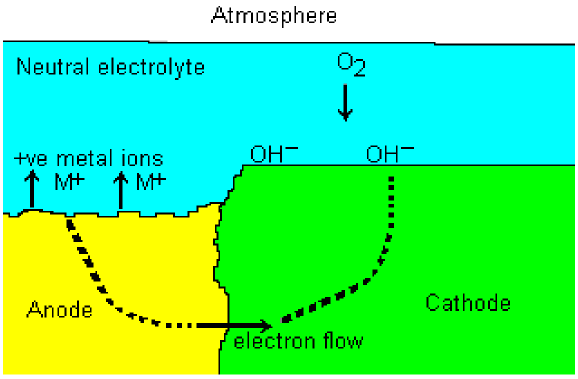


Fig. 1.3 Corrosion reaction involving current flow

1.1.3 Metal dissolution

In most corrosion processes, with the exception of cathodically controlled processes, metal will dissolve. An understanding of the principle behind how metal dissolves in a solution is necessary for understanding corrosion. Consider a piece of pure metal M in a solution, which contains its own ions, M^{z+}. In this case the metal has solubility in the solution in which it is placed. An example would be a piece of pure copper in a solution of copper sulfate. The general equilibrium reaction for a metal electrode in a solution of its own ions is: -

$$M = M^{z+} + z^{e-}$$

where M represents a metal atom, M^{z+} is the metal ion, Z is the possible valences and e^- represents an electron. At equilibrium there is no net current flow and the above reaction can be separated into two different reactions. One reaction produces metal ions in solution from metal atoms in the solid with the reaction: -

$$M = M^{z+} + z^{e-}$$

Again at equilibrium there is no net current, so the electrons produced in the reaction above are consumed in a reaction where all the electrons combine with metal ions in solution to deposit as atoms on the solid metal surface in contact with solution in the reaction: -

$$M^{z+} + z^{e-} = M$$

These individual reactions are called “half cell” reactions as another reaction either consumes or produces electrons for them to continue. These half-cell reactions are also called oxidation and reduction reactions (Fig. 1.3). Oxidation is a reaction that produces electrons. The ionization of metal atoms to ions is therefore an oxidation half-cell reaction. Reduction is a reaction that consumes electrons. De-ionization to form a metal atom is therefore a reduction half-cell reaction.

$$M = M^{z+} + z^{e-}$$

The above reaction is called a “REDOX” reaction because it contains both an oxidation and a reduction half-cell reaction. Both oxidation and reduction are important reactions. The oxidation reaction is the basis of corrosion as metal is dissolved whilst transforming from atoms to ions in a solution. The reduction reaction is also important as it is the basis of electroplating where ions in solution are deposited as atoms on a surface, for example chrome or gold plating (Revie, 2000). The ability of metals to resist corrosion to some extent depends upon their position in the electrochemical series.

The farther two metals are separated from one another in the electrochemical series, the more powerful is the electric current produced by their contact in the presence of an electrolyte. Also the more rapidly the metal towards the top of the table is attacked and the more will the metal towards the bottom of the table be protected. It must be remembered, however, that the order in the above series may vary under special corrosive conditions, and the galvanic series in service media, e.g. seawater, are often more useful from the corrosion aspect.

1.1.4 Corrosion in marine environments

Seawater corrosion or also called, as marine corrosion is a form of corrosion of metal exposed to seawater. The exposed metal is a structural component of a vessel (ship or boat) or a fixed structure either on the shore, offshore or under water. The exposure of components can be continuous or intermittent. Seawater is only electrolyte containing a relatively high concentration of salts that occurs commonly in nature and it is the most familiar and one of the most severe of natural corrosion agent.

The salts concentration of seawater is about 3.5 weight percent, mostly as NaCl and is slightly alkaline with pH of 8. Most of the elements that can be found on earth are present in sea water at least in trace amounts but there are eleven of the constituents account for 99.95 % of the total solutes, (grams per kilogram of water), with chloride ions being by far the largest constituent (19.354), followed by sodium ion (10.77), sulfate (2.712), magnesium (1.290), calcium (0.4121), potassium (0.399), bicarbonate (0.140), bromide (0.0673), strontium (0.0079), boron (0.0257), fluoride (0.0013). In addition, microbiological organisms, clustering of weed, limpets as well as deposits of sand, silt or slime not only exclude oxygen but also often create locally corrosive conditions, which aggravate corrosion attack. Sulphate reducing bacteria, left undisturbed in marine silt or mud deposits, will produce concentration of hydrogen sulphite, which is particularly aggressive to copper alloys.

The general marine environment includes a great diversity of sub-environments, such as full-strength open-ocean water, coastal seawater, brackish and estuarine waters, bottom sediments, and marine atmospheres. Because of the high degree of variability of seawater, it is difficult to simulate this environment in laboratories. Often, stored seawater is used rather than synthetic replacements in order to try and create a laboratory atmosphere as close to a natural environment as possible. However, stored seawater has been known to exhibit corrosive behavior that is different than that of the open ocean from which it was taken. This difference is due to the fact that the minor constituents, including the living organisms and their dissolved organic nutrients, are in a delicate balance in the natural environment. The laboratory cannot simulate this balance and the equilibrium is upset as soon as the sample is isolated from the parent water mass. It is important to recognize the difference in corrosion behavior between laboratories created tests and open ocean field tests. Whenever possible, changes in the corrosion behavior of a material is monitored and accounted for as corrosion properties are being determined.

Year upon year the cost of marine corrosion has increased until it is estimated today at 4.2 % of the Gross National Product (Trethewey, 1996). An enlightened approach to materials selection, protection and corrosion control is needed to reduce this burden of wasted materials, wasted energy and wasted money. Many different types of destructive attack can occur to structures, ships and other equipment used in seawater service. The term 'aqueous corrosion' describes the majority of the most troublesome problems encountered in contact with seawater, but atmospheric corrosion of metals exposed on or near coastlines, and hot salt corrosion in engines operating at sea or taking in salt-laden air are equally problematical and like aqueous corrosion require a systematic approach to eliminate or manage them. All metals and alloys when in contact with sea water have a specific electrical potential (or corrosion potential) at a specific level of sea water acidity or alkalinity - the pH.

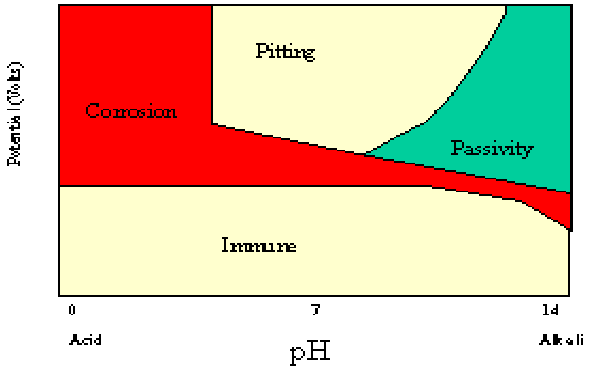


Fig. 1.4 Potential Vs pH

Figure 1.4 shows the regions where the metal will freely corrode; the region of passivation where stable oxide or other films form and the corrosion process is stifled; the region of pitting corrosion where the corrosion potential of the metal exceeds that of its oxide; and the region of immunity where the metal is normally fully safe to use (Fontana, 1986). More resistant alloys mean less corrosion, metals like gold platinum and tantalum can resist virtually all corrosion, but for marine service the final choice will always be a compromise with cost.

Most corrosion resistant metals rely on an oxide film to provide protection against corrosion. If the oxide is tightly adherent, stable and self-healing, as on many stainless steels and titanium, then the metal will be highly resistant or immune to corrosion. If the film is loose, powdery, easily damaged and non-self repairing, such as rust on steel, then corrosion will continue unchecked. Even so, the most stable oxides may be attacked when aggressive concentrations of hydrochloric acid are formed in chloride environments. Seawater, by virtue of its chloride content, is a most efficient electrolyte. The omni-presence of oxygen in marine atmospheres, sea sprays and splash zones at the water line, and sometimes surprisingly at much greater depths, increases the aggressiveness of salt attack. The differential concentration of oxygen dissolved at the waterline or in a droplet of salt spray creates a cell in which attack is concentrated where the oxygen concentration is lowest.

1.1.5 Polluted seawater

For test to yield meaningful results, knowledge of the environment that exists under actual service conditions is necessary. In order to conduct realistic corrosion tests, variation in seawater conditions must be taken into account. The bulk environmental condition can be clean seawater, e.g. water around offshore structures and some power stations, in other instances, polluted water or brackish water and variety of water qualities that are encountered during ship's service. The main effect of polluted seawater arises from a combination of low oxygen contents and generally decreased pH together with the presence of sulphite ions and /or ammonia (Efrid, 1979). These factors can lead to quite different corrosion mechanisms, resulting in the formation of very different corrosion product layer compared to those formed in natural sea water.

It has frequently been observed that the exposure of certain metals, copper alloys, to alternatively polluted and oxygen containing seawater gives the most detrimental conditions (Eiselstein, 1982; Kato, 1984). Similar effects are found under circumstances where sulphite ions are produced more or less continuously in oxygenated seawater, e.g. sulphite produced in mud layers being carried away by flowing seawater. Organic matter entering in a cooling water system can be deposited in layers in some area rather than being either filtered off and rejected or allowed to pass through the system. Such layers become anaerobic and yield significant amounts of sulphide, which are introduced into the cooling water and so become available for reaction with adjacent metal surface (Smith, 1985). In particular, a number of copper alloys will be affected by these high sulphide levels and become more susceptible to pitting. Pollution can also occur when biofouling present in systems decays to produce sulphur-containing compounds. In a large cooling system this can result in significant amounts of biological matter being generated in the form of thick layers of barnacles, mussels and shellfish. During stagnant or low flow water conditions, the system is likely to become anaerobic, resulting in death of the organisms followed by their gradual decomposition.

1.1.6 Marine environments

Seawater is a biologically active medium that contains a large number of microscopic and macroscopic organisms. Many of these organisms are commonly observed in association with solid surfaces in seawater, where they form biofouling films. Immersion of any solid surface in seawater initiates a continuous and dynamic process, beginning with adsorption of nonliving, dissolved organic material and continuing through the formation of bacterial and algae slime films and the settlement and growth of various macroscopic plants and animals. This process, by which the surfaces of all structural materials immersed in seawater become colonized, adds to the variability of the ocean environment in which corrosion occurs (Rodgers, 1968).

The amount of oxygen and other gases dissolved in seawater depends on the temperature and the salinity of the seawater and the depth. In some seawater compositions, hydrogen sulfide is also present. Hydrogen sulfide is formed in seawater by the action of sulfate-reducing bacteria (SRB), usually under deposits where oxygen is depleted or when the seawater is stagnant or polluted and becomes anaerobic, even in large volumes. Silt deposits in estuarial waters are also contributory. Mineral and organic materials are also carried in suspension by the seawater, particularly near the mouths of rivers (Craig, 1995).

Since seawater is a complex, delicately balanced solution of many salts containing living matter, suspended silt, dissolved gases, and decaying organic material, the individual effect of each of the factors affecting the corrosion behavior is not readily separated. Because of the interrelation between many of the variables in the seawater environment, an alteration in one variable may affect the relative magnitude of the other variables. The roles of oxygen, biological activity, temperature, velocity, salinity, and pH are discussed below (Fink, 1993).

a) Oxygen

The dissolved oxygen content is a major factor affecting the corrosivity of seawater. The oxygen level in seawater many range up to 12 ppm. Photosynthesis of green plants, wave action, etc., tends to increase the oxygen level, whereas the biological oxygen demand of decomposing dead organisms will reduce it. For a given location, seasonal variation in oxygen level will influence corrosion behavior. For metals like copper and iron, complete elimination of oxygen will reduce the corrosion to negligible amounts. However, metals that depend on formation of a passive film for corrosion protection, e.g., stainless steels, often corrode rapidly where the oxygen supply to the metal surface is restricted.

b) Biological activity

When a metal or other surface is first immersed in seawater, a biological slime tends to develop in a matter of hours. During an active season, a great variety of organisms are found on an immersed surface. From a corrosion point of view, the sessile organisms are of most concern. They arrive at the slime-covered surfaces in minute embryonic form and become firmly attached. Once attached, they rapidly transform to the mature form and become immobile. Organisms, which build hard shells, are: annelids, barnacles, encrusting bryozoans, mollusks, and corals. Organisms without hard shells are: marine algae, filamentous bryozoa, coelenterates or hydroids, tunicates, and calcareous and silaceous sponges.

c) Temperature

An increase in temperature is normally expected to speed up a chemical reaction according to thermodynamic considerations. This also would be the case for the corrosion reaction in seawater where it is possible to hold all other variables fixed. Since it is not normally possible to do this, the effect of temperature has to be established indirectly. Oxygen solubility decreases with increase in temperature, biological activity increases as the water temperature increases, and the chemical equilibrium involved in the precipitation of calcium carbonate and magnesium hydroxide is altered so that calcareous scale is more likely to deposit on the metal as the temperature is increased. For temperature variations of a seasonal nature, iron, copper, and many of their alloys show a high rate of attack during the warm months.

d) Velocity

Many metals are sensitive to velocity effects in seawater. For metals like iron or copper, there is a critical velocity beyond which corrosion becomes excessive. Stainless steel and certain nickel-chrome-molybdenum alloys tend to be more resistant in high-velocity seawater. Special forms of corrosion are associated with seawater velocity, e.g., (1) erosion-corrosion caused by high-velocity silt-bearing seawater, (2) impingement attack, where air bubbles are present, and (3) cavitations, where collapsing vapor bubbles cause mechanical damage and often corrosion damage as well.

e) Salinity

The major oceans of the world are completely connected and mixing is continuous. The average salt content of the sea is 3.5 wt % with the composition comprised mainly of the following ions: sodium, magnesium, calcium, potassium, chloride, bromide, carbonate, and sulfate. In addition, seawater contains measurable quantities of iodide, fluoride, phosphate, gold, silver, arsenic, rubidium, copper, barium, manganese, lithium, lead, iron, strontium, and zinc ions. Ammonia is also present, with free oxygen, nitrogen, and other gases. Variations in salinity in open-ocean surface water typically range from 3.25 - 3.75 wt %.

f) pH

The pH of seawater may vary slightly depending on the photosynthetic activity. Plant matter consumes carbon dioxide and affects the pH during the daylight hours. The carbon dioxide in seawater is influenced, close to the surface, by the exchange with carbon dioxide in the atmosphere. The slight daily shift in pH has little direct effect on the corrosion behavior, however it can be a factor in calcareous-scale deposition, which affects the corrosivity. As pressure is increased, pH is reduced according to thermodynamic considerations. Thus, at great depths, there is some evidence of fewer tendencies for protective carbonate-type scale formation.

1.1.7 Corrosion capabilities of various metals

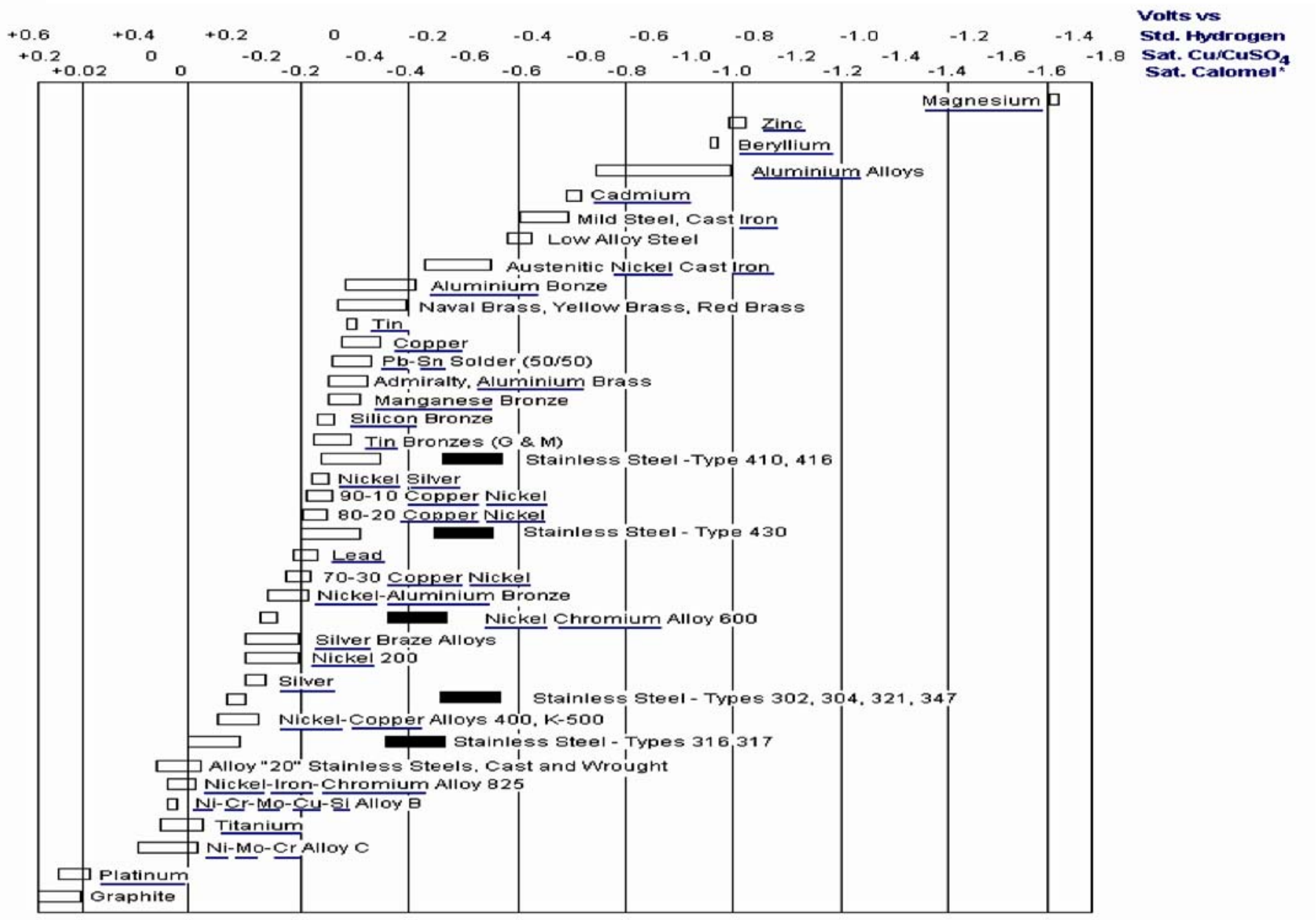
The luster, ability to conduct heat and electricity, malleability of some and ductility of others are only some of the main characteristics, which define metals. However, it is the varying ability of a metal to loose its electrons and form a positive ion that is essential in understanding the ranges of metals that are capable of corroding. It is this understanding which is used widely in industry as the number one measure for corrosion control (i.e. choosing a metal that will not corrode easily by giving up its electrons). The electrochemical field has developed a list, which details the range of most metals relative tendency to be oxidized, called an electromotive series. The list provides nearly all the information required to determine which metals are most susceptible to corrosion. The series tells us which species behaves best as the anode undergoing oxidation, and the cathode undergoing reduction. The list begins with metals most easily oxidized, and ends with the metal least capable of oxidation, or with the greatest capability for reduction. In other words, the list begins with metals, which are most easily corroded (i.e. behave as the anode in the corrosion reaction), and ends with metals, which can best behave as the cathode in the corrosion reaction. The tendency of each metal to be oxidized is given in terms of the standard electrode potential or oxidizing potential and is expressed in volts, which is measured relative to the standard oxidation of hydrogen gas, which is assigned an arbitrary potential of 0 volts. Table 1.1 provides an electromotive series sa a list of major industrial metal. As you can see from the list, metals such as magnesium, zinc and iron will oxidize easier and therefore corrode easier than platinum or gold. This list should provide you with the sufficient background needed to predict which metals during the experiment should corrode more easily and/or to a greater extent. Furthermore, the electromotive series has a large influence on a particular type of corrosion, known as galvanic corrosion.

The electromotive series serves as a corrosion map for metals in particular concentrations of their own salts. It fails in describing the behavior of such metals in various corrosive environments based on varying temperature, humidity, salinity, etc. Therefore, a more general table developed by electrochemists, called the galvanic series is used in practical application. Table 1.2 provides a short galvanic series as a list of major industrial metals in seawater corrosive environments (Efrid, 1979).

Table 1.1 Electromotive potential series

Element/ Other	***Reaction***	***Electrode Potential (V)***
Gold	$Au^+ + e^- = Au$	*1.692*
Platinum	$Pt^{2+} + 2\,e^- = Pt$	*1.18*
Silver	*Ag+ + e- = Ag*	*0.7996*
Copper	$Cu^+ + e^- = Cu$	*0.521*
Copper	$Cu^{2+} + 2\,e^- = Cu$	*0.3419*
Hydrogen (acid)	$2\,H^+ + 2\,e^- = H_2$	*0*
Iron	$Fe^{3+} + 3\,e^- = Fe$	*-0.037*
Lead	$Pb^{2+} + 2\,e^- = Pb$	*-0.1262*
Tin	$Sn^{2+} + 2\,e^- = Sn$	*-0.1375*
Iron	$Fe^{2+} + 2\,e^- = Fe$	*-0.447*
Chromium	$Cr^{2+} + 2\,e^- = Cr$	*-0.913*
Titanium	$Ti^{2+} + 2\,e^- = Ti$	*-1.63*
Aluminum	$Al^{3+} + 3\,e^- = Al$	*-1.662*
Magnesium	$Mg^+ + e^- = Mg$	*-2.7*
Sodium	$Na^+ + e^- = Na$	*-2.71*
Calcium	$Ca^{2+} + 2\,e^- = Ca$	*-2.868*
Potassium	$K^+ + e^- = K$	*-2.931*
Lithium	$Li^{3+} + e^- = Li$	*-3.0401*
Calcium	$Ca^+ + e^- = Ca$	*-3.8*

Table 1.2 Galvanic series of metals in flowing seawater.



Just as in an electromotive series, the metals near the top of the list on the galvanic series tend to oxidize easiest (i.e. behave as the anode, and therefore undergo corrosion), while the metals near the bottom reduce easiest (i.e. behave as the cathode).

1.1.8 Types of corrosion

There are several forms of corrosion that can occur. Each form of attack has a specific arrangement of anodes and cathodes and the corrosion which occurs has a specific location and pattern. Each form of corrosion can be effectively controlled during design if it is anticipated. By understanding the various forms of corrosion, the conditions under which they occur, and how they are quantified, they can each be addressed and controlled. The most important Types of Corrosion are:

a) Uniform corrosion

Uniform corrosion results from the sites, not necessarily fixed in location, that are distributed over a metal surface where the anodic and cathodic reactions take place. Uniform corrosion damage, sometimes called wastage, is usually manifested in the progressive thinning of a metal part until it virtually dissolves away or becomes a delicate lace-like structure.

b) Pitting corrosion

The initiation of a pit occurs when electrochemical or chemical breakdown exposes a small local site on a metal surface to damaging species such as chloride ions. The sites where pits initiate are not completely understood, but some possibilities are at scratches, surface compositional heterogeneities (inclusions), or places where environmental variations exist. The pit grows if the high current density and the area of breakdown initiation are exceedingly small. If the rate of repassivation is not sufficient to choke off the pit growth, two new conditions develop. First, the metal ions produced by the breakdown process are precipitated as solid corrosion products (such as the $Fe(OH)_2$) which usually cover the mouth of the pit. This covering traps the solution in the pit and allows the buildup of positive hydrogen ions through a hydrolysis reaction. Then, chloride or another damaging negative ion diffuses into the pit to maintain charge neutrality. Consequently, the repassivation becomes considerably difficult because the solution in the pit is highly acidic, contains a large concentration of damaging ions and metallic ions, and contains a low oxygen concentration. Thereby the rate of pit growth accelerates.

The pit is the anode of an electrochemical corrosion cell, and the cathode of the cell is the non-pitted surface. Since the surface area of the pit is a very small fraction of the cathodic surface area, all of the anodic corrosion current flows to the extremely small surface area of the breakdown initiation site. Thus, the anodic current density becomes very high and pitting can be rapid.

c) Crevice corrosion

Crevice corrosion results when a portion of a metal surface is shielded in such a way that the shielded portion has limited access to the surrounding environment. Such surrounding environments contain damaging corrosion species, usually chloride ions. A typical example of crevice corrosion is the crevice formed at the area between two metal surfaces in close contact with a gasket or another metal surface. The environment that eventually forms in the crevice are similar to that formed under the precipitated corrosion product that covers a pit (Fig. 1.5). Similarly, an electrochemical corrosion cell is formed from the couple between the unshielded surface and the crevice interior exposed to an environment with a lower oxygen concentration compared with the surrounding medium. This combination of being the anode of a corrosion cell and existing in an acidic, high-chloride environment where repassivation is difficult to make the crevice interior to corrosive attack.

d) Stress corrosion cracking, hydrogen damage and corrosion fatigue

Stress corrosion cracking (SCC) is a form of localized corrosion, which produces cracks in metals by the simultaneous action of a corrodent and tensile stress. The electrochemical cell between the exterior and the interior environment of a crack is similar to that described above for a crevice. Because of the necessity for the application of stress, the breakdown of the passive layer on a metal surface in SCC is generally ascribed to mechanical causes but many suggest that electrochemistry is a significant factor because it controls the rate of repair of the passive layer ruptured by mechanical stress.

Corrosion fatigue has a somewhat similar mode of failure to SCC. It mainly differs from SCC in that it involves situations where the stress is applied cyclically rather than as a static sustained tensile stress. With both corrosion fatigue and SCC, the issues of film mechanical breakdown, repassivation, adsorption of damaging species, hydrogen embrittlement and electrochemical dissolution are to greater or lesser extents involved in determining susceptibility.

e) Intergranular corrosion

With the exception of metallic glasses, the metals used in practical devices are made up of small crystals (grains) whose surfaces join the surfaces of other grains to form grain boundaries. Such boundaries or the small regions adjacent to these boundaries can under certain conditions be considerably more reactive (by being more anodic) than the interior of the grains. The resulting corrosion is called intergranular corrosion. It can result in a loss of strength of metal part or the production of debris (grains that have fallen out).

f) Galvanic (and thermo galvanic) corrosion

Two metals having different potentials in a conducting electrolyte result in the more anodic metal usually being attacked by galvanic corrosion. Because of electrical contact between two different metals, galvanic corrosion differs from the other forms of corrosion described previously in that the anodic and cathodic sites of the corrosion cell reside separately on the two coupled different metals comprising the corrosion cell, while for the other forms of corrosion, the cathodes and anodes exist on the surface of the same metal.

The value for the differences in potential between two dissimilar metals is usually obtained from a listing of the standard equilibrium potentials for the various metals.

Another factor besides the coupling of two different metals that can lead to galvanic corrosion is a difference in temperature at separated sites on the same metal surface. Such a situation leads to thermo galvanic corrosion. This kind of corrosion can be found in heat exchanger systems where temperature differences are common.

g) Selective leaching

This type of corrosion occur when component of an alloy is removed selectively by corrosion because of differences in potential between different constituents of an alloy – a situation analogous to that of the galvanic corrosion of coupled dissimilar metals. This results in an increase in the concentration of the remaining components and selective leaching occurs. This type of corrosion is also called parting. The most common example is selective leaching out of zinc from brass (dezincification).

h) Erosion corrosion

Erosion corrosion is caused by the disruption of protective passive films by erosive or abrasive processes. Once the protective or passive film is removed in an aqueous electrolyte, the electrochemical processes for the types of corrosion described above take place.

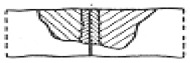
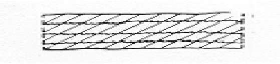
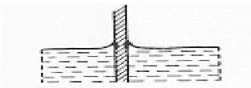
 **Uniform corrosion** The reaction starts at the surface and proceeds uniformly on surface.	 **Pitting corrosion** The metal is eaten away and perforated in places in the manner of holes, the rest of the surface being affected only slightly or not at all.	 **Wide pitting corrosion** Corrosion causes localized scarring.
 **Intergranular corrosion** Imperceptible or barely perceptible from outside, since the corrosion proceeds at the grain boundaries.	 **Transgranular (or) intragranular corrosion** The grain boundary material is retained, since the corrosion proceeds preferentially within the grain.	 **Galvanic corrosion** Increased corrosion in crevices or cracks or at contact surfaces between two metal articles.
 **Selective corrosion** Corrosive attack on structural constituents	 **Exfoliation corrosion** Occurs in deformed articles in "fiber orientation".	 **Interfacial corrosion**

Fig. 1.5 Different forms of corrosion

1.2 Corrosion testing

Before testing components in most practical applications, one should have knowledgeable of the corrosion properties of possible candidate materials, an idea of the type and complexity of testing desired and have a sufficient level of experience to comprehend possible materials interactions that a component may have with other material components and be able to interpret and translate the test results into the requirements of the service application (Ijsseling, 1989). The objective for performing a corrosion test should be identified during the initial phase of designing the testing procedure. The test conditions including specimen size, test environment or service environment, geometry, sample preparation, temperature, flow velocity, potential, and type of corrosion test (general, crevice, pitting resistance, galvanic, stress-related, dealloying, etc.) should be considered.

1.2.1 Laboratory evaluation

The corrosion behavior of metals or coatings is often evaluated in the laboratory rather than in an actual service environment due to time and / or budget limitations. Laboratory evaluation is generally of relatively short duration and is often used to study environmental effects on a metal's corrosion behavior because the specific environmental conditions can be controlled. The major disadvantage of testing in the laboratory is that the actual service environmental conditions may not be evaluated. Rather service conditions are being simulated, which involves accepting certain assumptions. It is important when testing in the laboratory to correlate field data with the laboratory data so that the validity of the laboratory information can be assessed (Treseder, 1985). Natural seawater is the referred environment for laboratory testing, but synthetic seawater solutions are often utilized. The term natural seawater refers to fresh seawater that is pumped directly into the laboratory, rather than seawater that has been stored and possibly shipped to an onshore location for the testing. Once seawater is removed from its natural environment, its composition changes and this can have a large impact on the resultant metal corrosion rate. Synthetic seawater solutions that are typically used include 3.5 weight percent sodium chloride (NaC1) and substitute seawater can be prepared as per ASTM D 1141. Both 3.5 % NaC1 and substitute seawater solutions do not contain the same organic and biological components as natural seawater. Substitute ocean water with heavy metals most nearly approximates the actual composition of natural seawater. The disadvantage in using any of the synthetic solutions is that, like the stored natural seawater, the composition varies from that of fresh natural seawater and thus the corrosion behavior of the metals evaluated can be considerably affected. However, one advantage of using 3.5 % NaC1 is that calcareous deposits will not form under cathodic polarization conditions in this solution. This is extremely useful in fracture surface evaluation of metal specimens, where the presence of calcareous deposits often prohibits examination of the surfaces unless the deposits are dissolved or mechanically removed, which could alter the original fracture surface.

Immersion testing is usually performed on panel specimens or small component parts such as fasteners. Specimens are exposed to the seawater environment in fully immersed, partially immersed, or alternately wetted and dried in a cyclic pattern. Sample weight loss, physical surface changes, visually assessed as well as surface compositional changes can be documented. For example, Long-term uniform corrosion testing is usually performed in test racks or in test loops. Immersion testing is useful to examine different variables such as environmental compositions, alloying elements, coating type, surface condition, controlled defects, etc. Immersion testing may be done in either natural or synthetic seawater. Natural seawater for laboratory immersion testing is often filtered to prevent macrofouling on the specimen surfaces. The filtering can be accomplished by passing seawater through a sequence of coarse to fine filters, with final filtering through 5-10 µm pore size filter cartridges. Stagnant natural seawater solutions are not recommended for testing due to decay of the marine biological organisms, which will alter the seawater composition and can affect the resultant corrosion behavior (Compton, 1971).

Salt spray (fog) testing is an accelerated laboratory method for assessing the corrosion behavior of coated and uncoated metals. The generally accepted methods in the United States for salt spray testing are discussed in ASTM B 117 (Method of Salt Spray (Fog) Testing) and G85 (Practice for Modified Salt Spray (Fog) Testing) and GM9540P. These tests have been successfully used to screen both coated and uncoated metals as well as to evaluate coating performance, particularly in terms of thickness uniformity and porosity. Cyclically acidified salt spray tests have also been used to determine the exfoliation corrosion resistance of aluminum alloys. Although salt spray testing is commonly used as a screening test, this method is not reliable for accurately predicting the corrosion rate of a metal in its service environment (Davis, 1987).

Laboratory test methods include a number of direct current measurement techniques that are commonly used in electrochemical testing. Specific methods include potentiodynamic polarization, potentiostatic polarization, galvanostatic polarization, Tafel extrapolation, and polarization resistance determinations. In seawater, passive film forming alloys like aluminum or stainless steel require an induction time for pitting to occur, and thus the scan rate in a potentiodynamic test can significantly influence the results obtained. Also, the dynamic nature of these test methods may prevent the natural formation of films on a metal or alloy surface, which can cause the distorted results. Potentiostatic and galvanostatic polarization methods are often applied in studying localized corrosion. Electrochemical methods to measure the susceptibility of alloys to pitting corrosion are reviewed elsewhere (Szlarska-Smialowska, 1986; Sedriks, 1996). The disadvantages associated with selecting the proper scan rate in the potentiodynamic method do not apply to the potentiostatic and galvanostatic methods.

The Tafel extrapolation test is capable of determining very low metal corrosion rates in a short period of time. When conditions are ideal, its accuracy is equivalent to or better than weight loss measurements. However, to maintain accuracy, the Tafel regions must encompass at least one order of magnitude of current. Also, this method can only be applied to systems that have one reduction process or the Tafel region may be distorted and corrosion rate determinations will be inaccurate. Finally, the Tafel method only yields an average, uniform corrosion rate and is not sensitive to localized corrosion. Therefore, use of this technique in seawater is considered to be limited primarily to obtaining an indication of the corrosion rate within an order of magnitude (Fontana 1967; Siebert 1985). Many of the disadvantages discussed above for the Tafel extrapolation method can be eliminated by using the polarization resistance technique. This non-destructive method can be used on systems that have either activation or diffusion controlled reactions. Very low corrosion rates can be determined accurately, quickly, and monitored as a function of time. Polarization resistance can also be used to measure the corrosion rate of a component such as a seawater tank or piping system, where inspections and weight loss tests are difficult if not prohibitive (Fontana, 1967)]. The major disadvantage with this technique is that, like the Tafel extrapolation method, the calculated corrosion rate represents a uniform value and does not indicate localized corrosion (Mansfeld, 1982).

Electrochemical impedance spectroscopy (EIS) is useful for examining the corrosion behavior of non-conductive coated metals (Sedriks, 1996; MacDonald, 1981). This method is essentially non-destructive and does not cause any acceleration of the corrosion reaction. The EIS technique can be used to monitor corrosion of a system or coating resistance as a function of time. Decreases in the measured coating resistance suggest that the electrolyte has permeated through the coating or that there are defects in the coating. Electrochemical voltage or current noise can determine the onset of pitting or crevice attack (Mansfeld, 2001; Berthome, 2001).

A variety of high velocity tests have been designed to evaluate cavitation and erosion properties in seawater environments. Specific tests are as follows: (a) high velocity flow tests which include venturi tubes, rotating disks, and ducts with specimens positioned in the throat sections, (b) high frequency vibration tests that utilize magnetostriction or piezoelectric devices (described in ASTM G32 (Cavitation Erosion Using Vibratory Apparatus)) and (c) impinging jet tests where rotating or stationary specimens are exposed to a high-velocity jet or droplet impact as per ASTM G73, Liquid Impingement Erosion Testing (Lichtman, 1971).

There are a number of disadvantages in high velocity laboratory testing. First, the results from these tests can vary widely due to differences in test technique, specimen size and shape, and environmental conditions like salinity, pH, temperature, and oxygen content. Secondly, these tests are designed to expose small specimens to high intensity flow conditions; however, the use of small specimens can alter the edge and turbulent flow conditions in such a way that the results do not simulate the service environment. The flow dynamics and conditions produced by the different high velocity techniques vary significantly. Although these high velocity laboratory tests may not accurately simulate the desired service condition, they are still useful in ranking different metals according to their resistance to velocity effects. For reproducibility among laboratory test, it is important to run a standard control material along with the candidate test materials so that the data can be normalized with respect to well understood and documented standard material (Lichtman, 1971).

A wide variety of stress corrosion cracking and hydrogen embrittlement tests have been developed to study different environmental cracking phenomena such as the susceptibility of materials to stress corrosion cracking and hydrogen embitterment. These tests, which employ either a static or a dynamic load, can vary widely in terms of specimen configuration, cost, test duration etc. These tests may include the effects of cathodic protection on the susceptibility of materials to environmental cracking.

1.2.2 Field evaluation

In-service testing provides the advantage of examining the corrosion behavior of a metal in the actual service environment. The advantages and disadvantages of some of these tests are briefly described below. Small specimen testing allows a large number of variables to be evaluated with minimal cost. Also, small specimens can be designed to determine specific types of corrosion; for example, creviced specimens can be exposed to assess localized corrosion. Although small specimen testing allows examination in the actual service environment, the corrosion rate determined on a small specimen is usually not consistent with the corrosion rate of a large scale piece of equipment predominantly because it is difficult to duplicate all of the metallurgical conditions of the large equipment on a small specimen. In addition, it is difficult to simulate erosion-corrosion by small specimen testing, since small specimens can shield each other from turbulence, thus providing inaccurate results. Electrical resistance probes are small in size and can be easily installed in the service environment; however, the walls of the test equipment must be penetrated for the probes to be installed and consequently, care must be taken to avert leakage in the system. The usefulness of the probes is limited in that they provide a measurement of uniform corrosion and can be continuously monitored, but provide no information on localized corrosion such as pitting or crevice corrosion. In addition, errors can result in the probe data if the temperature is varied during the time of the measurement. The ultrasonic thickness measurement method is quite popular for in-service corrosion testing. The major advantage of this method is that the equipment is portable and very easy to use.

The major disadvantage is that a bare metal surface is required for accurate measurements. The presence of coatings and / or corrosion products can introduce errors into the thickness measurements (Sedriks, 1996). Curved surfaces such as piping bends and small tubing diameters require special attention. Like in-service testing, simulated service testing provides the advantage of exposure to the actual environment. Fluctuations in the weather, the influence of geographical location, and bacteriological influences are part of the simulated service test environment and these factors that cannot be simulated in the laboratory (Davis, 1987). Simulated service testing in seawater typically consists of panel specimens exposed on test racks suspended from a pier or a float (Compton, 2001). Testing in this environment is discussed in ASTM G52. Specimens may be exposed in full immersion, splash / spray, or tidal conditions. The disadvantage of exposing panel specimens in the full seawater immersion environment is the occurrence of extensive macrofouling on the panel surfaces. The presence of these organisms prohibits inspection of the test panels during the exposure period and can result in the difficult task of removing the macrofouling after testing to obtain accurate weight loss measurements. For coated specimens, removal of the macrofouling after testing could cause partial removal of the coating as well, making an accurate corrosion assessment impossible.

1.3 Copper – zinc alloys

The copper alloys may be endowed with a wide range of properties by varying their composition and the mechanical and heat treatment to which they are subjected. For this reason they probably rank next to steel in importance to the engineer. The important alloys of copper and zinc from an industrial point of view are the brasses comprised within certain limits of zinc content. That portion of the constitutional diagram, which refers to these alloys, is given in Fig 1.6. The addition of zinc to copper results in the formation of a series of solid solutions which, in accordance with usual practice, are referred to in order of diminishing copper content as the α, β, γ etc., constituents. Table 1.3 shows copper-zinc alloys composition.

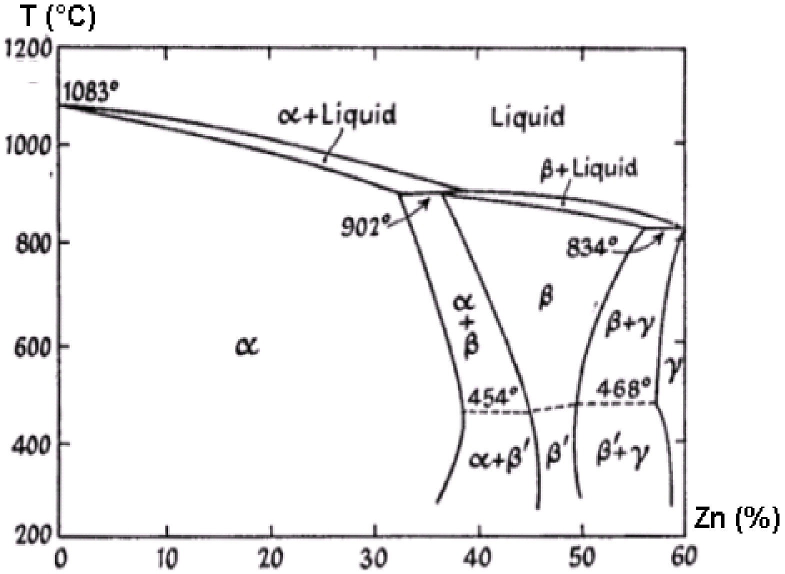


Fig. 1.6 Constitutional diagram of the copper-zinc alloys

Table 1.3 Copper-zinc alloys composition

Percentage composition		Constituent just below the freezing point	Constituent after slow cooling to 400°C
Copper	Zinc		
100 to 67.5	0 to 32.5	α	α
67.5 to 63	32.5 to 37	α + β	α
63 to 61	37 to 39	β	α
61 to 55.5	39 to 45.5	β	α + β’
55.5 to 50	45.5 to 50	β	β’
50 to 43.5	50 to 56.5	β	β ` + γ
43.5 to 41	56.5 to 59	β + γ	B’ + γ

Further changes in composition of α and β phases below 400°C are only observed after prolonged annealing. There is a certain connection between the properties and the microstructure, which may be expressed, in general terms. The tensile strength increases with increase in zinc content, rises somewhat abruptly with the appearance of β and reaches a maximum at a composition corresponding roughly to equal parts of α and β. It falls off rapidly at the appearance of the γ constituent. Elongation rises to a maximum and begins to fall again before the composition reaches the limit of the solution. It falls considerably as the amount of β increases and is very small in the presence of γ.

The constituent shows the greatest resistance to shock. This is diminished by the presence of α, β and the alloy becomes extremely brittle when γ is present. Hardness is greatly increased by the presence of β and still further when γ appears. Alloys containing α phase only are especially suitable for cold working and may be hot or cold rolled. Those containing α and β will suffer very little deformation without rupture in the cold rolling and may only be hot rolled. The β constituent may also be forged, rolled or hot extruded, but alloys containing γ should invariably be avoided for any mechanical treatment.

1.3.1 Designation system of brasses

Copper and zinc content often designate the brasses of industrial importance.

a) C 23000 - Red brass (85 Cu, 15 Zn)

This alloy is used for ornaments and for cheap jewellery, which is to be gilded: it withstands cold-work, cupping, etc. On account of the range of solidification, the cast material has a dendrite structure. If cooled very slowly or annealed, diffusion takes place, yielding polyhedral grains of uniform composition. The process of diffusion is assisted by mechanical deformation of the grains by hot- or cold work followed by annealing. The changes, which occur in rolling and annealing are similar to those described for 70:30 brasses.

b) C 26000 - Cartridge brass (70 Cu: 30 Zn)

This alloy, which is used widely for tubes, sheets and wires also shows a dendrite structure of the solid solution when chill fast. The β constituent does not begin to appear in the cast structure until the zinc exceeds 32 % except in the presence of an additional element like aluminum or tin. After annealing, the alloy consists of homogeneous solid solution and it is especially suitable for cold working. To withstand this treatment, especially drawing, it is necessary that the brass should be perfectly sound and free from impurities.

Without admixture of any but the cleanest scrap, these impurities are chiefly inclusions of oxides / silicates or charcoal. Such inclusions, if present, frequently lead to failure of the material during manufacture or in use. They become entrapped in the solidifying metal either by splashing or by rapid solidification in moulds of small cross section.

It is a frequent procedure in casting brass to draw it into rod to employ very long moulds of very small cross section in order to minimize subsequent mechanical treatment. Ingots made in such moulds are most liable to contain inclusions and to show piping to a great depth resulting in central unsoundness over a considerable length of the ingot. To ensure soundness, it is necessary to cast in a mould such that the cross section is large enough to give relatively slow cooling. The mould and stream of molten metal should be so arranged as to avoid splashing; the dimensions of the mould and speed of pouring should be such as to result in the ingot solidifying from bottom upwards. The effect of cold work on the microstructure is to break down the crystal grains by plastic deformation and so crush them into debris. Annealing after cold-work results in recrystalization and subsequent crystal growth.

d) C 28000 - Muntz metal (60 Cu: 40 Zn)

The molten metal begins to freeze at about 905°C and dendrites of the β solution are formed. With sufficiently slow cooling through the range of solidification the alloy consists of homogeneous β constituent but further cooling, this solution retains less copper and at 770°C the constituent separates from the homogeneous β and increases in amount as the temperature falls. The structure on reaching atmospheric temperature is therefore a mixture of α and β which may be controlled to some extent by the rate of cooling.

For example, a thin section of 60:40 brass quenched from 800°C consists of homogeneous β. With a larger section it is impossible to suppress completely the separation of α but a specimen rapidly cooled from this temperature always contains more β than a specimen more slowly cooled. These micro structural characteristics are accompanied by changes in mechanical properties, which can be deduced from the known hardness and brittleness of the β constituent and the softness and ductility of the constituent. Hot-rolled 60:40 brasses, the rolling of which has been stopped above 700°C, shows a uniform structure in longitudinal and transverse directions. After the separation, α and β constituents are elongated in the direction of rolling giving the normal structure of rolled 60:40 brass. The lower temperature of finishing, the smaller will be the grain size. If, however, rolling is continued much below 600°C, recrystalization does not keep pace with the deformation and the metal is cold-worked.

e) Brazing solder (50 Cu: 50 Zn)

This alloy, if cooled sufficiently slowly through the range of solidification, consists of homogeneous β solution, which, however, may decompose on cooling if the copper content is less than 50 %. At atmospheric temperature the β solution will retain a maximum of just 50 % of zinc if no impurities are present but any content of zinc over 50% causes the separation of the β constituent, which increases in amount as the temperature falls. Its presence renders the alloy extremely hard and brittle.

The components designed for use in seawater and freshwater have failed by dezincification in such applications as condensers, valves, taps, and pipe work, as well as screw, nuts and bots. The problem of dezincification was overcome by the addition of very small amount of arsenic, usually about 0.05 %. The 70:30 alloys with the arsenic addition become known as Admiralty brass (inhibited) and today, most commercial production of 70:30 brasses contains arsenic for this purpose. Uninhibited 70:30 brasses should never be specified for uses involving immersion in either freshwater or seawater.

Unfortunately, the addition of arsenic does not significantly affect the susceptibility of the 60:40 alloys and this problem of dezincification has remained. Efforts have been made to find the elemental additions, which might alleviate the corrosion. The addition of 1 % tin to muntz metal, an alloy widely claimed to have greatly reduced susceptibility to dezincification, though there is little evidence to support it. Rogers (1968) states that Naval brass does not provide improved resistance and there is no reliable method of inhibiting the dezincification.

1.3.2 Corrosion of brass

Dezincification is the most common form of dealloying. Copper-zinc alloys containing more than 15% zinc are susceptible to a dealloying process, called dezincification. Selective removal of zinc from the brass leaves behind the spongy mass of copper with poor mechanical strength.

1.3.3 Types of dezincification

a) Uniform layer type

In the uniform layer type, the active component of the alloy is leached out over a broad area of the surface. This is similar to general corrosion except that there is preferential dissolution of zinc from the surface leaving copper in the lattice. The surface appears to be just covered with a tarnish layer. The bulk of the alloy does not have enough strength due to slow removal of zinc and if flow of liquid is sufficiently high, this may result in the busting of the tube. The layer type of dezincification is found when the environment is acid and brass is of high zinc content.

b) Plug-type

This type of attack generally leads to more rapid failure than in the uniform layer type. This usually proceeds with greater speed and it is localized in nature. The plug type of attack penetrates deep into the metal, forming porous plugs of copper. The entire surface is not affected. A study of kinetics and mechanism of brass dezincification process is quite important for corrosion research as it has several practical applications. Brass dissolution process mainly depends upon the nature of the composition (Chawla et al., 1993;

Verink et al., 1972; Jones, 1996) and the corrosive medium such as acidic, alkaline and neutral solutions.

1.3.4 Mechanism of dezincification of brass

The kinetics and mechanism of dezincification of brass have been widely studied (Hieidersbach et al., 1972; Lueey, 1966; Fink, 1993).

a) Preferential dissolution of zinc

Bassett (1992); Polushkin et al. (1945); Langenegger et al. (1968) have reported that dezincification occurs due to selective removal or preferential dissolution of zinc taking place at the brass surface in contact with a corrosive medium. Accelerated dezincification under both anodic stimulation and freely corroding conditions revealed that the separation of zinc must be compensated by the diffusion of zinc atoms with the alloy lattice. It was believed that zinc is preferentially attacked at the active dezincification sites progressively inwards. The exclusive extraction of zinc from the brass matrix is only possible theoretically. In practice, some copper unavoidably gets dissolved together with zinc. The dezincified phase, therefore, only represents the skeleton structure of the original brass matrix and is porous enough to allow the non-restricted outward diffusion of zinc ions.

b) Simultaneous dissolution of copper and zinc

A work by Evans (1960) indicated that zinc atoms couldn’t easily leave the alloy unless copper atoms accompany them. He explained that a slow dezincification of brass placed in NaCl solution takes place especially in the β-phase of α-β brass, or at the grain boundaries of insufficiently annealed α- brass, where relatively zinc rich areas exist. At such places zinc passes into solution leaving residual copper. These residual copper sites act as cathodes in the galvanic cell that is set up in the alloy. At the cathode, copper is deposited in amount equivalent to the copper entering the solution at the anode. Sugawara et al. (1967*)* studied the dezincification of brass by means of a potentiostat and an electron microscope analyzer and reported that the mechanism of dezincification was mainly due to the redeposition of copper. The presence of both copper and zinc were identified during the electrode position of copper as reported by Horton (1970).

Popumin et al. (1982) used a combination of electrochemical and radiotracer techniques to study the dezincification of brass in HCl solution under the conditions of continuous addition of copper ions by means of anodic dissolution of auxiliary copper electrode. A relationship was established between the electrochemical characteristics of the alloy and the process of its dezincification as affected by the redeposition of copper from the solution. EL Warraky (1997) investigated the ratio of Cu and Zn by solution analysis under immersion. He suggested that zinc content higher than that of the bulk alloy indicate that simultaneous dissolution of both Cu and Zn was followed by the redeposition of copper in the dezincification process.

c) Combination of the above two mechanisms

Langenegger and Callaghan (1972) used the potential shift technique to determine the rate of dezincification of $\alpha + \beta$ brass in the chloride medium and reported that zinc preferentially got dissolved in the initial stages of dezincification and redeposition of copper appeared to be a second step. Heidersbach and Verink (1972) have studied the mechanism of dezincification of single phase alpha and alpha + beta brasses using x-ray diffraction, electron microscope, metallographic, atomic absorption and electrochemical techniques, where the specimens were subjected to accelerated corrosion testing in non-oxidising 1N NaCI and 5N HCl solutions. They reported that both the above mechanisms could occur on the same specimen.

Natarajan et al. (1975) focused on dezincification of cartridge brass and reported that a selective removal mechanism might operate over a short distance from the electrolyte boundary which appears to shift progressively into the interior of the sample through the porous layer of copper and that the mechanism of dezincification was due to the redeposition of copper. Itoh and Hikage (1976) observed the dezincification rate of α and α+β brasses by thermogravimetry over the temperature range of 500-800°C in vacuum and discussed the results in the light of the structural changes occurring in the diffusion layer and explained that dezincification reaction proceeded through three stages. In stage I, the weight loss was shown to obey the parabolic rate law as expected from an ordinary diffusion mechanism. In stage II, the dezincification rate was accelerated and in stage III, the weight loss was found to be nearly proportional to the square root of time. These three stages were characterized by the structural changes occurring during the dezincification process.

Pchelnikov et al. (1981) studied the kinetics and the mechanism of dezincification in alpha brass in NaCI by radiotracer and electrochemical techniques, and proposed two stage mechanism of dezincification. After the short primary preferential dissolution which is controlled by the volume diffusion of zinc and subsequent simultaneous dissolution of alloy, a steady state secondary preferential dissolution due to the redeposition of copper started when a certain concentration of copper in the solution had been reached. At this stage, the non-steady state volume of zinc in the alloy limited the process. The increase in the corrosion rate of α- brass with time was due to the slow oxygen reduction on the alloy surface process, which became oxidized to cupric oxide by oxygen with these ions being more effective depolarisers than oxygen.

Pushpa Gupta et al. (1982) attempted to study the mechanism of dezincification in 70:30 brass in dilute H_2SO_4 by solution analysis as well as electrochemical techniques and observed that in the initial stage, the rate of dissolution of zinc was greater than that of copper. They suggested that in the initial stages, due to the establishment of the galvanic cell (Cu-Zn), there is preferential dissolution of zinc in the solution but as a porous copper - copper oxide film is formed on the surface of the electrode, the rate of dezincification (i.e. the `z' value decreases) is accompanied by a decrease in the current density. The second stage of the mechanism of dezincification begins with the formation of a porous Cu-CuO layer on the surface of metal. During this stage the current density decreases with the formation of the Cu-CuO porous film. Under these conditions, a simultaneous dissolution of copper and zinc takes place followed by the redeposition of copper from the solution.

Abbas (1991) studied the effect of temperature on dezincification and corrosion of α-brass in 0.5M H_2SO_4 and reported that below $50^{\circ}C$ dezincification initially took place by preferential dissolution of zinc and latter, in a second stage, by simultaneous dissolution of copper and zinc. Above $50^{\circ}C$ dezincification initially occurred by dissolution of both copper and zinc at the same rate and in the second stage by the redeposition of copper from the solution onto the brass surface. Rehim et al. (1995) employed the cyclic voltammetry technique to study the copper rich brass (13-39% Zn) in aerated NaCI solutions and reported that preferential dissolution of the less noble zinc component was produced first whereas both components of the alloy were dissolved simultaneously second. They suggested that the preferential dissolution of zinc was limited by a non-steady diffusion of zinc atoms from the bulk of the alloys to its surface. The rate of preferential dissolution was found to increase with increasing zinc content, NaCl concentration and scan rate. The rate of simultaneous dissolution decreased with an increasing Zinc content in the passive film of the alloy. It is probable that the presence of ZnO in the passive film of the alloy could increase its protectiveness.

Therefore, the mechanism of dezincification of brass in corrosive media could be broadly divided into two types of reaction sequences or a combination of the following two.

- Preferential dissolution of zinc from the copper-zinc alloy.
- Simultaneous dissolution of both copper and zinc followed by the redeposition of copper on the surface of the brass.

1.3.5 Dezincification of brass in various environments

a) Atmosphere

Sterling et al. (1990) worked on the atmospheric corrosion of 90:10, 70:30 brass and copper using three accelerated atmospheric tests such as acidified, neutral spray salt test and reported that among these alloys, 70:30 brass exhibited dezincification. Alloying with P, Sn or Si did not improve atmospheric resistance. The higher corrosion rate was attributed to residual contaminants from rolling. Mattsson arid Holm (1968, 1980) investigated the atmospheric corrosion of copper and its alloys and reported that the formation of green patina (Cu (I) oxide and one or more basic Cu salts) ($CuSO_4$ CuCI, $CuCO_3$) on the surface of metals indicated that the brass underwent dezincification leaving copper matrix on the surface.

Fontinha and Salta (1999) used copper and its alloys such as six bronze and brass statues exposed to urban and urban marine atmosphere with ages between 30-200 years old. Using weight loss, scanning electron microscope, X-ray diffraction and electron diffraction spectroscope method, they observed that the atmospheric conditions (climatic and pollution characteristics) influenced the corrosion process.

Panchenko and Strekalov (1999) observed the protective properties of a chemically produced passive film on brass 1162 and Cu-38 in ship's instruments in a marine climate. They had used a D62 brass ship's instrument with coatings of gold and palladium and exposed it in the marine environment for a period of 14-20 years. They reported from their works that the dezincification products of the brass substrate emerged through the pores of the coating form strains and salt films on its surface. Due to the clogging of the pores, the products become responsible for the blistering of the plate. The corrosion weight loss was found to be linearly correlated with the surface accumulation of chlorides. It was also indicated that the thicker the coating, the smaller the damaged area of the substrate, but in the center the corrosion wear is deeper (Panchenko and Strekalov, 2000).

The behaviour of copper and zinc in the marine environment of the Yucatan peninsula in Mexico was studied by Veleva et al. (1997) using photoacoustic technique. For both copper and zinc, the changes in the thermal diffusivity were mainly governed by the oxide layers (Cu_2O and ZnO for the Cu and Zn samples) whereas a decrease in the thermal effusivity was apparently related to the growth of the chloride layers (paratacamite $Cu_2Cl(OH)_3/Cu_2O$) for Cu and simonkolleite ($ZnO/Zn_5(OH)_8\ Cl_2H_2O$ and sodium zinc chlorohydroxy sulphate ($NaZn_4Cl(OH)_6SO_46H_2\ O$) for zinc.

Chung et al. (1999) studied the initial stages of zinc atmospheric corrosion in the presence of chloride using ex situ electrochemical impedance spectroscopy (EIS) in a non-aqueous electrolyte (methanol), FTIR, XRD techniques and reported that the zinc hydroxy carbonate and zinc oxide were found responsible for the protectiveness of this surface layer against contaminated chlorides i.e., zincite, (ZnO), hydrozincite, [$Zn_5(CO_3)_2(OH)_6$] and showed it to be protective against a chloride environment. These corrosion products react with aggressive chloride ions from contaminated soluble NaCl to form insoluble simmkolleite providing protectiveness and reducing aggressive soluble chlorides.

Herman and Castillo (1974) studied short term atmospheric corrosion of various copper based alloys after two and four year exposure to natural environments (at New Haven, Connecticut, Brooklyn, New York and Daytona Beach, Florida) and reported significant changes in the percentage elongation of alloys Cu 70:30 Zn and Cu 56:25 Zn. Metallographic investigation revealed plug type dezincification of 70/30 brass at all locations and pitting coupled with plug type dezincification of Cu 56:25 Zn at the industrial and industrial marine sites respectively. They reported the lack of localized corrosion of this alloy in the marine environment strongly suggesting that nickel, as an alloying element, was beneficial with reference to corrosion resistance of a Cu-Zn system in marine atmospheres.

b) Acidic environments

Saber et al. (1991) investigated the effect of various pretreatment procedures on the surface composition of 70/30 α-brass using X-ray diffraction (XRD) and Auger electron spectroscopy (AES) and reported that in general, wet cleaning caused dezincification, cleaning with acids (HNO_3, HCl, H_2SO_4 or acid brightener and electrochemical cleaning in H_3PO_4 caused surface dezincification. Zembura el al. (1982) studied Cu-1 5Zn α-brass by rotating disc technique in argon, air or oxygen saturated 2M H_2SO_4 in the temperature range 10-65^{0}C. The dissolution rates of copper and zinc from Cu-15 Zn alloy were similar to that of copper corroding in similar conditions indicating that dezincification of α - brass did not occur.

Vora et al. (1997) reported that 63:37 brasses in souring substances used as food additives containing organic acids was responsible for the corrosion of brass and observed that a film was formed over the surface of the brass specimen. The dezincification mechanism of α -brass 70/30 in acidic solutions under various stress conditions was investigated by (Badawy et al., 1998). The preferential dissolution rate of zinc was found to destroy the Cu (I) passive film and higher rates of corrosion were observed in the presence of stress. Torchio et al. (1986) studied Al-brass in Cl^- ions in acidic sulphate solution; a Cl^- ion stimulating effect was observed either in environmental conditions in which competition between the precipitate of Cu_2O and CuCl could occur or in conditions in which Cu_2O was thermodynamically stable but the presence of a critical amount of Cl^- could induce an alteration of its defect structure. An inhibiting effect was observed at high Cl^- ion concentrations where CuCl was the prevailing stable phase. Jennane et al. (1996) suggested a divacancy mechanism of brass dezincification by self-diffusion parameters in (β-brass (Zn65 in Cu-Zn alloy).

c) Neutral environments

Morales et al. (1995) observed passivation and localized corrosion of α, β and α + β brass in borate - boric acid buffer solution (pH 9) in 0.5M NaCl solution by electrochemical techniques and X-ray diffraction studies. They observed the potential values to be slightly more negative than the breakdown potential of copper and markedly positive with respect to the presence of a complex $ZnO.2H_2O/Cu_2O$ - CuO layer which was less positive towards Cl^- ions attack than the Cu_2O-CuO layer formed on Cu. The pitting resistance increased from α + β and β-brasses to α - brass, the latter approaching the Cu behavior. The increase in resistance of brass to pitting corrosion with respect to zinc is due to the formation of a Cu-rich layer at the alloy/oxide layer interface which was immune to corrosion at negative potential where the pitting corrosion of zinc took place in N_2O containing solutions.

Al Kharafi and Badawy (1997) investigated the corrosion and passivation behavior of brass alloys α, $\alpha + \beta$ (Cu 24 Zn, Cu 30 Zn, Cu 39 Zn) in aqueous solutions at different pH (2.0, 7.0, and 12.0) by polarisation, EIS, XRD and SEM techniques and reported that it was dependent upon the stability of the passive Cu (I) compound. The presence of O_2 or oxidizers in acidic solutions besides the selective leaching of the alloy enhanced the disproportionation of the Cu (II) compound, leading to passive film breakdown and appearance of copper on the alloy surface. Copper patches initiated active galvanic couples and flawed regions, which increased the rate of corrosion of the alloy. Panagopoulos et al. (1998) studied the hydrogen induced cracking and blistering in α- brass (70:30) and reported that the hydrogen charging of α - brass could result in the formation of intergranular and transgranular cracks and hydrogen blisters. The current density increased from 15 to 25 $mAcm^{-2}$ resulting in more severe cracks and from 35 to 85 $mAcm^{-2}$, increasing the number of blisters. Pitting attacks on admiralty brass in brackish water by electrochemical and X-ray diffraction measurements were reported by Zia, et al. (1990)

Arvia el al. (1998) studied the α and β brass in aqueous borate / boric acid buffer (pH 9) in NaCl in the temperature range 5°- 45°C. They observed pitting corrosion when the breakdown potential (E_b) was exceeded. At constant temperature, the value of E_t, shifted negatively as either NaCl or the zinc content in the alloy was increased. For β-brass the value of E_t, decreased slightly with temperature. For α-brass, from 5°-25°C, the value of E_b was close to that reported for copper, whereas for $T > 25°C$ it approached those values measured for β-brass. The dealloying measurements indicate that zinc surface enrichment of α-brass was responsible for the decrease in pitting corrosion resistance at temperatures greater than 45°C.

Newman and Shahrabi (1993) have indicated how dezincification of α - brass occurs in crevices. Oxygen reduction on relatively bare parts of the brass surface supported diffusion controlled copper dissolution (as $CuCl_2$) under deposits or corrosion products that acted as diffusion barriers. The solution on the corroding surface was equilibrated with copper in the alloy and dezincification started. Diffusion controlled partial anodic current density of' copper was much less than that achievable by zinc. The latter varied with the chloride concentration, temperature, alloy zinc concentration and cold work. Especially, the presence of alloyed arsenic inhibited zinc dissolution was probably by reducing the surface self-diffusion co-efficient of copper. This dezincification only occurred when there was $CuCl_2$ in the solution and this might be interpreted as evidence for a Cu^+ exchange or dissolution - redeposition mechanism but no evidence exists for this occurring.

Grezegorzewicz and Kuznicka (1998) carried out failure analysis studies on brass tubes of a heat exchanger and indicated that the water flow rate through the heat exchanger was reportedly close to the turbulent flow rate. Aaltonen et al. (1996) studied the industrial brass, Cu20Zn, Cu37Zn and CoZnAIFe alloy subjected to electrochemical oxidation in tap water resulting in the selective dissolution of zinc by low temperature internal friction. For dezincified brass in the temperature range of 230 - 300K a complex two-component peak was observed. This peak was considered to be caused by dissolution of excessive vacancy interaction and is of a non-relaxation nature.

Badawy and Kharafi (1999) investigated the α-brass (70%Cu) and leaded brass (58%Cu) in Kuwaiti tap water by electrochemical polarisation, EIS and morphology techniques. The effect of anions such as phosphate, chloride etc., and oxygen was also investigated. The rate of corrosion was found to increase in oxygen rich water. This was attributed to enhance disproportionation reactions, which destroyed the surface passivity of the alloy.

Redd and Breslin (2000) studied Cu 37 Zn brass alloy in borate buffer (at pH 9.2 and 13.0) in 0.025 M NaCl solutions by potentio-dynamic polarisation, cyclic voltametry and complex impedance spectroscopy under the influence of UV illumination. Significant decreases in the breakdown potential on increase in the passive current density and lower charge transfer resistance values were observed on illumination of brass in pH 9.2 solutions. A much lower photo activation effect was observed at pH 13 solutions. These findings may be explained in terms of the photodecomposition of ZnO, which existed in the complex passive layer formed on CuZn alloy,

Sahoo (1998) studied the corrosion of yellow brass SeBiLOYIII alloy in near aqueous environments by spectroscopy. The spectrum of dezincification tests ranging from very aggressive to natural simulation showed that grain refined SeBiLoylll alloy and grain refined C85800 containing 36% zinc were prone to dezincification particularly at any center-line porosity in permanent mold castings.

Studies on α-brass were attempted by Badawy et al. (1999) in naturally aerated, oxygen saturated and oxygen free acidic, neutral and basic solutions at a constant pH using polarization and surface analysis techniques. The electrochemical behavior of α-brass was dependent on the pH of the ambient electrolyte. The alloy passivity was due to the formation of a Cu (I). Compound (mainly Cu_2O), which was relatively stable in neutral and basic solutions. The corrosion rate of the alloy increased in oxygen-rich acidic solutions due to the oxidation of the Cu (I) passive film to the soluble Cu (Il). The presence of oxidizers such as dichromate ($Cr_2O_7{}^{2-}$) ions enhanced the oxidation reactions in the acidic solutions, leading to a high corrosion rate. The preferential dissolution of zinc was found to destroy the Cu (I) passive film, especially in the acidic solutions leading to higher rate of corrosion.

d) Polluted environments

Lee and Shih (1966) were able to report on the effect of halide ions in aqueous environments using 67:33 α-brass by electrochemical, slow strain rate tension (SSRT) and scanning electron microscope techniques. Electropolarisation analysis confirmed that a passive Cu_2O film could be formed on α-brass in 0.1 M NaF solutions. This passive film could however break down. Film rupture and slip dealloying may be involved in intergranular stress corrosion cracking (IG SCC) of 67:33 α-brass in NaF- solution. In 0.1 M CI^-, Br^- and I^- solutions no SCC susceptibility was observed which could be due to the formation of soluble cuprous complexes controlling the dealloying process through precipitation of metal ion salts on the surface of α-brass. Pore formation during dezincification at different temperatures has been reported by (Kuperonan and Troiani, 1996).

Rylkina and Kuznetsov (1999) studied copper, zinc and brass (L 63:64, 36 at % Cu) in neutral media (borate buffers with pH 7.4) with activators of inorganic acid salts of sodium Nax (x^- = F^-, CI^-, BrI^-, SO_4^{2-}, $NO4^-$, NO_3^- and CIO_4^-). Brass L63 was less stable to pit formation as compared with copper in the borate buffer containing CI^- anions. The stability was higher in the presence of I^- ions. The pit formation potential was independent of the nature of anion - activators. Shams Eldin et al. (1981) reported galvanic corrosion of Cu, Zn and brass in O.1 M KCI, KNO_3 and Na_2SO_4 solution by galvanic corrosion test and potential scanning.

Torchio (1986) observed stress corrosion cracking of admiralty brass condenser tube in sulphate solution. The cracking was intergranular in strongly acidic solutions and transgranular in a wide range of moderately acidic solutions. According to Newman and Burstein (1980) the Cl^- anions which directly might well cause blunting of incipient cracks in pure metals but could cause SCC in alloys owing to additional features such as de-alloying coarse slip and grain boundary chemical heterogeneity in 0.1 M KCl, KNO_3 and Na_2SO_4 solution as shown by galvanic corrosion test and potential scanning. It was concluded that both techniques took place between pairs involving copper and any of the three brass alloys, or between pairs of the Cu-Zn alloys.

Findings of Jin-Yun Zou et al. (1997) showed corrosion of α -brass in $Na_2SO_{4,}$ NaCl, H_2SO_4 and $CuCl_2$ solutions by chromo-amperometry and positron annihilation methods and indicated that the transient currents were caused by the sole dissolution of zinc from α-brass at the constant potential much more negative than the potential of onset of dissolution of copper in brass in the solution. They reported that the current time relations followed the Cottrell Law in the initial period of dissolution of alloy and there was no effect of stirring solution on the transient current. Thus a solid-state diffusion process controlled the selective dissolution of zinc from brass. The positron lifetime spectra have been measured for α,β and ε- brass specimens before and after dezincifying in l% $CuCl_2$ solution. The variation of the mean positron lifetime (Δm) and 2/b value of corroded specimens suggested that the solid-state diffusion of zinc atoms occurs via (di) vacancies created on the alloy surface during corrosion of brass.

Malki and Legris (1999) studied the corrosion of yellow brass (Cu - 37 Zn) in sodium nitrite by slow strain rate loading tests. There existed a critical stress below which no embrittlement occurred. Such a threshold need not be necessarily associated to the cracking of the oxide film that could instead, be related to the nature of the chemical bonding in the oxide film and at both metal / electrolyte interfaces.

Giordano et al. (1997) studied α -brass (Cu 35 Zn, Cu 30 Zn, Cu 20 Zn, Cu 10 Zn) in cupric nitrate by polarisation, SCC and SEM techniques. The effect of Cu^{2+} concentration on the stress corrosion crack propagation rate (CPR) was measured. A linear relationship between the logarithm of the CPR and the logarithm of the Cu^{2+} concentration was found in all the alloys studied. The slope of this relationship was very close to that reported for the cuprous ion exchange current density and the cupric ion concentration ($\delta \log i_o$ ($Cu^+ \rightarrow$ Cu) / δ log [Cu^{2+}]). All the cracks were transgranular in nature and the crack propagation mechanism could be explained through the surface mobility mechanism. Increasing the Cu^{2+} ion content in the solution accelerated CPR. The relationship between the CPR and the Cu^{2+} ion concentration followed the predictions of the surface mobility SCC mechanism.

Dehri and Erbil (1999) went on to study the corrosion of 63137 brass in neutral aqueous solution containing $SO4^{2-}$, NH_4^+ and Cl^- ions by semi ellipse model in EIS and reported that the ammonia ion was corrosive to brass and the charge transfer resistance R, values decreased with an increase in ammonia concentration in the electrolyte. The formation of $[Zn(NH3)_4]^{2+}$ complex ion was easier than the formation of $Zn(OH)_2$ in a medium containing OH^- and NH_3, since NH_3 was a stronger ligand than OH^- and also $Zn(OH)_2$ dissolved more readily in aqueous solutions that contained NH_3. They also suggested that when the $(NH_4)_2$ SO_4, concentration increased in the solution; this equilibrium was displaced towards the right hand side and the NH_3 concentration increased. The chloride ions were not effective in the corrosion of brass. This was due to the rate of corrosion being controlled by diffusion of Cl^- to the surface of the electrode through a porous layer of CuCl film.

Tromans (1997) studied the corrosion of α -brass in NH_3 solution using polarization studies. Potential - pH diagrams for the $Cu-NH_3-H_2O$ and $ZnNH_3$ - H_2O systems have been constructed for 15M NF_3 solutions commonly used for studying SCC of α-brass. The anodic polarisation tests indicated that formation of the zinc tetramine complex in ammonia might involve transient zincate ions. Lu et al. (1998) observed that corrosion induced tensile stress of the alloy Cu 38 In brass in 1 mol/l NH4OH + 5 g/L $CuCl_2$ solution and further noted that an additional tensile stress would be generated at the metal/dezincification layer interface during original corrosion of brass. The steady value of the additive tensile stress was 24.4 MPa (about1/5 of the yield strength).

Natesan et al. (1988) reported that the monel exhibited superior corrosion resistance due to the formation of a compact film and the other alloys such as admiralty brass, Al-brass, 90/10 Cu-Ni and 70/30 Cu-Ni alloy initially corroded and subsequently formed corrosion product film to protect the metals in synthetic sea water. Xie et al. (1998) studied copper alloys (HSn 70-1+ AS and B 30) in H_2O containing S^{2-} ions by electrochemical and surface analysis and observed dezincification. Kermani and Scully (1979) investigated the stress corrosion of α-brass in ammonical solution containing Cl^- and Br^- ions by constant strain rate technique. The increasing Cl^- ion or Br- ion caused a decrease in crack velocity due to black tarnish film.

e) In the presence of microorganisms

The microbiologically influenced corrosion (MIC) of copper and its alloys is not very well understood. This is probably due to the general belief that copper is toxic to microorganisms, which is not, however, the case for all microorganisms. As an example, bacteria of the genus Thiobucillu.S may tolerate copper concentrations up to 2%. Early histories of MIC on copper and its alloys have been reported from piping systems and heat exchangers where heat transfer problems have been observed with growing biofilms, wherein the corrosion has been found to increase after the death of the microorganisms within the biofilm. This is believed to be due to the production of ammonia and carbon dioxide upon the death of cells that may result in pitting corrosion and / or stress corrosion cracking (SCC) for copper and its alloys. The production of hydrogen sulfide by Sulfide Reducing Bacteria (SRB) is also believed to be a cause for pitting corrosion and SCC on copper and copper alloys. In this case, the corrosion is due the formation of a thick non-adherent layer of chalwite (Cu_2S) or covellite (CuS). Pitting corrosion may occur where the copper sulfide film has been removed with the cathodic reaction-taking place on the intact copper sulfide film (Thierry et al., 1991).

Microbiologically induced pitting corrosion has also been observed in copper pipes used for potable water system (Fisher et al., 1990). This has been observed in both warm and cold water systems. Generally a biofilm is observed under a black deposit of copper (II) oxide. However, it has been suggested that the role of biofilm could be predominantly conversion of copper (I) oxide to copper (II) oxide (Chamberlain et al., 1969).

Subramanian et al. (1995) studied 70:30 brass and copper in seawater by culture media using SEM, optical metallurgical microscope and XPS measurements and observed that biofilmed coupons of brass experienced less corrosion in culture media than that of commercial copper. The bio-filmed coupons of Cu and brass experienced corrosion due to the hostile $H_2S - O_2$ environment created by aerobes and SRB. The nature of the sulfide film and susceptibility to pitting corrosion were confirmed by surface analysis.

1.4 Estuarine system

An estuary is a semi-enclosed coastal body of water with one or more rivers or streams flowing into it and with a free connection to the open sea (Pritchard, 1967). They are affected by both marine influences, such as tides, waves, the influx of saline water; and riverine influences, such as flows of fresh water and sediment. As a result they may contain many biological niches within a small area and so are associated with high biological diversity.

Estuaries are typically the tidal mouths of rivers (*aestus* is Latin for tide) and they are often characterized by sedimentation or silt carried in from terrestrial runoff and frequently, from offshore. They are made up of brackish water. The terms are not mutually exclusives ecosystems; many estuaries are under threat from human activities such as pollution and over fishing (Ross, 1995).

Estuaries are marine environments whose pH, salinity, and water levels vary, depending on the river that feeds the estuary and the ocean from which it derives its salinity (oceans and seas have different salinity levels). The time it takes an estuary to completely cycle is called its flushing time **(**Tomczak, 2008).

- Estuarine circulation is common in estuaries; this occurs when fresh or brackish water flows out near the surface, while denser saline water flows inward near the bottom.
- Anti-estuarine flow is its opposite, in which dense water flows out near the bottom and less dense water circulates inward at the surface.

These two terms, however, have a broader oceanographic application that extends beyond estuaries proper, such as in describing the circulation of nearly closed ocean basins.

Estuaries are more likely to occur on submerged coasts, where the sea level has risen in relation to the land; this process floods valleys to formrias and fjords. These can become estuaries if there is a stream or river flowing into them. Large estuaries, like Chesapeake Bay and the Gulf of St.Lawrence, often have many streams flowing into them and can have complex shapes. Where an enormous volume of river water enters the sea (as, for example, from the Amazon into the South Atlantic) its estuary could be considered to extend well beyond the coast.

The Cochin estuary houses the second largest port along the west coast of India. Historically, this area is known for trade, commerce and cultural activities with countries like Arabia, Portugal and Holland. This harbor and its neighboring environment are natural and have a free permanent connection (Cochin gut–tidal inlet) with the sea. The tropical estuarine environment shows multitudinal features, which characterize freshwater and seawater mixing and provide breeding ground for marine organisms. The extent of freshwater–seawater mixing in Cochin tidal inlet, with partially mixed conditions in May and a salt wedge in August–October. From November to January, partially mixed conditions prevail, whereas in June, moderately stratified to partially mixed waters are observed. Cochin estuary face serious environmental threats by inter-tidal land reclamation, pollution discharges, expansion for harbour development, dredging activities and urbanization. The sedimentation features at the Cochin port vary according to season(s). There are three seasonal conditions prevailing in this estuary, i.e. monsoon (June–September), post-monsoon (October–January) and pre-monsoon (February–May). During the monsoon period, heavy rainfall results in high river discharge, which eventually reaches the estuary and waterways of Cochin port. Stratification often develops and results in conditions with less dense river water at surface and high dense seawater at the bottom layers. Such typical hydrographic features and circulation pattern complicate the sedimentation characteristics of the estuarine channels. In post-monsoon, river discharge gradually diminishes and tidal influence gains momentum as the estuarine conditions change to a partially mixed type, weakening stratification. This is mainly a transitional period. In pre-monsoon, the river discharge is minimum and seawater influence is maximum upstream; the estuary is well mixed and homogeneity exists in the water column. The development of turbidity maxima during high tide within the estuary is very noticeable. The circulation pattern helps to bring more silt and clay into the estuary and especially during the tide slack period, sedimentation is highest. The sedimentation feature results from the heavy discharge of water plus sediments brought out to the Cochin gut and deposited in the outer harbour. Simultaneous processes (turbulence due to currents) in the inner harbour lead to re-suspension of sediments and hence accumulations reduced.

Estuarine chemical variability is complex and highly variable compared to other marine environments. The dominant feature controlling the distribution and reactivity of chemical components within estuaries is the mixing of fresh and saline waters. Differences in the nature of the fresh and saline mixing components produce gradients and transitions of physical-chemical properties within an estuary in response to the circulation and mixing pattern. Estuaries are characterized by complex gradients of salinity, tidal action, current velocity, bottom erosion and sediment accumulation. They are subject to major and often unpredictable variations in response to river flow as well as wind and storm patterns. In an estuary, mixing occurs between natural waters of very different-chemical composition and physico-chemical properties. Although the salinity of seawater is high as compared with the total salt content of the river waters, the plant nutrient elements nitrogen, phosphorus and silicon are higher in fresh water than in seawater. Ionic strength and physico-chemical parameters such as pH and redox potential may change during estuarine mixing. Estuarine waters also contain suspended solids derived from the in flowing river or seawater or by resuspension of bedload sediment as a result of tidal stirring. Cochin estuary is subjected to semi-diurnal tidal influence with a variation of about 1 m. As per the environmental (protection) act, 1985 (29 of 1986), Cochin backwaters (estuary) have been classified under the ecologically sensitive zone and the act envisages the zone should be safe and relatively free from hazardous chemicals like pesticides, heavy metals. However, higher values of heavy metals, sewage disposal and petroleum hydrocarbons have been recorded in Cochin bar mouth area (Shunmugaraj et al., 2002).

1.5 Epoxy coating

Epoxy coatings are commonly used to protect metals against corrosion. The most common types are amine cured epoxy, epoxy ester, epoxy polyamide and epoxy coal tar and epoxy coatings are extremely durable, tough and smooth with excellent adhesion and resistance to blistering, peeling and undercutting. They also posses excellent resistance to salt water and to most chemicals. Epoxy contains at least one and normally two (or more) epoxy (Glycidyl) groups. The bulk of the epoxy resins in commercial use today are based upon the di-epoxide of bisphenol ‘A’ known as BPA. They are produced by the condensation of epichlorohydrin with bisphenol ‘A’. Various additives may also be incorporated to tailor network properties. Inorganic particulate fillers such as alumina, carbon black and silica are used for a variety of reasons. The hardener consists of polyamine monomers, for example triethylinetetramine. When these compounds are mixed together, the amine groups react with the epoxide groups to form a covalent bond. Each NH group can react with an epoxide group, so that the resulting polymer is heavily crosslinked and the crosslinking results in making the coating rigid and strong and such a coating has lower permeability and hence better corrosion resistance (Amy Forsgren, 2006).

The efficacy of these coatings, which provide thin, tough and durable barriers to the substrate, depends on many factors like the suitability of organic materials, application methods, condition of corrosive environment etc. Epoxy resins have attracted a great deal of attention, particularly in view of their striking successes achieved in applications where corrosion resistance is required. Epoxy coatings are the workhorses of the protective coatings industry. They have excellent chemical and corrosion resistance, high mechanical strength, good adhesion to a variety of substrates and a combination of other properties that have made them a material of choice for providing cost effective, long term protection on industrial, marine and offshore structures.

The major limitations of epoxy coatings are their relatively slow cure in cold climates and poor exterior color and gloss retention (McCarthy, 1997; Mowrer, 1997). Slow cure at low temperatures is a continuing problem. In general, the epoxy types have enjoyed the most commercial success because they are user friendly and reduce the cost of surface preparation while providing excellent long-term corrosion protection. A new generation of fast reacting, surface tolerant epoxy coating has been developed that offers improvements compared to state-of-the-art. The coating is based on unique epoxy resin / modified polyamine - polyamide chemistry and proprietary formulation technology. The process "curing", can take minutes to hours. Some formulations benefit from heating during the cure period, whereas others simply require time and ambient temperatures (Crivello et al., 1977).

The applications for epoxy-based materials are extensive and include coatings, adhesives and composites. Epoxy coatings are also widely used as primer to improve the adhesion of automotive and marine paints especially on metal surfaces where corrosion (rusting) resistance is important. Epoxy is extensively used in the offshore industry and in aggressive and chemically polluted environments. They are also used in less polluted environments for long term protection (Salem, 1996). Epoxy resins used as binder for industrial coatings have become increasingly important because of the best combination of corrosion resistance and mechanical properties and they provide outstanding service under service condition (Shaw, 1993). The epoxy acts barrier coating, which can block the passage of oxygen and water reaching the metal surface (Mungaer, 1994).

The ability of the epoxy ring to react with a variety of substrates gives the epoxy resins versatility. Some of the characteristics of epoxy resins are high chemical and corrosion resistance, good mechanical, thermal properties, outstanding adhesion to various substrates, low shrinkage upon cure, good electrical insulating properties, and the ability to be processed under a variety of conditions (McAdams et al., 1991). Depending on the specific needs for certain physical and mechanical properties, combinations of choices of epoxy resin and curing agents can usually be formulated to meet the market demands (May, 1988; McGarry, 1996). Kanitkar (2006) and Mayne et al. (1957) shown that the organic coating and cations ions (sodium, potassium, calcium) present in a solution interact, causing a gradual reduction in resistance of the coating.

Epoxy coating works well but over time the barrier coating can fail due to prolonged exposure to the environment. The organic coating can develops what is called under-coating corrosion which initiates from weak spots and develop into blisters leading to corrosion. The organic coating (barrier coating) fails by separation process known as delamination caused by the separation at the coating / metal interface (Sweeney, 1953; Fernandes, 1985). Epoxy-resin-based paints generally offer very good corrosion-protective properties and are widely used in harsh environments such as the sea. They are two-pack systems, the curing agent normally used being polyamines or polyamides (Dhanalakshmi, 1997).

The corrosion behavior of epoxy coatings on aluminum was studied by (Vesna et al. 2001) and they found that the corrosion resistance was increased with epoxy coating. The corrosion behavior of epoxy-poly amide primer attached to galvanized steel was assessed (Gonzalez et al., 2001) and they found that the corrosion resistance was increased with epoxy coating. Kotnarowska (1994) studies shown that the aging of the epoxies coating caused deterioration of its mechanical properties such as hardness, tensile strength, and unit elongation. The epoxy coated steel in tidal zone provided better anti-corrosion ability than polyurethane resin and acrylic resin (Yen-chin Lin et al., 2003). Kondrashin et al. (2000) found that modifying the surface of brass with polysilane coating decelerates general corrosion and hamper selective dissolution and its protective effect is based on shielding the alloy surface. Eric Bescher and John Mackenzie (2003) studied the effectiveness of sol-gel organic and inorganic hybrid coatings as barrier coating on brass and they found that the coating delayed corrosion on brass.

1.5.1 Fundamental mechanisms of corrosion control by coating

The application of organic coatings to metal is the oldest means of corrosion control and dates back to antiquity. Surface coatings can only stop the corrosion process for a limited time. However, the selection of a suitable coating can reduce the corrosion reaction to a rate that the structural integrity of the steel can be maintained for the lifetime of the structure. Three main methods of using coatings to control the corrosion of ferrous substrate are barrier, cathodic and inhibitive protection.

Barrier protection provides high resistance to the diffusion of water, ions and oxygen through the paint film to the substrate. It has also been reported that barrier coatings can act as ionic filters (Hare, 1997), which means that although water appears to readily permeate most paint films, the same is not true of ions. Any water that does penetrate the coating is relatively ion-free and hence has a high resistance, which inhibits the corrosion process at the paint / substrate interface. Therefore barrier coatings should be formulated to resist the transmission of ionic species as well as oxygen permeation.

Whether protecting by resistance inhibition or oxygen deprivation, the fundamental requirements of the barrier system are that the coating should be (1) impermeable to ionic moieties and if possible to oxygen and that it should maintain adhesion to the metal under wet service conditions. Impermeability to ionic solutions and oxygen are entirely more practical objectives, however, these factors are thought to be rate determining for corrosion beneath barrier films. Permeability of the film to water is generally thought to have greater direct consequence on deadhesion leading to corrosion. It has been noted that corrosion beneath barrier film can begin only after deadhesion has taken place and that if adhesion can be maintained under wet service conditions then protection is assured (Funke, 1985).

Cathodic protection is usually achieved by pigmenting the coating with zinc dust, which acts as a sacrificial anode in contact with the steel substrate as the cathode. Loading of the anodic zinc dust pigment must be high enough to ensure a continuous current flow through the film itself and across the interface (Hare, 1983) and as long as the conductivity of the metal is sufficient to just sustain current flow from the film to the environment, the steel remains protected.

Two fundamentally different classes of zinc rich primer have been developed, the organic zinc rich primer and inorganic zinc-rich primer. Organic zinc rich primers are based on a variety of resin systems including epoxy/polyamaide, moisture cured urethanes, high styrene resins, chlorinated rubbers and epoxy esters. Control of the volumetric ratio of conductive pigment to dry nonconductive binder ensures that the binder sheath around each particle of pigment (zinc) does not become so thick that the current transfer is too greatly reduced or so depleted that cohesion and film strength are lost (Munger, 1975).

Inorganic zinc rich primers are fundamentally different to the organic. Instead of employing a binder, which encapsulates the zinc, these materials employ a reactive binder, usually inorganic silicates (Munger, 1984). Reactions involve loss of solvent or water and hydrolysis of the silicate to the reactive acid (silicic acid) which then undergoes self-condensation and chemically react with zinc atoms on the zinc dust surface, forming a primary valance bonded matrix of tetrahedral linked (poly) silicone oxide bridges between adjacent particles of zinc. The resultant film matrix is entirely inorganic, open and much more porous than the organic zinc film. As long as sufficient zinc remains to act as an anode, even in the presence of chloride solution, the primer will retain its ability to protect steel at least in the short term.

Inorganic zinc rich films are harder, stronger and for more adherent than are the organic zinc rich films. The performance levels realized from the inorganics are superior to those realized from the organic. In both organic and inorganic zinc-rich primers, the duration of cathodic activity is finite and the effect of zinc polarization and the generation of zinc corrosion product gradually coverts protection from the galvanic mechanism to a barrier mechanism (Feliu, 1993). The interval of galvanic protection before conversion to the secondary protecting mechanism depends on the type and composition of system and nature of the environment. In epoxy zinc rich primers, the cathodic protection phase is small (Svoboda, 1984).

Inhibitive protection works by pigmenting coatings with specific compounds such as anticorrosive pigments, which chemically change the environment at the primer / substrate interface. Inhibitive primers that control corrosion by modifying the interfacial (primer / metal) environment so that passivation of the substrate metal may be achieved and maintained (Funke, 1983). Inhibitive metal primer facilitates sufficient water absorption into the film so that soluble inhibitive ions may be released by the pigment and carried to the metal surface beneath the primer where passive films may be established. It is difficult to understand how passivating films may form on metal bearing tightly adherent organic films. It has been suggested that inhibition may not become established until some initial adhesive breakdown in a quasi-barrier protection has occurred.

1.6 Statement of the problem

Different types of corrosion can occur to the structures, ships and equipments made up of copper and copper based alloys when exposed to seawater, which is a good electrolyte that can cause corrosion. Brass possesses attractive properties, namely good corrosion resistance, mechanical workability, excellent electrical and thermal conductivities and good resistance to biofouling. Corrosion resistance of brass has been attributed to a protective cuprous oxide layer formed upon exposure. However, this alloy can deteriorate due to the local gradient of pH and oxygen under seawater condition and distinctive attacks are impingement attack, dezincification of brasses and pitting. The dezincification of brass is one of the forms of selective corrosion and it has attracted the attention of researchers for the last two decades. The survey of literature clearly indicates that many of the dezincification mechanistic studies were performed in noncomplex media and hence their conclusions cannot be extended to estuarine water, which is of great significance in connection with the extensive use of brass in marine environment. It is particularly relevant to Cochin region where various industries extensively use brass in marine application in the form of condenser, pipe work, valves, screws, and nuts and bolts.

Severe corrosive conditions are encountered in power stations and ships, which draw their cooling water from estuaries and harbours. Cochin estuarine water is having large quantity of suspended sediments with organic matter causing an anoxic condition. The main effect of estuarine water arises from a combination of low oxygen content and generally decreased pH together with the presence of sulphite ions or ammonia. These factors can lead to quite different corrosion mechanisms, resulting in the formation of very different corrosion product layer compared to those formed in natural seawater. Estuarine water is polluted to varying extent depending on location and the seasons. Corrosion initiated by polluted water may often continue even after changing to clean water. For corrosion test to yield meaningful results, knowledge of the environment that exists under actual service conditions is necessary. In order to conduct realistic corrosion tests, variation in seawater conditions must be taken into account. There is inadequate data on the effect of the estuarine water on the corrosion rate of brasses. The earlier study on corrosion behavior of brass in natural environment shows that the weight loss measurement alone does not reliably predict corrosion performance of brass and therefore localized corrosion is more important and should be considered together with weight loss / gain data. The review of literature reveals that there has been lack of investigations about dezincification behaviour of brass in Cochin estuarine water.

Inhibited α brasses are largely immune to dezincification, but the effect of tin and arsenic addition to α / β brasses is not so predictable in controlling the problem. There have been many cases of dezincification in duplex brasses in both fresh water and seawater. There is no reliable method of inhibiting the dezincification of two-phase brass despite there is some protection methods such as inhibitors, electro deposition and electro polymerization. Organic coatings are effectively used for the protection of metals due to their capacity to act as a physical barrier between the metal surface and corrosive environment. Hence, epoxy coating is selected for this study as it has anti-corrosion effects on brass.

1.7 Objectives and scope of the present study

This investigation focuses on the corrosion (dezincification) behavior of the brass and epoxy-coated brass in Cochin estuarine water with the following objectives

- to evaluate the dezincification behavior of brass in Cochin estuary
- to assess the dezincification behavior of epoxy coated brass in Cochin estuary
- to characterize the corrosion products formed on brass exposed in Cochin estuary
- to analyze the corrosion products formed on epoxy coated brass in Cochin estuary

The present study has amied at the investigations of corrosion behaviour (dezincification) of brass and epoxy coated brass in Cochin estuary for a specific period of one year which coincides with three different seasons. The corrosion behaviour (dezincification) of brass and epoxy coated brass in Cochin estuary has been studied by weight loss method as well as electrochemical polarization technique. The results have been highlighted in terms of corrosion rate, weight gain / weight loss, corrosion current and corrosion potential. The marine fouling in terms of biomass on brass and epoxy coated brass in Cochin estuary has been assessed and documented.

Open circuit potentials of the systems have been monitored to substantiate the corrosion behaviour data. Dezincification of brass and epoxy coated brass in Cochin estuary has been evaluated by dezincification factor (Z). The mechanical properties, such as tensile strength, yield strength, percentage elongation and percentage reduction in area, of the brass and epoxy-coated brass subjected to the effect of Cochin estuarine water have been investigated. To validate dezincification data, surface characterization on brass and epoxy coated brass has been performed by Scanning Electron Microscope and Energy Dispersive Spectroscopy. Corrosion product has been analysed by X-Ray Diffraction method to assess the nature of corrosion products.

The role of Cochin estuarine water characteristics, climate atmospheric data on corrosion behaviour of brass and epoxy coated brass has been investigated. The investigation of this study will be of paramount important to the marine engineering community.

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Chapter 2

MATERIALS AND METHODS

Contents

2.1 Sample preparation and exposure test
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2.1 Sample preparation and exposure test

Brass panels (Cu 56 41 Zn) with dimension of 5 × 4 cm were polished with emery paper, rinsed several times with distilled water, degreased with acetone, washed again with distilled water and dried (Champion, 1952). Epoxy resin and hardener were purchased from Vani paints Pvt Ltd, Madurai, Tamil Nadu and applied on pretreated brass panels after mixing in 2:1 ratio by a brush and allowed to cure at 30^0 C to get dry film thickness of 100 ± µm. The brass panels and epoxy-coated brass panels for immersion were taken in 12 triplicates. The panels were weighed and fixed on fiberglass strips with PVC nuts and bolts and immersed in estuarine water at the far end of jetty which belongs to School of Marine sciences, Cochin University of Science and Technology (3 m depth and 1 m above the estuarine bed). At high tide the water depth in the selected site was 4 m deep and at low tide the water depth was 2 m and so the brass panels were always below water surfaces at least by 1 m (Palraj et al., 2002). At the end of each exposure month, brass panels were retrieved one after another. The retrieved panels were used for visual observation and data collection after rinsing gently with fresh estuarine water to remove any non-adhering bacteria and diatoms (Figs. 2.1 – 2.7).

2.2 Weight change method

The difference between initial weight prior to deployment and final weight, before corrosion products were removed, was used for calculation of weight gain for brass (Sawant, 1995; Davis, 1987). The difference between initial weight prior to deployment and final weight, after the corrosion products removed by standard method (Bastos, 2008), was used for calculation of corrosion rate of brass by using the following formula:

$$mdd=W/(A*T) \qquad (1)$$

where mdd is the corrosion rate expressed in terms of metal loss (mg) [per decimeter square area per day], W the loss in weight (mg), A the area of panels (dm^2), and T the exposure time (days).

The difference between initial weight prior to applying of coating and final weight, after removal of epoxy coating with out removal of corrosion products underneath the coating was used for calculation of weight gain for epoxy coated brass. At the end of each exposure period, the coatings were removed first by the epoxy diluents (butyl glycidyl ether) and then mechanically using an acrylic knife (Kouloumbi, 1994). The corrosion rate of epoxy-coated brass was calculated by the difference between initial weight prior to applying of coating and final weight, after the corrosion products removed by standard method.

2.3 Electro chemical test

A conventional three – electrode cell was used with a saturated silver/silver chloride reference and a coiled platinum wire counter electrode. The working electrode for corrosion studies was cut from a 2 mm thick sheet of brass and they were polished using emery paper, degreased with acetone and rinsed with demonized water. The electrochemical measurements were performed using a potentistat / galvanostate / frequency response analyzer (AOTULAB PGSTAT 30, FRA 2) and a flat cell. Only 1 cm^2 of the brass electrode / epoxy coated brass was exposed to estuarine water (electrolyte). The polarization curves were measured at a scan rate of 1mv s-1 from cathode to anode potentials. The corrosion potential (E_{corr}) and corrosion current density (I_{corr}) were determined using the Tafel extrapolation (Siebert, 1985; Kharafi, 2004; Winston Revie, 2000).

2.4 Open circuit potential measurement

The open circuit potentials of brass panels and epoxy coated brass immersed in estuarine water in a flask connected to the reference electrode via a KNO_3 salt bridge were measured exposure - wise with a digital multimeter (Fontana, 1967).

2.5 Dezincification factor

During the above test period, the concentration of Cu^{2+} and Zn^{2+} in the solutions after each measurement was determined by atomic absorption spectrometer. Using the Cu^{2+} and Zn^{2+} concentration and Cu and Zn in brass alloy, dezincification factor (Z) was calculated according to the following equation:

$$Z = (Zn/Cu)_{sol} \ / \ (Zn/Cu)_{alloy} \qquad (2)$$

where $(Zn/Cu)_{sol}$ is the ratio between Cu^{2+} and Zn^{2} ions in solution and $(Cu \text{ and } Zn)_{alloy}$ is the ratio between the two elements in the alloy (Heiderback, 1972).

2.6 SEM/EDS

The morphology of the brass panels and epoxy coated brass panels before and after removal of the corrosion products was imaged by Scanning Electron Microscopy (JEOL Model JSM - 6390LV) and Energy Dispersive Spectroscopy (JEOL Model JED – 2300) was used for the identification of the corrosion products. The corrosion products were removed by dipping the panels for 5-10 minutes in a solution of sulphuric acid and potassium dichromate, according to standard procedure.

2.7 XRD

Surface of corroded brass samples and epoxy coated brass after respective exposure periods were scrapped and dried at room temperature for 10 days. The products comprising of corrosion products and biomass were finely powdered with a mortar and fine powders of respective removal were examined with X-Ray Diffraction method (Bruker AXS D8 Advance) for identifying the compounds of inorganic nature of oxides, chlorides, carbonates, hydroxides and oxychlorides of calcium, magnesium and iron.

2.8 Estuarine water characteristics

Estuarine water was collected from the study area at each exposure period and analyzed for identifying the seawater characteristics such as salinity, dissolved oxygen, temperature and pH. Salinity and temperature were recorded using a salinity-temperature bridge while dissolved oxygen content using

Winkle’s method. A portable pH meter was used to measure the pH (Wagh, 1982; Howell Furman, 1962). The major ions present in the estuarine water were analyzed using respective techniques (Howell Furman, 1962).

2.9 Mechanical Properties

The deterioration of the brass and epoxy-coated brass subjected to the estuarine water, exposure-wise, were experimented using Universal tensile testing machine. The specimens were prepared as per the ASTM recommendation. The changes in mechanical properties of the panels were recorded as a measure of the following factors, such as yield strength, ultimate strength, and percentage elongation and percentage reduction in area (Fig. 2.8).

2.10 Assessment of fouling

Fouling on brass panels and epoxy coated brass panels were assessed, exposure-wise, in terms of biomass. Biomass was calculated after scrapping the mass adhered on the metal surface and drying in air oven for an hour at 60°C (Mathiarasu, 1998).

2.11 Climate data

Wave data such as Wind velocity, Wind direction, Wave velocity were collected regularly (INCOIS,2007; 2008) and meteorological data on Tempertaure, Rain fall and Relative humidity were collected regularly and presented in terms of monthly average vales (IMD, 2007; 2008).

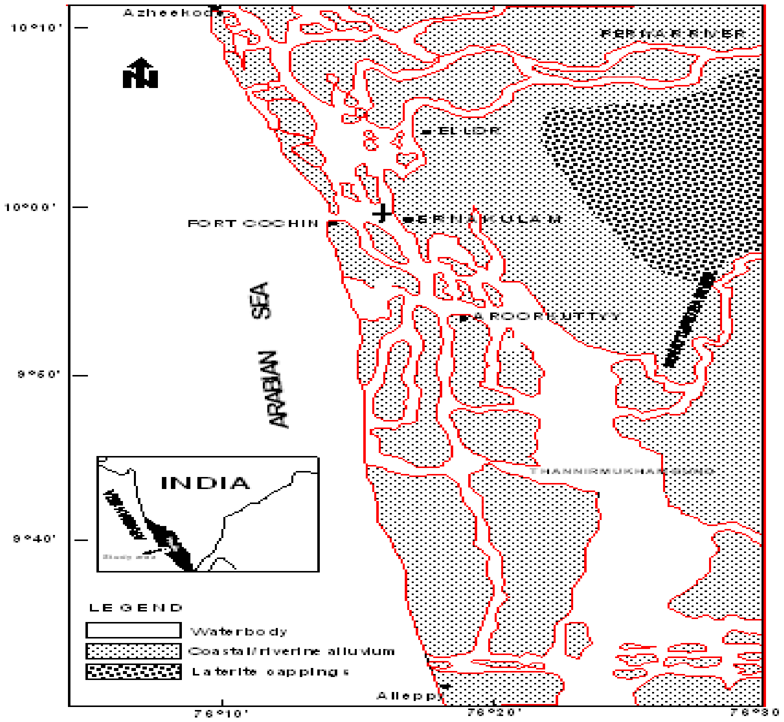

Fig. 2.1 Location of test site (+)

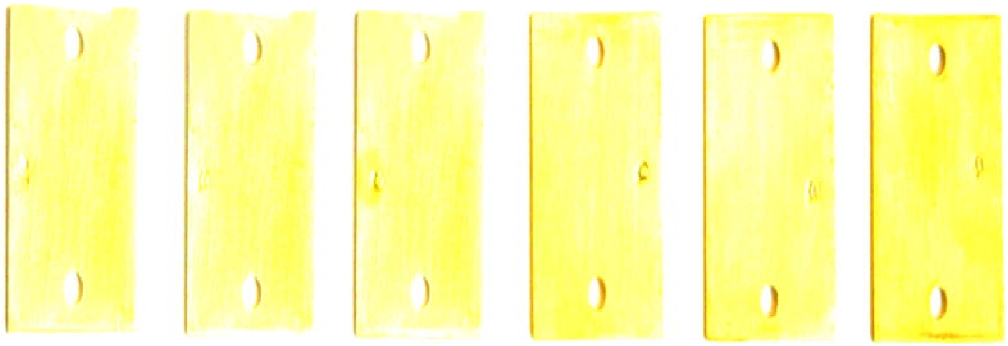

Fig. 2.2 Brass panels after cleaning as per standard procedure

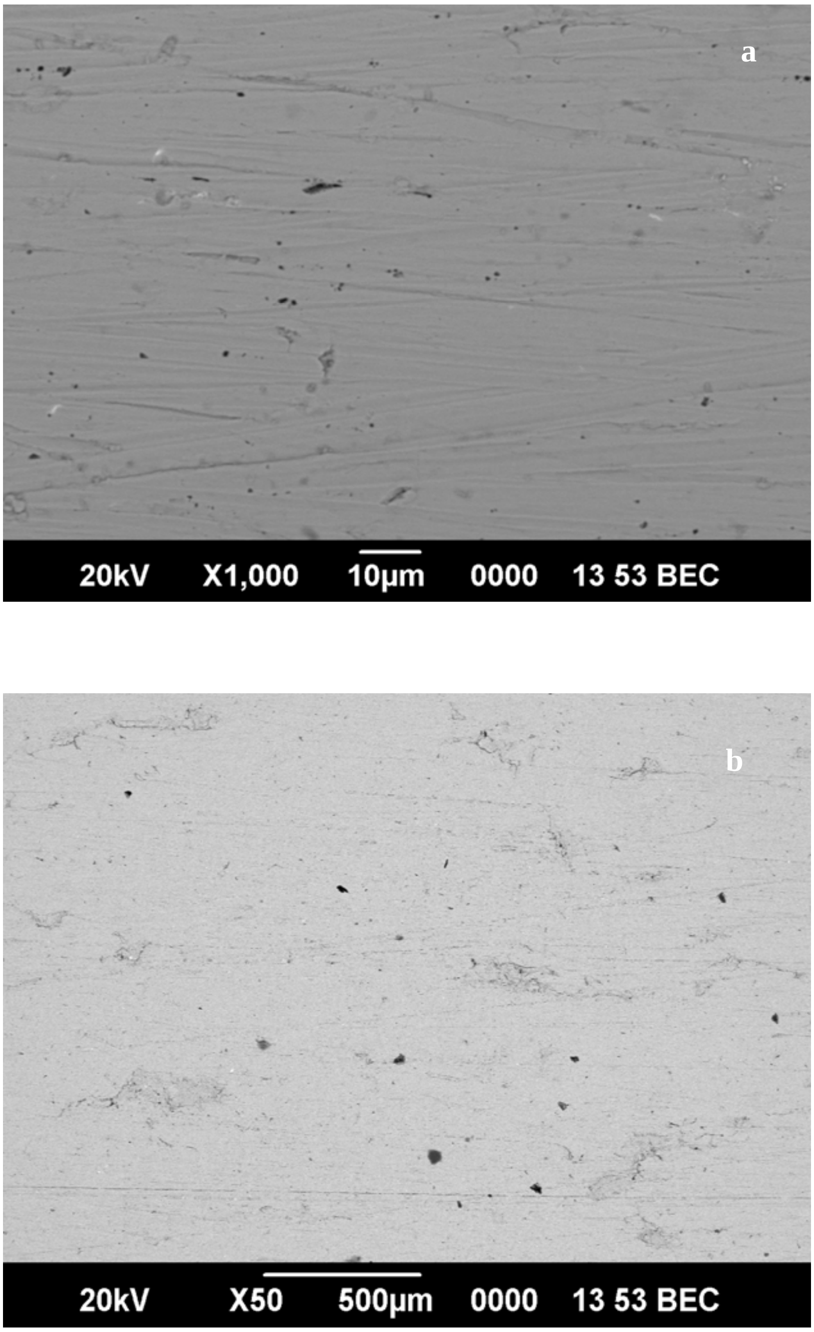

Fig. 2.3 a, b SEM image of brass as received

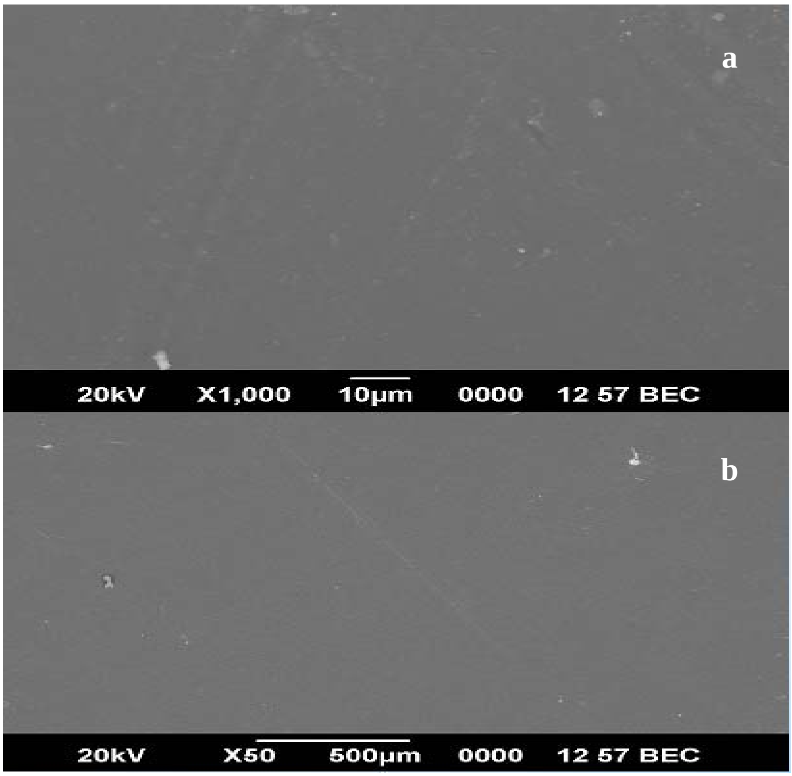

Fig. 2.4 a, b SEM image of epoxy coated brass before immersion

Fig. 2.5 Brass panels deployed in to Cochin estuarine water

Fig. 2.6 Brass panels retrieved after every exposure period

Fig. 2.7 Brass panels retrieved after every exposure period and visually observed

Fig. 2.8 Brass specimen for tensile test

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Chapter 3

DENZINCIFICATION OF BRASS

Contents

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The survey of literature, presented in Chapter 2, clearly indicates that many of the dezincification mechanistic studies were performed in noncomplex media and hence their conclusions cannot be extended to estuarine water, which is of great significance in connection with the extensive use of brass in marine / esruarine environment. It is particularly relevant to Cochin region where number of industries extensively uses different kind of brasses in marine applications in the form of condenser, pipe work, valves, screws, nuts and bolts. Corrosion behaviour is very intensive in polluted harbour and estuaries where the ebb and flow of tides cause daily changes from anoxic, polluted brackish water to relatively fresh / aerated seawater.

Some of the most corrosive conditions are encountered in power stations, port and ships which draw their cooling water from estuaries and harbors. These waters are polluted to varying extents depending on the location and the period in a year. Corrosion initiated by polluted water may often continue even after changing to clean water. However, there is inadequate data on the effect of estuarine water on the corrosion of brasses.

Results of dezincification of brass in terms of corrosion rate, weight gain by gravimetric method and electrochemical polarization, open circuit potential, dezincification factor, hydrochemical properties, biomass and mechanical properties are presented in this chapter.

3.1 Climate characteristics

The climate data in Cochin are presented in Table 3.1. The wind velocity is lowest in Mar. 08 and highest in Jun. 08. The wind direction is southwest from April to September and northeast from October to March. Wave velocity is minimum of 0.18 m/sec in the month of Feb. 08 and maximum of 1.852 m/sec in Jul. 08. The currents along the coast of Cochin consist of tide, wave and wind induced components. As per observations the maximum current velocities at the Cochin inlet during the non-monsoon periods is of the order of 3 knots, which increase to as high as 5.5 knots during the monsoon periods. Inside the harbour the current velocity is low and is of the order of 0.5 knots only, with directions varying at different locations.

Table 3.1 Data on climate factors during exposure Periods (Sep. 07-Aug. 08)

Months	Wind velocity m/s	Wind direction	Wave velocity m/sec
Sep.07	6.86	S/W	1.14
Oct.07	3.89	N/E	0.58
Nov.07	2.28	N/E	0.19
Dec.07	3.05	N/E	0.87
Jan.08	2.81	N/E	0.58
Feb.08	4.29	N/E	0.18
Mar.08	1.84	N/E	0.22
Apr.08	4.87	S/W	0.34
May 08	4.93	S/W	0.39
June 08	8.68	S/W	0.39
July 08	7.51	S/W	1.852
Aug.08	5.57	S/W	1.51

Cochin estuary is subjected to semi-diurnal tidal influence with a variation of about 1 m and maximum speed of current varies from 1 to 1.5 knots, while ebb current always has greater intensity and during monsoon months it varies from 2.5 to 3.5 knots. The wave climate is governed by the southwest monsoon when wave action can be strong with prevailing wave direction from northwest to southwest. Deep - water (15 m) wave observation in the past indicates the significant wave heights of 4 m, 2 m and 1 m at water depths of 10m, 5m and 2m respectively, the predominant wave direction being west. Wave action inside the harbour is insignificant because of narrow entrance at the Cochin inlet. Generally calm conditions prevail in the harbour region throughout the year except during the times of extreme wind action.

3.2 Atmospheric parameters

The monthly variations of atmospheric parameters during exposure period i.e. Sep. 2007 – Aug. 2008 in the Cochin are given in Table 3.2. The data presented in Table 3.2 reveal that temperature at Cochin varies from about 23.8° to 34.2° C. There is no much distinct seasonal variation in the temperature, which is more or less uniform throughout the year. However, highest temperatures tend to occur in the months of March – April. The humidity is high all through the year. It ranges from approximately 77% in the morning during winter months to approximately 93 % in the monsoon period. The maximum rainfall usually occurs during the southwest monsoon period i.e., from June 08 to September.

Table 3.2 Monthly variations of atmospheric parameters during exposure period i.e. Sep. 2007 – Aug. 2008 at Cochin coast.

Month	Temperature ^{0} C		Rain fall mm	Relative humidity %
	Minimum	Maximum		
Sep.07	24.2	29.4	667.3	93
Oct.07	24.2	29.5	522.1	90
Nov.07	24.1	30.3	66.1	87
Dec.07	24.2	30.8	9.8	87
Jan.08	23.8	33.5	1.9	77
Feb.08	24.9	33.3	1.4	77
Mar.08	25.8	34.2	9.2	77
Apr.08	26.7	34.3	146.5	75
May 08	28.8	33.5	193.5	79
June 08	26.4	29.5	815.0	93
July 08	24.2	29.5	1132.8	91
Aug.08	24.7	30.0	480.1	93

The southwest monsoons, which arrives in June and continue up to September, is characterized by heavy rainfall and high velocity winds. It is very often results in the dilution of seawater and also influences the bio fouling. Cochin estuary is a well mixed estuary from June - August, partially stratified during December-January, highly stratified from September – November; transition from September - November thus suggesting that except during monsoon period (June to August) salinity variation is highly significant (Menon et al., 2000).

The corrosivity of the atmosphere at any ocean side location can be expected to vary widely with the direction of prevailing winds relative to the ocean and the topography of the shoreline which affects wave action and the amount of salts particles thrown into the air by the surf (Tracy, 1956). Corrosion rates and the type of corrosions are often dependent on the environmental factors such as fluid flow and the availability of appropriate species required to derive electrochemical reactions (Poulson, 1983). A change in the motion of a corroding metal or alloy relative to its environment by fluid flow can increase corrosion rates by removing protective films or by increasing the diffusion or migration of deleterious species. However, an increase of seawater in fluid flow can decrease corrosion rates by eliminating aggressive ion concentration or enhancing passivation or inhibition by transporting the protective species to the fluid / metal interface.

Under high seawater flow speed conditions, corrosion may take the form of impingement, erosion corrosion, or cavitation (Boyd, 1978). The effect of seawater velocity on a metal's corrosion rate varies with the particular alloy. Alloys such as 304 and 316 stainless steel or nickel-chromium-molybdenum alloys exhibit deep pitting under low flow conditions, yet at a high seawater velocities their corrosion rates decrease to < 25 gm / yr. Contrary to this, iron and copper show significantly lower corrosion rates at low flow velocities than under high seawater flow conditions as seawater turbulence can substantially alter the flow rates and subsequent corrosion rate of metals. In designing a piping system, turbulent areas should be considered and accounted for in choosing appropriate materials (Tuthill, 1971). As seawater flow rate increases, corrosion rates remain low due to the tenacity of the protective surface film. However, when the velocity exceeds a critical value for a given geometry, the shear stress acting on the film can lead to its breakdown resulting in high corrosion rates (Powell, 2000).

3.3 Weight gain and loss

The weight gain and loss on brass immersed in estuarine water at Cochin at each exposure period is shown in Table 3.3. There is no variation in weight gain for Sep. 07 and Oct. 07 and it reduces in Dec. 07 and thereafter increases up to Feb. 08. Subsequently it drops drastically in Mar. 08 and afterwards increases up to Jun. 08 with little fluctuation for Jul.08 and Aug. 08. The lowest weight gain is observed in March 08 while the highest weight gain is noticed in Jun. 08. The weight loss increases from Sep. 07 to Nov. 07 and then reduces up to May 08 with minor variation in between and again increases for the remaining period.

Table 3.3 Weight gain and weight loss on brass panels immersed in estuarine water at Cochin each exposure period

Months	Initial weight	Final weight before removal of corrosion products	Final weight after removal of corrosion products	Weight gain g/cm^2	Weight loss g/cm^2
Sep.07	26.01	26.57	25.95	0.028	0.003
Oct.07	25.91	26.47	25.83	0.028	0.004
Nov.07	26.02	26.53	25.93	0.025	0.005
Dec.07	26.48	26.90	26.41	0.021	0.004
Jan.08	26.19	26.68	26.13	0.024	0.003
Feb.08	26.14	26.70	26.10	0.028	0.002
Mar.08	26.70	26.90	26.65	0.01	0.003
Apr.08	26.29	26.82	26.22	0.026	0.002
May 08	26.23	26.92	26.21	0.034	0.001
June 08	26.08	26.89	26.05	0.040	0.002
July 08	26.34	27.02	26.29	0.034	0.003
Aug.08	26.50	27.23	26.42	0.036	0.004

The lowest weight loss is observed in May. 08 whereas the highest weight loss is observed in Nov. 07. Higher weight loss can be related to higher corrosion rate. The high amount of weight loss is due to the large dissolution of zinc and copper from the samples. The weight loss curve is a measure of the electrochemical reaction occurring under the fouling and scale (Bogar et al., 1985). The results are in agreement with results reported elsewhere (Santos et al., 2006).

3.4 Corrosion rate by gravimetric method

The variation of the corrosion rate against time is plotted in Fig. 3.1. The monthly corrosion rate value of brass varies from 0.5 to 10 mdd. The results indicate that there is steady declining trend in the corrosion rate from Sep. 07 to May 08 and thereafter it increases slightly till the end of study. The corrosion rate values are decided by various factors such as surface temperature of seawater, dissolved oxygen concentration, wave action, salinity, monsoon rain and settlement and growth of marine organisms on brass panels.

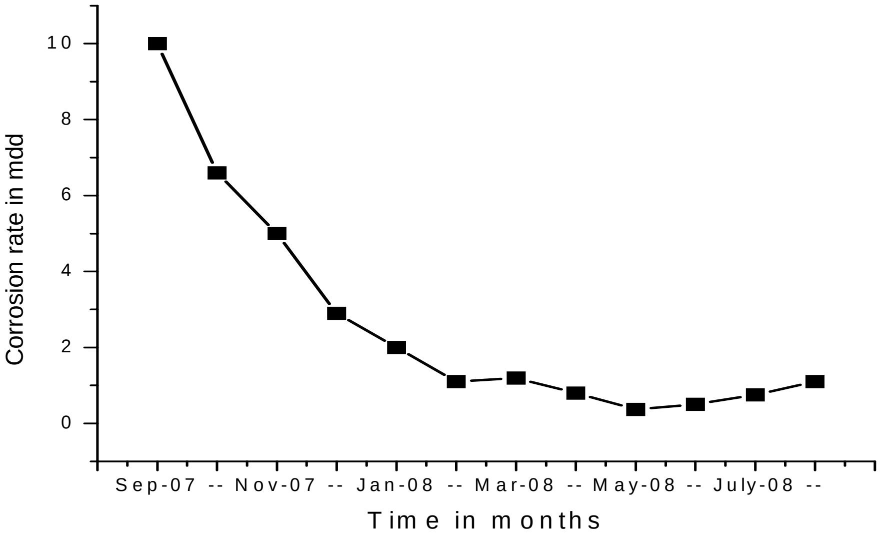

Fig. 3.1 Monthly Corrosion rate of brass panels immersed in Cochin estuarine water

The low corrosion rate is related to protecting film formed completely over brass panel. In contrast, the increase of corrosion rate after May 08 is associated with removal of protective film due to prolonged exposure in the water. The drastic decrease in the corrosion rate values of brass over the period of time implies the protective nature of corrosion products and biomass. This behavior can be explained on the basis that fouling assemblage and corrosion products on brass provides a shielding effect. The increase of corrosion rate experienced by the brass in estuarine water is mainly attributed to the turbulence and soft fouler and micro and macro algae that fouled on brass.

This is also evidenced from the fact that formation of corrosion products and accumulation of biomass acts as barrier between the metal interface and estuarine water, thereby reducing diffusion of oxygen and possess excellent resistance when uniform corrosion is considered. The declining trend of corrosion rate of brass in this study is comparable with corrosion of brass in natural seawater of Ericeira Beach, Portugal (Santos et al., 2006). The study conducted by Palraj et al. (2002) revealed that the corrosion rate of brass (60/40) in Palk Bay waters of Mandapam, India was uniform throughout the year except during October and December 1996 and January 1997. The corrosion rate of brass in this study is relatively low compared to that of Bombay coastal water (Sreenivasa Rao, 1978) and this could be ascribed to the higher levels of pollutants in Bombay water than Cochin water. The monthly corrosion rate of brass in Palk Bay coastal water is relatively higher than that reported by Prabha Devi et al. (1992) in Goa coastal water. The study on corrosion rate of brass in Tuticorin harbour water by Mathiyarasu et al. (1998) revealed that the corrosion rate was higher during the initial periods and it decreased with time as observed similarly in the present study.

The results rekindled the controversy about the relationship between corrosion and biofouling in copper and its alloy. In experimenting with copper alloy at Kure beach, Efrid et al. (1975) found that the alloys not fouled even after 14 years of exposures. This need further investigation on the throwing power of copper and lead (Efrid, 1976) to contradict the famous leaching theory of Laque and Clapp, (1945) which postulates that the antifouling property of copper resolves around the nature of corrosion products. In the present study, pitting corrosion is observed on the monthly exposure of brass. This implies that in general brass metal experiences uniform corrosion but pitting corrosion in estuarine water, which is in contrary to results reported elsewhere (Laque, 1945; Shibal et al., 1967, 1968, 1971, 1975).

Initial higher corrosion in brass can be attributed to the synergistic effect of multifarious factors such as turbulence in sea caused by relatively high wave velocity, dissolved oxygen concentration near the vicinity of the metal/electrolyte interface and slime forming bacteria. The exponential decrease in the corrosion rate is indicative of the protective nature of corrosion products such as cuprous oxide and cupric hydroxy chloride, which are formed along with marine growth accumulation (Mansfield, 1994) Santos et al. (2005, 2006) in their study observed higher weight gains and higher corrosion rates on the brass samples immersed in natural seawater.

Gamal et al. (2005) concluded that ZnO layer provides passivity of brass until is ruptured by dissolution, which leads to a high corrosion rate during the initial stages of immersion and also dezincification is accelerated in an acidic chloride medium with high temperature. Feng et al. (1996) explained that an increase of corrosion rate is caused by the reduction of the film thickenss under turbulence. Bastos et al. (2008) observed higher weight gains, corrosion products and higher corrosion rates on brass immersed in anaerobic condition.

The decreased corrosion rate is correlated with the structure of the corrosion product layers (Badawy, 1998; Torchio, 1986). Brass corrosion proceeds with oxygen depolarization, and is almost completely controlled by the diffusion delivery of oxygen. In acidic to weakly acidic and even neutral media, dissolved oxidized copper accumulates during brass corrosion. In aerated chloride solutions, it significantly promotes the cathodic process (auto catalytic effect). Therefore, the corrosion rate of brasses, even insusceptible to dezincification, can appear higher than in the case of dezincing. Dezincing, conversely, decreases the corrosion rate (Marshakov, 2005).

The higher rate of corrosion of copper and its alloys in coastal water is attributed to the higher concentration of dissolved oxygen and temperature at the site. Secondly, in coastal water erosion corrosion is more pronounced which is caused by the removal or break down of the protective film by mechanical forces due to local turbulence or impingement (Sheir, 1977). The initial higher corrosion rate of copper alloys is due to higher weight loss in marine condition (Kucera et al., 1987). According to Winston Revie (2000), the corrosion rate of brass in seawater is 0.008-0.12 mm/yr (2-24 mdd). The increase in weight loss observed in the first few months is due to the non-uniform coverage of the corrosion layer over the surface. This is probably due to the formation of nonadherent corrosion products on the surface. The film of corrosion product becomes denser with continued exposure, thus affording a thicker, more protective coating (De la Fuente, 2007).

3.5 Biofouling

Biomass on brass sample immersed in estuarine water of Cochin at each exposure period is given in Table 3.4 and Fig. 3.2. The monthly biomass value of brass varies from 1.25 to 4.65 g/cm^2. Biomass on brass shows a decline from

Sep. 07 to Nov. 07 (Fig. 3.2) and thereafter it increases steadily up to May 08 representing the maximum of 4.65 g/cm^2 in this study. Then it reduces to 3.5 g/cm^2 in Aug. 08. Settlement of fouling is low up to Nov. 07 as the salinity in this period and toxic effect of brass are increased and thereafter fouling is increased with little variation in between.

Table 3.4 Monthly biomass on brass panels immersed in Cochin estuarine water at each exposure period

Biomass g/sq.cm	Total biomass g/panel	Biomass g/cm^2
Sep.07	58	2.9
Oct.07	49	2.45
Nov.07	25	1.25
Dec.07	31	1.55
Jan.08	47	2.35
Feb.08	42	2.1
Mar.08	82	4.1
Apr.08	78	3.9
May 08	93	4.65
June 08	68	3.4
July 08	60	3.0
Aug.08	70	3.5

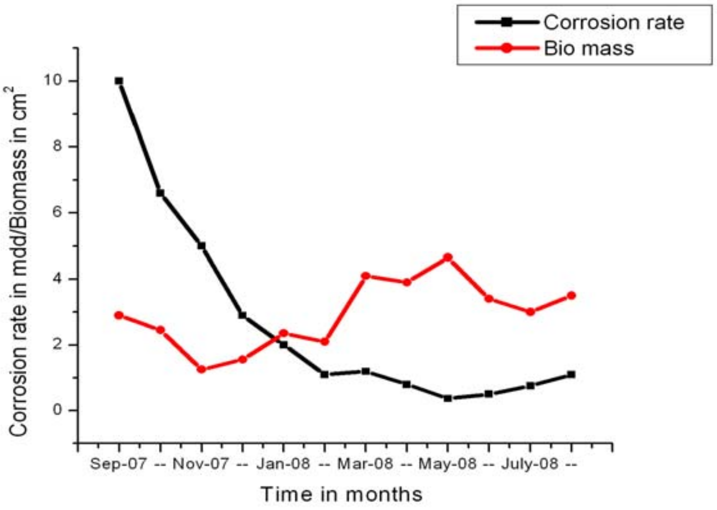

Fig. 3.2 Monthly Corrosion rate and biomass of brass panels immersed in Cochin estuarine water

Hydrochemical parameters and loss of toxic effect of brass can be the reasons for increase of biomass. With longer exposure, the toxic effect of brass is reduced and thereby enhanced bio-adherence could occur on brass surface. In general, accumulation of fouling organisms on monthly exposure is low for the first three months. The increase of fouling after Nov. 07 indicates the reduction in corrosion rate. The decline in the corrosion rate values and an increase in biomass accumulations imply the protective nature of the biomass over the period of exposure. Settlement of organisms is also influenced by temperature of seawater, salinity, tidal waves and flood water currents. Sunlight played a major role in influencing the settlement of bio-organisms. In the absence of fouling, the corrosion products formed over brass are sloughed off frequently thereby enhancing corrosion rate.

The initial higher corrosion rate on brass panels could have been affected by bacteria, micro algae (diatoms). Differential cells produced by bacterial extra cellular polymers can cause micro biologically induced corrosion as reported elsewhere (Popplewell, 1978; Vreeland, 1974). It is evident from the present study that the biomass on brass is relatively less, compared to that in Palk Bay waters of the Mandapam coast where fouling load was heavily increased as time increased (Palraj et al., 2002).

Marine biological organisms have both micro (bacterial) and macro (algae, barnacles) forms. These organisms can affect corrosion behavior of metals and alloys in a number of ways (a) influencing one or both the anodic and cathodic reactions occurring, (b) influencing the formation and / or maintenance of protective films, (c) producing deposits on metal surfaces, and d) creating a corrosive environment. The causes listed above can act singly or can be combined to alter a metal's corrosion behavior (Fontana, 1967). Biological organisms can attach and multiply on any solid surface in seawater.

Within two hours of immersion, a bacterial slime film develops and creates a partial barrier to diffusion between the liquid / metal interface and the bulk seawater environment. These slime films are usually not continuous and can create oxygen or chemical concentration cells on the metal surface, which can result in accelerated localized corrosion (Davis, 1987). Huang et al. (2004) noticed that the sulfate reducing bacteria (SRB) attached on the alloy surface formed a biofilm which led to intergranular corrosion. Consequently, a significant decrease in the polarization resistance was observed.

Marszalek et al. (1979) and Tevors et al. (1990) have suggested that colonization of toxic metals may be related to the ability of adhered microbial species to secrete exopolymer material. The acidic groups in the exopolymers may interact with copper, protecting the cells from the metallic ions and their investigation showed inverse relationship between corrosion rate and some of the micro fouling parameters and this is due to the protective film formed over the surface by micro fouling. The micro fouling on brass panel surface occurred due to the fact that some species of bacteria and diatoms of micro fouling community possess resistance to toxicity of copper ions (Sawant et al., 1995). According to Efrid (1975) the fouling resistance of copper is not only because of leaching rate (10 $\mu g/cm^2/day$) but also due to cuprous oxide corrosion product that is toxic to the settled organisms. Rao et al. (1993) stated that the activity of SRB comprises the removal of cathodic hydrogen or formation of iron sulphide and the presence of this aggressive sulphide ion will break down the formation of the passive film and accelerates the process of anodic dissolution. Naguib et al. (2001) and Raul Sandoval et al. (2006) have suggested that the biofilm formation by the microorganism provided a certain capacity to protect the metals despite the formation of sulphite on the interface of metal.

According to Southwell et al. (1974) the settlement of organisms on the exposed surface may also be modified by the time of the year at which the fresh surface is exposed. Since many algae/animals are seasonal in their reproduction habit and the settlement over the newly exposed surface depends on which reproductive stages are present in the sea at the time of exposure and all forms of fouling, ranging from algae to very heavy barnacles cover will exclude oxygen sufficiently from fouled surface to permit the development of SRB. The presence of micro-organisms and their metabolic activity are known to induce modifications in the electrochemical parameters, which control the corrosion behavior of passive-active alloys such as stainless steel, Ni-alloys in marine environments (Dexter et al., 1987).

Jean Buezennec (1988) reported that the increase of potential with increased presence of the sulphate reducing bacteria through the aging of biofilm, can justify the high probability of localized corrosion onset. Ruimu et al. (1984) pointed out that an uneven surface beneath the barnacle provides appropriate conditions for the localized corrosion and the shell has a less rigid contact with the metal surface and metabolic products, products of decay and growth of sulphate reducing bacteria (SRB) provide acidic condition inside the shell facilitating the initiation of pits. Terry et al. (1986) stated that protection from corrosion on stainless steel and aluminum could be due to the obstruction of oxygen diffusion beneath the barnacle shell caused by their direct adhesion on the metal surface. Differential aeration, selective leaching, under-deposit corrosion and cathodic depolarization have been reported as mechanisms of microbiologically influenced corrosion of copper alloys (Pope, 1985; Dexter, 1986; Miller, 1970).

Fouling can shield the metal surface from oxygen thereby creating condition conducive to the formation of differential cells and decaying fouling can also produce sulphides, which modify the environment at the metal surface. Fouling also has catalyzing effects (Scotto et al., 1985). Macro fouling films can develop over slime films within 2-3 days after immersion in seawater. If the macro fouling is continuous along the solid surface, the film can decrease the amount of dissolved oxygen present at the surface and thus decrease the overall metal corrosion rate. If, however, the macro fouling is discontinuous, the film acts in the same manner as discontinuous slime films where oxygen or chemical concentration cells can be formed and result in localized corrosion of the metal (Davis, 1987). When exposed to quiet conditions for long periods, some macro fouling will occur eventually but is loosely attached and will slough away at intervals or can be easily removed by finger pressure or a light scraping action (Boulton, 1999).

3.6 Open circuit potential

The open circuit potential (OCP) of brass panels immersed in estuarine water sample as a function of exposure time is given in Fig. 3.3 and Table 3.5. The open circuit potential of monthly exposure varies from - 0.22 to 0.30 mV. The experimental results show almost constant value of - 0.22 mV Vs. SCE during Sep. 07 and Oct. 07 and then decreases abruptly to -28 on Jan. 08 and thereafter it sustains at this potential up to Aug. 08. The drop of the potential after Oct. 07 also substantiates the fact that there can be pitting corrosion coupled with dezincification after two months. According to Mansfield et al. (1992), the sustainable noble potentials (more positive values) mean that the metal or alloy retains its normal corrosion resistance, whereas, if localized corrosion has occurred, the OCP drops to the active potentials indicating localized corrosion. Santos and Mendonca (2006) related the negative shift of the OCP at longer time with the decrease of O_2 in seawater.

Table 3.5 Open circuit potential of brass sample immersed in estuarine water, Cochin at each exposure period

Months	Open circuit potential (V)
Sep.07	-0.22
Oct.07	-0.22
Nov.07	-0.25
Dec.07	-0.27
Jan.08	-0.28
Feb.08	-0.28
Mar.08	-0.28
Apr.08	-0.28
May 08	-0.28
June 08	-0.28
July 08	-0.28
Aug.08	-0.28

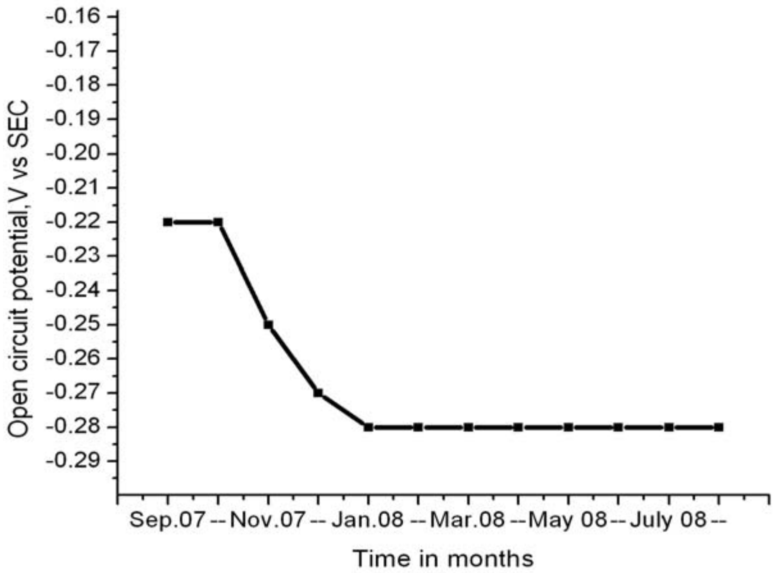

Fig. 3.3 Open circuit potential of brass sample immersed in estuarine water, Cochin at each exposure period

Kharafi et al. (2004) observed selective dissolution of brass at various potentials and chloride concentrations and concluded that chloride promotes the dissolution of copper and also zinc. It is evident from the earlier work that only zinc is leached from brass, while it has also been claimed that both zinc and copper are dissolved. Both mechanisms are possible, but the factor, which determines the type of behavior, is the corrosion potential. Trethewey et al. (1988) noticed the E_{corr} of muntz metal shifting from –235mV SCE to –380 mV SCE when solution deoxygenated and there is a potential difference between the cathodic areas on the outside of the specimen, where oxygen is readily available and the corroding interface deep within the metal, where there can be little oxygen, this potential difference constitutes a major driving force. MacDonald et al. (1979) stated that accelerated corrosion of the copper based alloys in sulphite-polluted seawater is caused by a shift in corrosion potential to active values.

Dos Santos et al. (2007) found that the breakdown of the passivity in deoxygenated, non - buffered media occurred easier and at much higher rate on passive bronze than on copper. The open circuit potential values of bronze samples in non-deoxygenated nonbuffered samples over a period of 30 days shown less negative potential and this potential can be assigned to the formation of cuprite Cu_2O and / or nantokite CuCl. Malik et al. (1999) indicated that the shift of OCP towards the more noble direction is due to the fact that cathodic process control is the predominant process than the anodic process attributing the healing condition of the passive film.

The open circuit potential transients of copper in non-deoxygenated, on-buffered synthetic seawater indicate pitting from the beginning of the exposure, in agreement with volta metric data. Data from weight loss studies are in quite good agreement with the conclusion from OCP: Copper starts to corrode during the initial period of immersion, leading to the formation of a passive film. Then, after a three-month period, V_{corr} starts to increase at quite a high rate reaching higher values in 0.5 M NaCl solution. Then breakdown of passivity takes place (Ferreira et al., 2004).

3.7 Electrochemical polarization studies

Table 3.6 and Figs. 3.6-3.8 illustrate the polarization curves of the brass sample immersed in estuarine water, Cochin after every month exposure. Corrosion rate of brass sample in 3.5 % NaCl solution is 0.3073 mm/year (Fig. 3.4). The corrosion rate of brass from Sep. 07 shows a steady increase upto Dec. 07 and then reduces till Mar.0 8 while it drastically increases through Apr.08 and May 08 (Fig. 3.5). Again it abrubtly reduces for the remaining months (Jun. 08-Aug. 08).

The results shown in Table 3.6 and Fig. 3.5 indicate that the low corrosion rate is prevailed throughout the period of study except Apr. 08 and May 08 where high corrosion rate is noticed. The corrosion value in May 08 is 3 times higher than Apr.08 and more than 5 times higher than the rest of the period. The high values of corrosion rate experienced by the brass during Apr. 08 and May 08 can be attributed to soft fouler and micro and macro algae that fouled on brass. The low corrosion rate of brass implies the protective nature of corrosion products and biomass.

Table 3.6 Polarization data of brass panels immersed in estuarine water, Cochin for different exposure period

Months	I_{corr} A/cm^2	E_{corr} V	b_c V/dec	b_a V/dec	R_p Ohm	Corrosion rate mm/yr	Corrosion rate mm/yr
Sep.07	1.761x10^{-5}	-0.232	0.3451	0.2694	3.73x10^{3}	3.604x10^{-1}	0.3604
Oct.07	3.591 x10^{-5}	-0.234	0.7897	0.1862	1.823x10^{3}	7.346 x10^{-1}	0.7346
Nov.07	2.852 x10^{-9}	-0.349	0.0844	0.0769	6.13 x10^{6}	5.834 x10^{-1}	0.583
Dec.07	4.14 x10^{-5}	-0.222	0.4929	0.29	1.915 x10^{3}	8.471 x10^{-1}	0.8471
Jan.08	3.158 x10^{-5}	-0.229	0.943	0.2296	2.54 x10^{3}	6.462 x10^{-1}	0.6462
Feb.08	5.389x10^{-8}	-0.289	0.946	0.0578	2.892 x10^{5}	1.103 x10^{-3}	0.00113
Mar.08	2.896 x10^{-6}	-0.636	0.3118	1.5483	3.893 x10^{4}	5.925 x10^{-2}	0.05925
Apr.08	7.673x10^{-5}	-0.372	0.5557	0.5279	1.532 x10^{3}	1.57 x10^{-0}	1.57
May 08	2.409 x10^{-4}	-0.213	0.5264	0.5031	4.638 x10^{2}	4.928 x10^{-0}	4.928
June 08	1.852 x10^{-5}	-0.25	0.3764	0.1699	2.745 x10^{3}	3.789 x10^{-1}	0.3789
July 08	1.232 x10^{-7}	-0.521	0.1365	0.1025	2.063 x10^{5}	2.52 x10^{-3}	0.0025
Aug.08	6.802 x10^{-6}	-0.267	0.4198	0.1585	7.347 x10^{3}	1.392 x10^{-1}	0.1392

In general corrosion potential (E_{corr}) values for copper alloys will not be having many variations over the period of time. But in the present study the variation in the E_{corr} values of monthly exposures could be mainly attributed to the corrosion products formation and biofouling development, depending upon the local environment conditions (Seawater chemistry in the immediate vicinity of the metal/electrolyte interface, dissolved $O_{2,}$ wave action, role of micro algae, slime forming bacteria in the bio fouling consortia) prevailed during period of study in Cochin estuarine water, which has been evidenced from the well documented studies carried out elsewhere (Miller, 1970; Obuekwe, 1981; Patricia wagner, 1993). The b_a and b_c values for monthly exposure are in tune with E_{corr} and I_{corr} values of respective exposure.

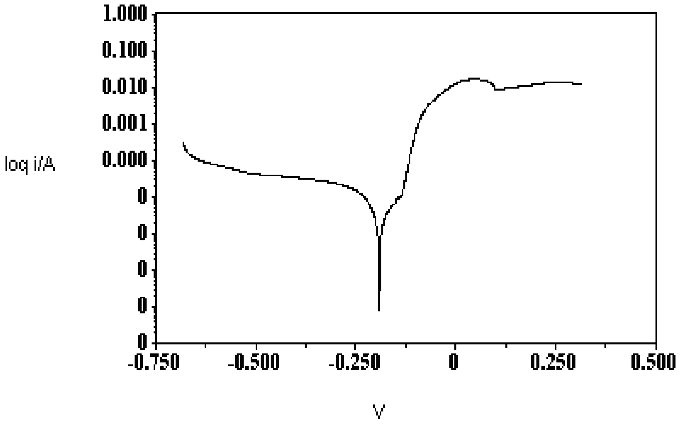

Fig. 3.4 Polarization curve of brass sample before exposed to estuarine water Cochin

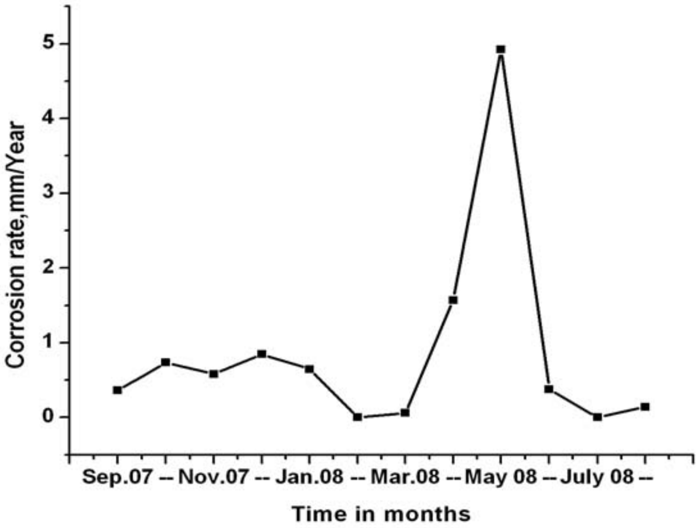

Fig. 3.5 Month wise corrosion rate of brass exposed to estuarine water Cochin

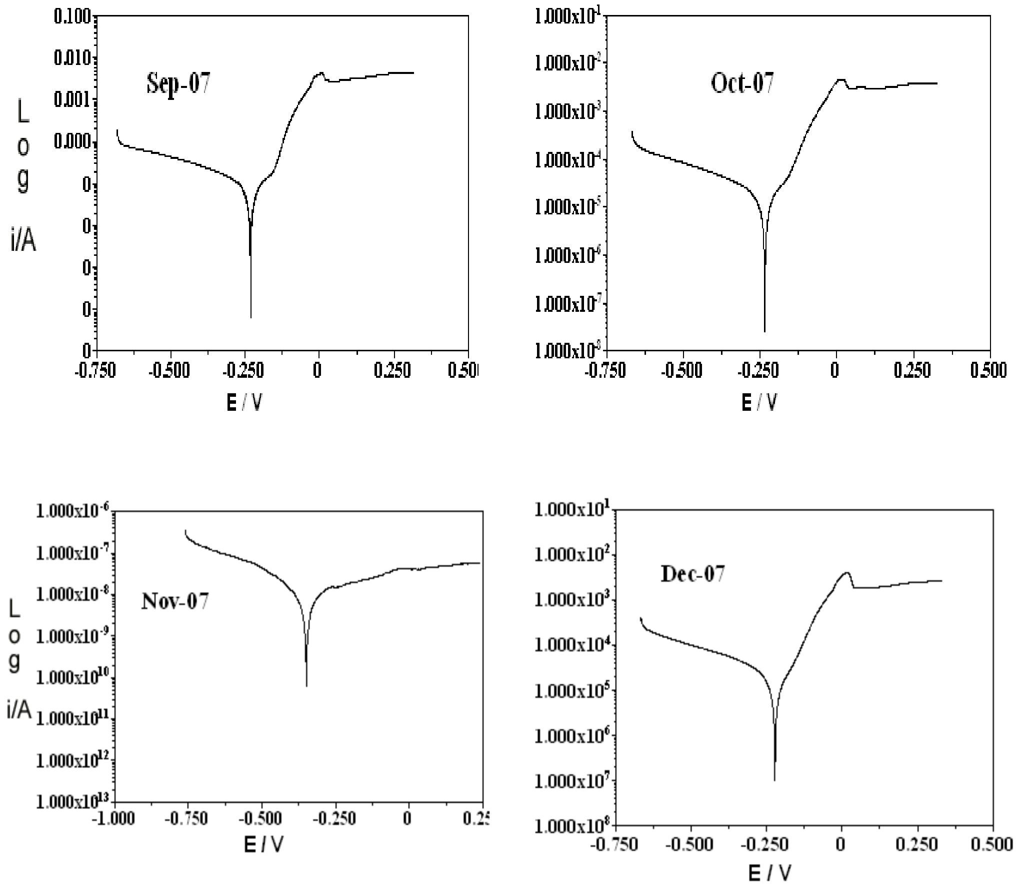

Fig. 3.6 Polarization curve of brass panels immersed in estuarine water, Cochin for Sep. 07, Oct. 07, Nov. 07 and Dec. 07 months

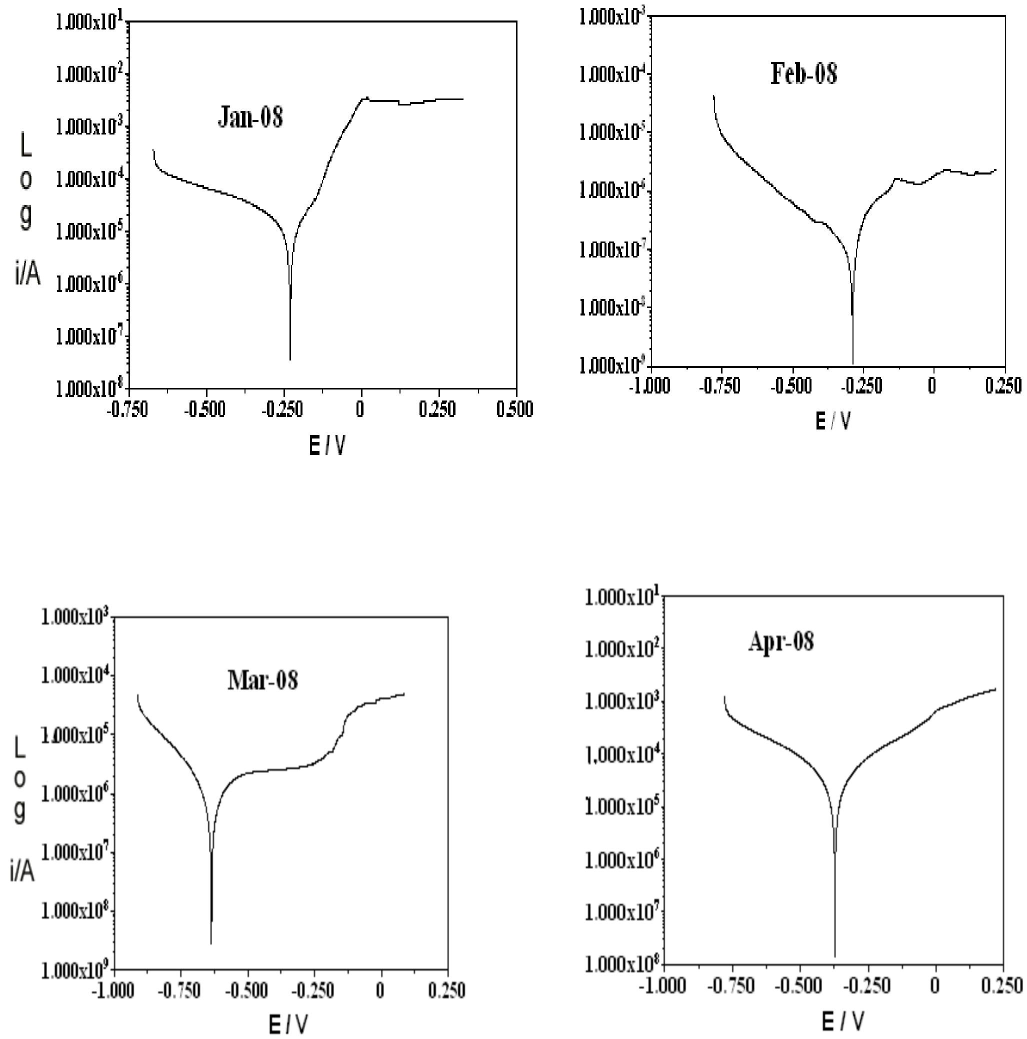

Fig. 3.7 Polarization curve of brass panels immersed in estuarine water, Cochin for Jan. 08, Feb. 08, Mar. 08 and Apr. 08 months

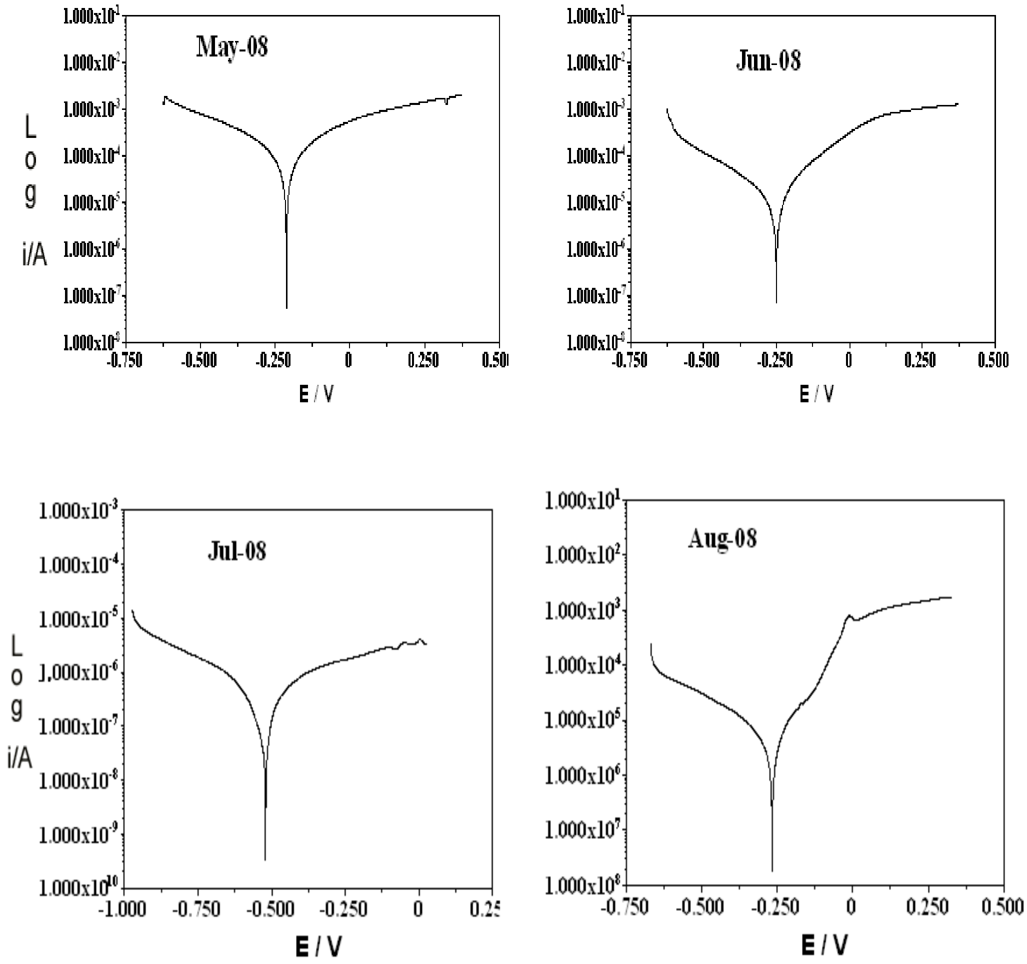

Fig 3.8 Polarization curve of brass panels immersed in estuarine water, Cochin for May. 08, Jun. 08, Jul. 08 and Aug. 08 months

From the above results of E_{corr}, $I_{corr,}$ b_a and $b_{c,}$ it implicits that higher corrosion during the exposure (April 08 and May 08) is owing to the fact that the levels of dissolved oxygen concentration available at the meta/electrolyte interface is higher. On the contrary, the decrease of corrosion rate during the rest of exposure can be attributed to the less access of dissolved oxygen at the metal / electrolyte interface, owing to the formation of corrosion products and bio mass. This is in agreement with studies carried out elsewhere (Peter, 1982; Bomberg, 1955). Mansfield et al. (1994) concluded that the increase of corrosion rate of copper alloys with increasing mass transport at constant E_{corr} is due to acceleration of both anodic and cathodic reaction. Under anaerobic condition, the cathodic reactant may be H_2O and/or organic compounds, or products from the microbial activity, particularly in NSW, or in contaminated ASW.

3.8 Dezincification factor

Table 3.7 summarizes percentages of leaching of zinc from the matrix of brass and the extent of dezincification over a period of one year. Dezincification factor for brass as a function of exposure time is given in Fig. 3.9. The percentage leaching of zinc from brass increases for all months. Copper leaching percentage also increases for all months except small fluctuation in the first three months.

Table 3.7 Dezincification of brass panels during exposure period in estuarine water, Cochin

Periods	Leaching of Cu %	Leaching of Zn%	Dezincification factor Z
Sep.07	44.2	16	0.50
Oct.07	40.8	18	0.61
Nov.07	41.0	32	1.07
Dec.07	45	35	1.07
Jan.08	49.4	41	1.14
Feb.08	55	42	1.05
Mar.08	60.0	44	1.01
Apr.08	63.0	47	1.02
May 08	65.1	52	1.10
June 08	69.3	53	1.05
July 08	72.1	55	1.05
Aug.08	74.5	58	1.07

Dezincification factor is more than one for all months except Sep. 07 and Oct. 07, which indicates that dissolution of zinc has occurred from the matrix of brass. Dezincification factor higher than one denotes preferred dissolution of zinc. It is concluded that leaching of zinc increases with respect to time of exposure. This is in confirmation with results reported elsewhere (Beccaria, 1989; Abbas, 1991). The studies carried out in the Palk Bay waters of Mandapam coast reveal that the Z factor is less than one whereas in Gulf of Mannar water of Mandapam the Z factor is greater than one. Kharafi et al. (2004) observed dezincification of brass at various potentials and chloride concentrations and concluded that chloride promotes dissolution of copper and zinc.

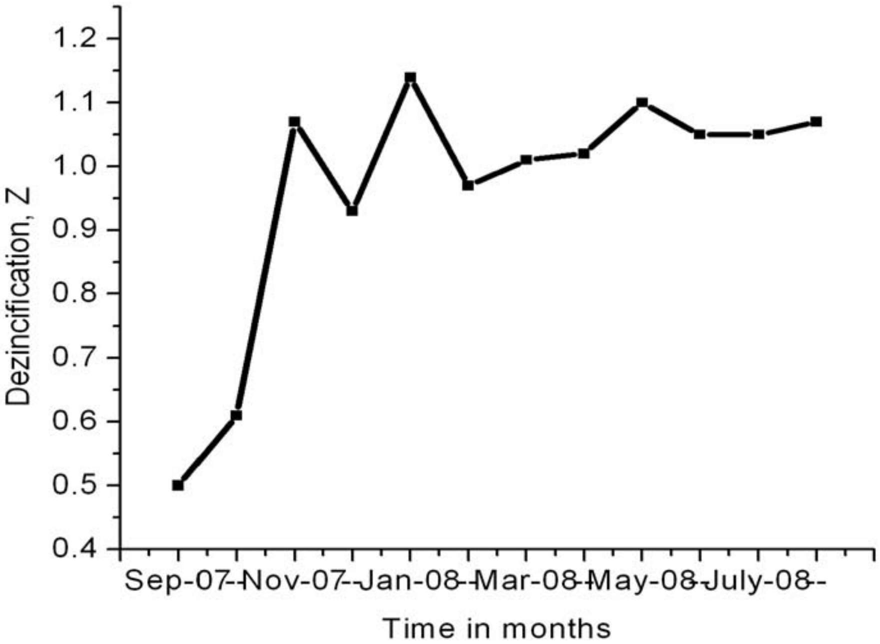

Fig. 3.9 Dezincification of brass panels at each exposure period in estuarine water, Cochin

The abnormal behavior can be due to the synergistic effects of biofilm consortia (aerobic and anaerobic) dissolved oxygen caused by turbulence in the estuary and differential concentration cells on the surface during the study period.

The contradictory behavior can be explained on the basis that during the study period, Cochin estuary is characterized by production of biogenic sulfides by anoxic condition. The smell of H_2S gas has also been sensed from a distance 10 m away from the bank. This has caused black tarnishing on the brass panel exposed in the Cochin estuary.

3.9 Physicochemical properties

Variation in different physicochemical parameters of Cochin estuarine water during the period of observation is presented in Table 3.8 and Fig. 3.10. At the initial stage of the study, in Sep. 07, salinity is 16.1$‰_0$ but the value increases to maximum of 29 $‰_0$ in Dec. 07. It reduces to single digit in June, July and August 08 (Table 3.9) due to freshwater influx during the monsoon period.

Table 3.8 Variation of dissolved oxygen, pH, salinity, temperature of water samples at each exposure period in estuarine water, Cochin

Months	Dissolved oxygen ml/l	pH	Salinity ‰	Temperature °C
Sep.07	4.0	7.1	16.1	27.3
Oct.07	1.90	6.5	17.5	29.0
Nov.07	3.1	6.8	19.3	24.0
Dec.07	3.6	7.0	29	25.0
Jan.08	4.3	7.4	26.2	26.8
Feb.08	4.0	7.5	26	29.5
Mar.08	3.9	7.4	28.3	30.5
Apr.08	4.7	6.9	19.3	30.5
May 08	5.1	6.5	19.8	31.6
June 08	4.9	6.2	2.9	29.5
July 08	4.6	7.3	1.2	27.5
Aug.08	4.9	7.5	0.8	24.5

Higher salinity in marine environment accelerates metallic corrosion (Winston Revie, 2000). Temperature is initially 27.3 ºC and reduces to 24 ºC on Nov. 07 and then increases to maximum 31.6 ºC in May. 08 and thereafter the values decreases marginally (Fig. 3.10) due to influx of freshwater during monsoon period. Dissolved oxygen (DO) is 4 ml/l at the Sep. 07 and then it drops to 3.1ml/l on Nov. 07 and increases to 3.6 ml/l on Dec. 07 and afterward increases to 4.3 ml/l and 4.0 ml/l on Jan. 08 and Feb. 08, while reduces to 3.9ml/l on Mar. 08. It again increases to 5.1 on May. 08 and then remains at 4.9 for June 08 and Aug. 08 except July 08 where it is at 4.6 ml/l.

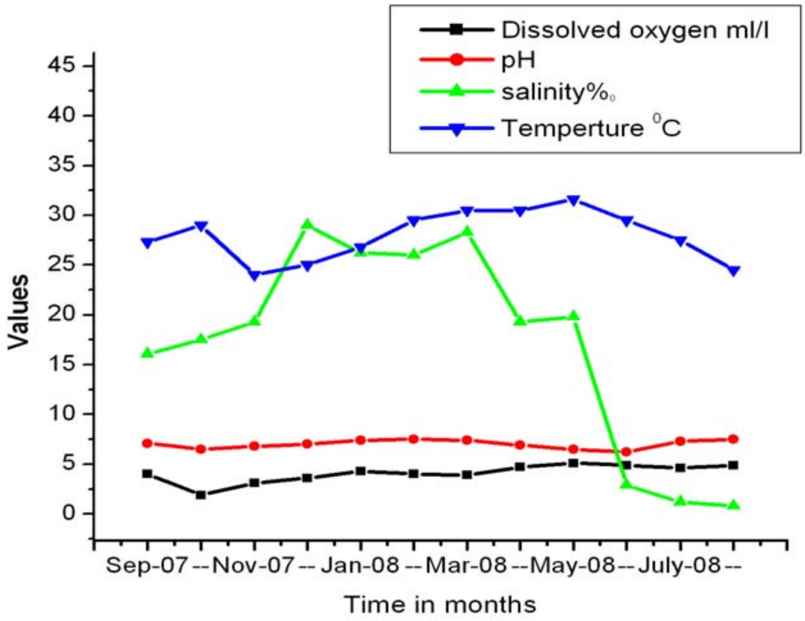

Fig. 3.10 Variation of dissolved oxygen, pH, salinity, temperature sample at each exposure period in estuarine water, Cochin

pH of the water is 7.1 on exposure of sample and increases to 7.5 on Feb. 07 and then reduces to 6.2 on Jun. 08 and after that increases to 7.5 on Aug. 08. An initial increase of salinity and temperature can be the reason for initiation of corrosion of brass in the initial period of exposure in Cochin estuary.

Physicochemical conditions of this estuary are controlled by freshwater drainage and precipitation during monsoon and seawater intrusion during high tide. Hydrological parameters during July-August (Monsoon); November-December (winter) and April-May (Pre-Monsoon) in near shore environment of Cochin. The surface water temperature varied from 23.3o C to 31o C. While lowest temperature was recorded in July-August, the highest temperature during April-May. The salinity in Cochin Backwaters varied between three distinct periods in a year (i) a period of low salinity (June-September), (ii) a period of gradual rise in salinity (October- January) and (iii) a period of high salinity (February to May). pH varied from 6.7 to 8.3 during monsoon, 6.5 -8.6 during post- monsoon and 6.7 – 8.1 during pre-monsoon. DO in the surface waters varied from 3.9 to 5.27 mg/ l in pre-monsoon, 3.59 to 5.39 mg/ l during monsoon and 3.44 to 5.59 mg/ l during post-monsoon. Nitrate content in water varied from 0.80 to 7.86 mmol/ l in monsoon, 0.92 to19.16 mmol/l in post-monsoon and 5.25 to 11.8 mmol/l in pre-monsoon. The nitrite concentration ranged from 0.20 to 1.63 mmol/ l in pre-monsoon, 0.07 to 0.4 mmol/ l in post-monsoon and 0.14 to 1.27 mmol/ l in monsoon season. Phosphate content varied from 1.02 to 4.92 mmol/ l in pre-monsoon, 0.44 to 3.29 mmol/ l in post-monsoon and 1.84 to 17.7 mmol/ l in monsoon season. Silicate content varied from 62.87 to 410.78 mmol/ l in pre-monsoon, 5.7 – 51.0 mmol/ l in post-monsoon and 139.6 to 717.4 mmol/ l in monsoon period (Shunmugaraj et al., 2002).

It is reported that the microbial activity may contribute to lower the pH (Bastos et al., 2008). But settlement of organisms was influenced by the hydrochemical parameters particularly salinity and temperature. The loss of zinc is accelerated by high temperature, and increased chloride content and differential aeration (Trethewey, 1996). As a general rule, the corrosion reaction rate in seawater increases with temperature. However, other variables such as oxygen concentration and biological activity must also be considered. The solubility of oxygen decreases as the temperature increases. Biological activity generally increases with increasing temperature and calcareous deposits and other protective scales are also more likely to form/deposit on metal surfaces at higher temperatures. Temperature variations due to seasonal changes also affect metal corrosion rates in seawater. For many copper and iron alloys, the corrosion rate increases in the warmer months of the year (Davis et al., 1987).

A chloride ion promotes the dissolution of Zn and Cu and hence increases the rate of dissolution of the alloy. The high corrosion resistance of the copper-nickel alloys in aerated salt water is due to a slower cathodic reaction, presumably oxygen reduction (Zia et al., 1990). The poor catalytic nature and/or poor conductance of the outer porous layer force the oxygen level to diffuse within the pore electrolyte to sites deep in the porous layer. These deep sites may be of a catalytic nature and where electrons are readily available for reduction of the oxygen. The oxygen diffusion step in the pore electrolyte partially or completely limits the rates for the overall corrosion reaction. The role of this film in reducing corrosion is controversial since the behavior is greatly affected by oxygen content, velocity, temperature, pollutants and biological organisms.

Temperature and dissolved oxygen of seawater is directly related to corrosion of mild steel while organic matter of the corrosion products was inversely correlated with the corrosion of mild steel and therefore a metal - organic matter complex is probably involved in developing a passive film on the metal surface (Bhosle et al., 1992). The dissolved oxygen concentrations in the coastal areas are lower than those of the offshore. This is caused by enrichment of the water derived from the land and the decaying process of organic materials that require oxygen (Anugerah Nontji, 2004). The reduction of oxygen is directly coupled with the metal oxidation process and accordingly it influences all factors, which alter the availability of oxygen at metal surface and affects the corrosion behavior. The oxygen concentration affects the actively corroding metals in a way of the corrosion potential and corrosion current (Schumacher, 1979).

An increase in the water temperature reduces the corrosion resistance and intensifies the dezincification of brasses. In aerated chloride solutions, it significantly promotes the cathodic process (autocatalytic effect). Therefore, the corrosion rate of brasses, even insusceptible to dezincing, can appear higher than in the case of dezincing. Dezincing, conversely, decreases the corrosion rate (Marshakov, 2004). The dissolved oxygen content has a major influence on seawater corrosivity. The oxygen content in seawater can be as high as 12 ppm. The oxygen level increases due to photosynthesis by marine plants and by the action of the waves; the oxygen level decreases due to the demand for oxygen created from the decomposition of organic matter. The combined influence of the above results in a dissolved oxygen content that varies as a function of the season at any given location (Boyd, 1978). The general rule is that if the temperature or the salinity decreases, the dissolved oxygen content increases (Dexter, 1986; Davis, 1987).

The surface salinity of open ocean water typically varies from 32 to 37.5 $\%_0$. Generally, this degree of variation does not alter metal corrosion rates. At the mouth of a river, seawater is more diluted than in open ocean water. Dilute seawater is undersaturated in carbonates, which reduces the likelihood of forming protective calcareous films on a metal surface. Also, the reduction or complete elimination of marine organisms in dilute seawater reduces the probability of forming protective biofilms and could result in increased metal corrosion (Boyd et al., 1978). Variations in salinity can also alter the localized corrosion resistance of metals in seawater. As the salinity increases, the chloride ion activity increases which can result in increased pit and crevice corrosion initiation and propagation (Davis, 1987).

The alloys used in seawater systems are not greatly influenced by variation with the normal pH range of 7.8-8.3. However, higher pH values will lower the solubility of calcium and magnesium oxides, hydroxides and salts and results in formation of the so called calcareous layers which can exert a beneficial influence by preventing oxygen from reaching the surface (Compton, 1975). The pH of open ocean water varies from approximately 7.5 to 8.3. This variation in pH does not affect the corrosion of most metals, except for aluminum (Dexter, 1986). Although changes in the pH do not directly alter the corrosion behavior of most metals, the variations can influence the formation of protective calcareous scales, which do affect the metal's corrosion rate. At the surface water, ocean are normally supersaturated with calcium carbonates and therefore precipitation of these carbonate scales will influence the corrosion reaction at the metal surface. Apart from its direct influence on corrosion rate, temperature can also be operative in modifying the properties of corrosion products and passive or calcareous layers and seawater temperature affect the free corrosion potential level and thereby the susceptibility to pitting (Ijsseling et al., 1982).

An increase in the temperature of seawater makes it more corrosive even at low oxygen level and erosion of alloys by aerated high velocity seawater becomes more sever even as the temperature of the water increase (Greies, 1968). The equilibrium values of oxygen content are disturbed by the action of marine plants and organisms. The lower oxygen content appears to have a more potent effect in reducing corrosion than the lowering of pH accelerating it. Decomposition of marine organisms results in loss of oxygen and generation of hydrogen sulfide in the environment which lowers the pH well below 8. Higher pH values can be anticipated when photosynthesis occurs near surface while lower level of oxygen prevails where the decomposition of organisms is active (Redfield, 1963 and Parvizi et al., 1988).

Reinhart et al. (1972) observed that the rate of corrosion of copper alloys is closely related to the concentration of oxygen in the environment. Oxygen accelerates the corrosion of steel by serving as a cathodic depolarizer and it retards the corrosion of stainless steel by the development and repair of oxide films responsible for passivity. The surfaces with the smallest oxygen concentration suffer accelerated corrosion as anodes in a differential aeration.

3.10 Mechanical properties

The change in mechanical properties such as ultimate strength and yield strength of brass exposed in Cochin estuarine water is shown in Table 3.9. The exposure of brass subjected to tension testing over the period of experimentation is, as received, monthly (one month), quarterly (three months), half yearly (six months), nine months and yearly. It is observed that both ultimate and yield strength are a similar pattern of declining trend over the period of exposure.

Table 3.9 Change in mechanical properties of brass due to exposure in Cochin estuary

Periods/Properties	Ultimate load (X Newton)	Ultimate strength mpa	Yield load (X Newton)	Yield strength mpa	Area reduction	Elongation %
As received	687	429	480	300	64	51
Monthly	623	388	420	266	51	33
Quarterly	552	345	390	243	50	32
Half yearly	450	281	344	215	40	37
9 months	447	250	325	203	37	23
Yearly	370	231	315	196	35	19

The extent of deterioration experienced by brass owing to exposure in Cochin estuarine water is determined by monitoring the change in mechanical properties of the materials such as ultimate strength, yield strength, ultimate load, yield load, percentage elongation and percentage reduction in area over the period of exposure. It is evident that the loss in tensile strength is directly proportional to weight loss over the period of time. This is in agreement with the results reported elsewhere (Forgeson et al., 1961; Southwell et al., 1965, 1968). The notable increase in loss in mechanical properties of brass after six months period is mainly attributed to the loss in antifouling properties after six-month period. This is also substantiated from the fact that studies carried out on copper alloys for 16 years in the Pacific Ocean near Panama Canal Zone experienced only 45.5% loss in tensile strength wherein there was no significant fouling observed (Schumacher et al., 1979).

3.11 Summary and conclusions

Corrosion rates decreases significantly from Sep. 07 to May. 08. The low corrosion rate is related to the protecting film formed almost completely on brass panel. This behavior is due fouling assemblage and corrosion products. The corrosion products and fouling assemblage remained on brass acted against corrosion to proceed further. The increase of corrosion rate after May 08 is related to the removal of protective film due to prolonged of brass in estuarine water.

The increase of fouling after Nov. 07 indicates reduction of corrosion rate. The decline in the corrosion rate values and up trend values of biomass accumulations imply the protective nature of the biomass over the period of exposure. The biomass on brass is initially low but increases with time as evidenced from the present study. Hydrochemical parameters and loss of toxic effect of brass can be the reasons for the increase of biomass.

The sustainable noble potentials (more positive values) of -0.22 Vs. SCE during Sep. 07 and Oct.07 indicate that the metal or alloy retains its normal corrosion resistance and then decreased abruptly to –0.28 on Jan. 08 and thereafter it sustains at this potential up to Aug. 08. The drops of the potentials after Oct. 07 also indicate the onset of pitting corrosion coupled with dezincification from Nov. 07 to Dec.07.

A low corrosion rate is prevailed throughout the period except in Apr. 08 and May 08 during which periods the corrosion rates are very high. The high values of corrosion rate experienced by the brass in the estuarine water can be attributed to soft fouler and micro and macro algae that fouled on brass. The low corrosion rate values of brass imply the protective nature of corrosion products and biomass. The higher corrosion during (April 08 and May 08) is owing to the fact that the level of dissolved oxygen concentration available at the metal/electrolyte interface is higher. On the contrary, the decrease of corrosion rate during the rest of exposure can be attributed to the less access of dissolved oxygen at the metal/electrolyte interface, owing to the formation of corrosion products and biomass.

In general the E_{corr} values for copper alloys will not be having many variations over the period of time. But in the present study the variation in the E_{corr} values of monthly exposures could be mainly attributed to the formation of corrosion products and biofouling development, depending upon the local environment conditions (estuarine water chemistry in the immediate vicinity of the metal/electrolyte interface, dissolved $O_{2,}$ wave action, role of micro algae, slime forming bacteria in the biofouling consortia) prevailed during the study period.

Dezincification factor is more than one for all months except Sep. 07 and Oct. 07, which indicate that dissolution of zinc from the brass for all months except the above two months. An increase in the temperature of estuarine water makes it more corrosive even at low oxygen level and intensifies the dezincification of brass. Higher salinity can also alter the localized corrosion resistance of metals in estuarine water. With increase of salinity, the chloride ion activity increases resulting in increased pitting. Higher temperature and salinity reduce the oxygen content while microbial activity reduces the pH. There is not much variation in dissolved oxygen and pH and therefore could not be correlated with corrosion of brass. The notable increase in loss in mechanical properties of brass after six months period is mainly attributed to the loss in antifouling properties after six-month period.

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Chapter 4

SURFACE CHARACTERIZATION OF BRASS

Contents

4.1 Visual Observation of corroded brass
4.2 Surface characteristics of brass before removal of corrosion products
4.3 Surface compound analysis
4.4 Surface morphology of brass after removal of corrosion products
4.5 Summary and conclusions

Results of surface characterization of brass in estuarine water in terms of visual photos, surface morphology, elements, and compounds using photographs, SEM, EDS and XRD are presented in this chapter. Visual observation, elements and compounds of corrosion products obtained from brass panels combined with surface morphology of brass before and after removal of corrosion products can reveal the protective nature of the brass and the effect of estuarine water on the corrosion behavior of brass.

4.1 Visual Observation of corroded brass

According to Little et al. (1993), the corrosion of freshly polished copper alloys in seawater involves the cathodic reactions of

$$O_2 + 2H_2O + 4e^- \text{-----} 4OH^-$$

And the anodic reaction of

$$Cu \text{ ---- } Cu^{+} + e$$

If seawater contains (Cl^{-}, SO_4^{2-}, HCO^{-}_3) the possible reaction with copper is the formation of cuprous chloride complex

$$Cu^{+} + 2Cl^{-} \text{ ------ } CuCl^{-2}$$

The decrease of corrosion rates of copper alloys during longer exposure periods in natural seawater is believed to be due to the formation of cuprous oxide (Cuprite) as

$$2CuCl^{-}_2 + 2OH^{-} \text{ ------------} Cu_2O + H_2O + 4Cl^{-}$$

which is further oxidized to the less protective cupric hydroxy chloride (Atacamite)

$$Cu_2O + 1/2\, O_2 + Cl^{-} + 2H_2O \text{------} Cu_2(OH)_3Cl^{-} + OH^{-}$$

$$4Cu + SO_4^{2-} + 6H_2O \text{------} CuSO_4.\ 3Cu(OH)_2 \text{ (bronchanite/antlerite)} + 6H^{+} + 8e$$

Figs 4.1 – 4.3 show the visual examination of the brass panels for various exposures periods. In Sep. 07 and Oct. 07, brass surfaces show heterogeneous patina mainly with brownish color and small-scattered green patches while in Nov. 07 the brass surface has turned to greenish color with brown patches and this has continued up to Jan. 08. Then the surface of brass has changed with more area of brownish colored layer and little of green batches with few white spots for Feb. 08, which has observed till May. 08. In the rest of months, surface has appeared as blend of brownish and green color with more white spots. There is no appearance of pink and blue color on brass surface.

Visual examinations of the brass sample show that the different regions have slightly different colors, indicating that they are of different compositions. Pourbaix, (1972) showed that the possible formation of different layers of products occurred in the following order (starting from metal surface): Cu_2O, CuCl, $Cu(OH)_2$, and $CuCl_2$. The copper compound $CuCl_2$ or Cu_2O is possibly appearing as brownish color and greenish color zone and is possibly atacamite and / or bronchantite/antlerite. Zinc in the alloy may also contribute to the formation of the following corrosion compounds: hydrated zinc basic chloride-sulphates, $Zn_{12}(OH)_{15}Cl_3(SO_4)_35H_2O$, zinc hydroxide chloride, $Zn_5(OH)_8Cl_2H_2O$ (simonkoleite), zinc hydroxides, $Zn(OH)_{2,}$ Zinc carbonates, $Zn_2CO_3(OH)_6$ (hydrozincite). The zinc compound, in general, is white or pinkish while the copper compounds, i.e. Atacamite/paraatacamite, bronchantite/antlerite have green color.

The white spots are possibly due to hydrated zinc basic chloride-sulphates, $Zn_{12}(OH)_{15}$ $Cl_3(SO4)_3$ $5H_2O$. The exponential decrease in the corrosion rate of brass can be attributed to the protective nature of corrosion products such as cuprous oxide and cupric hydroxy chloride, which are formed along with marine growth accumulation (Mansfield, 1994). Gomez de Saravia et al. (1990) postulated that the modification in the metal/solution interface properties of copper based alloys could be characteristic of the corrosion products beneath bacterial colonies.

Morales et al. (1995) reported that in neutral and alkaline solutions, the passivity of brass involves in the formation of a complex $ZnO.XH_2O$ and Cu_2O layer as supported from electrochemical, XPS and Auger Spectroscopy data. The passivity break down depends on the composition of the alloy, the aggressive environment and temperature. Mathiyarasu et al. (1998) concluded that the surface film of copper based alloys consisted of mainly a mixture of Cu_2O, $Cu_2(OH)_3$ and CuS in natural seawater of southeast Coast of India, Tuticorin. Visual observation of bronze samples show a thin film slightly red with white zones and some greenish precipitates of Cu_2O mixed with SnO_2 and chloride salts i.e. atacamite, paraatacamite and /or botalkide. The amount of greenish corrosion products were much higher on samples immersed in the non-buffered synthetic seawater (Dos Santos et al., 2007). Barbucci (1990) reported that the structure of protective layer of copper alloys is generally ascribed to an outer layer of CuO / $Cu(OH)_2$ and an inner layer of Cu_2O and the protective action of the passive film seems to be dependent on good adherence to the metal.

According to North et al. (1970) and Blundy et al. (1972), the corrosion resistance of copper alloys is due to the formation of a protective film of cuprous oxide (Cu_2O). Sawant et al. (1995) observed two distinct layers of corrosion products. The outer layer was dark green while the inner was brown on copper alloys and their XRD analysis of corrosion products revealed the presence of Cu_2O as the major component in the inner layer, whereas the outer layer indicated presence of atacamite. Ferreira et al. (2004) stated that the passivation of copper in sulfate / chloride containing solution is due to passive layers composed of CuO_2, CuCl, CuO/$Cu(OH)_2$, Cu_2Cl, $Cu_2Cl(OH)_3$ (atacamide) and/or $CuSO_4$3Cu(OH)3 (brochantite) and type of compound forms on brass depends on the polarization potential and on the relative concentration of Cl^- and SO_4^{-2} ions. The presence of chalcocite (Cu_2S) was an indicator of SRB induced corrosion of copper alloys (McNeil and Little, 1990).

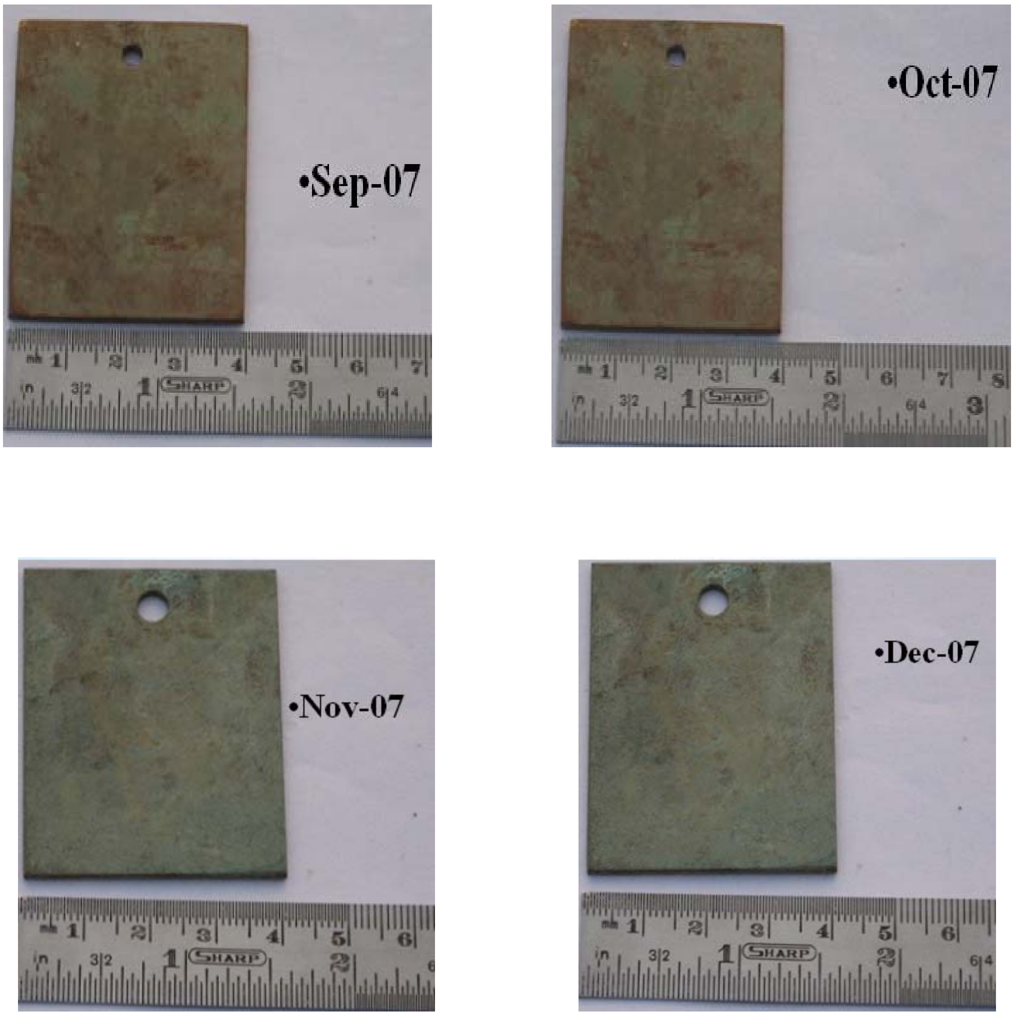

Fig. 4.1 Brass panels after Sep. 07, Oct. 07, Nov. 07 and Dec. 07 in Cochin estuarine water

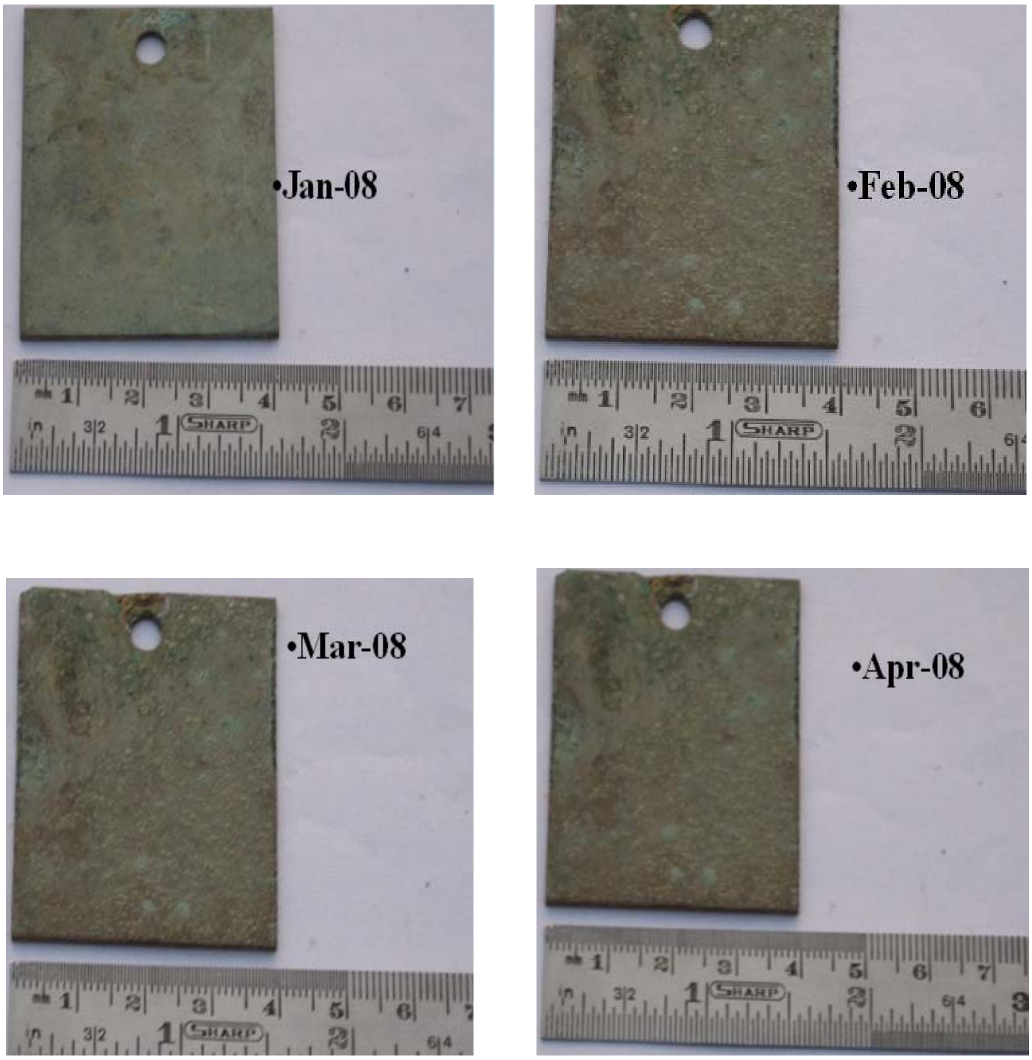

Fig. 4.2 Brass panels after Jan. 08, Feb. 08, Mar. 08 and Apr. 08 in Cochin estuarine water

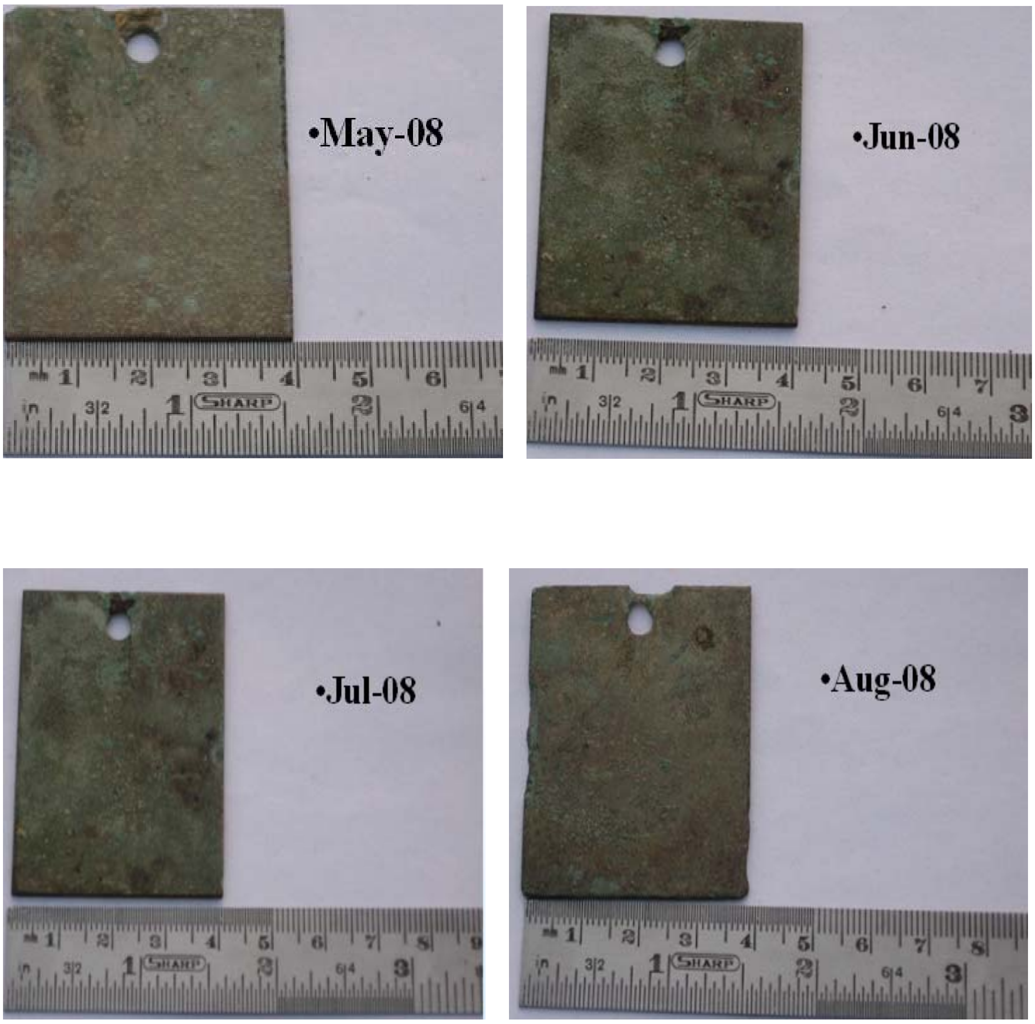

Fig. 4.3 Brass panels after May 08, Jun. 08, Jul. 08 and Aug. 08 in Cochin estuarine water

4.2 Surface characteristics of brass before removal of corrosion products

SEM images and EDS spectra of this study are shown in Figs. 4.4 - 4.15. Surface characteristics of brass show extensive stains and voids for the month of Sep. 07 and Oct. 07 (Figs. 4.4 - 4.5). The brass surface for Nov. 07 to Apr. 08 show extensive stains and progressive fine crystalline grains indicating extensive dezincification from Nov. 07 to Apr. 08 while the stains and crystalline grain are insignificant for the remaining months (Fig. 4.6 - 4.15). The SEM images through Figs 4.4 - 4.15 reveal that the extent of dezincification increases up to Apr.08 due to increase of density of crystalline grains from Nov. 07 - Apr. 08 and then reduces till Jul. 08 with slight increase for Aug. 08 as the density of crystalline grains decrease with little increase for Aug. 08. Dezincification of brass could be attributed to the role of biofilm consortia-differential aeration cells/concentration cell. The above trend is in tune with results reported elsewhere (Langenegge, 1968). The presence of fouling on brass is characterized by localized corrosion on selective areas with preferential dissolution and fine crystalline grains. The results are in tune with open circuit potential, extent of leaching of zinc, Z factors of respective exposure and extent of loss of mechanical properties of brass.

EDS spectra of brass for Sep. 07 in Cochin estuarine water, before the removal of corrosion products are show in Fig 4.4 and Table 4.1. EDS data indicate different spots and various types of elements on brass. Spot one has high O, followed by Si, Cu, Fe, Al, C, In and Mg. Spot two has high O, followed by Si, Al, Fe, Tb, C, K, and Mg. Spot three has high O, followed by Si, Al, K, C, and Mg. Spot four has high O, followed by Si, Al, Fe, C and Mg. The highly enriched element on the brass sample in this month exposure is O and the second highest element is Si which can be from suspended sediments in estuarine water. Sodium and chloride are not present on corrosion product while carbon content is found in this month which can come from the organic material dissolved in estuarine water. Other elements can be from the bottom sediment, which is rich in trace elements.

Figure 4.5 and Table 4.2 indicate the presence of various elements on corroded brass panel of the Oct. 07. It was observed that the zone one has high O, followed by Si, Al, Fe, and Mg. Zone two has high Cu, followed by O, Si, Mo, C, Al and Cl while zone three has high Cu, followed by O, Tl, C, Cl, Si, Pd, P, Al, and Mg. Zone four has high C, followed by Cu, O, Mo, Si, P, Cl and Al. The highly dominant element on the brass sample in this month exposure is carbon, which can be from the organic material dissolved in estuarine water. The second highest element is copper while third highest element is oxygen. Sodium is absent but chloride (maximum of 3.64 %) is present on corrosion product. Other elements can be from the bottom sediment, which is rich in trace elements. The resuspension of bottom sediments by the ebb and flow of water can cause for the enrichment of elements.

Various elements found on the brass panel for Nov. 07 are given in Fig 4.6 and Table 4.3 and spot one has high O, followed by Si, Fe, Al, K, Mg and Ti but Spot two has high Cu, followed by Cl and Zn. Spot three has high O, followed by Zn, Si, C, Mo, Fe, Mg and Na. Spot four has high Cu, followed by Zn, O, Si, C, Mo, Fe, P, Al, and Mg. The most predominant element on the brass sample in this month exposure is copper. The second highest element is oxygen and third highest element is zinc (maximum of 26.28 %). Sodium and chloride (maximum of 24.40 %) are present on corrosion product which can be responsible for initiation of dezincification. Carbon content can be come from the organic materials dissolved in estuarine water. Sulfur is absent in this month. Other elements can be from the sediments, which is rich in trace elements.

The spot analyses of corroded brass panel for the Dec. 07 are shown in Fig. 4.7 and Table 4.4. The spot one has high Zn, followed by Cu, O, Cl, Tl, S and P whilst Spot two has high Mo, followed by O, Na, S and Cu. Spot three has high Cu, followed by O, Cl, Rb, Si, Fe, Al, Na and Mg. Spot four has high O, followed by Cu, Si, Al, Cl, Zn, In, Fe, Mg and S. The most predominant element on the brass sample in this month exposure is Mo, which can be from the sediments. Second highest element is copper, which can be from brass. Third highest element is oxygen and fourth one is zinc (maximum of 27.04 %). Sodium and chloride (maximum of 16.96 %) are present but carbon is absent on corrosion product as the organic material dissolved in estuarine water is absent in this month. Other elements can be from the sediments, which is rich in trace elements. Sulphur is present in the fourth month indicating that the water is polluted.

The EDS spectra of the corroded brass of Jan. 08 show different elements. The spot one has high O, followed by Si, Fe, Al, K, Mg, C, Ti and Na while spot two has high Zn, followed by Cl, O and Cu. Spot three indicate high O, followed by Si, Cu, Al, Mo, Fe, Mg, Zn, C, Ca, and K while spot four has high Zn, followed by O, Cu, Mo, Cl, Tl, C, S and Si (Fig. 4.8 and Table 4.5). The highest Zn values (maximum of 58.63 %) on the brass sample observed for Jan. 08. The second highest concentrated element is oxygen and third highest element is silicon. Sodium and chloride (maximum of 21.64 %) are present on corrosion product. Carbon content is seen in this month and carbon could be drawn from the organic material dissolved in estuarine water. Other elements can be from the sediments, which is rich in trace elements. Sulphur is present in this month indicating that the water is polluted.

The corrosion product analysis of brass for Feb. 08 by EDS is given in Fig. 4.9 and Table 4.6. Spot one has high O value, followed by Si, Al, C, Fe, Cu, Mg, K, and Na but spot two has high Zn, followed by Cl, O, Cu, Tl, Fe, and Si while spot three has high O, followed by Si, Mg, C, Al, Cu, Fe and Zn. Spot four has high O, followed by Cu, Zn, Si, Mo, C, Al, Fe, Cl, Mg and P. The highly concentrated element on brass in this month exposure is oxygen, which can be from suspended sediments from estuarine water. The second highest element is zinc (maximum of 38.89 %) which can be from brass. Third highest element is silicon. Sodium and chloride (maximum of 16.82 %) are present on corrosion product. Carbon content is also found in this month while carbon can be derived from the organic material dissolved in estuarine water, other elements can be from the bottom sediments, which is rich in trace elements. Sulphur is not present in the brass panel of Feb. 08 indicating that sulphide pollution is not prevailed.

The results of corrosion product of brass panel for Mar. 08 are shown in Fig 4. 10 and Table 4.7. Spot one has high O value, followed by Si, Al, Cu, Fe, K, Mg and Zn while spot two has high Zn, followed by Cl, O and Cu. Spot three has shown high Cu, followed by O, Cl, Si, Zn, Al, Fe and Mg. Spot four has high Zn , followed by O, Cu, Cl, Si, S and Al. The highly intensified elements in this month is zinc (maximum of 54.68 %) followed by oxygen which can be from estuarine water. The third highest element is copper. Sodium and carbon are absent but more chloride (maximum of 23.52 %) is present on corrosion product. Other elements can be from the sediments, which is rich in trace elements. Sulfur presence indicates that the water is polluted**.**

From Fig. 4.11 and Table 4.8, it is noticed that the spot one has high Zn, followed by O, Cl, Cu, Si, Fe, and Al. Spot two has high Zn, followed by Cl, O and Cu. Spot three has high Cu, followed by O, Fe, Zn, Cl, Si, Al, P, Mg and

Ca. Spot four has high O, followed by Si, Cu, Al, C, Fe, Cl, K and Zn. The most predominant element on the brass panel in Apr. 08 exposure is zinc (maximum of 59.50 %). The second highest element is copper. Third element is oxygen. Sodium is absent but Chloride (maximum of 21.46 %) is present on corrosion product. Carbon content is found in this month and carbon can come from the organic material dissolved in estuarine water. Other elements can be from the sediments, which is rich in trace elements.

The different spots on corroded brass for the month of May 08 reveals the different elements and Spot one has high O, followed by Cu, Zn, Cl, Si, Al, Fe, P, Mg and S. Spot two has high Cu, followed by Sn, O, Cl, Zn, Mo, Fe, P and Si. Spot three has high O, followed by Si, K, Al, Cu, Cl and Fe. Spot four has high O, followed by Si, Fe, Al, Mg B, K and Ti (Fig. 4.12 and Table 4.9). The most enriched element on the brass sample in this month exposure is oxygen, which can be from seawater. The zinc content in this month is 9.87%. The second highest element is copper. Sodium is absent while sulfur and chloride (maximum of 9.91 %) are present on corrosion product. Carbon content is not seen in this month. Other elements can be from the sediments, which is rich in trace elements.

Figure 4.13 and Table 4.10 indicate the presence of various elements on corroded brass panel of the June 08 in Cochin estuarine water. The spot one has high Cu, followed by O, Zn, Si and Al while spot two has high Ca followed by C, O and Na. Spot three has high Cu, followed by O, Zn, Cl, Sn, C, Mo, Fe, P, Si, Al and Mg. Spot four has high O, followed by Si, Fe, Ca, Al, Mg, Cu, Zn and Na. The most dominant element on the brass sample in this month exposure is copper. The second highest element is Calcium, which can be from mud or sand in seawater. Oxygen is third highest element. The zinc content in this month is 7.49 %. Sodium and chloride (maximum of 6.43 %) are present on corrosion product. Carbon content is found in this month and carbon can come from the organic material dissolved in estuarine water. Other elements can be from the sediments, which is rich in trace elements.

The spot analyses of corroded brass panel for the July 08 is shown in Fig. 4.14 and Table 4.11 and the spot one has high O, followed by Si, Al, Cu, Fe, Zn, Mg, Cl, K and Na. Spot two has only high O, followed by Si. Spot three has high Cu, followed by O, Zn, Cl, C, Si and Ca. Spot four has high Cu, followed by O, Zn, Mo, Cl, Fe, Ca and Si. The most predominant element on the brass sample is copper. The second highest element is oxygen, which can be from seawater. Third highest element is Silicon. The zinc content in this month is 5.87%. Sodium and chloride (maximum of 4.03 %) are present on corrosion product. Carbon content is observed in this month and carbon can come from the organic material dissolved in estuarine water.

In the month of Aug. 08, the EDS spectra of corroded brass in Cochin estuary show different elements and spot one has high Cu, followed by O, C and Zn. Spot two has high O, followed by Si, Al, Na, Cu, Ca, C and Fe. Spot three has high Cu followed by O, Zn, Cl, Tl, Mo, Sn, C, Fe, S, P and Si. Zone four has high Cu followed by O, Zn, Sn, Cl, P, Fe, Si and S (Fig 4.15 and Table 4.12). The element which has high concentration on the brass sample in this month is copper. The second highest element on the brass sample is oxygen, which can be from seawater. Third highest element is silicon. The zinc content in this month is 17.70 %. Sodium and chloride (maximum of 6.57 %) are present on corrosion product. Carbon content in this month can come from the organic material dissolved in estuarine water. Sulfur is present in this month as the medium is polluted. Other elements can be from the sediments, which is rich in trace elements.

Table 4.1 Results of EDS of brass for Sep. 07 in Cochin estuary

Point-001

Element	Mass%	Compound	Mass%
C	4.33	C	4.33
O	36.81	-	-
Mg	1.73	MgO	2.87
Al	9.42	Al_2O_3	17.80
Si	17.00	SiO_2	36.36
Fe	10.16	FeO	13.06
Cu	16.92	CuO	21.18
In	3.64	InO_2	4.40
Total	100		100

Point-003

Element	Mass%	Compound	Mass%
C	3.85	C	3.85
O	45.54	-	-
Mg	0.93	MgO	1.54
Al	12.35	Al_2O_3	23.34
Si	28.14	SiO_2	60.20
K	9.19	K_2O	11.07
Total	100		100

Point-002

Element	Mass%	Compound	Mass%
C	3.64	C	3.64
O	41.86	-	-
Mg	1.17	MgO	1.93
Al	14.64	Al_2O_3	27.66
Si	20.78	SiO_2	44.46
K	2.08	K_2O	2.50
Fe	10.72	FeO	13.79
Tb	5.12	Tb_4O_7	6.02
Total	100		100

Point-004

Element	Mass%	Compound	Mass%
C	4.74	C	4.74
O	45.27	-	-
Mg	3.03	MgO	5.02
Al	16.02	Al_2O_3	30.26
Si	23.64	SiO_2	50.57
Fe	7.31	FeO	9.41
Total	100		100

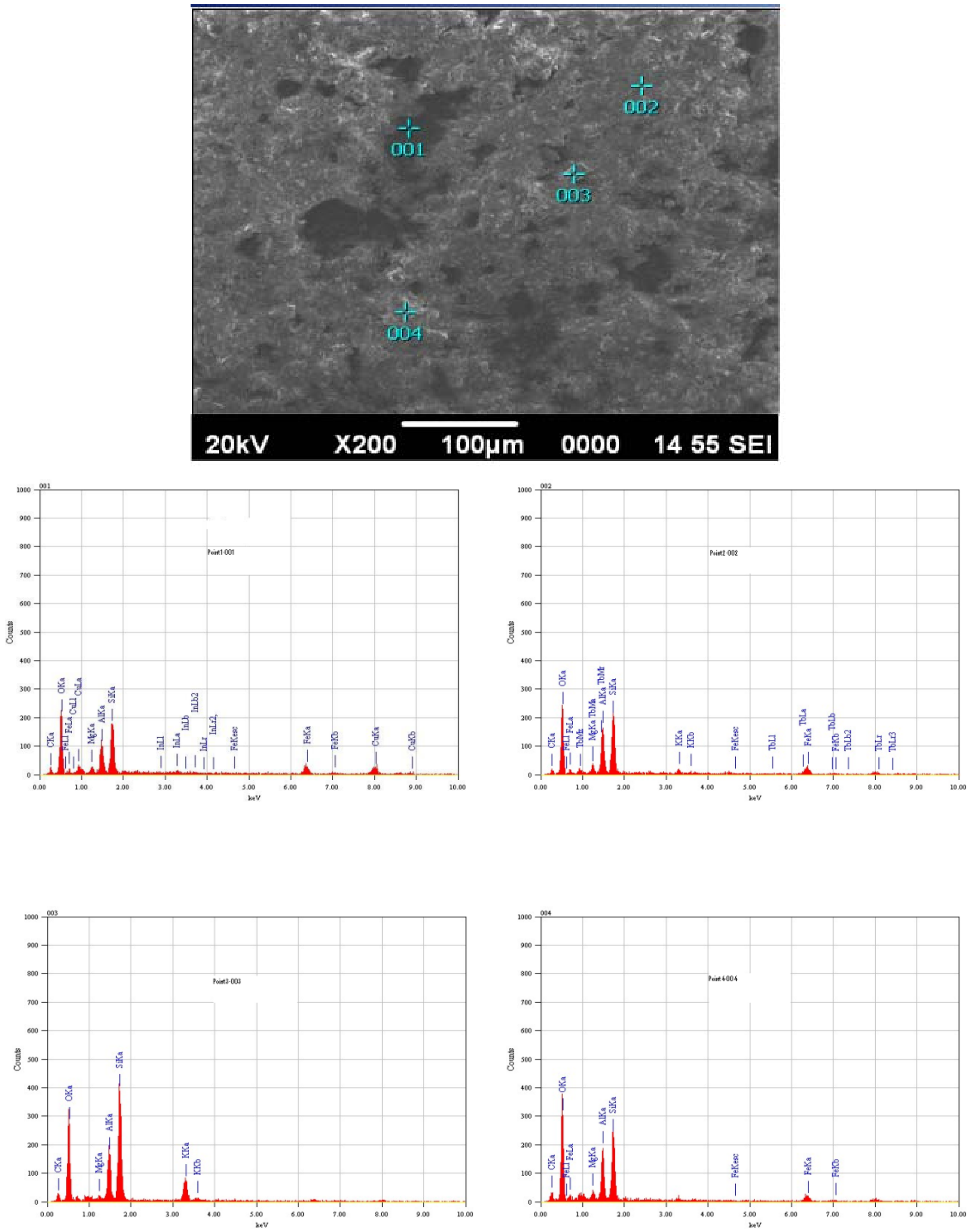

Fig. 4.4 EDS spectra of 4 spots selected from SEM image of brass for the month of Sep. 07

Table 4.2 Results of EDS of brass for Oct. 07 in Cochin estuary

Point-001

Element	Mass%	Compound	Mass%
O	48.84	-	-
Mg	3.39	MgO	5.62
Al	12.25	Al_2O_3	23.15
Si	29.95	SiO_2	64.07
Fe	5.57	FeO	7.16
Total	100		100

Point-003

Element	Mass%	Compound	Mass%
C	6.20	C	6.20
O	21.94	-	-
Mg	0.60	MgO	0.99
Al	1.86	Al_2O_3	3.52
Si	3.11	SiO_2	6.65
P	1.59	P_2O_5	3.65
Cl	3.64	Cl	3.64
Cu	52.51	CuO	65.73
Pd	2.04	PdO	2.35
Tl	6.50	Tl_2O_3	7.27
Total	100		100

Point-002

Element	Mass%	Compound	Mass%
C	7.44	C	7.44
O	29.07	-	-
Al	4.71	Al_2O_3	8.89
Si	9.71	SiO_2	20.78
Cl	2.51	Cl	2.51
Cu	38.13	CuO	47.73
Mo	8.43	MoO_3	12.65
Total	100		100

Point-004

Element	Mass%	Compound	Mass%
C	53.44	C	53.44
O	15.09	-	-
Al	2.02	Al_2O_3	3.82
Si	3.23	SiO_2	6.90
P	2.43	P_2O_5	5.58
Cl	2.32	Cl	2.32
Cu	17.16	CuO	21.49
Mo	4.30	MoO_3	6.46
Total	100		100

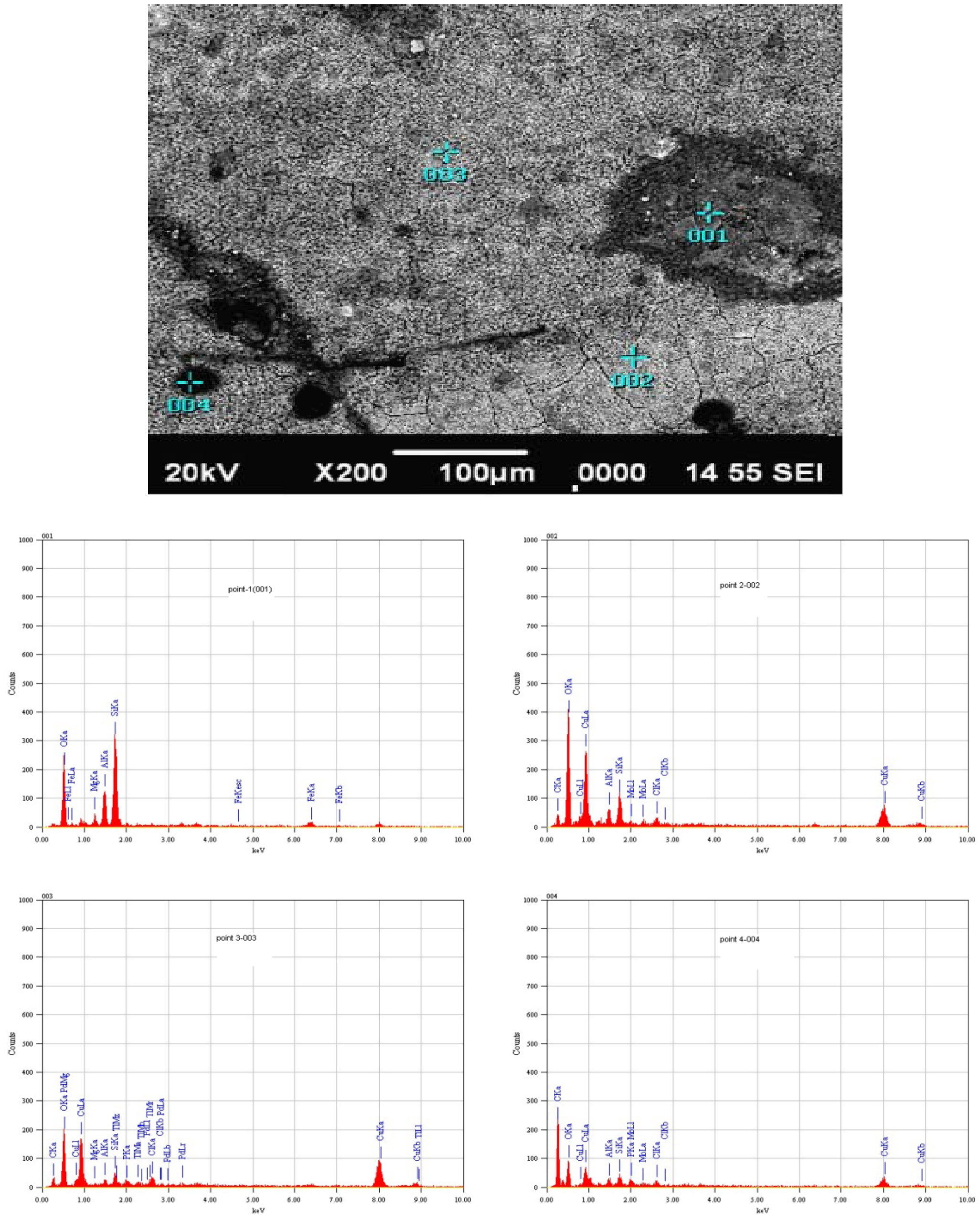

Fig. 4.5 EDS spectra of 4 spots selected from SEM image of brass for the month of Oct. 07

Table 4.3 Results of EDS of brass for Nov. 07 in Cochin estuary

Point-001

Element	Mass%	Compound	Mass%
O	42.35	-	-
Mg	4.42	MgO	7.33
Al	12.75	Al_2O_3	24.09
Si	18.58	SiO_2	39.74
K	4.84	K_2O	5.82
Ti	2.79	TiO_2	4.66
Fe	14.27	FeO	18.36
Total	100		100

Point-003

Element	Mass%	Compound	Mass%
C	10.78	C	10.78
O	31.14	-	-
Na	1.17	Na_2O	1.57
Mg	1.97	MgO	3.26
Si	14.95	SiO_2	31.98
Fe	4.14	FeO	5.32
Zn	26.28	ZnO	32.71
Mo	9.59	MoO_3	14.38
Total	100		100

Point-002

Element	Mass%	Compound	Mass%
O	15.11	-	-
Cl	24.40	Cl	24.40
Cu	44.06	CuO	55.15
Zn	16.43	ZnO	20.45
Total	100		100

Point-004

Element	Mass%	Compound	Mass%
C	3.70	C	3.70
O	25.65	-	-
Mg	1.52	MgO	2.53
Al	1.71	Al_2O_3	3.24
Si	4.21	SiO_2	9.01
P	1.71	P_2O_5	3.92
Fe	2.38	FeO	3.07
Cu	28.16	CuO	35.24
Zn	25.06	ZnO	31.19
Mo	2.72	MoO_3	4.09
Sn	3.16	SnO_2	4.02
Total	100		100

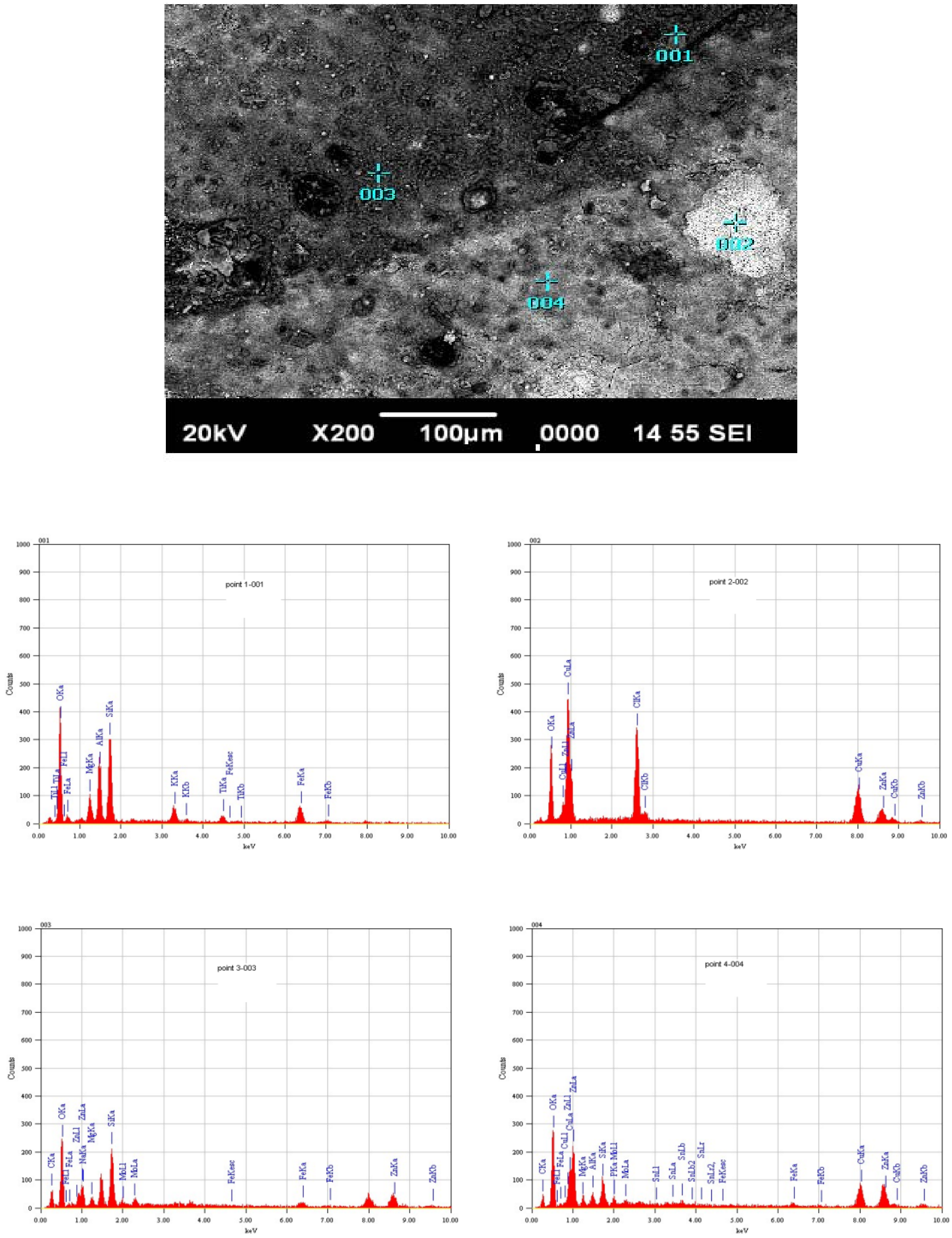

Fig. 4.6 EDS spectra of 4 spots selected from SEM image of brass for the month of Nov. 07

Table 4.4 Results of EDS of brass for Dec. 07 in Cochin estuary

Point-001

Element	Mass%	Compound	Mass%
O	18.51	-	-
P	0.81	P_2O_5	1.86
S	2.11	SO_3	5.27
Cl	14.82	Cl	14.82
Cu	25.09	CuO	31.41
Zn	27.04	ZnO	33.65
Tl	11.62	Tl_2O_3	12.98
Total	100		100

Point-003

Element	Mass%	Compound	Mass%
O	21.08	-	-
Na	1.54	Na_2O	2.07
Mg	0.60	MgO	1.00
Al	2.37	Al_2O_3	4.48
Si	4.07	SiO_2	8.72
Cl	16.96	Cl	16.96
Fe	3.31	FeO	4.26
Cu	40.10	CuO	50.20
Mo	3.49	MoO_3	5.23
Rb	6.47	Rb_2O	7.08
Total	100		100

Point-002

Element	Mass%	Compound	Mass%
O	35.08	-	-
Na	14.46	Na_2O	19.49
S	5.23	SO_3	13.06
Cu	1.64	CuO	2.06
Mo	43.59	MoO_3	65.39
Total	100		100

Point-004

Element	Mass%	Compound	Mass%
O	35.42	-	-
Mg	1.74	MgO	2.88
Al	8.36	Al_2O_3	15.80
Si	14.61	SiO_2	31.27
S	1.36	SO_3	3.40
Cl	5.82	Cl	5.82
Fe	4.64	FeO	5.97
Cu	17.68	CuO	22.13
Zn	5.52	ZnO	6.87
In	4.85	In_2O_3	5.87
Total	100		100

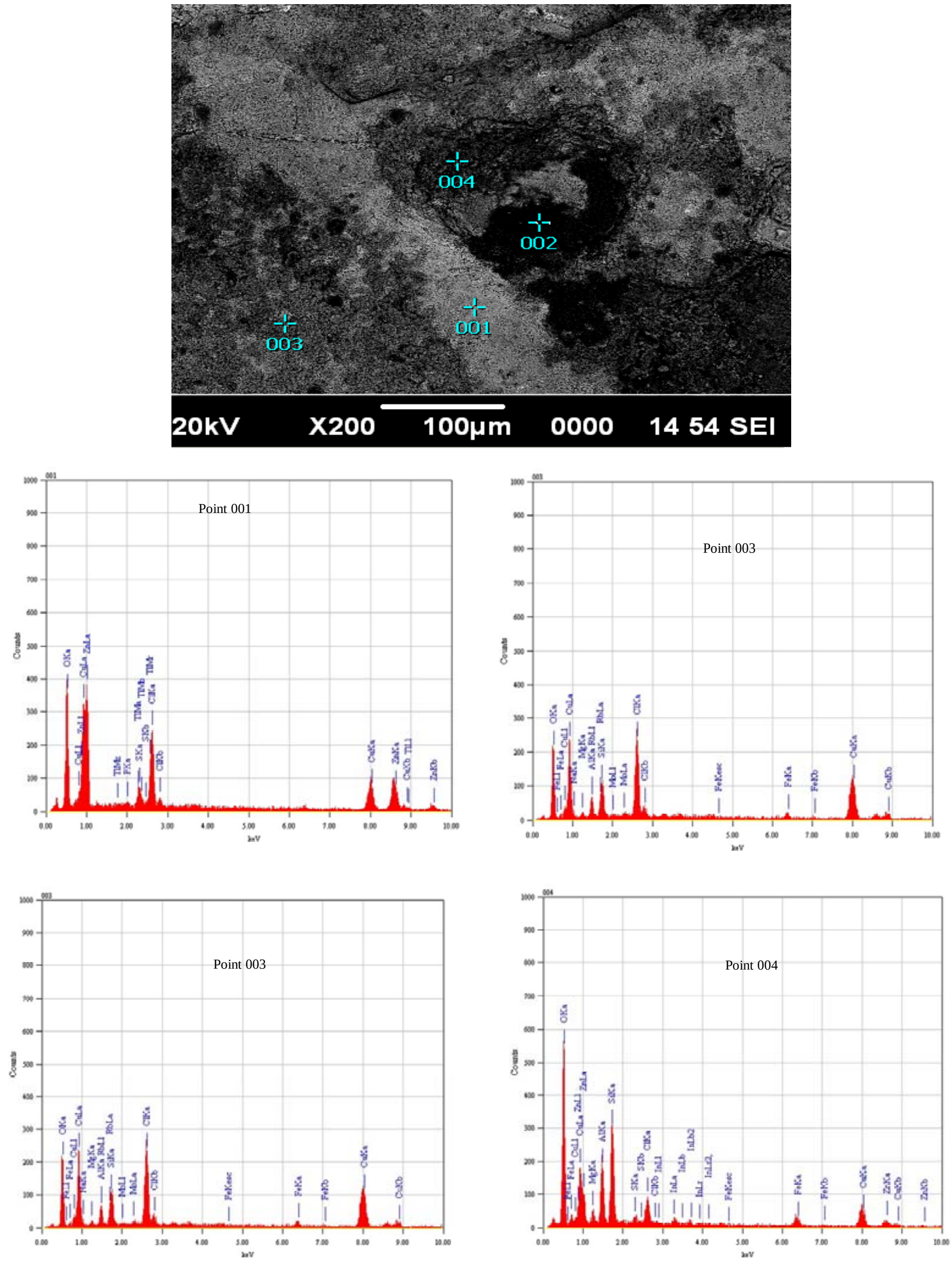

Fig. 4.7 EDS spectra of 4 spots selected from SEM image of brass for the month of Dec. 07

Table 4.5 Results of EDS of brass of Jan. 08 in Cochin estuary

Point-001

Element	Mass%	Compound	Mass%
C	2.97	C	2.97
O	43.12	-	-
Na	1.31	Na_2O	1.76
Mg	3.93	MgO	6.52
Al	7.29	Al_2O_3	13.78
Si	24.91	SiO_2	53.29
K	5.25	K_2O	6.33
Fe	8.80	FeO	11.32
Ti	2.42	TiO_3	4.03
Total	100	100.00	100

Point-002

Element	Mass%	Compound	Mass%
O	15.43	-	-
Cl	21.64	Cl	21.64
Cu	4.29	CuO	5.37
Zn	58.63	ZnO	72.99
Total	100		100

Point-003

Element	Mass%	Compound	Mass%
C	3.24	C	3.24
O	38.99	-	-
Mg	3.46	MgO	5.74
Al	9.36	Al_2O_3	17.69
Si	17.23	SiO_2	36.87
K	1.36	K_2O	1.64
Ca	2.90	CaO	4.06
Fe	4.76	FeO	6.12
Cu	10.27	CuO	12.86
Zn	3.30	ZnO	4.10
Mo	5.12	MoO_3	7.68
Total	100		100

Point-004

Element	Mass%	Compound	Mass%
C	2.22	C	2.22
O	23.66	-	-
Si	0.75	SiO_2	1.60
S	2.06	SO_3	5.15
Cl	3.79	Cl	3.79
Cu	14.60	CuO	18.28
Zn	36.34	ZnO	45.24
Mo	13.58	MoO_3	20.38
Tl	3.00	Tl_2O_3	3.35
Total	100		100

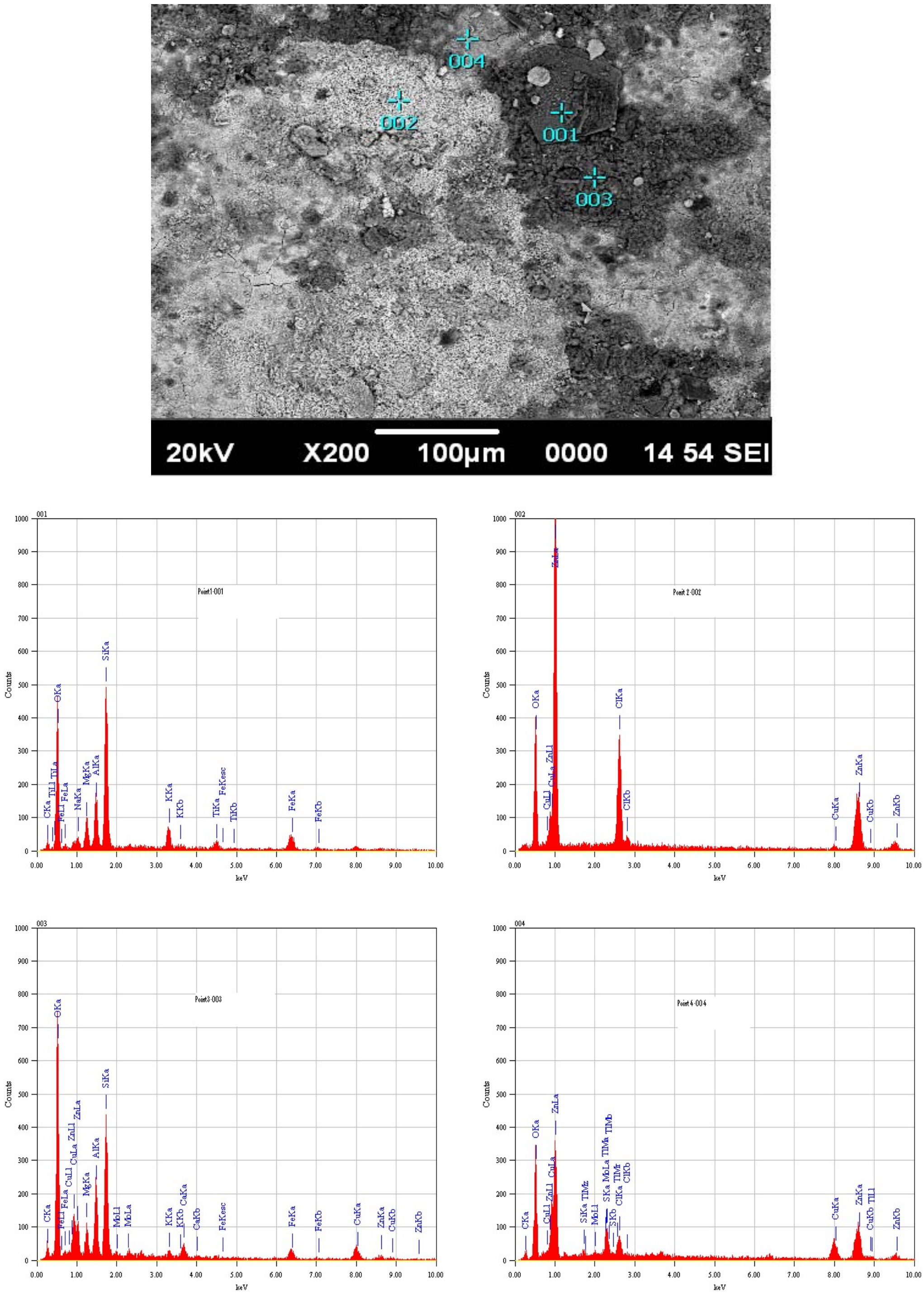

Fig. 4.8 EDS spectra of 4 spots selected from SEM image of brass for the month of Jan. 08

Table 4.6 Results of EDS of brass for Feb. 08 in Cochin estuary

Point-001

Element	Mass%	Compound	Mass%
C	5.28	C	5.28
O	44.92	-	-
Na	1.22	Na_2O	1.64
Mg	2.22	MgO	3.68
Al	9.19	Al_2O_3	17.37
Si	28.67	SiO_2	61.34
K	1.72	K_2O	2.07
Fe	4.14	FeO	5.33
Cu	2.63	CuO	3.29
Total	100		100

Point-003

Element	Mass%	Compound	Mass%
C	4.04	C	4.04
O	45.75	-	-
Mg	15.05	MgO	24.95
Al	2.65	Al_2O_3	5.01
Si	28.46	SiO_2	60.88
Fe	1.45	FeO	1.86
Cu	1.91	CuO	2.40
Zn	0.69	ZnO	0.86
Total	100		100

Point-002

Element	Mass%	Compound	Mass%
O	16.77	-	-
Na	-	-	-
Si	1.81	SiO_2	3.88
Cl	16.82	Cl	16.82
Fe	3.02	FeO	3.88
Cu	12.36	CuO	15.47
Zn	38.89	ZnO	48.40
Tl	10.33	Tl_2O_3	11.55
Total	100		100

Point-004

Element	Mass%	Compound	Mass%
C	5.43	C	5.43
O	31.15	-	-
Mg	1.72	MgO	2.85
Al	5.30	Al_2O_3	10.02
Si	8.93	SiO_2	19.11
P	1.57	P_2O_5	3.59
Cl	1.93	Cl	1.93
Fe	4.61	FeO	
Cu	15.78	CuO	19.76
Zn	15.62	ZnO	19.44
Mo	7.94	MoO_3	11.91
Total	100		100

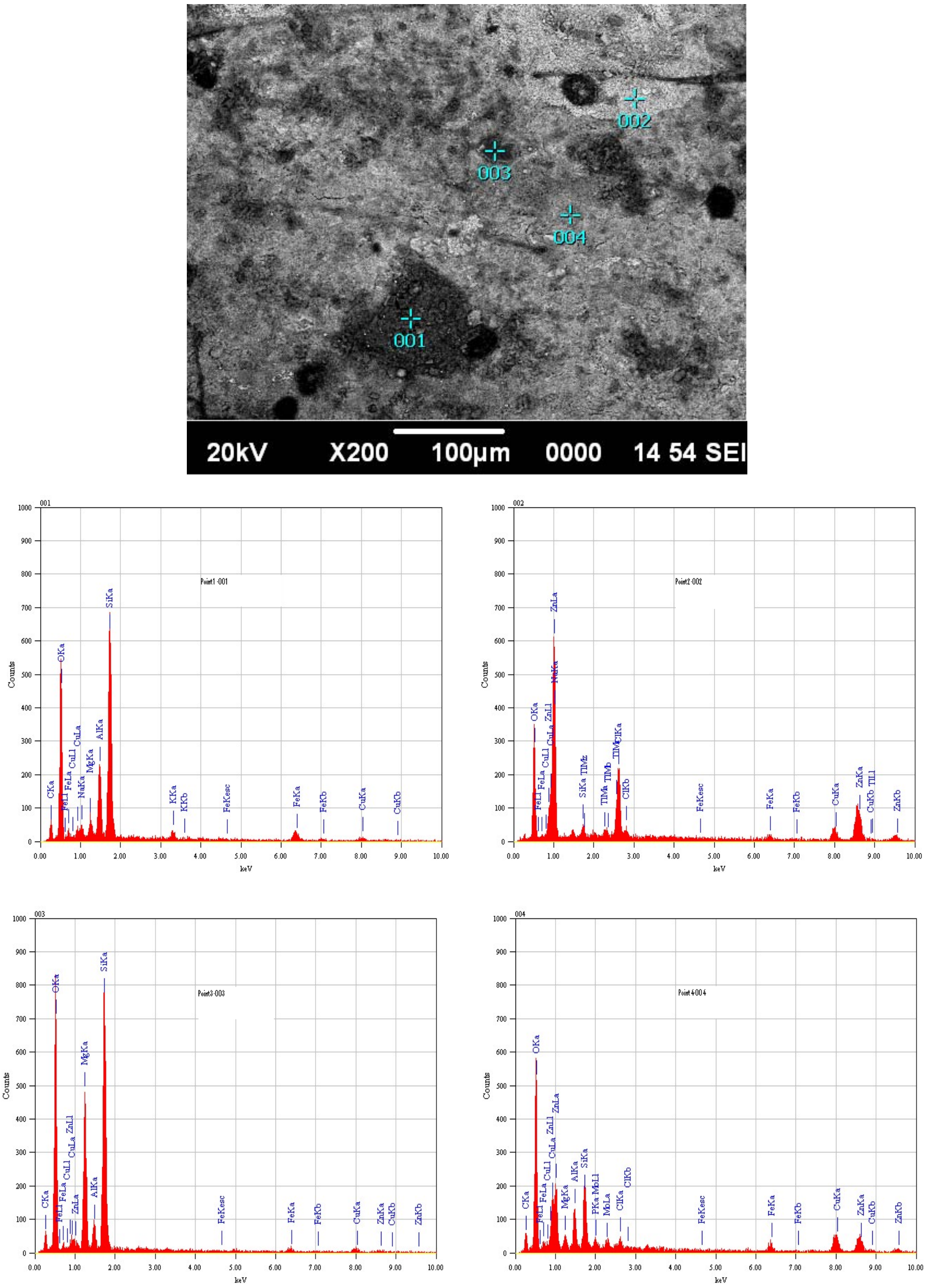

Fig. 4.9 EDS spectra of 4 spots selected from SEM image of brass for the month of Feb. 08

Table 4.7 Results of EDS of brass for Mar. 08 in Cochin estuary

Point-001

Element	Mass%	Compound	Mass%
O	43.67	-	-
Mg	3.03	MgO	5.02
Al	11.74	Al_2O_3	22.18
Si	23.42	SiO_2	50.10
K	3.86	K_2O	4.65
Fe	5.29	FeO	6.80
Cu	7.16	CuO	8.96
Zn	1.84	ZnO	2.29
Total	100		100

Point-003

Element	Mass%	Compound	Mass%
O	27.30	-	-
Mg	1.46	MgO	2.43
Al	4.73	Al_2O_3	8.93
Si	9.29	SiO_2	19.88
Cl	11.68	Cl	11.68
Fe	3.72	FeO	4.78
Cu	35.52	CuO	44.46
Zn	6.30	ZnO	7.84
Total	100		100

Point-002

Element	Mass%	Compound	Mass%
O	15.07	-	-
Cl	23.52	Cl	23.52
Cu	6.72	CuO	8.41
Zn	54.68	ZnO	68.07
Total	100		100

Point-004

Element	Mass%	Compound	Mass%
O	26.53	-	-
Al	1.30	Al_2O_3	2.46
Si	5.81	SiO_2	12.43
S	3.37	SO_3	8.42
Cl	7.21	Cl	7.21
Cu	7.38	CuO	9.24
Zn	48.40	ZnO	60.25
Total	100		100

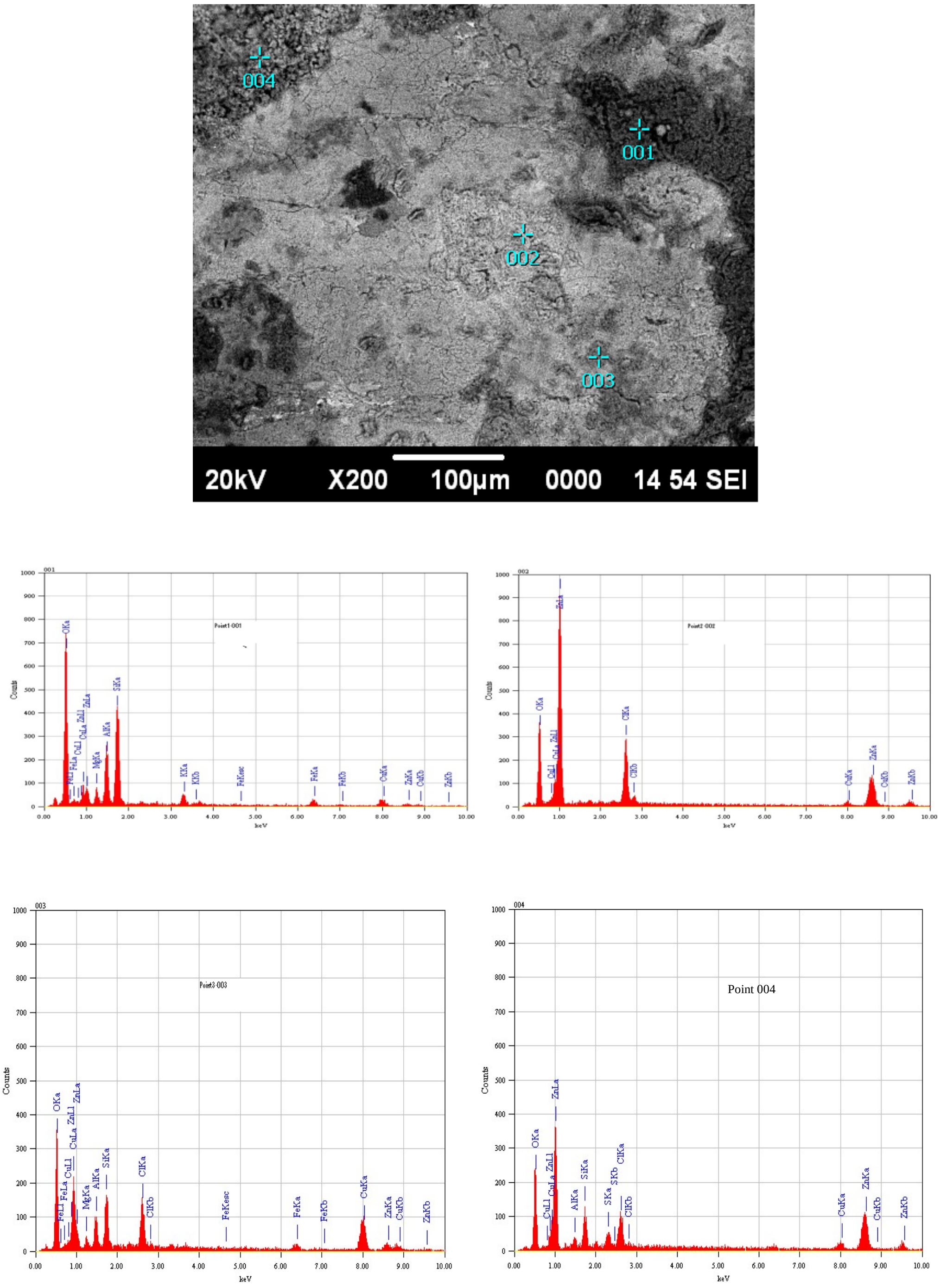

Fig. 4.10 EDS spectra of 4 spots selected from SEM image of brass for the month of Mar. 08

Table 4.8 Results of EDS of brass for Apr. 08 in Cochin estuary

Point-001

Element	Mass%	Compound	Mass%
O	19.56	-	-
Al	1.79	Al_2O_3	3.38
Si	3.36	SiO_2	7.19
Cl	18.32	Cl	18.32
Fe	3.28	FeO	4.22
Cu	8.66	CuO	10.84
Zn	45.02	ZnO	56.04
Total	100		100

Point-003

Element	Mass%	Compound	Mass%
O	24.48	-	-
Mg	1.50	MgO	2.50
Al	2.10	Al_2O_3	3.97
Si	3.13	SiO_2	6.71
P	1.57	P_2O_5	3.60
Cl	5.61	Cl	5.61
Ca	1.00	CaO	1.39
Fe	11.78	FeO	15.15
Cu	42.97	CuO	53.79
Zn	5.86	ZnO	7.29
Total	100		100

Point-002

Element	Mass%	Compound	Mass%
O	15.46	-	-
Cl	21.46	Cl	21.46
Cu	3.57	CuO	4.47
Zn	59.50	ZnO	74.06
Total	100		100

Point-004

Element	Mass%	Compound	Mass%
C	7.96	C	7.96
O	37.84	-	-
Al	8.71	Al_2O_3	16.46
Si	21.42	SiO_2	45.83
Cl	2.02	Cl	2.02
K	1.45	K_2O	1.74
Fe	5.99	FeO	7.70
Cu	13.50	CuO	16.90
Zn	1.11	ZnO	1.38
Total	100		100

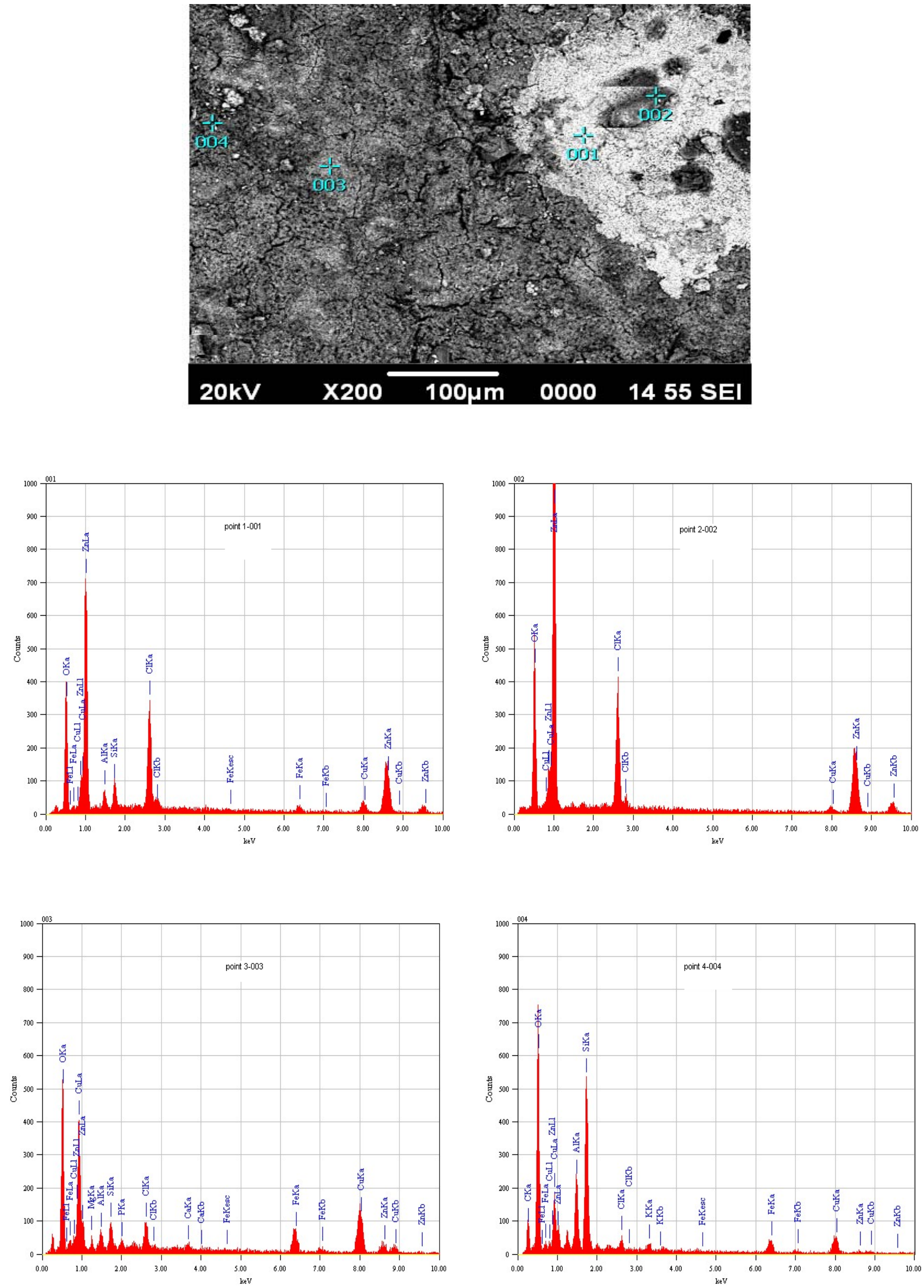

Fig. 4.11 EDS spectra of 4 spots selected from SEM image of brass for the month of Apr. 08

Table 4.9 Results of EDS of brass for May 08 in Cochin estuary

Point-001

Element	Mass%	Compound	Mass%
O	30.13	-	-
Mg	1.58	MgO	2.63
Al	5.17	Al_2O_3	9.77
Si	8.47	SiO_2	18.11
P	1.79	P_2O_5	4.11
S	1.18	SO_3	2.94
Cl	9.11	Cl	9.11
Fe	3.44	FeO	4.43
Cu	29.25	CuO	36.62
Zn	9.87	ZnO	12.28
Total	100		100

Point-003

Element	**Mass%**	**Compound**	**Mass%**
O	44.60	-	-
Al	9.67	Al_2O_3	18.27
Si	28.51	SiO_2	61.00
Cl	1.29	Cl	1.29
K	10.99	K_2O	13.24
Fe	0.84	FeO	1.08
Cu	4.09	CuO	5.12
Total	100		100

Point-002

Element	**Mass%**	**Compound**	**Mass%**
O	22.13	-	-
Si	1.79	SiO_2	3.82
P	1.98	P_2O_5	4.54
Cl	9.97	Cl	9.97
Fe	3.16	FeO	4.06
Cu	42.76	CuO	53.52
Zn	8.30	ZnO	10.33
Mo	5.04	MoO_3	7.56
Sn L	30.13	SnO_2	6.20
Total	100		100

Point-004

Element	**Mass%**	**Compound**	**Mass%**
O	39.78	-	-
Mg	7.48	MgO	12.40
Al	9.10	Al_2O_3	17.19
Si	17.14	SiO_2	36.67
K	3.89	K_2O	4.69
Fe	16.43	FeO	21.14
Ba	4.35	BaO	4.85
TiK	1.84	TiO_2	3.07
Total	100		100

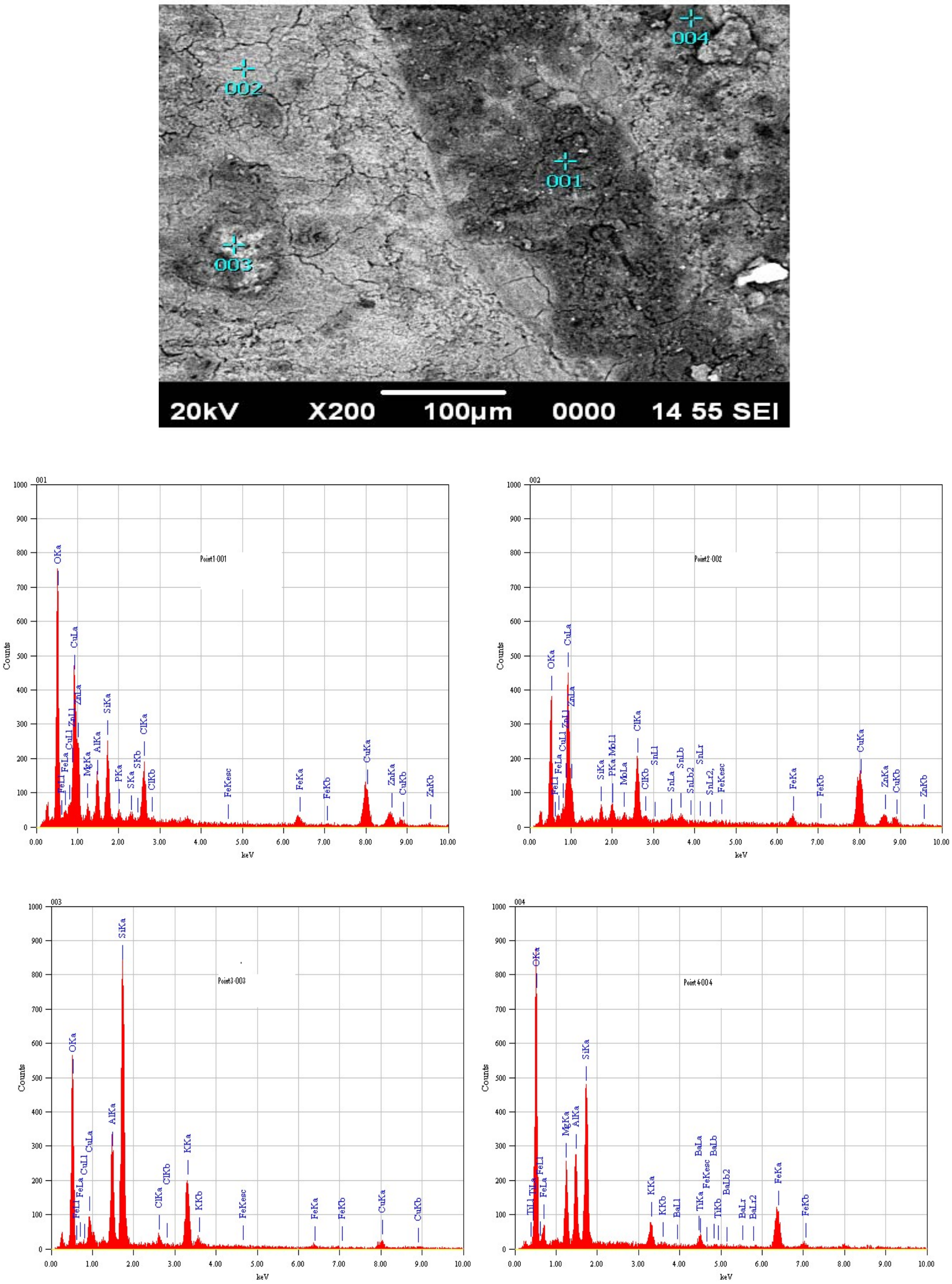

Fig. 4.12 EDS spectra of 4 spots selected from SEM image of brass for month of May 08

Table 4.10 Results of EDS of brass for Jun. 08 in Cochin estuary

Point-001

Element	Mass%	Compound	Mass%
O	21.14	-	-
Al	0.65	Al_2O_3	1.22
Si	1.01	SiO_2	2.17
Cu	73.59	CuO	92.12
Zn	3.61	ZnO	4.49
Total	100		100

Point-003

Element	Mass%	Compound	Mass%
C	4.14	C	4.14
O	22.68	-	-
Mg	0.94	MgO	1.56
Al	1.08	Al_2O_3	2.04
Si	1.72	SiO_2	3.68
P	2.21	P_2O_5	5.06
Cl	6.43	Cl	6.43
Fe	3.23	FeO	4.15
Cu	41.20	CuO	51.58
Zn	7.49	ZnO	9.32
Mo	3.30	MoO_3	4.95
Sn	5.58	SnO_2	7.09
Total	100		100

Point-002

Element	Mass%	Compound	Mass%
C	24.62	C	24.62
O	21.46	-	-
Na	1.21	Na_2O	1.62
Ca	52.71	CaO	73.75
Total	100		100

Point-004

Element	Mass%	Compound	Mass%
O	40.71	-	-
Na	0.88	Na_2O	1.18
Mg	3.57	MgO	5.92
Al	5.40	Al_2O_3	10.20
Si	21.21	SiO_2	45.37
Ca	9.90	CaO	13.85
Fe	15.18	FeO	19.53
Cu	2.59	CuO	3.24
Zn	0.57	ZnO	0.71
Total	100		100

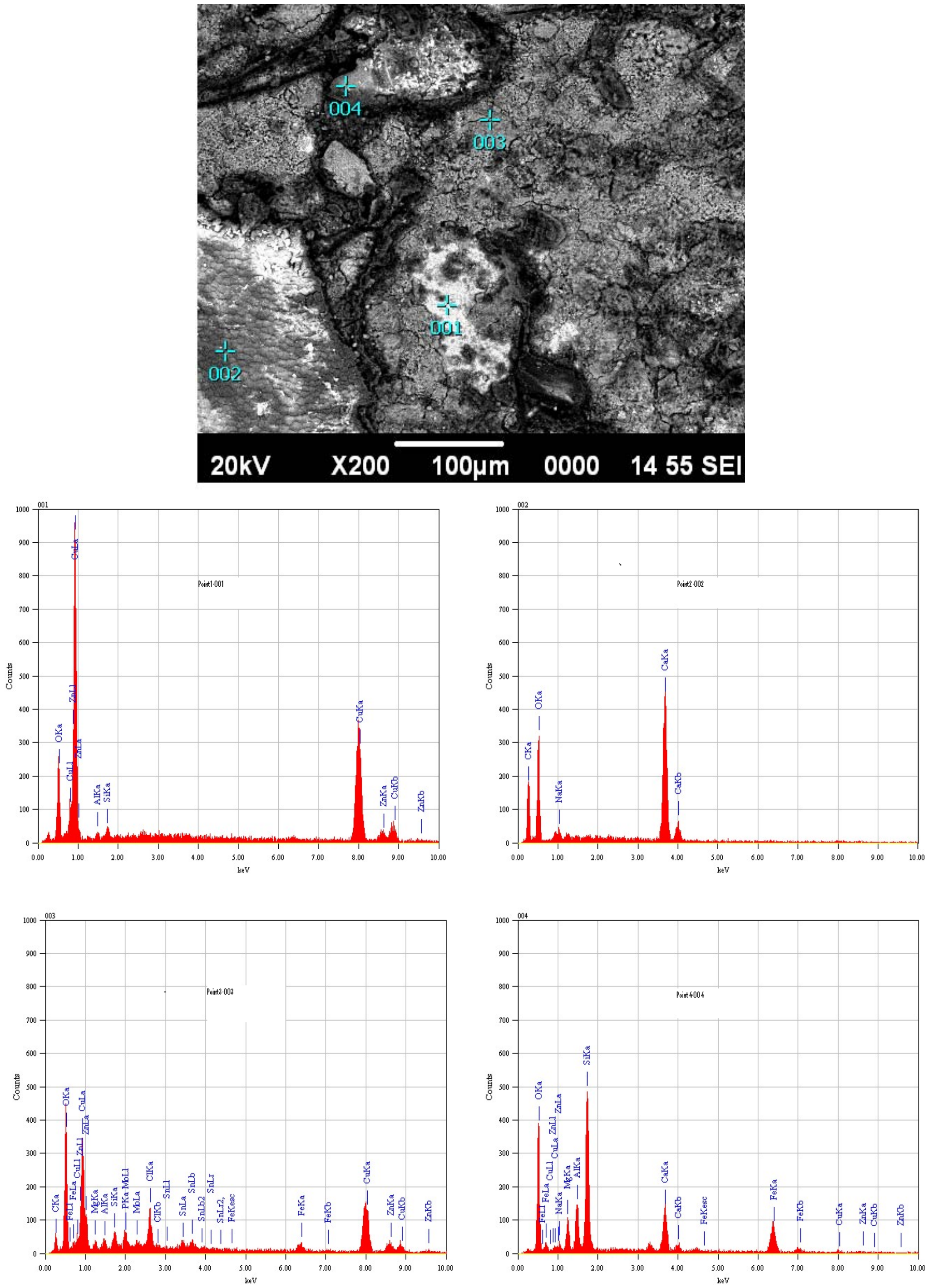

Fig. 4.13 EDS spectra of 4 spots selected from SEM image of brass for the month of Jun. 08

Table 4.11 Results of EDS of brass for Jul. 08 in Cochin estuary

Point-001

Element	Mass%	Compound	Mass%
O	44.43	-	-
Na	1.05	Na_2O	1.41
Mg	2.39	MgO	3.97
Al	10.90	Al_2O_3	20.59
Si	25.46	SiO_2	54.46
Cl	1.14	Cl	1.14
K	1.05	K_2O	1.27
Fe	5.16	FeO	6.64
Cu	5.35	CuO	6.70
Zn	3.07	ZnO	3.82
Total	100		100.00

Point-003

Element	Mass%	Compound	Mass%
C	2.48	-	2.48
O	19.55	-	-
Si	0.96	SiO_2	2.05
Cl	4.03	Cl	4.03
Ca	0.82	CaO	1.15
Cu	66.31	CuO	83.00
Zn	5.87	ZnO	7.30
Total	100		100

Point-002

Element	Mass%	Compound	Mass%
O	53.26	-	-
Si	46.74	SiO_2	100.00
Total	100		100.00

Point-004

Element	Mass%	Compound	Mass%
O	21.03	-	-
Si	1.06	SiO_2	2.28
Cl	4.01	Cl	4.01
Ca	1.10	CaO	1.53
Fe	2.21	FeO	2.84
Cu	61.90	CuO	77.49
Zn	4.63	ZnO	5.76
Mo	4.05	MoO_3	6.08
Total	100		100

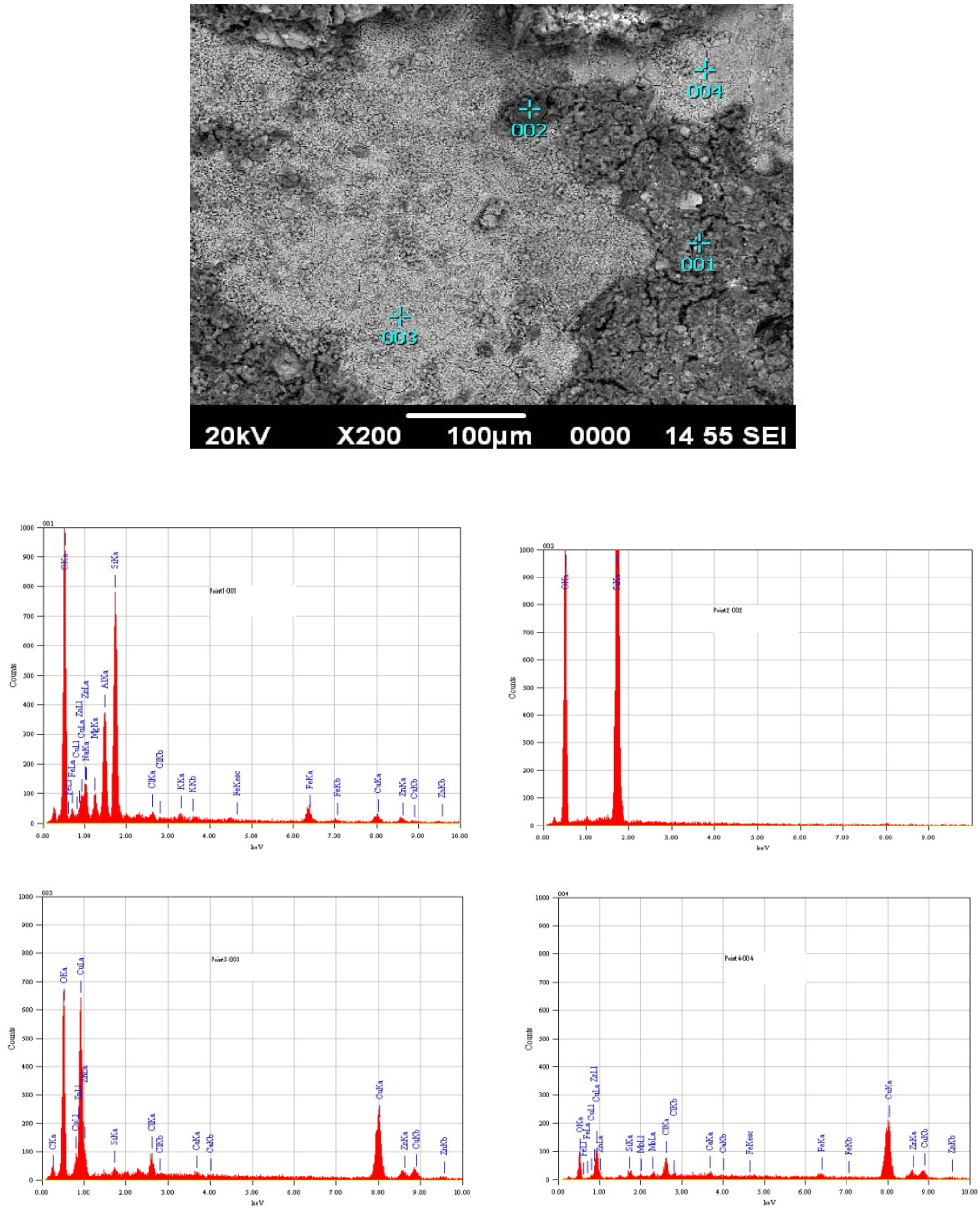

Fig. 4.14 EDS spectra of 4 spots selected from SEM image of brass for the month of Jul. 08

Table 4.12 Results of EDS of brass for Aug. 08 in Cochin estuary

Point-001

Element	Mass%	Compound	Mass%
C	1.42	C	1.42
O	19.82	-	-
Cu	77.83	CuO	97.43
Zn	0.93	ZnO	1.16
Total	100		100

Point-003

Element	Mass%	Compound	Mass%
C	3.15	C	3.15
O	21.93	-	-
Si	1.15	SiO_2	2.46
P	1.35	P_2O_5	3.10
S	1.52	SO_3	3.79
Cl	6.57	Cl	6.57
Fe	2.26	FeO	2.91
Cu	38.05	CuO	47.62
Zn	10.20	ZnO	12.69
Mo	4.34	MoO_3	6.52
Sn	3.92	SnO_2	4.97
Tl	5.56	Tl_2O_3	6.21
Total	100		100

Point-002

Element	Mass%	Compound	Mass%
C	1.73	C	1.73
O	46.70	-	-
Na	3.97	Na_2O	5.35
Al	12.69	Al_2O_3	23.98
Si	27.94	SiO_2	59.77
Ca	2.79	CaO	3.90
Fe	1.25	FeO	1.61
Cu	2.93	CuO	3.67
Total	100		100

Point-004

Element	Mass%	Compound	Mass%
O	24.38	-	-
Si	2.18	SiO_2	4.67
P	3.11	P_2O_5	7.13
S	0.74	SO_3	1.86
Cl	3.15	Cl	3.15
Fe	2.33	FeO	2.99
Cu	41.93	CuO	52.49
Zn	17.70	ZnO	22.03
Sn	4.48	SnO_2	5.68
Total	100		100

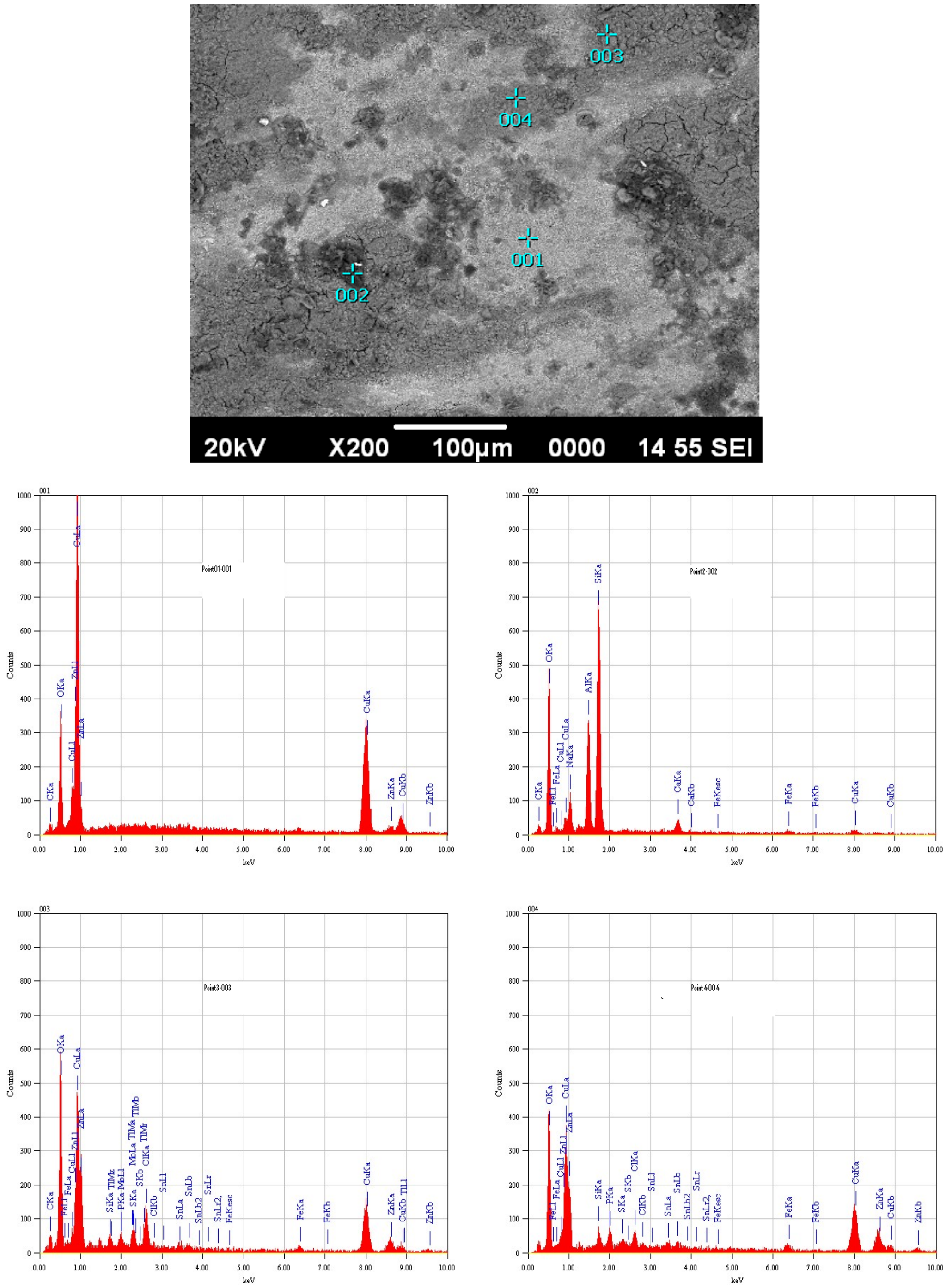

Fig. 4.15 EDS spectra of 4 spots selected from SEM image of brass for the month of Aug. 08

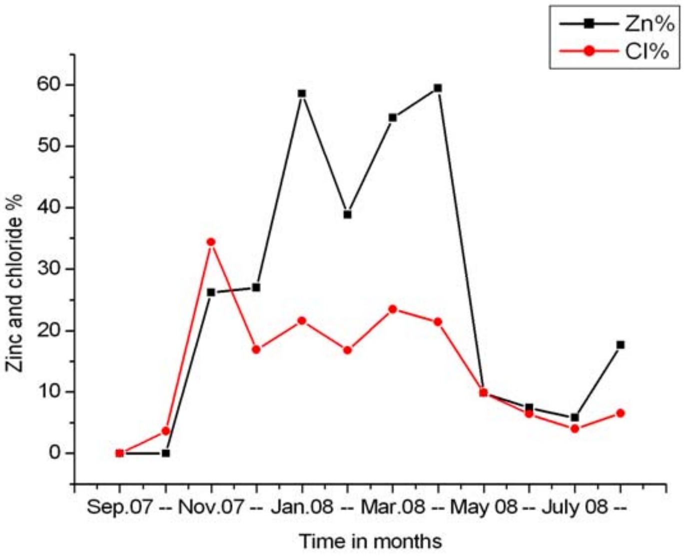

Fig. 4.16 Percentages of zinc and chloride Vs time

EDS data reveals that dezincification has not occurred in first two months as there is no zinc content in these months. Dezincification initiated from Nov. 07 and has continued till Aug. 08. The results are in tune with dezincification factor Z_f of respective exposure and extent of loss of mechanical properties of brass. Chloride ions promote the dissolution of brass and hence increase the rate of dissolution the brass. It is perceived from the Fig. 4.16 that the chloride ion value above 3.64 % is sufficient for dezincification of brass and the percentage of zinc increases up to Apr. 08 with minor variation in between. Then the reduction of zinc % after Apr. 08 to Jul. 08 with slight increase for Aug. 08 is observed as increase of rain fall neutralize the effect chloride ions in these months. Since chloride ions form strong complexes with Cu ions and weakest complexes with Zn ions, chloride ions affect the equilibrium potentials and hence it tends to cause dissolution of the Cu and Zn components of brass.

The presence of sulphide ions leads to modification of the oxide layer on copper based alloys. Acceleration of corrosion is due to enhancement of the cathodic process (Kota et al., 1984). Sulphides are present in polluted seawater and can also occur under stagnant conditions due to decomposition of organic matter. The localized pitting can occur in the presence of sulphides (Parvizi, 1988). Eiselstein et al. (1983) indicated that corrosion films formed in sulphide-free environment offered some protection against accelerated attack than samples exposed to aerated polluted water. The presence of Fe^{2+} can reduce the extent of sulphide-induced corrosion when exposed to polluted conditions (North et al., 1968).

The SEM images at lower magnification show a porous layer indicating the selective dissolution of zinc leaving almost pure copper (Santos et al., 2006). Satendra Kumar et al. (2006) indicated that the presence of sulphide ions in 3.4% NaCl cause a significant increase in the extent of corrosion attack on brass. The porous nature of the Cu_2S film and the catalyzing ability of the sulphide ions are responsible for the increased corrosion attack.

Eiselstein and Syrett (1983) reported that the cuprous oxide was the dominant product in all the materials. However cuprous sulphide was also observed on the surface layer, indicating that the outer layer was highly attacked by the sulphide ions in polluted seawater. It was porous, thick, and scaly adherent where as the inner layer was thin and it was mainly contain Cu_2O. The results of study concluded by Syrett (1981) stated that the surface of the copper and admiralty were attached with small size barnacle which could be due to the precipitation of copper salts, adsorption of organic film, adherence of biological materials and formation of sulphur compound. Further the corrosion product layer formed over brass panel was not uniform.

SEM images of bronze sample exposure in non-buffered synthetic seawater show significant difference in morphology: a uniformly cracked surface and a surface with large and spherical precipitates. After the removal of corrosion products, decuprication process was well visible and size and intensity of pits were high on brass exposed to non-buffered synthetic seawater (Dos Santos et al., 2007). Brenda Little et al. (1989) found that the exposure of Cu-Ni welded alloy to fresh aerated estuarine water resulted in the rapid spalling of surface deposits rendering these surfaces anodic to the sulphate coated area. When sulfide-polluted deareated seawater is replaced by unpolluted aerated seawater, the cathodic reaction rate also increase thereby the corrosion rate increases sharply. Cu^+ ions diffusion through the porous sulphide scale combine with dissolved oxygen to produce Cu_2O and the sulfide scale itself is slowly transformed to the oxide or elemental sulfur. The transformation of sulfide to oxide results in a change in volume that weakens the bond between the thick black scale and the oxide type subscale and leads to spalling and uncovered area repassivates forming cuprous oxide (Syrett et al., 1980). Copper alloys suffer accelerated corrosion when they are exposed to seawater polluted with sulphides. Several surveys and reports (Chattopadhyay, 1973; North, 1970) show the adverse effect of dissolved sulphides on copper alloy tubing and piping in service situations. The principal sources of sulphides in seawater are the actions of sulphate reducing bacteria under anoxic (oxygen free) conditions on the natural sulphate content of the seawater and decay of organic sulphur compounds (proteins, etc.) from sanitary or industrial sewage (Blundy, 1972).

In the seabed sediment, serious local corrosion occur mainly because of the oxygen concentration cell between the steel specimens (Kazuaki, 1968). The steel plates were acted as cathode where oxygen could diffuse into them while oxygen could not easily diffuse to the bottom of the seabed sediment and hence the steel plates became anodes which accelerate corrosion (Kazuaki Zen, 1968). The steel plates were best protected at the estuarine water/seabed sediment interface, where the corrosion was almost similar in the case of individually hanging steel plates (Yantao, 1999). Components such as CO_2, H_2S, NH_3, organic and inorganic acids present in seawater as results of higher biological activity in coastal waters may also accelerate localized corrosion (Pope, 1984)

The presence of CO_2 in aqueous solution may increase the solubility of corrosion products which usually form on the copper-base alloys so that they do not have opportunity to stifle the corrosive action and the corrosiveness of natural fresh water depends on concentration of mineral matter, gases, organic matter, sand and debris (Bulow, 1947). Xuejun Xie et al. (2007) found that sulphide in water accelerate the corrosion of copper alloys.

4.3 Surface compound analysis

X-ray powder pattern of the corrosion products formed on brass at each exposure months in Cochin estuarine water is shown in Figs. 4.17 - 4.19. Various types of compounds are found on brass with different months. The corrosion products on brass surface are characterized by the presence of copper oxide in Sep. 07 and Oct. 07, while copper oxide, copper sulfide and Cu-Zn are found in Nov. 07.

The corroded brass surface indicates the presence of silicon oxide, copper sulfide, copper oxide and Cu-Zn in Dec. 07 while zinc silicate hydroxy hydrate, zinc oxide and Cu-Zn are noticed in Jan. 08 month. Again copper oxide is reformed on brass for Feb. 08 whereas molybdenum sulfide, copper zinc chloride hydroxide and copper oxide are detected in Mar. 08. Silicon oxide, iron sulfide, copper oxide are found on surface of corroded brass in Apr. 08 but silicon oxide, copper oxide are noticed in May. 08. The presence of silicon oxide, iron oxide and copper oxide are identified in Jun. 08. The corrosion products comprising of silicon oxide, copper oxide are observed in Jul-08 while copper sulfide, copper hydroxide phosphate, copper chloride, and copper oxide are seen in Aug. 08.

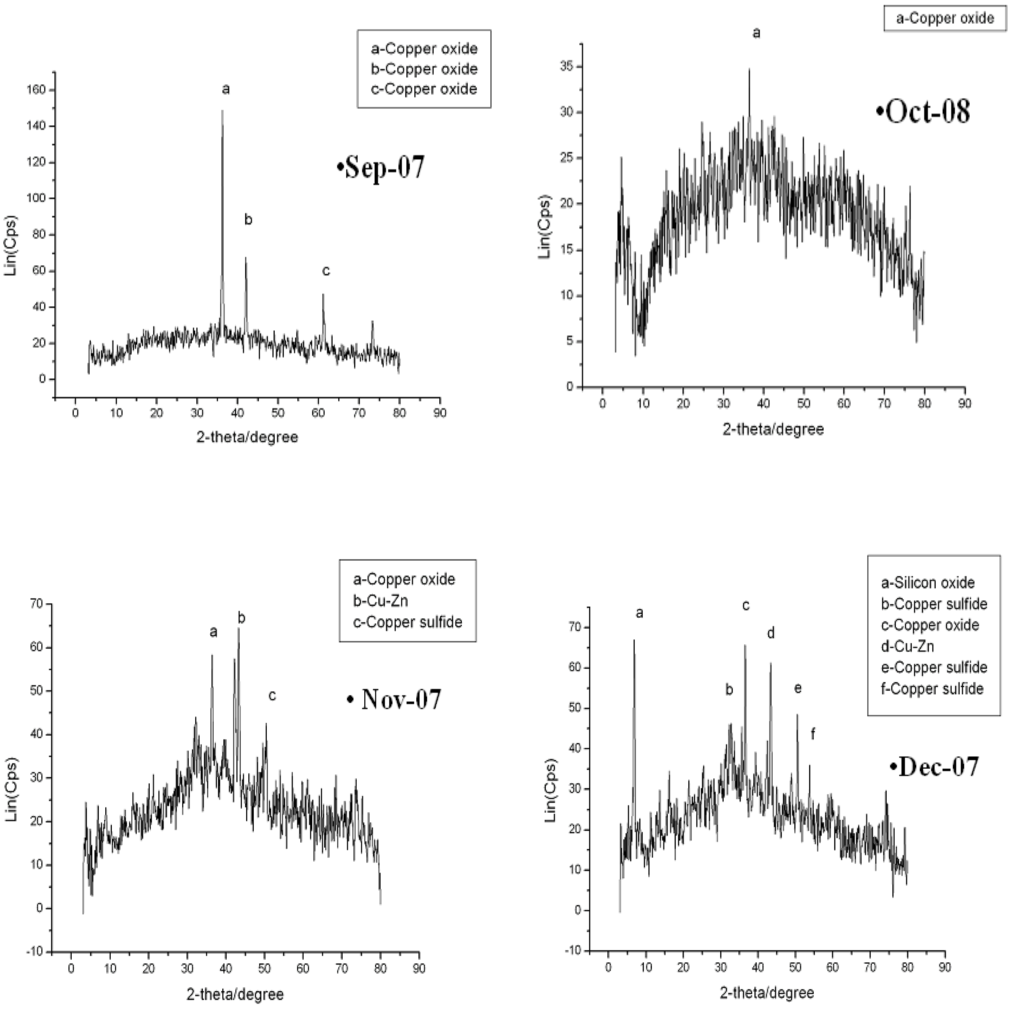

Fig. 4.17 X-ray pattern of the corrosion products on brass exposed to Cochin estuarine water over Sep. 07, Oct. 07, Nov. 07 and Dec. 07 months.

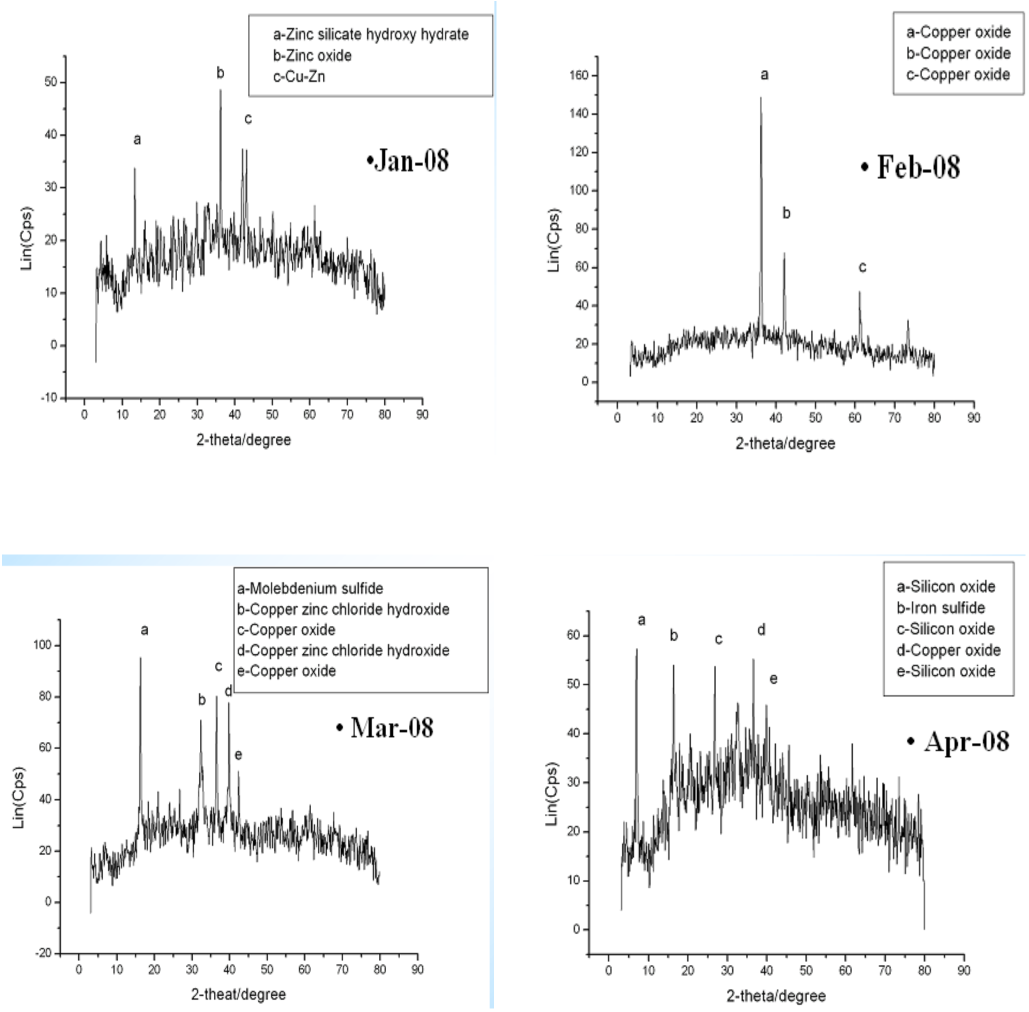

Fig. 4.18 X-ray pattern of the corrosion products on brass exposed to Cochin estuarine water over Jan. 08, Feb. 08, Mar. 08 and Apr. 08 months.

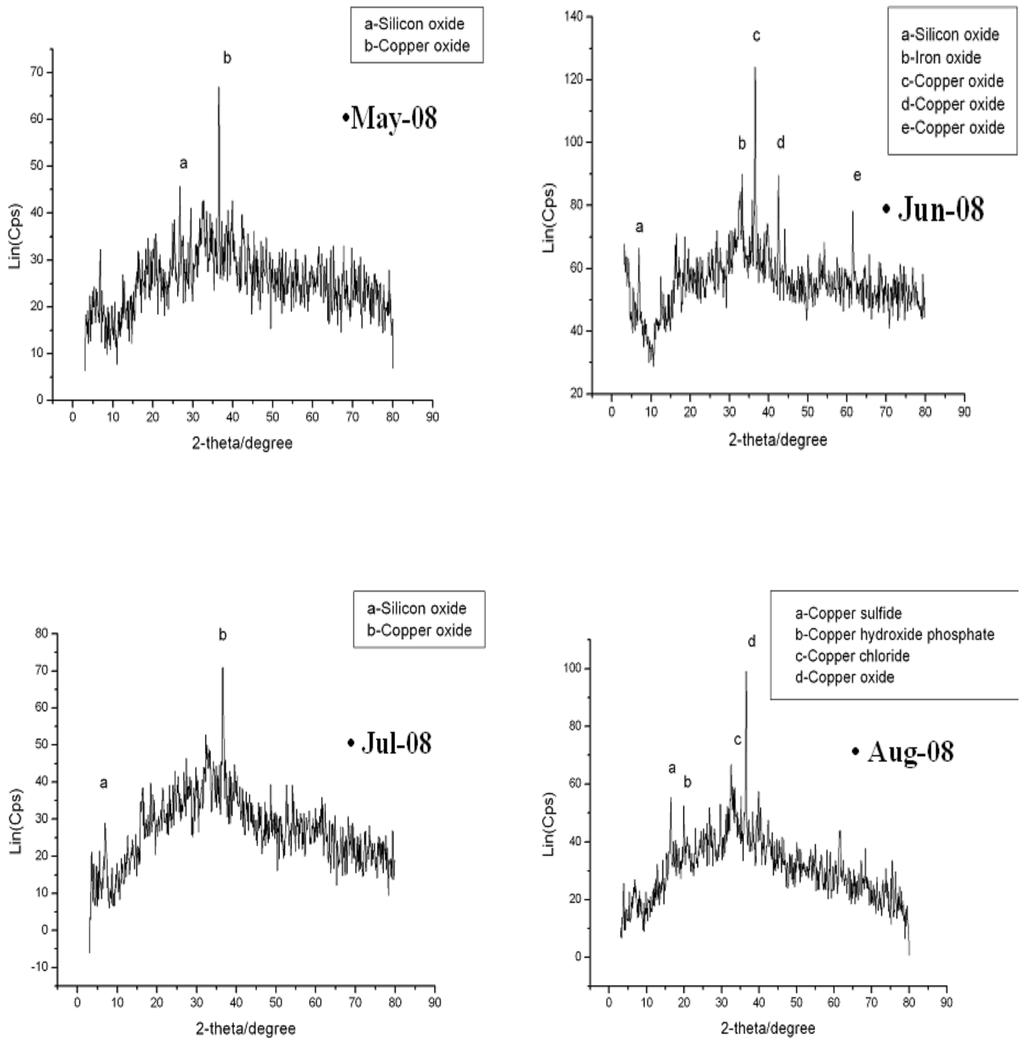

Fig. 4.19 X-ray pattern of the corrosion products on brass exposed to Cochin estuarine water over May 08, Jun. 08, Jul. 08 and Aug. 08 months.

XRD data reveal the presence of copper oxide almost in all the months attributing the protective nature of brass against uniform corrosion. It can be concluded that the Cochin estuarine water has affected the nature of the crystalline corrosion products, which are mainly copper oxide, silicon oxide, copper sulfide, Cu-Zn, molybdenum sulfide, copper zinc chloride hydroxide, iron sulfide, copper hydroxide phosphate and copper chloride.

The corrosion behavior of copper based alloys depends on the presence of oxygen and other oxidizers because it is cathodic to the hydrogen electrode. During the primary anodic reaction, a cuprous oxide film is produced and corrosion is predominately responsible for the corrosion protection. The products of corrosion reactions can react with compounds in seawater to form, for example, $CuCl_2$ 3Cu. $(OH)_2$ or $Cu_2(OH)_3Cl$ and in so doing, build a multi layered structure (Kienits, 1972). The medium does not significantly attacked the nature of corrosion products which were mainly hydrated zinc basic chloride-sulphates $Zn_5(OH)_{18}Cl_2\ H_2O$, copper compounds such as atacamite, $Cu_2Cl(OH)_3$ and paraatacamite $Cu_2(OH)_3Cl$ (Santos et al., 2006).

Palraj et al. (2002) reported that the protective corrosion products consisting of Cu_2O, CuO, ZnO and $Zn(OH)_2$ were formed and with increased duration of exposure calcareous, corrosion products of copper hydroxide, copper chloride and copper carbonate were formed. XRD data showed that dealloying of zinc from brass was reduced considerably and ultimately copper corrosion products predominately were formed on the metal surface after longer periods of exposure. With prolonged exposure, the toxic effect on brass was reduced and thereby enhanced bio-adherence on the metal surface and for shorter exposure duration, the tendency to fouling was minimized. Vinicius et al. (2000) concluded that the lower corrosion resistance of the brass in comparison to pure Cu was attributed to the anodic layer structure consisting of a complex $ZnOXH_2O/Cu_2O$-CuO layer which is less protective than the Cu_2O-CuO passive layer produced onto Cu. Selective dissolution of zinc was not detected being their electro dissolution rate higher than that of pure Cu and smaller than that of pure zinc.

The hydrated zinc basic chloride-sulphate and $Zn_5(OH)_8Cl_2$ was observed only in the first month of exposures in natural seawater. The hydrated zinc basic chloride-sulphate occurs in all the samples. Bastos et al. (2008) concluded that the removal of dissolved O_2 and buffering at pH 9 contribute to enhanced corrosion of brass in seawater. According to Sutter, (1995), Cu_2O is the main compound on Cu in 0.5 M aerated chloride solution under open circuit potential.

Components such as CO_2, H_2S, NH_3, organic and inorganic acids which are present in sea water as a results of higher biological activities in coastal water, may also accelerate localized corrosion (Miller, 1970; Sheir, 1977; Pope, 1984; Dexter, 1986). Sulfides can also be produced from the decay of organic matter within the slime film, resulting in increased corrosion of some alloys. Thus, the presence of the slime film on the metal surface can locally change the environment at the liquid/metal interface such that the corrosion behavior of a metal can be considerably altered. For a metal that has a relatively low corrosion rate in seawater, the slime film can alter the local environment at the liquid/metal interface to create conditions where the corrosion rate is accelerated.

Stoffyn-Egli et al. (1998) identified metallic Cu, djurleite ($Cu_{1.96}S$), cuprite (Cu_2O), atacamite ($Cu_2Cl(OH)_3$), spertiniite ($Cu(OH)_2$) and hydrozincite ($Zn_5(CO_3)_2(OH)_6$) as corrosion products on brass exposed in marine condition. However, they also revealed the presence of a mineral not previously known to exist and tentatively identified as $Cu_{14}Zn_{14}Cl_5 (SO_4)_5(OH)_{41}.H_2O$. This new mineral seems to have a stability field in E^H-pH diagrams similar to that of connellite ($Cu_{19}Cl_4SO_9$ $(OH)_{32}2H_2O$). Hoar et al. (1965) have indicated that the black film covered on brass in a chloride medium is Cu_2O. Faita et al. (1975) who worked with aerated 0.5 NaCl solutions indicated that the protective film is CuO. For the Cu–37Zn alloy, the XRD pattern show less cuprous oxide in the corrosion product, as well as increased amounts of cupric oxide and chlorides as basic zinc chlorides and there is also strong component of ZnO formed as a result of dezincification (Mariappan Natesan et al., 2008).

4.4 Surface morphology of brass after removal of corrosion products

Different **s**urface morphologies of brass after removal of corrosion products is shown in Figs 4.20-4.22 SEM image for Sep. 07 and Oct. 07 in Fig. 4.20 shows very few black spots related to pits and few white spots indicating few remaining corrosion products. There is no indication of cracked surface exhibiting dezincification. SEM images for Nov. 07 to Dec. 07 in Fig. 4.20 show large area of black spots related to pits and cracked area where dezincification has occurred. SEM images for Jan. 08 to Apr. 08 (Fig. 4.21) show large area of black spots related to pits and cracked area where dezincification has occurred. Similarly SEM images from May 08 to Aug. 08 (Fig. 4. 22) show more black spots with cracked surface related to pits and dezincification with few white spots indicating few remaining corrosion products. The organic matter can make anaerobic condition and yield significant amounts of sulphide which will cause pitting of brass.

From the above results it is apparent that the nature of the medium has strongly influenced the morphology of the corrosion layer as well as the size and morphology of the pits underneath the corrosion products. SEM images also reveal the localized corrosion on selective area with preferential dissolution. The setting of a concentration cell can encourages localized corrosion or pitting due to corrosion products (Wyche et al., 1946). Bastos et al. (2008) observed that a white zone with a porous nature on brass immersed in ASW is probably related to dealloying “Dezincification”. After the removal of the corrosion products, the morphology of the structures corresponding to immersion in ASW presents a uniformly cracked surface along the boundaries, whereas these from immersion in NSW showed pits uniformly distributed along the whole surface. Kharafi et al. (2004) observed selective dissolution of brass at various potentials and chloride concentrations and concluded that chloride promotes the dissolution of copper and also zinc.

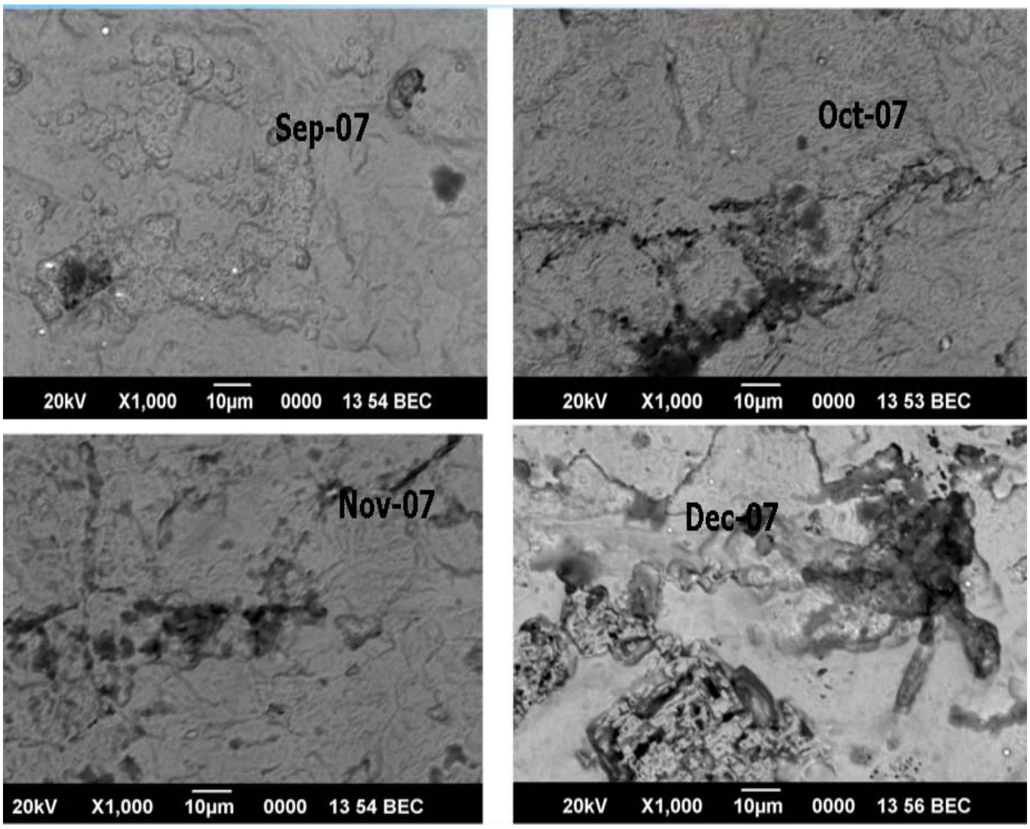

Fig. 4.20 SEM micrograph of brass for Sep. 07, Oct. 07, Nov. 07 and Dec. 07 months exposure in Cochin estuarine water after removal of corrosion products

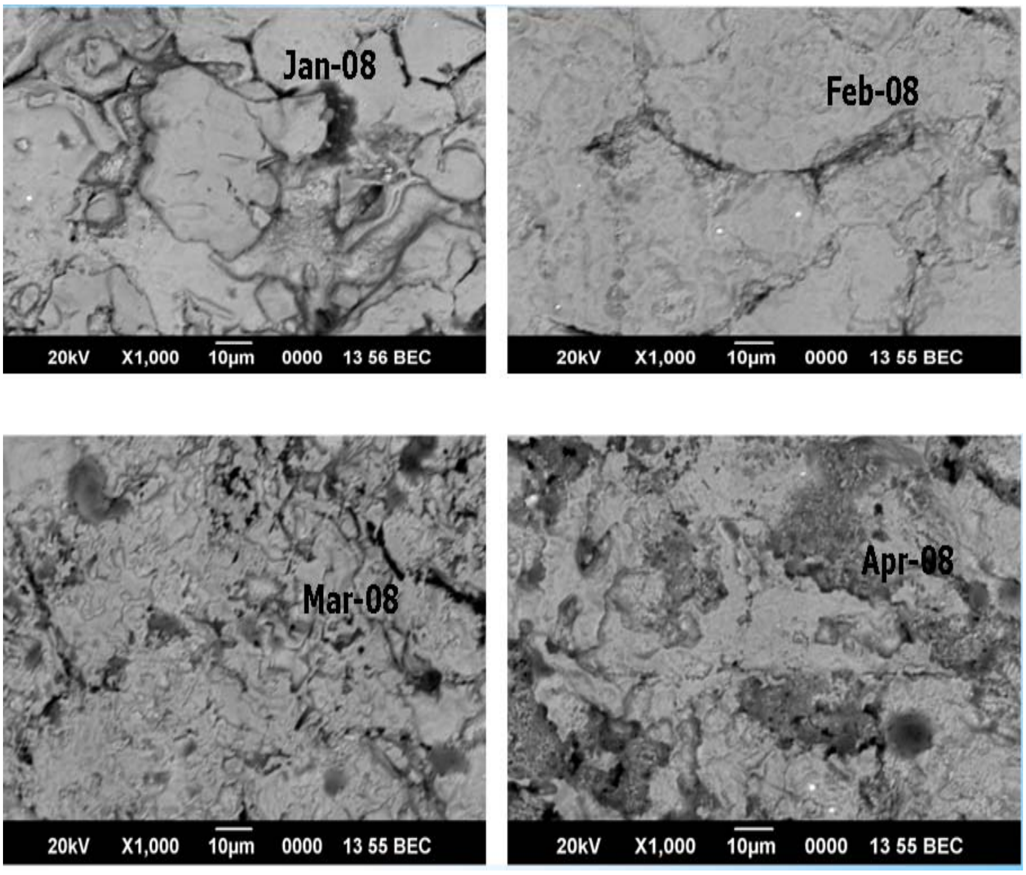

Fig. 4.21 SEM micrograph of brass for Jan. 08, Feb. 08, Mar. 08 and Apr. 08 months exposure in Cochin estuarine waterafter removal of corrosion products

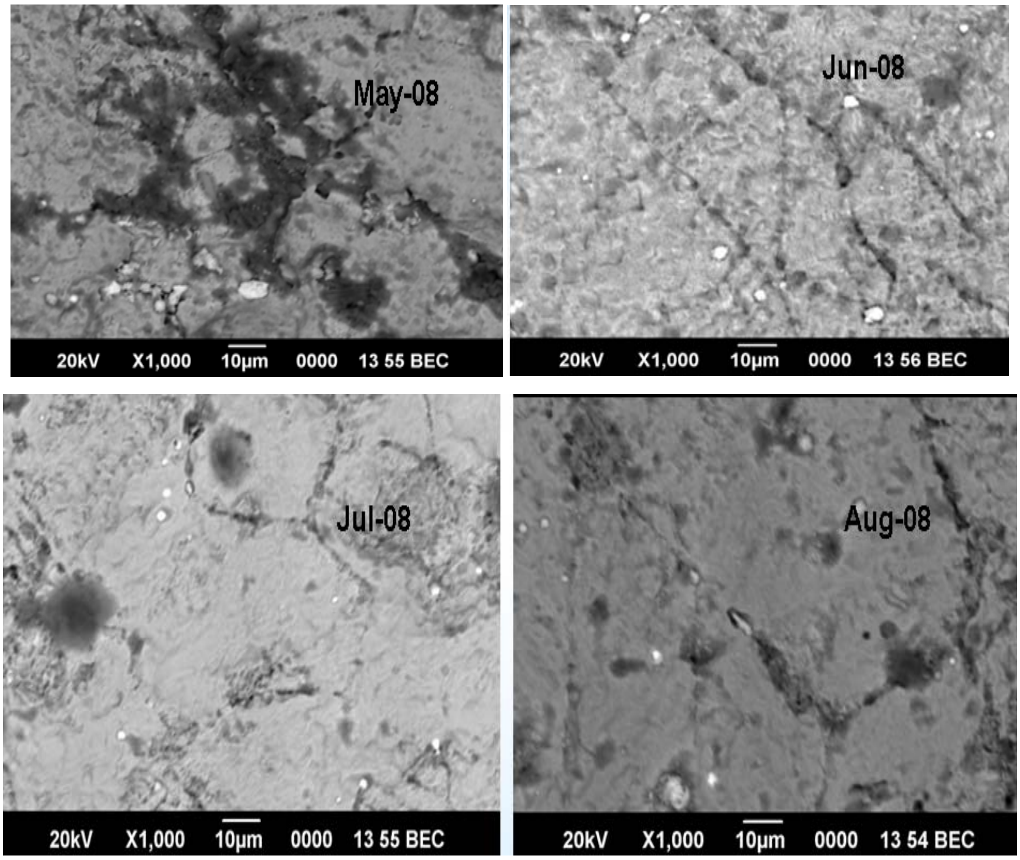

Fig. 4.22 SEM micrograph of brass for May. 08, Jun. 08,Jul. 08 and Aug. 08 months exposure in Cochin estuarine water after removal of corrosion products

According to Mankowski (1997), pit morphology and mechanism of pitting depend on the relative concentration of both anions and cations in chloride/sulfate containing solution. Higher concentrations of Cl^- ions are responsible for the pitting. SEM micrographs of copper samples with 1, 3, 6 and 9 months of immersion for both solutions show round pits covered by copper salts. Higher density of pits is observed on samples exposed in chloride solutions (0.5M NaCl), in comparison with those exposed in synthetic seawater. All the studies confirm that synthetic seawater is somewhat less aggressive than pure chloride solutions of identical concentration of NaCl (Ferreira et al., 2004).

The surface morphology of the corroded alloy indicates intergranular attack, which is believed to be the characteristic nature of copper alloy for seawater exposure (Sawant et al., 1995). The formation of the surface layer producing a black film containing cuprous oxide and sulphide is not as protective as those formed in clean water and higher corrosion rates and pitting can be experienced (Powell, 2000).

4.5 Summary and conclusions

Visual observation of brass panels exposed in Cochin estuary during the study period reveals that there was no appearance of either blue or pink color on brass surface indicating zinc compound. The copper compound $CuCl_2$ or Cu_2O is possibly appearing in brownish and greenish color zone and is possibly atacamite and /or bronchantite/antlerite. The exponential decrease in the corrosion rate of brass can be attributed to the protective nature of corrosion products such as cuprous oxide and cupric hydroxy chloride, which are formed along with marine growth accumulation.

The SEM images reveal that the extent of dezincification increases up to Apr.08 due to increases of density of crystalline grains from Nov. 07 to Apr. 08 and then reduces till Jul. 08 with slight increase for Aug. 08 as the density of crystalline grains decreases with little increase for Aug. 08. Dezincification of brass could be attributed to the role of biofilm consortia-differential aeration cells/concentration cell. The results are in tune with dezincification factor Z_f of respective exposure, open circuit potential and extent of loss of mechanical properties of brass.

EDS studies reveal that dezincification starts from Nov. 08 due to high amount of chloride ions and continue till Aug. 08. However, reduction of zinc % after Apr. 08 to Jul. 08 with slight increase for Aug. 08 are observed as increase of rain fall which neutralize the effect chloride ions in these months (May 08-Aug. 08). These months are peak mon-soon period.

XRD data reveal the presence of copper oxide almost in all the periods of study attributing the protective nature of brass against uniform corrosion. From the results, it can be concluded that the Cochin estuarine water has affected the nature of the crystalline corrosion products, which are mainly copper oxide, silicon oxide, copper sulfide, Cu-Zn, molybdenum sulfide, Cu-Zn chloride hydroxide, iron sulfide, copper hydroxide phosphate and copper chloride. The products of corrosion reactions can react with compounds in estuarine water to form different compound.

SEM images of brass after removal of corrosion products show that the nature of the medium has strongly influenced the morphology of the corrosion layer as well as the size and morphology of the pits underneath the corrosion products. SEM images of brass also reveal the localized corrosion (pitting) on selective area with preferential dissolution. The cracked area of brass surface from Nov. 07 – Aug. 08 indicates the dezincification process.

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Chapter 5

DEZINCIFICATION OF EPOXY COATED BRASS

Contents

5.1 Weight gain and loss
5.2 Corrosion rate
5.3 Biofouling
5.4 Open circuit potential
5.5 Electrochemical polarization studies
5.6 Dezincification factor
5.7 Mechanical properties
5.8 Summary and conclusions

Inhibited α brasses are largely immune to dezincification in most waters but the effect of tin and arsenic addition to α/β brasses is not so reliable or predictable in controlling the problem. There have been many cases of dezincification in duplex brasses in both fresh - water and seawater. Though there are some protection methods such as inhibitors electro deposition and electro polymerization, there is no reliable method of inhibiting the dezincification of two-phase brass. Organic coatings are effectively used for the protection of metals due to their capacity to act as a physical barrier between the metal surface and corrosive environment. Hence, epoxy coating on brass is applied and its effect against corrosion resistance and biofouling in Cochin estuarine water over a period of one year is studied. Review of literature reveals that no work of this nature has been carried out so far. Results of dezincification of epoxy-coating in terms of corrosion rate, weight gain by gravimetric method and electrochemical polarization, open circuit potential, dezincification factor, biomass and mechanical properties are presnted in this chapter.

5.1 Weight gain and loss

The weight gain and loss on brass immersed in the Cochin estuarine water during this study is shown in Table 5.1. A steady weight gain is noticed from Sep. 07 to Nov. 07. Then it reduces considerabily in Dec. 07 and Jan. 08. Since Feb. 08, there is steady weight gain till Aug. 08 with minor variation in between. The minimum weight gain is in Dec. 08 while the maximum for Aug. 08. The low weight gain is due to removal of corrosion products and de-addiction of biomass. The weight loss is less than 0.0025 g/cm^2 for the period from Sep. 07 to Apr. 08 with minor variation in between and then reaches a maximum of 0.004 g/cm^2 for Jun. 08 while it reduces from Jul. 08 to Aug. 08. The low weight loss is related to less corrosion rate.

Table 5.1 Weight gain and weight loss on epoxy coated brass panels immersed in estuarine water, Cochin at each exposure period

Months	Initial weight	Final Weight before removal of corrosion products	Final weight after removal of corrosion products	Wight gain g/cm^2	Wight loss g/cm^2
Sep.07	26.08	27.08	26.06	0.088	0.001
Oct.07	26.12	27.96	26.08	0.092	0.002
Nov.07	26.02	28.18	26.00	0.108	0.001
Dec.07	26.07	28.08	26.04	0.0505	0.0015
Jan.08	26.03	28.13	26.00	0.055	0.0015
Feb.08	26.22	28.90	26.17	0.134	0.0025
Mar.08	26.28	28.57	26.24	0.1145	0.002
Apr.08	26.34	28.67	26.29	0.1165	0.0025
May 08	26.51	29.53	26.44	0.151	0.0035
June 08	26.13	29.12	26.85	0.1495	0.004
July 08	26.17	29.10	26.11	0.1465	0.003
Aug.08	26.48	29.51	26.45	0.1515	0.0015

5.2 Corrosion rate

The Corrosion rate of epoxy coated brass samples immersed in estuarine water, Cochin at each exposure period is shown in Table 5.2 and Fig. 5.1. The results suggest that there was no much change in corrosion rate of epoxy coated brass for first two months (Sep. 07 to Oct. 07). A drastic reduction in corrosion rate is observed from Oct. 07 to Nov. 07. But from Nov. 07 to Aug. 08, the fluctuation in corrosion rate is marginal. The decrease of corrosion rate implies that the combined action of accumulation of biomass and adherent epoxy coating on brass as a barrier between the metal interface and seawater reduces the diffusion of oxygen and possess excellent resistance when uniform corrosion is considered. The corrosion rate of epoxy coated brass in this study is much lower than with corrosion rate of uncoated brass.

Table 5.2 Corrosion rate of epoxy coated brass panels immersed in estuarine water, Cochin at each exposure period

Months	Corrosion rate mdd
Sep.07	3.33
Oct.07	3.33
Nov.07	1.11
Dec.07	1.25
Jan.08	1.0
Feb.08	1.38
Mar.08	0.95
Apr.08	1.04
May 08	1.29
June 08	1.33
July 08	0.90
Aug.08	0.41

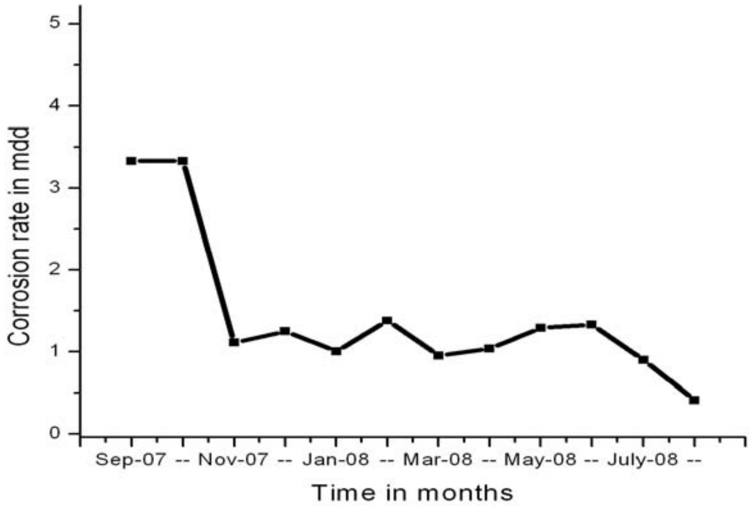

Fig. 5.1 Corrosion rate of epoxy coated brass panels in Cochin estuary at each exposure period

The instantaneous corrosion rate varies strongly with time which depends on the composition of the electrolyte (Ericsson et al., 1980). It was found that increasing oxygen concentration in the estuarine water causes rapid increase in corrosion rate (Funke and Haagen, 1975). According to Morcillo et al. (1991), corrosion rate increases as interfacial contamination increases while non-contaminated surface are free of corrosion. Higher dissolved oxygen content in the water will increase the rate of attack and leading to the higher risk of corrosiveness (Seoh et al., 2004).

The higher rate of corrosion in copper and its alloys in coastal water is attributed to the higher concentration of dissolved oxygen and temperature with in the water. Secondly, in coastal waters erosion corrosion is more pronounced which is caused by either removal or break down of the protective film by mechanical forces such as local turbulence or impingement (Sheri, 1977). Differential aeration (Pope, 1985), selective leaching (Dexter, 1986) under-deposit corrosion, cathodic depolarization (Miller, 1970) have been reported as mechanisms for microbiologically influenced corrosion of copper alloys. Polymer coating prevents corrosion of steel by interrupting or blocking the normal processes necessary for corrosion (Munger, 1986). When corrosion is controlled by diffusion of oxygen, the corrosion rate at a given oxygen concentration depends on the temperature and living organisms. At higher temperature the rate of attack might be lessened by the deposition of protective calcareous deposits and by loss of oxygen from solution resulting in decrease in potential (Uhlig, 1963).

5.3 Biofouling

Biomass on brass samples immersed in estuarine water, Cochin at each exposure period is given in Fig. 5.2 and Table 5.3. The biomass increases from Sep. 07 to Mar. 08 and then it reduces till Jun. 08. It again increases until the end of study period.

Table 5.3 Biomass on epoxy coated brass panels immersed in estuarine water, Cochin at each exposure period

Months	Total biomass g/panel	Biomass g/sq.cm
Sep.07	65	3.25
Oct.07	68	3.4
Nov.07	72	3.6
Dec.07	78	3.9
Jan.08	82	4.1
Feb.08	91	4.55
Mar.08	93	4.65
Apr.08	85	4.25
May 08	70	3.5
June 08	62	3.1
July 08	87	4.35
Aug.08	89	4.45

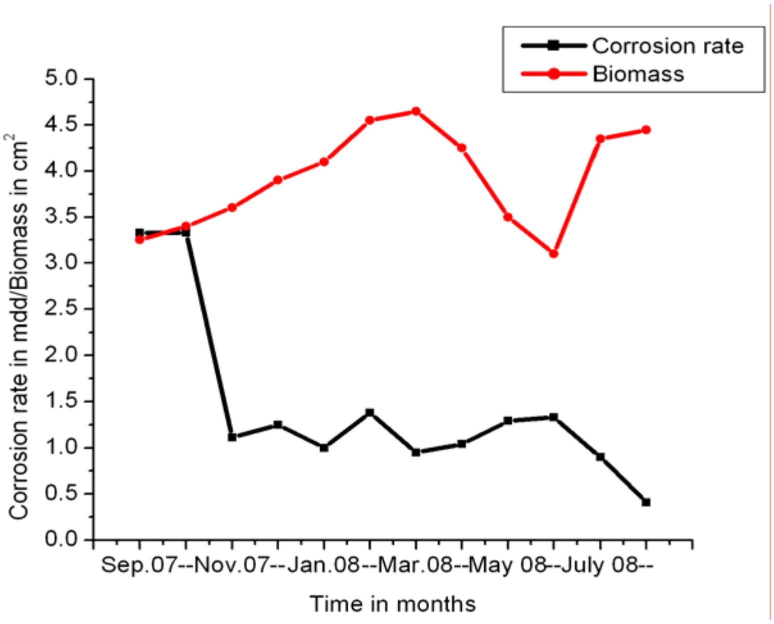

Fig. 5.2 Corrosion rate and biomass of brass panels in Cochin estuary at each exposure period

Earlier studies carried out in Mandapam coastal water on ferrous materials reveal higher corrosion on the coupons without fouling than coupons with the presence of fouling (Palraj et al., 2002). The accumulation of these biological organisms is dependent on the specific environmental conditions. Conditions which are most conducive to their development are (a) relatively shallow water like harbour, (b) warm temperatures, (c) low seawater flow, and d) smooth and hard surfaces (Fontana, 1967).

Similarly both macro and microfouling can have a major impact on the performance of marine components. Macro and microfouling organisms can break down protective paint films on a component surface. Fouling also shields the component surface from any oxygen supply thereby creating the possibilities that differential aeration cells can develop. Fouling can cause catalytic effects. Plant decay or secretion products from animal life can accelerate corrosion processes (Ijsseling, 1989).

5.4 Open circuit potential

The open circuit potential of epoxy coated brass samples immersed in Cochin estuary at each exposure period is given in Table 5.4 and Fig. 5. 3. The experimental results show a value of -0.15 V vs. SCE on Sep. 07 which then decreases to -17 V in Oct. 07 and Nov. 07. Thereafter it increases to –0.21 V in Dec. 07 and -0.2 V for Jan. 08 and Feb. 08 while it drobs to -0.19 V for Mar. 08. Then it sustains at this potential up to Aug. 08. The negative shifts of potential from Sep. 07 to Dec. 07 indicate that there can be localized corrosion. The positive shift of potential after Dec. 07 and sustainable noble potentials (more positive values) mean that brass retains its normal corrosion resistance. Though the OCP of plain brass and epoxy coated brass have decreased over the period of time, the more negative potentials were noticed for the brass than the epoxy-coated brass. The open circuit potential, anodic polarization curves and AC impedance spectroscopy and electrochemical measurement of Poly (o-anisidine) coated brass electrodes showed that POA films provided a physical barrier property to brass electrode (Ali Tuncay Ozyilmaz, 2008).

Table 5.4 Open circuit potential of epoxy coated brass panels immersed in estuarine water, Cochin at each exposure period

Months	Open circuit potential, V
Sep.07	-0.15
Oct.07	-0.17
Nov.07	-0.17
Dec.07	-0.21
Jan.08	-0.2
Feb.08	-0.2
Mar.08	-0.19
Apr.08	-0.19
May 08	-0.19
June 08	-0.19
July 08	-0.19
Aug.08	-0.19

According to Leidheiser (1979), the corrosion potential in combination with other methods can provide information about the mechanism of the reaction and the rate controlling process. The movement of the corrosion potential in the active (i.e. more negative) direction indicates the underfilm corrosion as cathodic/anodic ratio decreases.

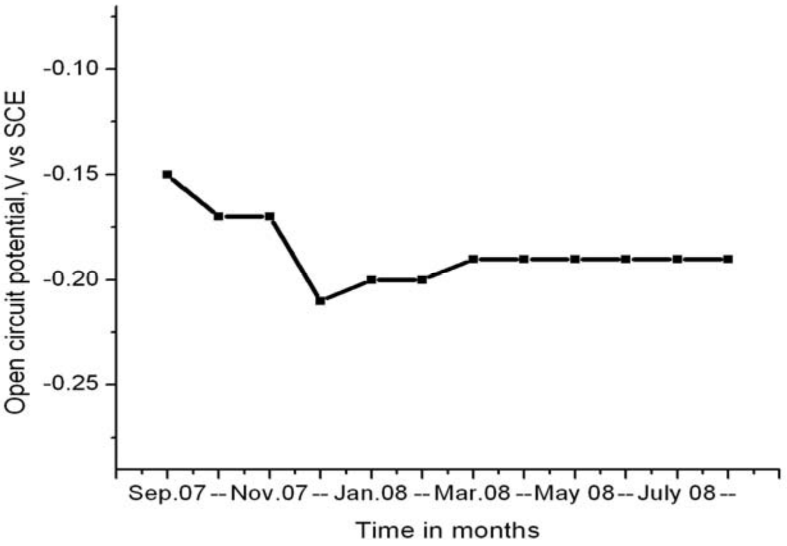

Fig. 5.3 Open circuit potential of epoxy coated brass panels in Cochin estuary at each exposure period

AL-Kharafi et al. (2004) reported that selective dissolution of zinc occurs with no detectable level of copper dissolution at more active potential and at more noble potential, dissolution of both components can occur. It is also shown that chloride ions promote the dissolution of both zinc and copper from the alloy.

The potential of the coating system closer to the corroding steel indicates the loss of barrier action of the coating (Dhanalakshmi et al., 1997). According to Trethewey et al. (1995), the free corrosion potential of the specimen becomes more anodic when the solution is deaerated. It is reasonable to assume that if coating becomes porous, then differential aeration cell develops. Corrosion potential for coated metals and the time dependence has been questioned with regard to their use as a technique for evaluating the anticorrosive resistance of organic coating (Wolstenholme, 1973). However, its changes as a function of the exposure time to aqueous media have been successfully used as a simple tool to study the corrosion protection offered by organic coatings (Morcillo et al., 1990).

It is also stated that OCP drops when surface becomes active (Kendig et al., 1983) or passive layer break down (Naderi et al., 2004). The decrease of potential (more active) with time on coated panels indicates that the chloride ion permeability of the coating has decreased while an increase of potential (more positive) with time suggests that the coating does not allow the transmission of corrosive ions into the surface (Selvaraj, 1997). The open circuit potential of metal exposed to flowing seawater are affected by velocity of flow and increase in velocity makes copper less noble and steel more noble. The differences in potential between filmed and unfilmed surface can lead to considerable acceleration of corrosion of unfilmed areas adjacent to filmed surfaces (Gilbert, 1968).

The corrosion potential provides a qualitative indication whether a given structure is in an active or a passive state. The lower potential of steel in natural seawater is due to the formation of deposits consisting of algae, diatoms, bacteria, inorganic salts and deleterious minerals which affect dissolution of metal in seawater. An increase of open circuit potential is due to the high concentration of dissolved oxygen which is consumed gradually by the living mass of micro-organisms (Brendat, 1991).

5.5 Electrochemical polarization studies

Figures 5.5 - 5.7 and Table 5.5 illustrate the polarization curves of the epoxy coated brass sample immersed in estuarine water, Cochin after every month exposure. The corrosion rate of brass for Sep. 7 is 0.1193 mm/yr which reduces for Oct. 07 and then increases till Dec. 07. Again the corrosion rate of brass reduces up to Mar. 08 while it increases for Apr. 08. Yet again the corrosion rate reduces in May 08 and afterwards it increases for the remaining period.

Table 5.5 Polarization data of epoxy coated brass panel immersed in estuarine water, Cochin for different exposure period.

Monhs	I_{corr} A/cm^2	E_{corr} V	b_c V/dec	b_a V/dec	R_p Ohm	Corrosion rate mm/yr	Corrosion rate mm/yr
Sep.07	4.518 x10^{-6}	-0.243	0.0542	0.0542	2.514 x10^{3}	1.193 x10^{-1}	0.1193
Oct.07	3.227 x10^{-6}	-0.243	0.0848	0.0657	4.984 x10^{3}	8.521 x10^{-2}	0.08521
Nov.07	2.082 x10^{-5}	-0.306	0.3478	0.1488	2.174 x10^{+3}	5.498 x10^{-1}	0.5498
Dec.07	5.787 x10^{-5}	-0.216	0.6683	0.1604	9.706 x10^{2}	1.528 x10^{+0}	1.528
Jan.08	6.564 x10^{-6}	-0.236	0.3646	0.1264	6.211 x10^{3}	1.734 x10^{-1}	0.1734
Feb.08	2.37 x10^{-6}	-0.156	0.1683	0.1015	1.16 x104	6.259 x10^{-2}	0.06259
Mar.08	2.329 x10^{-6}	-0.205	0.045	0.0612	4.838 x10^{3}	6.151 x10^{-2}	0.06151
Apr.08	5.002 x10^{-5}	-0.311	0.9421	0.2526	1.73 x10^{3}	1.321 x10^{+0}	1.321
May 08	2.795 x10^{-6}	-0.199	0.0764	0.0659	5.499 x10^{3}	7.381 x10^{-2}	0.07381
June 08	6.564 x10^{-6}	-0.236	0.3646	0.1264	6.211 x10^{3}	1.734 x10^{-1}	0.1734
July 08	2.082 x10^{-5}	-0.306	0.3478	0.1488	2.174 x10^{+3}	5.498 x10^{-1}	0.5498
Aug.08	3.858 x10^{-5}	-0.218	0.7692	0.2231	1.946 x10^{+3}	1.019 x10^{+0}	1.019

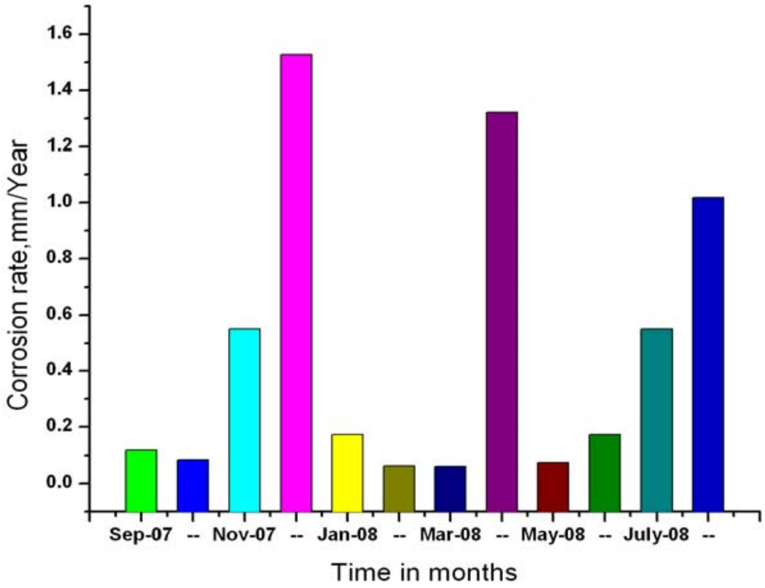

Fig. 5.4 Monthly wise corrosion rate of epoxy coated brass exposed to estuarine water Cochin

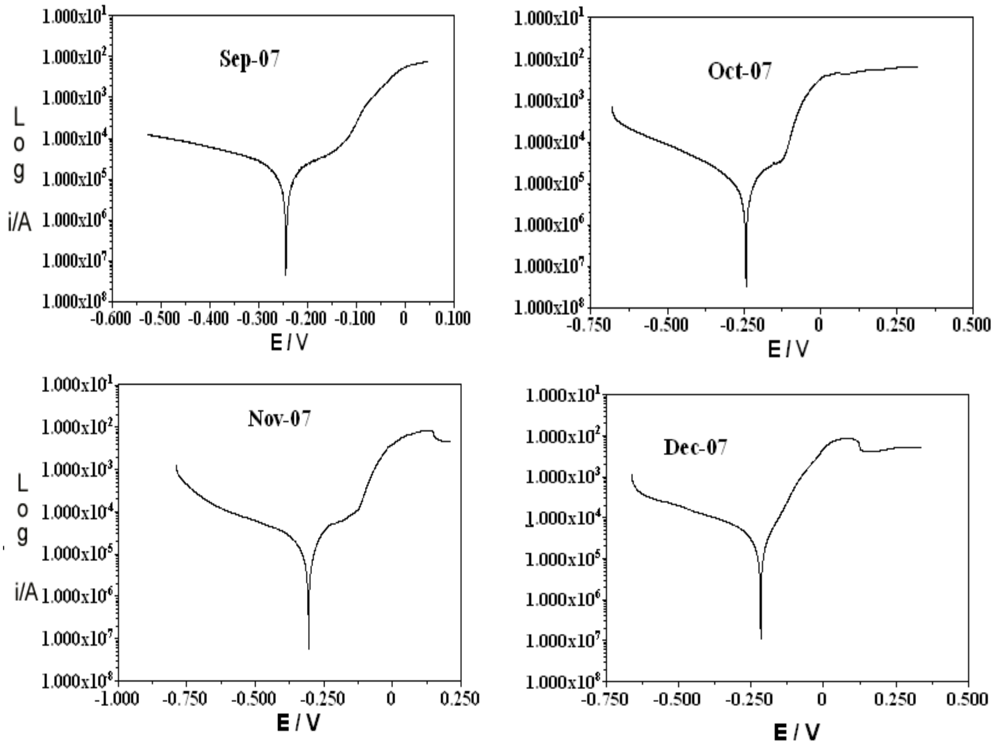

Fig. 5.5 Polarization curve of epoxy coated brass panels immersed in estuarine water, Cochin for Sep. 07, Oct. 07, Nov. 07 and Dec. 07 months

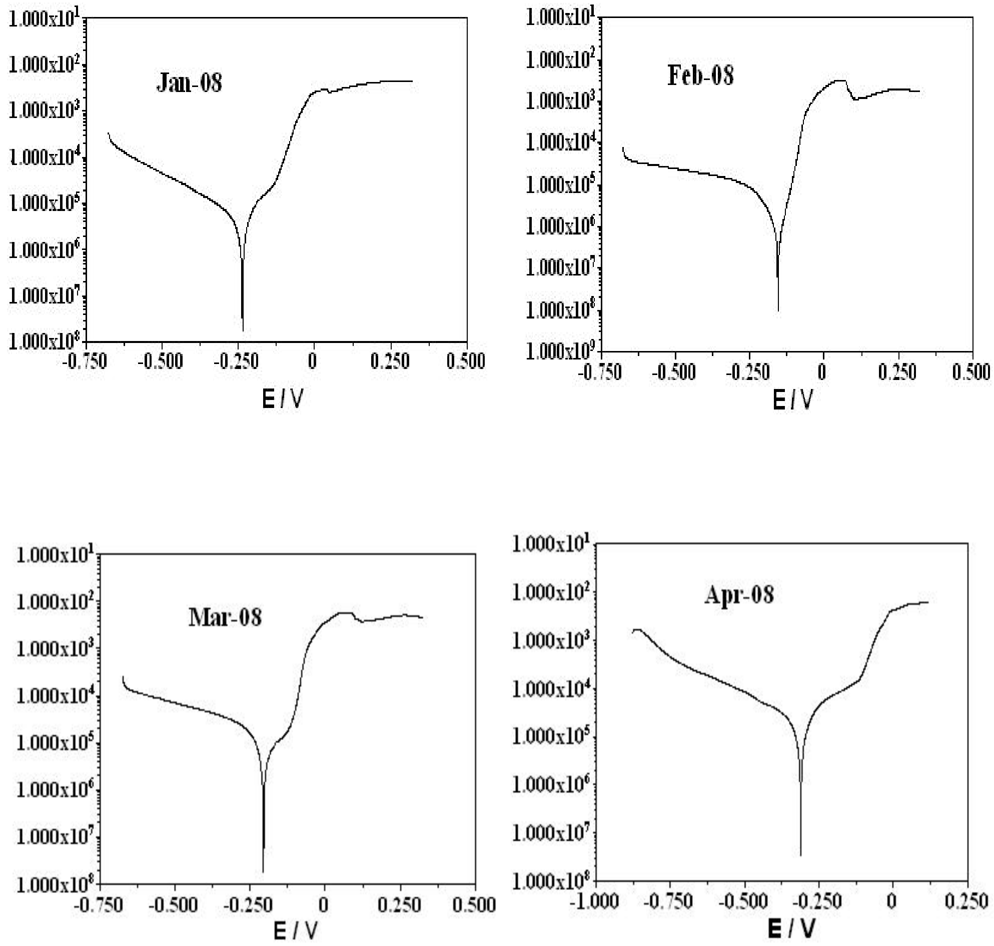

Fig. 5.6 Polarization curve of epoxy coated brass panels immersed in estuarine water, Cochin for Jan. 08, Feb. 08, Mar. 08 and Apr. 08 months

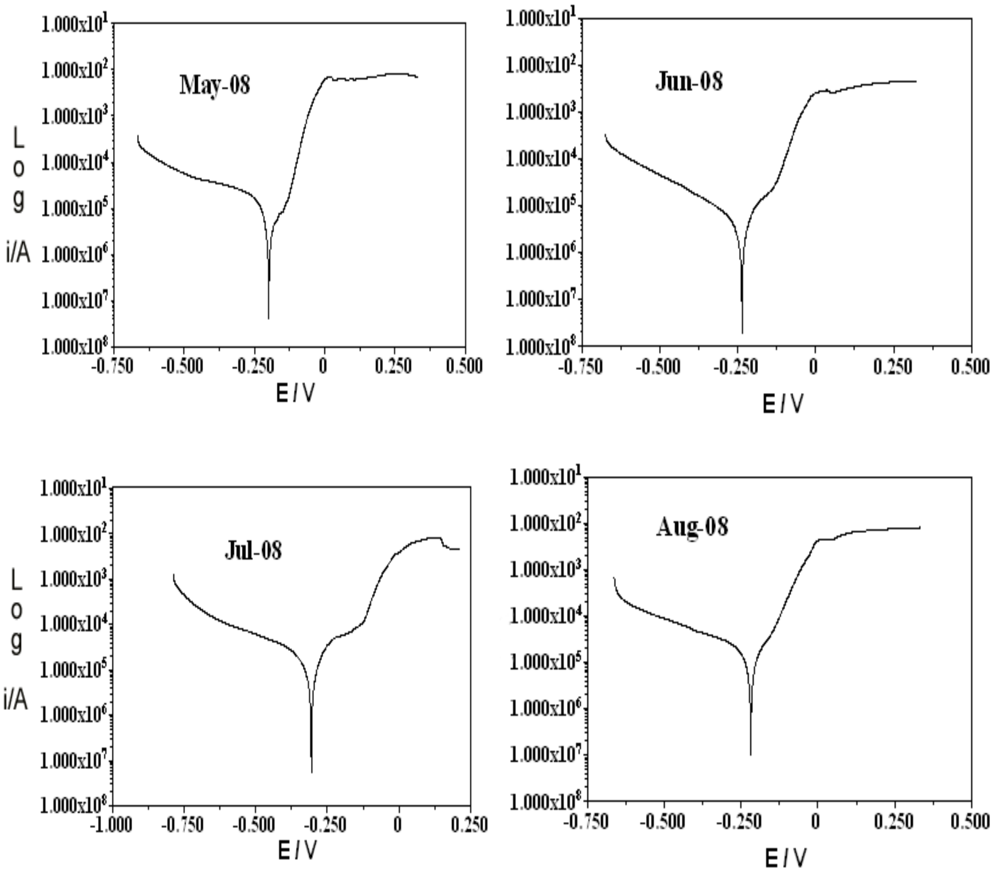

Fig. 5.7 Polarization curve of epoxy coated brass panels immersed in estuarine water, Cochin for May 08, Jun. 08, Jul. 08 and Aug. 08 months

The results show (Fig. 5.4 and Table 5.5) that low corrosion rate prevails throughout the study period except from Nov. 07 to Dec. 07; Apr. 08, and Jul. 08 to Aug. 08, where high corrosion rates are noticed. A low corrosion rate value of brass imply synergistic effect of barrier action of epoxy coating and fouling assemblage coupled with the adherent of sediments on epoxy-coated samples. On the other hand, an increased corrosion rate indicates local damage of epoxy coating due to prolonged exposure in the water thereby exposing bare brass to electrolyte. The higher values of corrosion rate observed on the epoxy coated brass in the water can also be attributed to the turbulence and soft fouler and micro and macro algae that fouled on epoxy-coated brass. The corrosion rates are normally decided by various factors such as surface temperature of seawater, dissolved oxygen concentration, wave action, salinity, monsoon rainfall and settlement of marine organisms.

The varying patterns of I_{corr} and E_{corr} values observed for brass and epoxy coated brass over the period of exposure imply the variance in corrosion rate over the period of exposure. The varying rates of corrosion can be ascribed to the role of environmental conditions at the vicinity of metal, electrolyte interface and role of micro and macro fouling organisms engulfed in the region as evidenced from the well documented studies reported elsewhere (Miller, 1970; Obuekwe, 1981; Mansfeld et al., 1992; Patrica et al., 1994). The b_a and b_c values are also in tune with E_{corr}, I_{corr} and corrosion rate of the respective exposure. The experimental results show that the corrosion rate of epoxy-coated brass is less compared to brass in Cochin estuarine water. The polarization resistance is inversely proportional to the corrosion current density, which can be transferred to a corrosion rate for uniform corrosion (Winston Revie, 2000).

Kondrashin et al. (2000) concluded that modifying the surface of α/β - brass with a polysiloxane coating decelerates general corrosion and hampers selective dissolution. The coating is most efficient at low concentrations of chlorides in neutral environments. The protective effect is based on partially shielding of the alloy's surface and decreasing the thermodynamic activity of copper at the electrode-corrosive environment boundary. Yen-Chin Lin et al. (2003) reported that epoxy coating has better anti-corrosion ability than polyurethane resin and acrylic resin. The interface of epoxy coating and low carbon steel substrate remain intact after the tidal wave simulation test. The organic protective coating (barrier coating) fails by separation process known as delaminating, caused by separation at the coating metal interface (Sweeney et al., 1953; Fernandez et al., 1985). In addition to quantitative information such as corrosion current and corrosion rate, the Rp value can provide the information to assess the relative ability of a material to resist corrosion and the polarization resistance is inversely proportional to corrosion current (Brett et al., 1994). It is supposed that decrease of corrosion current is the result of the enhancement of electrical resistance of oxide layer (Mahdavain et al., 2005).

The results show that the low corrosion current (I_{corr}) is due to the barrier action of epoxy coating on brass. It is well known that epoxy binders offer protection to mild steel structure by a barrier mechanism (Thomas, 1991). The protective behavior is probably related to the formation of a passive film due to the presence of oxygen containing water at the metal/coating interface, contributing in this way to establish a cathodic area at the surface (Ramírez, 2005). The corrosion current produced by epoxy coating is decreased with time, which indicates that the coating is intact on the surface (Selvaraj, 1997). The protective capabilities of coatings are related to electrochemical reaction taking place at the metal and coating interface of sample (Tsaneva et al., 2008).

5.6 Dezincification factor

Table 5.6 and Fig .5.8 show the percentages of leaching of zinc and Cu from the matrix of brass and the extent of dezincification over a period of one year.

The percentage of leaching of zinc from the matrix of brass is minimum (1.1%) for Feb. 08 while maximum (8.2%) for Dec. 07. It is found that leaching of zinc has not increased with time of exposure. The percentage leaching of copper from the brass is minimum (8%) for Apr. 08 while maximum (23%) is in Aug. 08.

Table 5.6 Dezincification of epoxy coated brass panels during exposure period in estuarine water, Cochin

Periods	Leaching of Cu %	Leaching of Zn%	Dezincification factor Z
Sep.07	20	5.2	0.49
Oct.07	12	5.8	0.91
Nov.07	18	2.4	0.25
Dec.07	16	8.2	0.96
Jan.08	11	3.5	0.60
Feb.08	15	1.1	0.13
Mar.08	13	5.0	0.72
Apr.08	8	3.6	0.84
May 08	14	2.7	0.36
June 08	19	1.3	0.12
July 08	21	4.6	0.41
Aug.08	23	8.1	0.66

Dezincification factor for brass as a function of exposure time is given in Fig. 5.8. A dezincification factor higher than one means preferred dissolution of zinc. In all the exposures periods, the dezincification factor is less than one, which indicates that dissolution of zinc has not occurred from the matrix of epoxy coated brass for all months. But the dezincification has occurred for brass except in Sep. 07 and Oct. 07. The abnormal behavior can be due to the synergistic effects of biofilm consortia (aerobic and anaerobic) absence of oxygen at the interface affected by barrier action of epoxy coating during the study period.

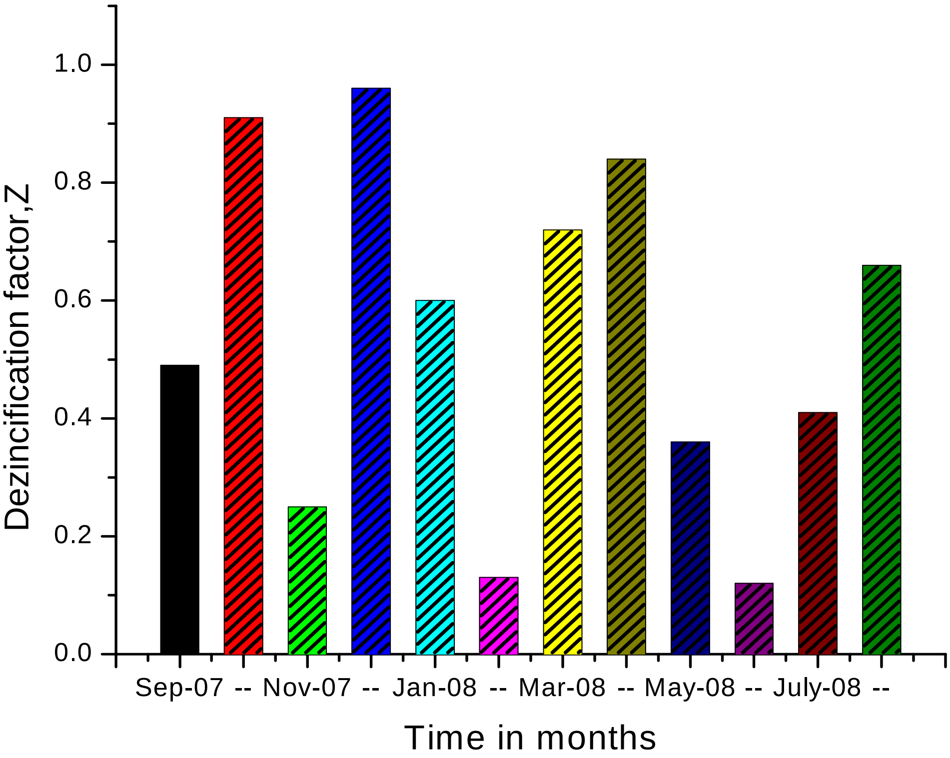

Fig. 5.8 Dezincification of epoxy coated brass panels at each exposure period in estuarine water, Cochin

5.7 Mechanical properties

The change in mechanical properties such as ultimate strength and yield strength of epoxy coated brass due to exposure in Cochin estuary is given in Table 5. 7. The exposure of epoxy coated brass subjected to tension testing over the period of experimentation is as received, monthly (one month), quarterly (three months), half yearly (six months), nine months and yearly.

Table 5.7 Change in mechanical properties of epoxy coated brass due to exposure in Cochin estuary

Periods/Properties	Ultimate load (X Newton)	Ultimate strength mpa	Yield load (X Newton)	Yield strength mpa	Area reduction	Elongation %
AS received	687	429	480	300	64	51
Monthly	666	423	479	296	62	49
Quarterly	662	415	460	293	59	46
Half yearly	660	400	459	285	56	40
9 months	657	395	455	277	51	37
Yearly	641	390	443	266	48	34

It is observed that both ultimate and yield strength have not varied much over the period of exposure. It is evident that the loss in tensile strength is directly proportional to weight loss over the period of time. As there is no much variation in the loss in tensile strength, there is no much weight loss during the period of exposure.

5.8 Summary and conclusions

Corrosion rate by weight loss method decreases after Oct. 07 owing to a combined action of biomass accumulation and epoxy coating on bare brass. The corrosion rate in epoxy coated brass is much lower than the corrosion rate of brass. The reason for lower corrosion rate of epoxy-coated brass is due to the lower level of available dissolved oxygen at brass surface. Increase of biomass from Sep. 07 to Mar. 08 and from Jun. 08 to Aug. 08 is due to local damages of coating and higher level of oxygen.

The negative shifts of potential from Sep. 07 to Dec. 07 indicate that there can be localized corrosion. The positive shift of potential after Dec. 07 and sustainable noble potentials (more positive values) mean that epoxy coated brass retains its normal corrosion resistance. Though Open Circuit Potential of plain brass and epoxy coated brass decreases over the period of time. The more negative potentials are noticed for the brass than the epoxy-coated brass.

The Electrochemical studies reveal that low corrosion rate prevails throughout the period except Nov. 07 to Dec. 07; Apr. 08, and Jul. 08 to Aug. 08, where high corrosion rate is noticed. The low corrosion rate values of brass imply synergistic effect of barrier action of epoxy coating and fouling assemblage coupled with the adherence of sediments on epoxy-coated samples. An increase of corrosion rate is associated with local damage of epoxy coating due to prolonged exposure in the water thereby exposing bare brass to electrolyte. The higher values of corrosion rate experienced by the epoxy coated brass in the water can also be attributed to the turbulence of water, and soft fouler and micro and macro algae that fouled on epoxy-coated brass.

The varying pattern of I_{corr} and E_{corr} values observed for bare brass and epoxy coated brass over the period of exposure imply the variance in corrosion rate. The experimental results show that the corrosion rate of epoxy-coated brass is lesser than plain brass in Cochin estuarine water over the exposure. Dezincification factor is less than one, which indicates that dissolution of zinc has not occurred from brass for all months.

It is evident that the loss in tensile strength is directly proportional to weight loss over the period of time. As there is no much variation in tensile strength, there is no much weight loss during the period of exposure.

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Chapter 6

SURFACE CHARACTERIZATION OF EPOXY COATED BRASS

Contents

6.1 Visual examination of epoxy coated brass
6.2 Surface characteristics of epoxy coated brass before the removal of corrosion products
6.3 Surface compound analysis
6.4 Surface morphology of epoxy coated brass after removal of corrosion products
6. 5 Summary and conclusions

Results of surface characterization of epoxy coated brass in estuarine water in terms of visual photos, surface morphology, elements and compounds using photographs SEM, EDS and XRD spectrum are presented in this chapter. The visual observation of epoxy-coated brass after every exposure indicates the kind of changes observed on the surface. XRD and EDS studies reveal the nature of compounds and types of elements found on the epoxy coated brass. The surface characterization of epoxy coated brass before and after removal of compound reveals the effect of estuarine water on epoxy coated brass.

6.1 Visual examination of epoxy coated brass

Figs 6.1- 6.3 show changes in color of epoxy coated brass surface after various exposure periods. Visual examination of samples reveal the presence of white patches in the partially covered black deposits in Sep. 07 while it has changed to green zone with black deposits in Oct. 07. The surface has completely covered with black deposits with white deposits in Nov. 07 but scattered black deposits and a very few white deposits have appeared in Dec. 07. Then the surface has fully covered by black deposits with dead microorganisms from Jan. 08 to Aug. 08.

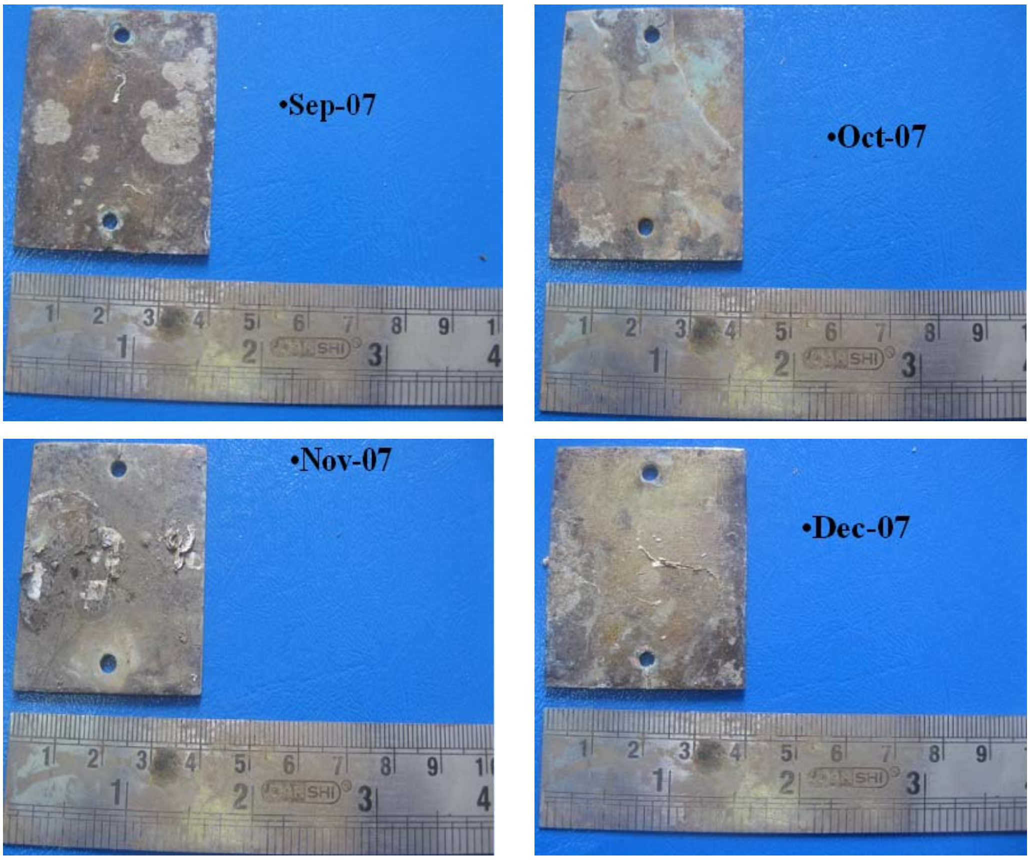

Fig. 6.1 Epoxy coated brass panels after Sep. 07, Oct. 07, Nov. 07 and Dec. 07 in Cochin estuarine water

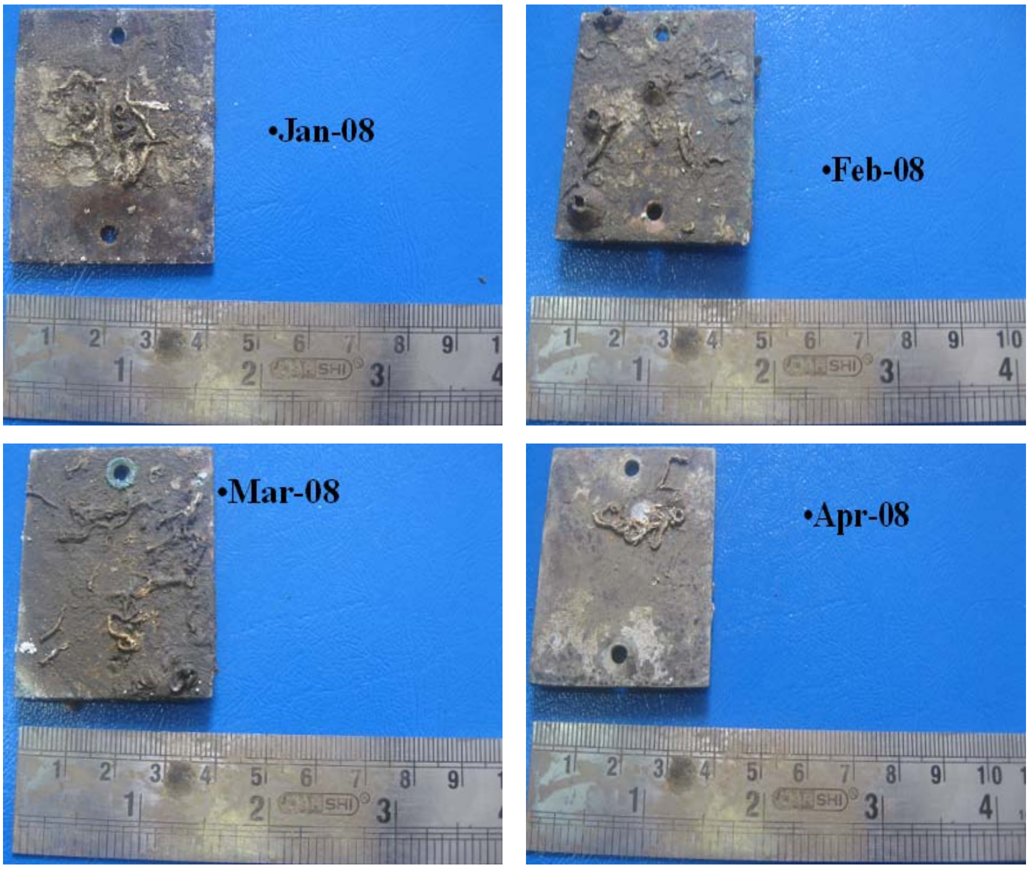

Fig. 6.2 Epoxy coated brass panels after Jan. 08, Feb. 08, Mar. 08 and Apr. 08 in Cochin estuarine water

Heavy growth of marine organisms can reduce corrosion by acting as barrier to the diffusion of oxygen to the metal surface so as to set up anaerobic conditions and can also eliminate acceleration of corrosion by a high velocity of water flow as there is no direct effect of velocity on metal surface. Deficiencies in oxygen supply under the discontinuous deposits are responsible for the initiation of accelerated attack in such regions due to corrosion cells formed by marine organisms and dead organisms. Continuous calcareous base are less damaging than species, which comes into direct contact with the underlying metal (Francis Laque, 1975). The green color generally denotes copper hydroxide sulphate or copper hydroxide chloride (Einar Mattsson, 1996). The brown color is due to $CuCl_2$ or Cu_2O mixed with other compounds (Santos et al., 2006).

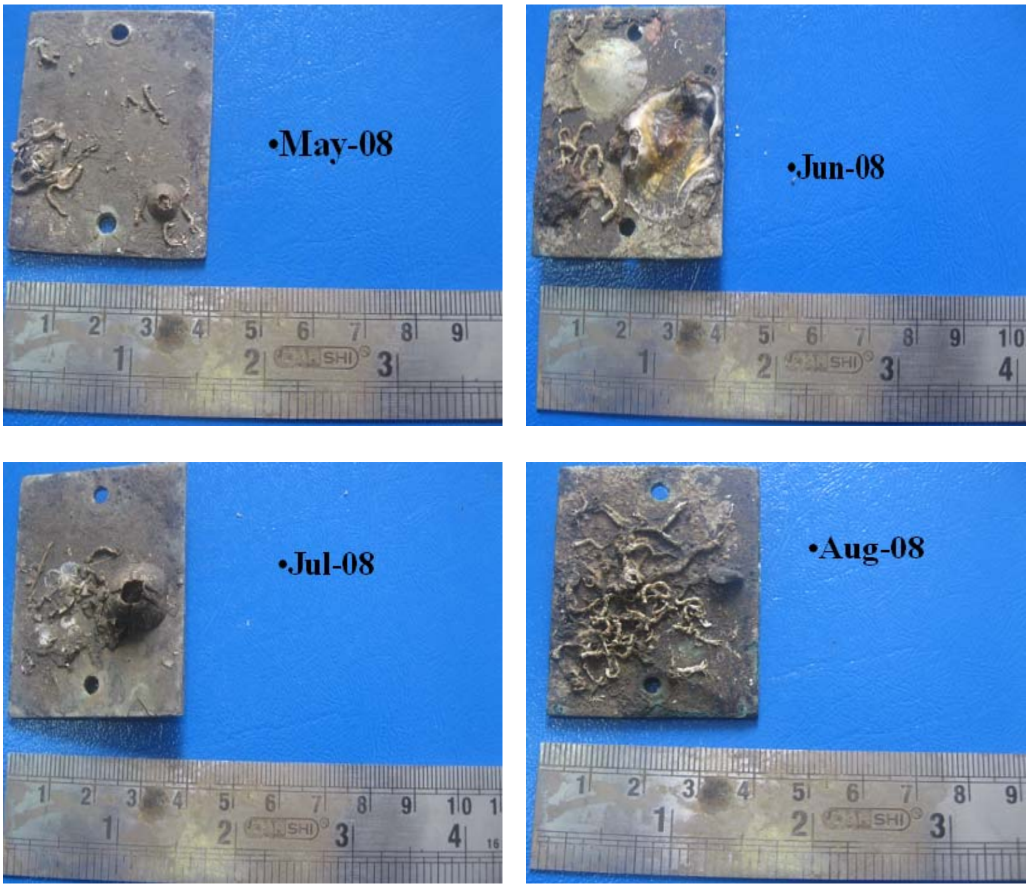

Fig. 6.3 Epoxy coated brass panels after May. 08,Jun. 08,Jul. 08 and Aug. 08 in Cochin estuarine water

6.2 Surface characteristics of brass before the removal of corrosion products

Results of SEM images and EDS spectra of surface morphology of epoxy-coated brass after each exposure period in Cochin estuary are shown in Tables 6.1- 6.12 and Figs 6.4 - 6.15. The four spots on the epoxy coated brass panel for Sep. 07 subjected to detailed EDS analysis reveal the following elements. Spot one has high C, followed by Si, Al, Cl, Mg, Fe, Mo and Ca. Spot two has high C, followed by O, Si, Cl, Mg, Al, Mo, Ca and Fe. Spot three has high O followed by C, Si, Al, Cl, Mg, Fe, Mo and Ca. Spot four has high C, followed by O, Cl, Na, Si, Al, Mg and P (Fig. 6.4 and Table 6.1). The highest element on the epoxy coated brass sample in this month is carbon, which may be due to adherence of organic matter dissolved in seawater. The next predominant elements found on panel are oxygen, sodium and chloride. Oxygen content is seen in all the four spots due to oxidative condition prevailing in this month. Other elements can be from the sediments, which is rich in trace elements.

Figure 6.5 and Table 6.2 indicate the presence of various elements on epoxy coated brass panel of the Oct. 07 immersed in Cochin estuarine water. It is observed that spot one has high C, followed by O, Ca, Cl, Si, Al, Mg, Mo, and Fe. Spot two has high C, followed by O, Cl, Ca, Mo, Si, Mg, Al and Fe. Spot three has high C, followed by O, Si, Al, Cl, Mg, Mo, Fe and Ca. Spot four has high C, followed by O, Si, Al, Ca, Cl, Mg, Mo and Fe. The predominant element found on the epoxy coated brass panel in this month is carbon that can be from organic matter dissolved in seawater. The second highest element is oxygen while chloride is present on corrosion product. Oxygen content is seen in all the four spots as oxidative condition prevails in this month. Other elements can be from the sediments, which is rich in trace elements.

Various elements found on the epoxy coated brass panel for Nov. 07 are given in Fig 6.6 and Table 6.3 and spot one has high C, followed by O, Si, Al, Ca, Cl, Mg, Mo, and Fe. Spot two has high O, followed by Si, C, Fe, Al, Ca, Cl, Mg and Mo. Spot three has high C, followed by O, Si, Al, Mg, Cl, Mo and

Ca. Spot four has high C, followed by O, Mg, Si, Cl, Al, Mo, and Ca. The highly dominant element on the epoxy coated brass sample in this month exposure is carbon, which can be from organic matter dissolved in seawater. The second highest element is oxygen while chloride is present on corrosion product. Oxygen content is seen in all the four spots as oxidative condition prevails in this month. Other elements can be from the sediments, which is rich in trace elements.

The spot analyses of epoxy coated brass panel for the Dec. 07 are shown in Fig. 6.7 and Table 6.4. The spot one has has high C, followed by O, Si, Al, Cl, Ca, Mg, Mo, and Fe. Spot two has high O, followed by C, Si, Al, Ca, Fe, Cl, Mo and Mg. Spot three has high O, followed by Si, C, Al, Cl, Fe, Mo, Mg and Ca. Spot four has high C, followed by O, Si, Cl, Al, Ca, Mo, Fe and Mg. The highly enriched element on the epoxy coated brass sample in this month exposure is carbon, which can be from organic matter dissolved in seawater. The second highest element is oxygen and chloride is present on corrosion product. Oxygen content is seen in all the four spots as oxidative condition prevails in this month. Other elements can be from the sediments, which is rich in trace elements.

In the month of Jan 08, the EDS spectra of epoxy coated brass in Cochin estuary show different elements and the spot one has high Ca, followed by O, C, Fe, Si, Cl, Mg, Mo, Al, and P. Spot two has high C, followed by Ca, O, Mg, Si, Al, Mo Cl, and P. Spot three has high Ca, followed by C, O, Si, Al, Mg, Fe and Cl. Spot four has high Ca, followed by C, O, Mg, Mo, Cl, Fe, Si, Al, S and P (Fig. 6.8 and Table 6.5). The most dominant on the epoxy coated brass sample in this month exposure is carbon, which can be from organic matter dissolved in seawater. The second highest element is calcium and chloride is present on corrosion product. Oxygen content is seen in all the four spots as oxidative condition prevails in this month. Other elements can be from the sediments, which is rich in trace elements.

The corrosion product analysis of epoxy coated brass for Feb. 08 by EDS is given in Fig. 6.9 and Table 6.6. The spot one has high C followed by O, Mo, Mg, Si, Al, Cl, and P. Spot two has high C, followed by O, Si, Al, Mg, Fe, P Cl, and S. Spot three has high C, followed by O, Al, Si, Fe, P, and Cl. Spot four has high C, followed by O, Si, Al, Fe, Mg, Mo, Ca, P, Cl, and S. The highly concentrated element on the epoxy coated brass sample in this month exposure is carbon, which can be from organic matter dissolved in seawater. The second highest element is oxygen and chloride is present on corrosion product. Oxygen content is seen in all the four spots as oxidative condition prevails in this month. Other elements can be from the sediments, which is rich in trace elements.

Different elements on corrosion product of epoxy coated brass panel for Mar. 08 are shown in Fig 6. 10 and Table 6.7 and spot one has high O followed by C, Si, Al, Mg, Fe, Ca, S and P. Spot two has high O followed by Si, C, Al and Mg. Spot three has high C, followed by O, Si, Al, Fe, Mg, Cl, Ca, Mo and P. Spot four has high C, followed by O, Si, Al, Fe, Ca, Cl, Mg, S and P. The highly intensified element on the epoxy coated brass sample in this month exposure is carbon, which can be from organic matter dissolved in seawater. The second highest element is oxygen and chloride is present on corrosion product. Oxygen content is seen in all the four spots as oxidative condition prevails in the fifth month. Other elements can be from the sediments, which is rich in trace elements.

From Fig. 6.11 and Table 6.8, it was noticed that the zone one has high O, followed by C, Si, Al, and Na. Spot two has high O followed by Si, C, Al and Mg. Spot three has high C, followed by O, Si, Al, Fe, Mg, Cl, Ca, Mo and P and S. Spot four has high C, followed by O, Si, Al, Fe, Ca, Mg, Cl, S and P (Apr. 08). The highly predominant element on the epoxy coated brass sample in this month exposure is carbon, which can be from organic matter dissolved in seawater. The second highest element is oxygen and chloride is present on corrosion product. Oxygen content is seen in all the four spots as oxidative condition prevails in this month. Other elements can be from the sediments, which is rich in trace elements.

The different zones on epoxy coated brass for the month of May 08 reveals the different elements and spot one has high Ca followed by C, O, Mo, Mg, Al, Si, and Cl. Spot two has high Ca followed by, C, O, Mo, Mg, Al, Si and Cl. Spot three has high Ca, followed by O, C, Si, Al, Mg, Si, Fe, P and S. Spot four has high C, followed by O, Ca, Si, Al Fe, Mg, Cl and S (Fig. 6.12 and Table 6.9). The most abundant element on the epoxy coated brass sample in this month exposure is calcium, which can be from organic matter dissolved in seawater. The second highest element is carbon and chloride is present on corrosion product. Oxygen content is seen in all the four spots as oxidative condition prevails in this month. Other elements can be from the sediments, which is rich in trace elements.

Figure 6.13 and Table 6.10 indicate the presence of various elements on epoxy coated brass panel of the June 08 in Cochin estuarine water. The spot one has high C followed by Ca, O, Mo, Al, Si, Mg, and Fe. Spot two has high C followed by, O, Ca, Mo, Si, Mg, Al, Cl and Fe. Spot three has high O followed by C, Si, Al, Fe, Mo, Mg, Ca, S, P and Cl. Spot four has high C, followed by Ca, O, Mo, Mg, Si, Cl and Al. The most dominant element on the epoxy coated brass sample in this month exposure is carbon, which can be from organic matter dissolved in seawater. The second highest element is oxygen and chloride is present on corrosion product. Oxygen content is seen in all the four spots as oxidative condition prevails in the fifth month. Other elements can be from the sediments, which is rich in trace elements.

The spot analyses of epoxy coated brass panel for the July 08 is shown in Fig. 6.14 and Table 6.11 and the spot one has high O followed by Si, Al, C, Mg, Fe and Cl. Spot two has high O followed by Mo, C, Si, Al, Fe, Mg, Cl and Ca. Spot three has high O followed by Si, Al, C, Fe, Mg, Cl, Mo, P, S and Ca. Spot four has high O, followed by Si, Al, Fe, C, Cl, Mg, Ca and P. The highly intensified element on the epoxy coated brass sample in this month exposure is oxygen, which can be from organic matter dissolved in seawater. The second highest element is silicon and chloride is present on corrosion product. Oxygen content is seen in all the four spots as oxidative condition prevails in this month. Other elements can be from the sediments, which is rich in trace elements.

In the month of Aug. 08, the EDS spectra of epoxy coated brass in Cochin estuary show different elements and spot one has high C, followed by O, Si, Al, Ca, Fe, Cl, Mo, Mg, S and P. Spot two has high C followed by, Ca, O, Si, Al, Fe, Mg, S, P, and Mo. Spot three has high O followed by Si, C, Al, Fe, Mg, Cl, Mo and P. Spot four has high O, followed by C, Si, Al, Mg, Mo, Fe, Cl and Ca (Fig. 6.15 and Table 6.12). The highly concentrated element on the epoxy coated brass sample in this month exposure is oxygen, which can be from organic matter dissolved in seawater. The second highest element is carbon and chloride is present on corrosion product. Oxygen content is seen in all the four spots as oxidative condition prevails in this month. Other elements can be from the sediments, which is rich in trace elements.

Table 6.1 Results of EDS of epoxy coated brass for Sept. 07 in Cochin estuary

Point 001

Element	Mass%	Compound	Mass%
C	45.76	C	45.76
O	-	-	-
Mg	3.41	MgO	3.41
Al	16.94	Al_2O_3	16.94
Si	23.76	SiO_2	23.76
Cl	3.42	Cl	3.42
Ca	1.35	CaO	1.35
Fe	2.82	FeO	2.82
Mo	2.53	MoO_3	2.53
Total	100		100

Point 003

Element	Mass%	Compound	Mass%
C	30.47	C	30.47
O	31.36	-	-
Mg	2.76	MgO	4.58
Al	10.48	Al_2O_3	19.8
Si	16.13	SiO_2	34.51
Cl	3.92	Cl	3.92
Ca	1.12	CaO	1.57
Fe	2.23	FeO	2.87
Mo	1.52	MoO_3	2.28
Total	100		100

Point 002

Element	Mass%	Compound	Mass%
C	86.57	C	86.57
O	5.27	-	-
Mg	1.07	MgO	1.77
Al	1.6	Al_2O_3	3.03
Si	2.34	SiO_2	5
Cl	2.12	Cl	2.12
Ca	0.24	CaO	0.34
Fe	0.03	FeO	0.04
Mo	0.75	MoO_3	1.13
Total	100		100

Point 004

Element	Mass%	Compound	Mass%
C	77.88	C	77.88
O	7.59	-	-
Na	2.68	Na_2O	3.61
Mg	1.74	MgO	2.88
Al	2.15	Al_2O_3	4.06
Si	2.38	SiO_2	5.08
P	0.69	P_2O_5	1.58
Cl	4.9	Cl	4.9
Total	100		100

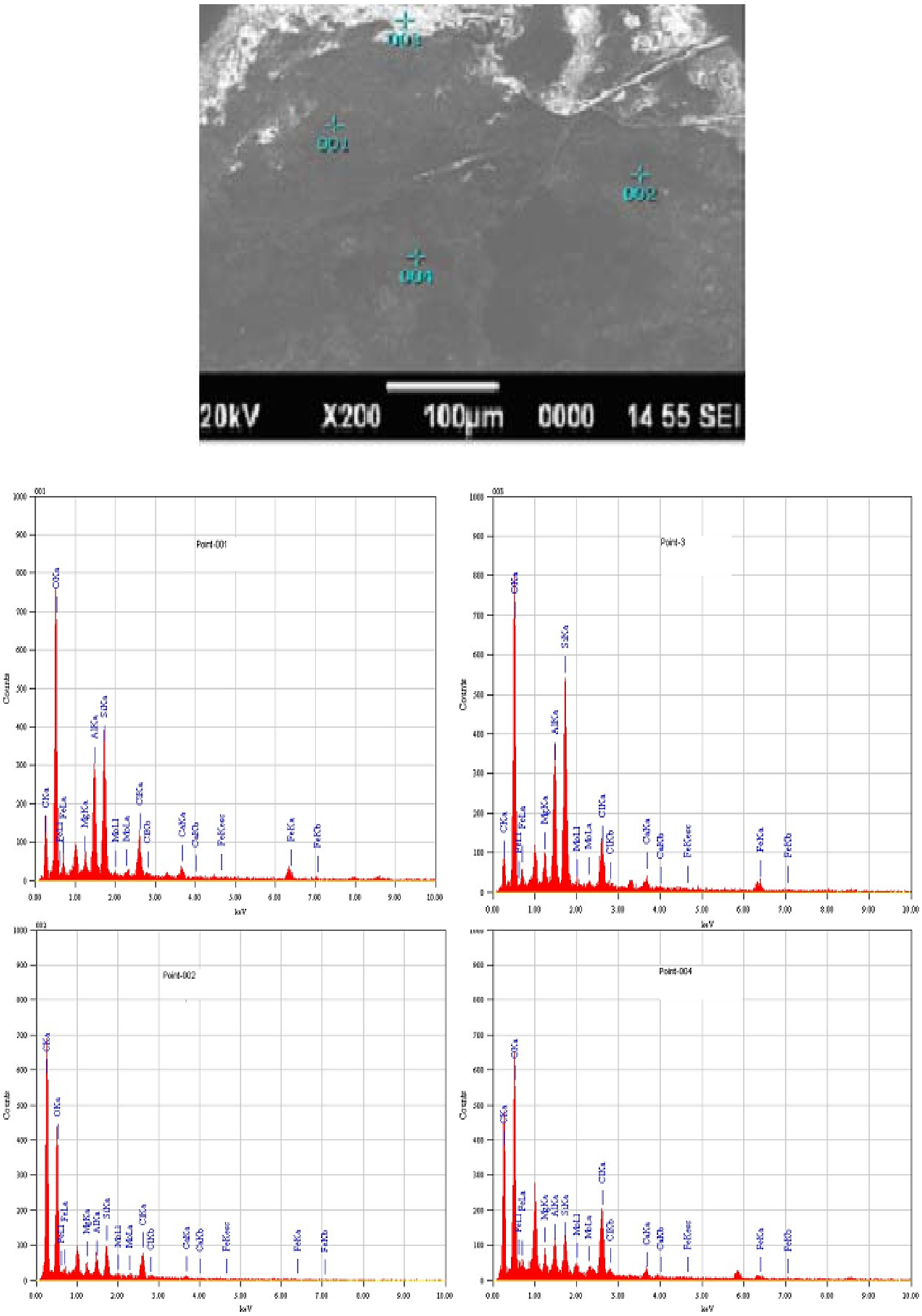

Fig. 6.4 EDS spectra of 4 spots selected from SEM image of epoxy coated brass for the month of Sep. 07

Table 6.2 Results of EDS of epoxy coated brass for Oct. 07 in Cochin estuary

Point 001

Element	**Mass%**	**Compound**	**Mass%**
C	64.09	C	64.09
O	11.91	-	-
Mg	1.69	MgO	2.8
Al	2.86	Al_2O_3	5.41
Si	3.3	SiO_2	7.05
Cl	5.16	Cl	5.16
Ca	9.05	CaO	12.67
Fe	0.37	FeO	0.48
Mo	1.56	MoO_3	2.34
Total	100		100

Point 003

Element	**Mass%**	**Compound**	**Mass%**
C	38.56	C	38.56
O	25.66	-	-
Mg	2.46	MgO	4.08
Al	8.45	Al_2O_3	15.97
Si	12.88	SiO_2	27.55
Cl	7.49	Cl	7.49
Ca	1.11	CaO	1.56
Fe	1.32	FeO	1.7
Mo	2.06	MoO_3	3.09
Total	100		100

Point 002

Element	Mass%	Compound	Mass%
C	74.51	C	74.51
O	7.43	-	-
Mg	1.63	MgO	2.71
Al	1.4	Al_2O_3	2.64
Si	1.8	SiO_2	3.85
Cl	5.93	Cl	5.93
Ca	5.15	CaO	7.2
Fe	0.32	FeO	0.41
Mo	1.82	MoO_3	2.74
Total	100		100

Point 004

Element	Mass%	Compound	Mass%
C	51.26	C	51.26
O	19.14	-	-
Mg	2.46	MgO	4.08
Al	5.86	Al_2O_3	11.07
Si	7.71	SiO_2	16.5
Cl	5.15	Cl	5.15
Ca	5.26	CaO	7.36
Fe	0.74	FeO	0.96
Mo	2.41	MoO_3	3.62
Total	100		100

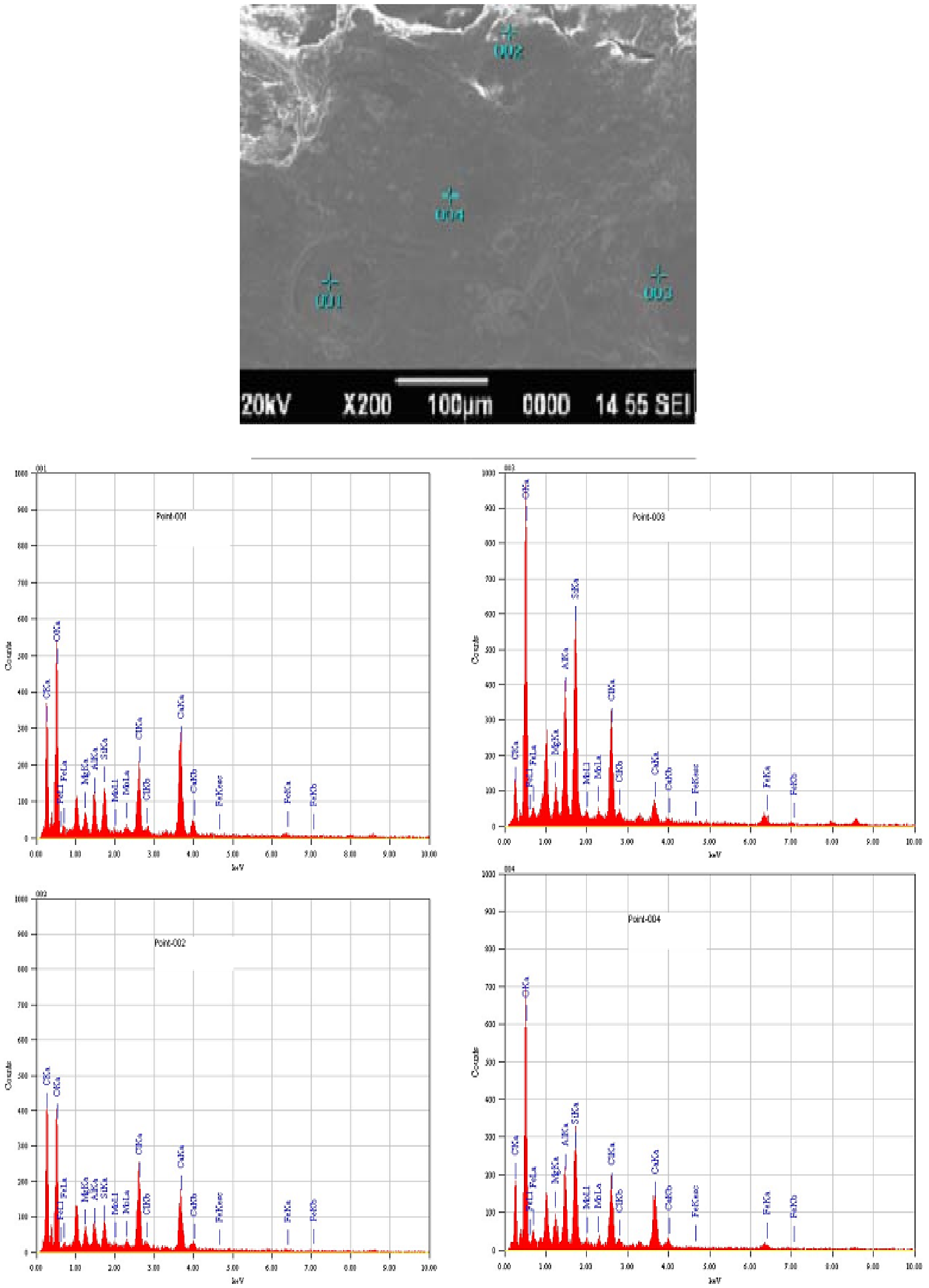

Fig. 6.5 EDS spectra of 4 spots selected from SEM image of epoxy coated brass for the month of Oct. 07

Table 6.3 Results of EDS of epoxy coated brass for Nov. 07 in Cochin estuary

Point 001

Element	Mass%	Compound	Mass%
C	39.95	C	39.95
O	24.1	-	-
Mg	2.95	MgO	4.89
Al	6.89	Al_2O_3	13.02
Si	10.44	SiO_2	22.32
Cl	5.48	Cl	5.48
Ca	6.22	CaO	8.71
Fe	1.53	FeO	1.97
	2.44	MoO_3	3.66
Total	100		100

Point 003

Element	Mass%	Compound	Mass%
C	62.35	C	62.35
O	17.32	-	-
Mg	3.73	MgO	6.19
Al	5	Al_2O_3	9.46
Si	8.75	SiO_2	18.72
Cl	1.95	Cl	1.95
Ca	0.07	CaO	0.1
Fe	-	-	-
Mo	0.83	MoO_3	1.24
Total	100		100

Point 002

Element	Mass%	Compound	Mass%
C	20.61	C	20.61
O	38.25	-	-
Mg	0.85	MgO	1.41
Al	2.77	Al_2O_3	5.23
Si	28.91	SiO_2	61.86
Cl	2.3	Cl	2.3
Ca	2.74	CaO	3.84
Fe	2.79	FeO	3.59
Mo	0.78	MoO_3	1.18
Total	100		100

Point 004

Element	Mass %	Compound	Mass%
C	89.94	C	89.94
O	3.99	-	-
Mg	1.41	MgO	2.33
Al	1.3	Al_2O_3	2.46
Si	1.39	SiO_2	2.98
Cl	1.31	Cl	1.31
Ca	0.17	CaO	0.24
Fe	-	FeO	-
Mo	0.49	MoO_3	0.74
Total	100		100

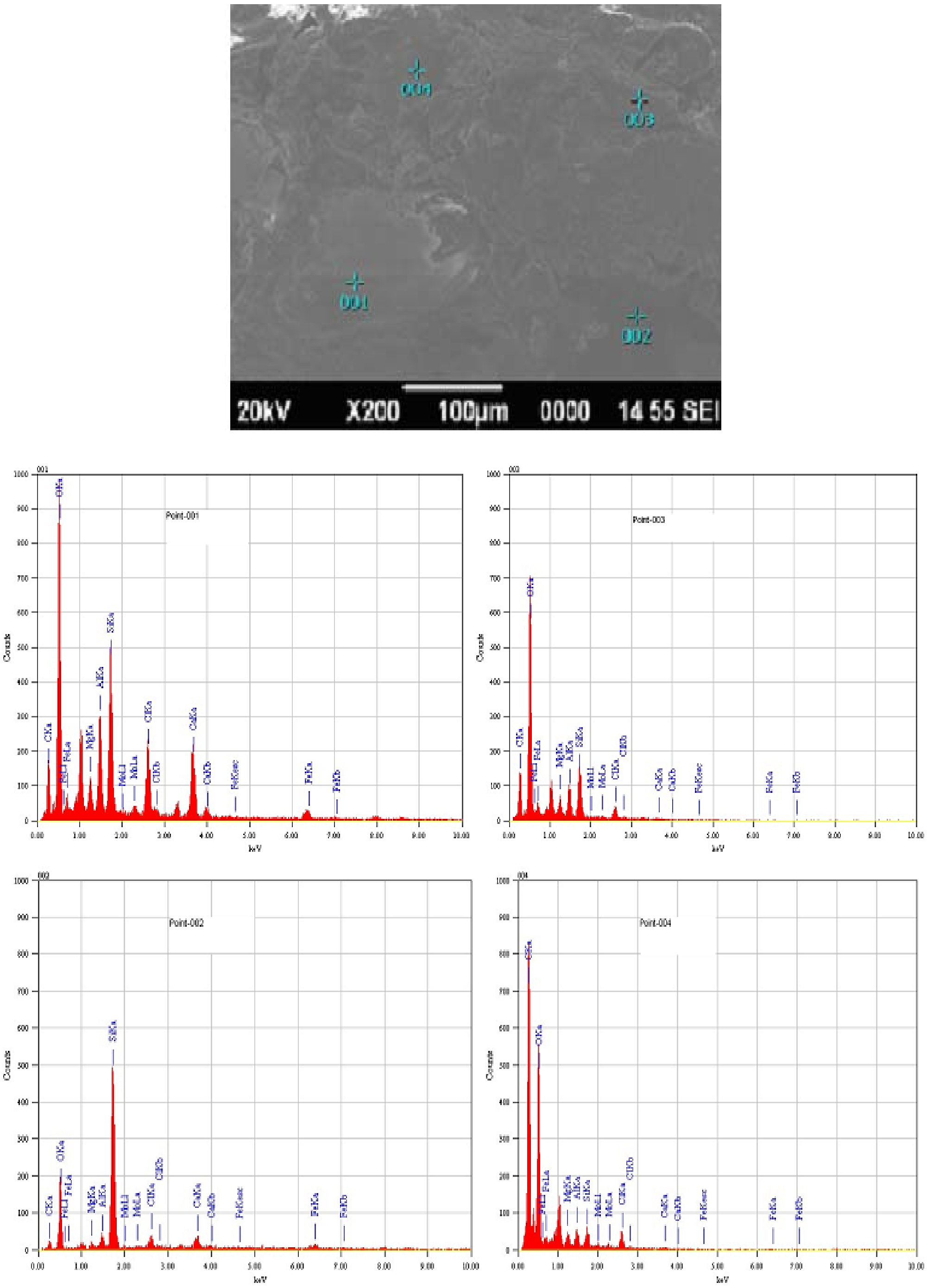

Fig. 6.6 EDS spectra of 4 spots selected from SEM image of epoxy coated brass for the month of Nov. 07

Table 6.4 Results of EDS of epoxy coated brass for Dec. 07 in Cochin estuary

Point 00

Element	Mass%	Compound	Mass%
C	38.96	C	38.96
O	25.09	-	-
Mg	3	MgO	4.97
Al	6.28	Al_2O_3	11.86
Si	12.45	SiO_2	26.63
Cl	5.78	Cl	5.78
Ca	3.08	CaO	4.31
Fe	2.67	FeO	3.43
Mo	2.7	MoO_3	4.06
Total	100		100

Point 003

Element	Mass%	Compound	Mass%
C	15.46	C	15.46
O	35.42	-	-
Mg	3.2	MgO	5.3
Al	9.71	Al_2O_3	18.34
Si	18.62	SiO_2	39.84
Cl	8.7	Cl	8.7
Ca	0.98	CaO	1.37
Fe	4.1	FeO	5.27
Mo	3.81	MoO_3	5.72
Total	100		100

Point 002

Element	Mass%	Compound	Mass%
C	28.82	C	28.82
O	31.57	-	-
Mg	1.71	MgO	2.83
Al	12.11	Al_2O_3	22.88
Si	14.54	SiO_2	31.1
Cl	3	Cl	3
Ca	3.33	CaO	4.67
Fe	3.21	FeO	4.13
Mo	1.72	MoO_3	2.58
Total	100		100

Point 004

Element	Mass %	Compound	Mass%
C	41.87	C	41.87
O	21.27	-	-
Mg	2.69	MgO	4.47
Al	5.52	Al_2O_3	10.42
Si	8.97	SiO_2	19.19
Cl	8.7	Cl	8.7
Ca	4.4	CaO	6.16
Fe	3.15	FeO	4.05
Mo	3.43	MoO_3	5.15
Total	100		100

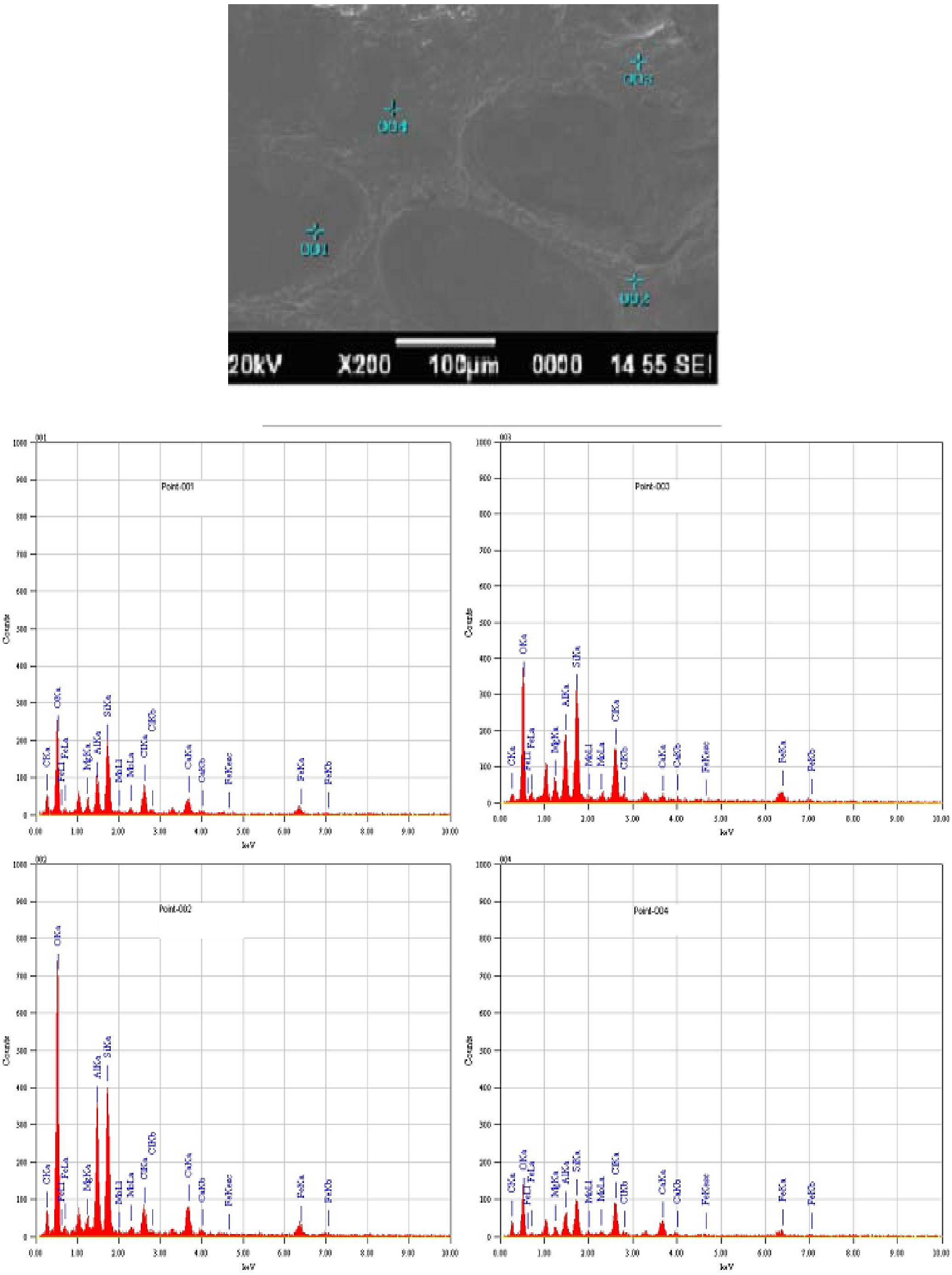

Fig. 6.7 EDS spectra of 4 spots selected from SEM image of epoxy coated brass for the month of Dec. 07

Table 6.5 Results of EDS of epoxy coated brass for Jan. 08 in Cochin estuary

Point 001

Element	Mass%	Compound	Mass%
C	20.76	C	20.76
O	24.33	-	-
Mg	1.51	MgO	2.5
Al	0.84	Al_2O_3	1.59
Si	5.07	SiO_2	10.85
P	0.48	P_2O_5	1.1
S	-	-	-
Cl	2.86	Cl	2.86
Ca	29.62	CaO	41.44
Fe	13.53	FeO	17.4
Mo	0.98	MoO_3	1.47
Total	100		100

Point-002

Element	**Mass%**	**Compound**	**Mass%**
C	56.9	C	56.9
O	14.78	-	-
Mg	5.29	MgO	8.78
Al	1.39	Al_2O_3	2.63
Si	1.99	SiO_2	4.26
P	0.14	P_2O_5	0.33
S	-	-	-
Cl	0.66	Cl	0.66
Ca	17.97	CaO	25.15
Fe	-	-	-
Mo	0.87	MoO_3	1.3
Total	100		100

Point-003

Element	**Mass%**	**Compound**	**Mass%**
C	28.65	C	28.65
O	22.45	-	-
Mg	1.87	MgO	3.11
Al	2.21	Al_2O_3	4.17
Si	2.63	SiO_2	5.63
P	0	P_2O_5	0
S	-	-	-
Cl	1.08	Cl	1.08
Ca	39.73	CaO	55.59
Fe	1.38	FeO	1.78
Mo	-	-	-
Total	100		100

Point-004

Element	**Mass %**	**Compound**	**Mass%**
C	29.58	C	29.58
O	21.15	-	-
Mg	4.12	MgO	6.82
Al	0.09	Al_2O_3	0.18
Si	0.12	SiO_2	0.26
P	0.02	P_2O_5	0.04
S	0.07	SO_3	0.17
Cl	0.34	Cl	0.34
Ca	40.97	CaO	57.32
Fe	0.12	FeO	0.15
Mo	3.42	MoO_3	5.13
Total	100		100

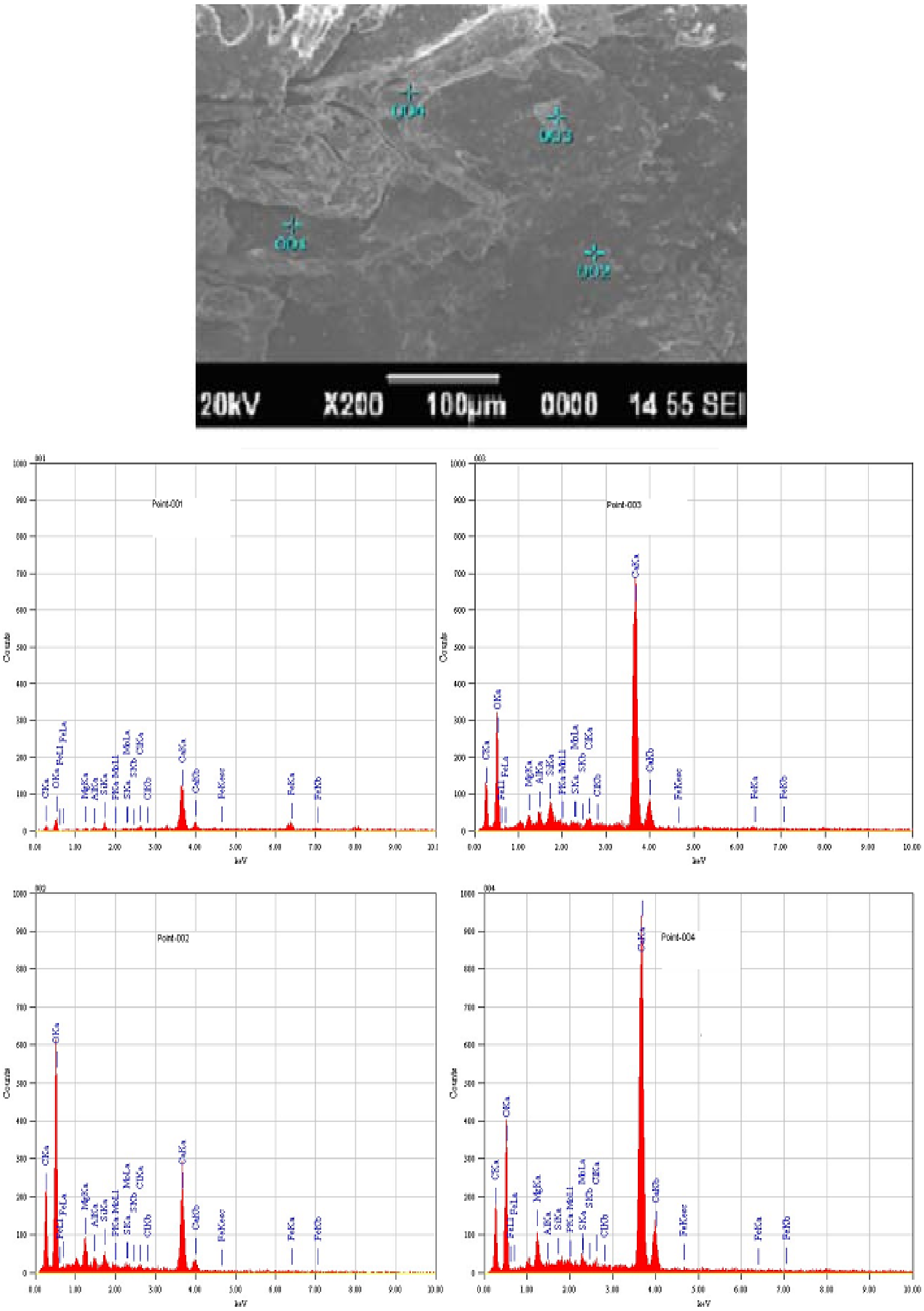

Fig. 6.8 EDS spectra of 4 spots selected from SEM image of epoxy coated brass for the month of Jan. 08

Table 6.6 Results of EDS of epoxy coated brass for Feb. 08 in Cochin estuary

Point 001

Element	Mass%	Compound	Mass%
C	97.87	C	97.87
O	0.89	-	-
Mg	0.29	MgO	0.49
Al	0.16	Al_2O_3	0.31
Si	0.26	SiO_2	0.55
P	0.08	P_2O_5	0.19
S	-	-	-
Cl	0.13	Cl	0.13
Ca	-	-	-
Fe	-	-	-
Mo	0.3	MoO_3	0.46
Total	100		100

Point-003

Element	Mass%	Compound	Mass%
C	98.16	C	98.16
O	0.84	-	-
Mg	-	-	-
Al	0.32	Al_2O_3	0.6
Si	0.32	SiO_2	0.68
P	0.12	P_2O_5	0.27
S	-	-	-
Cl	0.07	Cl	0.07
Ca	-	-	-
Fe	0.17	FeO	0.22
Mo	-	-	-
Total	100		100

Point-002

Element	Mass%	Compound	Mass%
C	74.17	C	74.17
O	12.93	-	-
Mg	0.75	MgO	1.24
Al	4.11	Al_2O_3	7.76
Si	7.47	SiO_2	15.98
P	0.08	P_2O_5	0.19
S	0.04	SO_3	0.11
Cl	0.07	Cl	0.07
Ca	-	-	-
Fe	0.37	FeO	0.48
Mo	-	-	-
Total	100		100

Point-004

Element	Mass %	Compound	Mass%
C	76.02	C	76.02
O	11.07	-	-
Mg	1.18	MgO	1.95
Al	3.53	Al_2O_3	6.66
Si	5.06	SiO_2	10.82
P	0.27	P_2O_5	0.62
S	0.03	SO_3	0.07
Cl	0.14	Cl	0.14
Ca	0.34	CaO	0.48
Fe	1.49	FeO	1.92
Mo	0.88	MoO_3	1.32
Total	100		100

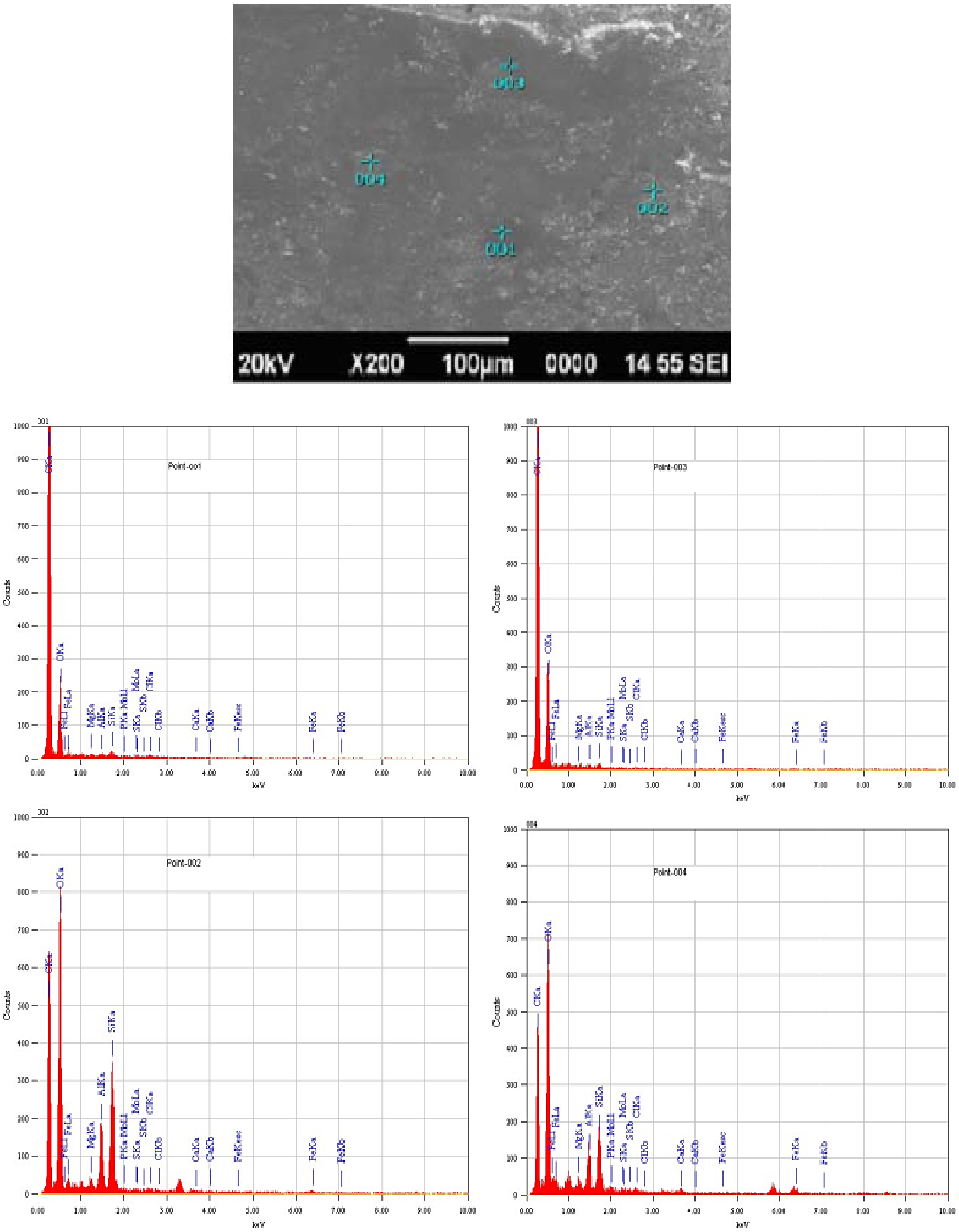

Fig. 6.9 EDS spectra of 4 spots selected from SEM image of epoxy coated brass for the month of Feb. 08

Table 6.7 Results of EDS of epoxy coated brass for Mar. 08 in Cochin estuary

Point 001

Element	Mass%	Compound	Mass%
C	28.47	C	28.47
O	36.47	-	-
Mg	0.8	MgO	1.33
Al	10.09	Al_2O_3	19.06
Si	23.13	SiO_2	49.49
P	0.1	P_2O_5	0.24
S	0.14	SO_3	0.35
Cl	0	Cl	0
Ca	0.37	CaO	0.52
Fe	0.41	FeO	0.53
Mo	-	-	-
Total	100		100

Point-003

Element	Mass%	Compound	Mass%
C	32.25	C	32.25
O	32.1	-	-
Mg	2.52	MgO	4.18
Al	9.94	Al_2O_3	18.78
Si	17.24	SiO_2	36.87
P	0.32	P_2O_5	0.73
S	-	-	-
Cl	0.91	Cl	0.91
Ca	0.71	CaO	0.99
Fe	3.5	FeO	4.5
Mo	0.52	MoO_3	0.78
Total	100		100

Point-002

Element	Mass%	Compound	Mass%
C	19.8	C	19.8
O	41.42	-	-
Mg	0.64	MgO	1.06
Al	9.87	Al_2O_3	18.66
Si	28.28	SiO_2	60.49
P	-	-	-
S	-	-	-
Cl	-	-	-
Ca	-	-	-
Fe	-	-	-
Mo	-	-	-
Total	100		100

Point-004

Element	Mass %	Compound	Mass%
C	66.14	C	66.14
O	16.7	-	-
Mg	0.67	MgO	1.11
Al	2.68	Al_2O_3	5.07
Si	10.96	SiO_2	23.44
P	0.28	P_2O_5	0.65
S	0.29	SO_3	0.73
Cl	0.57	Cl	0.57
Ca	0.77	CaO	1.08
Fe	0.93	FeO	1.2
Mo	-	-	-
Total	100		100

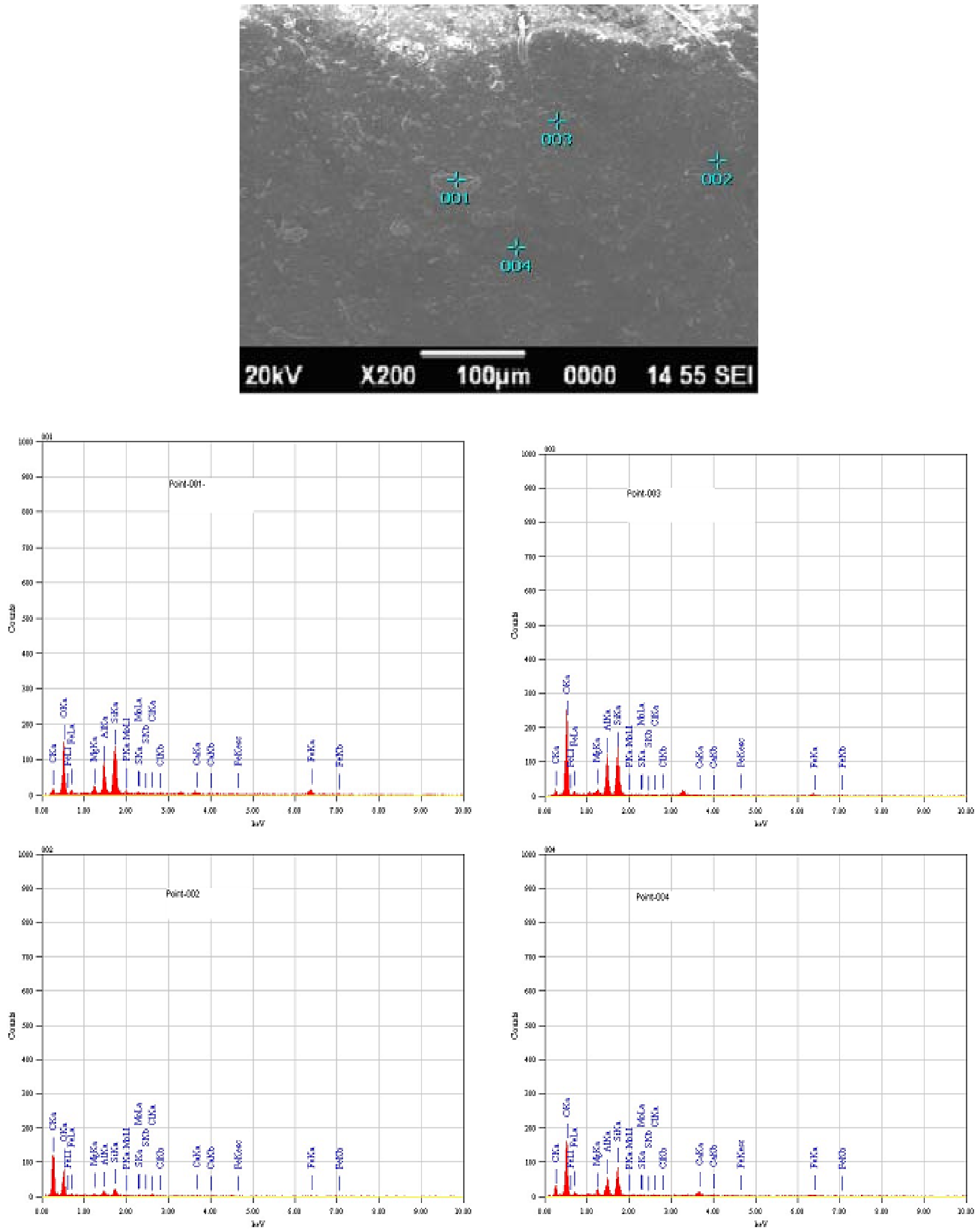

Fig. 6.10 EDS spectra of 4 spots selected from SEM image of epoxy coated brass for the month of Mar. 08

Table 6.8 Results of EDS of epoxy coated brass for Apr. 08 in Cochin estuary

Point 001

Element	Mass%	Compound	Mass%
C	25.9	C	25.9
O	35.79	-	-
Na	6.86	Na_2O	9.25
Al	9.72	Al_2O_3	18.37
Si	21.73	SiO_2	46.48
Total	100		100

Point-003

Element	Mass%	Compound	Mass%
C	32.25	C	32.25
O	32.1	-	-
Mg	2.52	MgO	4.18
Al	9.94	Al_2O_3	18.78
Si	17.24	SiO_2	36.87
P	0.32	P_2O_5	0.73
S	-	-	-
Cl	0.91	Cl	0.91
Ca	0.71	CaO	0.99
Fe	3.5	FeO	4.5
Mo	0.52	MoO_3	0.78
Total	100		100

Point-002

Element	Mass%	Compound	Mass%
C	19.8	C	19.8
O	41.42	-	-
Mg	0.64	MgO	1.06
Al	9.87	Al_2O_3	18.66
Si	28.28	SiO_2	60.49
P	-	-	-
S	-	-	-
Cl	-	-	-
Ca	-	-	-
Fe	-	-	-
Mo	-	-	-
Total	100		100

Point-004

Element	Mass %	Compound	Mass%
C	66.14	C	66.14
O	16.7	-	-
Mg	0.67	MgO	1.11
Al	2.68	Al_2O_3	5.07
Si	10.96	SiO_2	23.44
P	0.28	P_2O_5	0.65
S	0.29	SO_3	0.73
Cl	0.57	Cl	0.57
Ca	0.77	CaO	1.08
Fe	0.93	FeO	1.2
Mo	-	-	-
Total	100		100

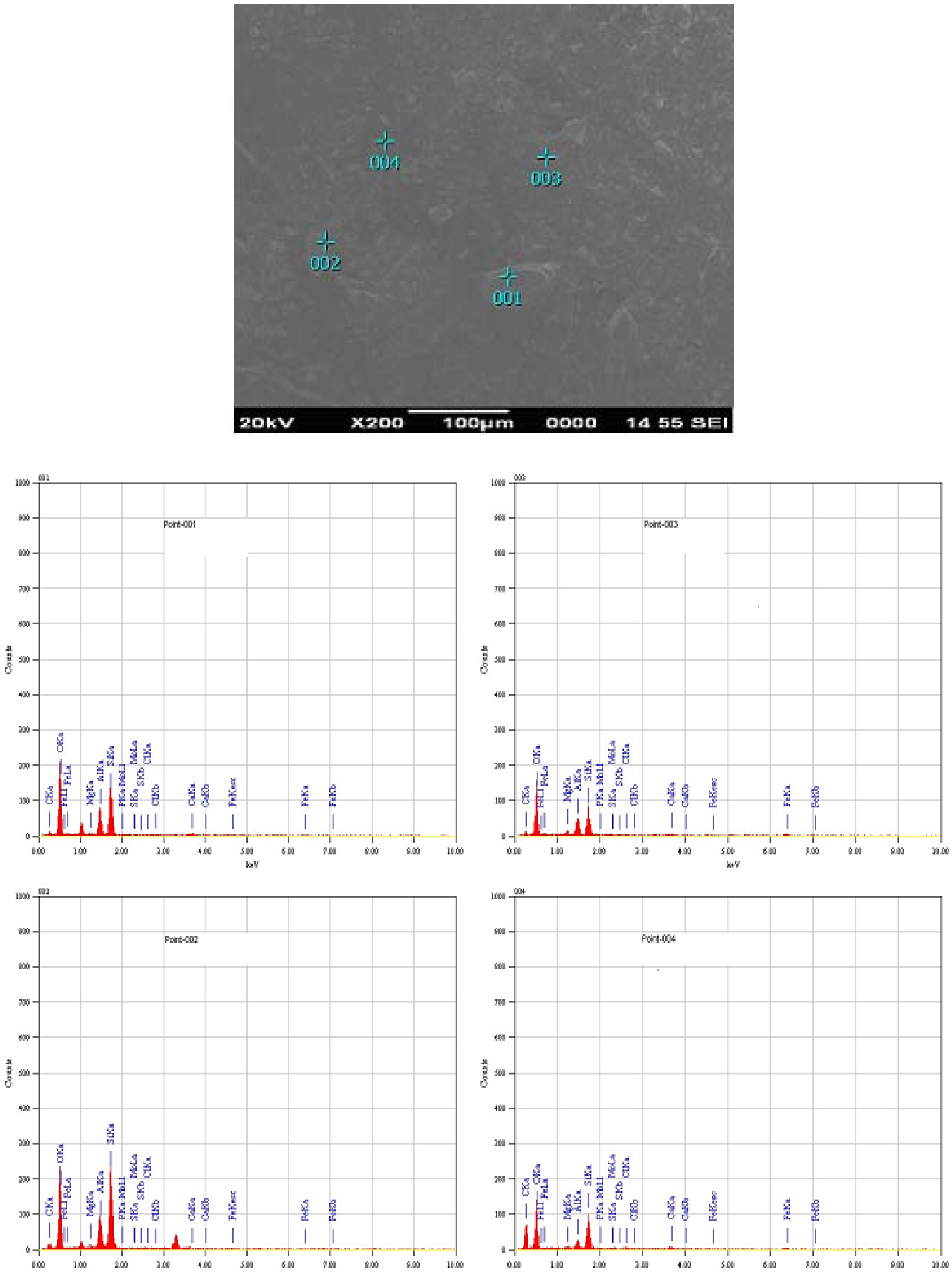

Fig. 6.11 EDS spectra of 4 spots selected from SEM image of epoxy coated brass for the month of Apr. 08

Table 6.9 Results of EDS of epoxy coated brass for May 08 in Cochin estuary

Point 001

Element	Mass%	Compound	Mass%
C	31.15	C	31.15
O	20.18	-	-
Mg	0.44	MgO	0.72
Al	0.39	Al_2O_3	0.74
Si	0.27	SiO_2	0.57
P	-	-	-
S	-	-	-
Cl	0.11	Cl	0.11
Ca	44.6	CaO	62.41
Fe	-	-	-
Mo	2.86	MoO_3	4.29
Total	100		100

Point-002

Element	Mass%	Compound	Mass%
C	23.35	C	23.35
O	23.17	-	-
Mg	1.92	MgO	3.19
Al	1.03	Al_2O_3	1.95
Si	0.81	SiO_2	1.73
P	-	-	-
S	-	-	-
Cl	0.12	Cl	0.12
Ca	46.97	CaO	65.72
Fe	-	-	-
Mo	2.62	MoO_3	3.93
Total	100		100

Point-003

Element	Mass%	Compound	Mass%
C	26.29	C	26.29
O	27.76	-	-
Mg	2.02	MgO	3.35
Al	4.48	Al_2O_3	8.47
Si	8.25	SiO_2	17.64
P	0.67	P_2O_5	1.52
S	0.17	SO_3	0.43
Cl	-	-	-
Ca	28.66	CaO	40.1
Fe	1.71	FeO	2.2
Mo	-	-	-
Total	100		100

Point-004

Element	Mass %	Compound	Mass%
C	38.32	C	38.32
O	25.04	-	-
Mg	1.84	MgO	3.05
Al	5.76	Al_2O_3	10.89
Si	9.26	SiO_2	19.81
P	-	-	-
S	0.59	SO_3	1.47
Cl	0.41	Cl	0.41
Ca	16.72	CaO	23.4
Fe	2.05	FeO	2.64
Mo	-	-	-
Total	100		100

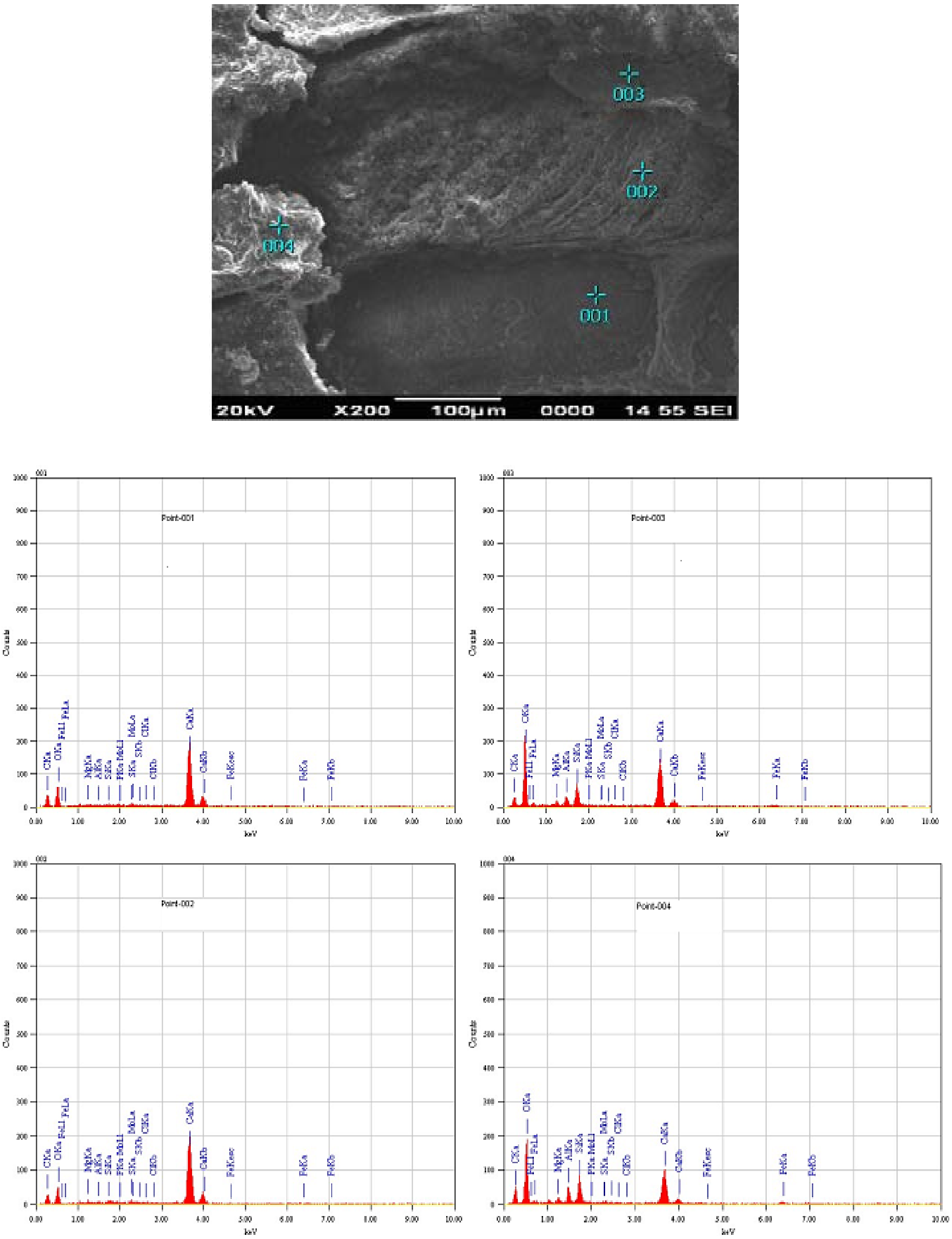

Fig. 6.12 EDS spectra of 4 spots selected from SEM image of epoxy coated brass for the month of May 08

Table 6.10 Results of EDS of epoxy coated brass for Jun. 08 in Cochin estuary

Point 001

Element	Mass%	Compound	Mass%
C	63.22	C	63.22
O	11.73	-	-
Mg	0.99	MgO	1.65
Al	1.36	Al_2O_3	2.56
Si	1.09	SiO_2	2.32
P	-	-	-
S	-	-	-
Cl	0.6	Cl	0.6
Ca	18.19	CaO	25.44
Fe	0.19	FeO	0.24
Mo	2.63	MoO_3	3.95
Total	100		100

Point-003

Element	Mass%	Compound	Mass%
C	25.97	C	25.97
O	35.69	-	-
Mg	1.4	MgO	2.32
Al	8.04	Al_2O_3	15.19
Si	20.91	SiO_2	44.74
P	0.29	P_2O_5	0.67
S	0.54	SO_3	1.35
Cl	0.12	Cl	0.12
Ca	0.94	CaO	1.31
Fe	3.83	FeO	4.93
Mo	2.26	MoO_3	3.39
Total	100		100

Point-002

Element	Mass%	Compound	Mass%
C	65.92	C	65.92
O	11.88	-	-
Mg	1.65	MgO	2.74
Al	0.96	Al_2O_3	1.81
Si	2.42	SiO_2	5.18
P	-	-	-
S	-	-	-
Cl	0.29	Cl	0.29
Ca	12.2	CaO	17.07
Fe	0.15	FeO	0.19
Mo	4.53	MoO_3	6.8
Total	100		100

Point-004

Element	Mass %	Compound	Mass%
C	80.26	C	80.26
O	6.57	-	-
Mg	1.42	MgO	2.36
Al	0.09	Al_2O_3	0.17
Si	1.08	SiO_2	2.32
P	-	-	-
S	-	-	-
Cl	0.35	Cl	0.35
Ca	7.84	CaO	10.97
Fe	-	-	-
Mo	2.38	MoO_3	3.56
Total	100		100

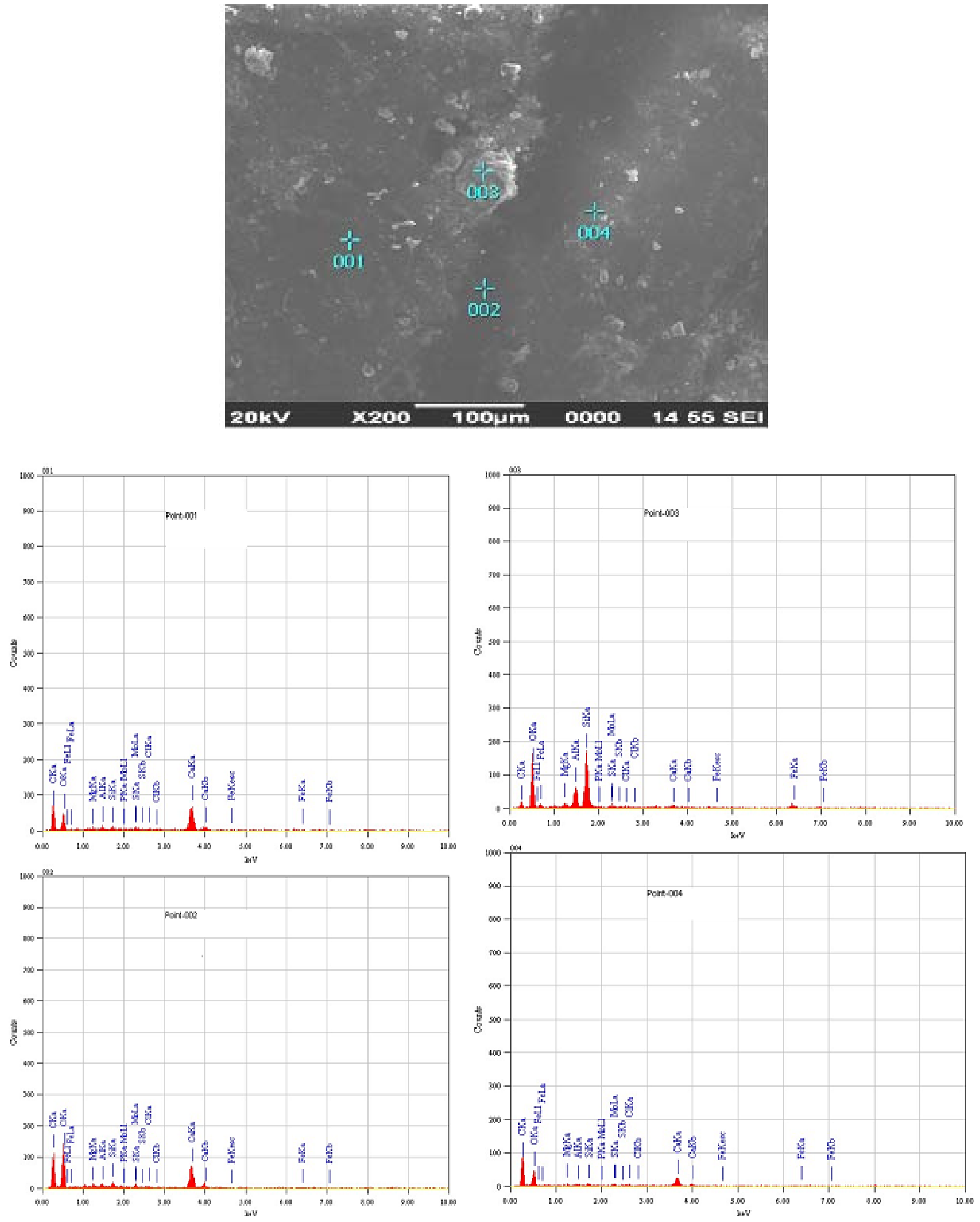

Fig. 6.13 EDS spectra of 4 spots selected from SEM image of epoxy coated brass for the month of Jun. 08

Table 6.11 Results of EDS of epoxy coated brass for Jul. 08 in Cochin estuary

Point 001

Element	Mass%	Compound	Mass%
C	6.43	C	6.43
O	47.98	-	-
Mg	0.77	MgO	1.28
Al	12.52	Al_2O_3	23.65
Si	31.82	SiO_2	68.07
P	-	-	-
S	-	-	-
Cl	0.18	Cl	0.18
Ca	-	-	-
Fe	0.31	FeO	0.4
Mo	-	-	-
Total	100		100

Point-003

Element	Mass%	Compound	Mass%
C	9.06	C	9.06
O	41.76	-	-
Mg	2.84	MgO	4.7
Al	13.7	Al_2O_3	25.89
Si	20.31	SiO_2	43.46
P	0.83	P_2O_5	1.91
S	0.41	SO_3	1.02
Cl	2.22	Cl	2.22
Ca	0.41	CaO	0.57
Fe	7.12	FeO	9.16
Mo	1.34	MoO_3	2.01
Total	100		100

Point-002

Element	Mass%	Compound	Mass%
C	15.27	C	15.27
O	33.32	-	-
Mg	2.78	MgO	4.61
Al	7.82	Al_2O_3	14.77
Si	9.78	SiO_2	20.93
P	-	-	-
S	-	-	-
Cl	2.48	Cl	2.48
Ca	0.59	CaO	0.82
Fe	3.92	FeO	5.04
Mo	24.05	MoO_3	36.08
Total	100		100

Point-004

Element	Mass %	Compound	Mass%
C	10.27	C	10.27
O	40.99	-	-
Mg	2.67	MgO	4.42
Al	12.32	Al_2O_3	23.28
Si	22.05	SiO_2	47.18
P	0.61	P_2O_5	1.4
S	-	-	-
Cl	3.13	Cl	3.13
Ca	0.68	CaO	0.95
Fe	7.28	FeO	9.37
Mo	-	-	-
Total	100		100

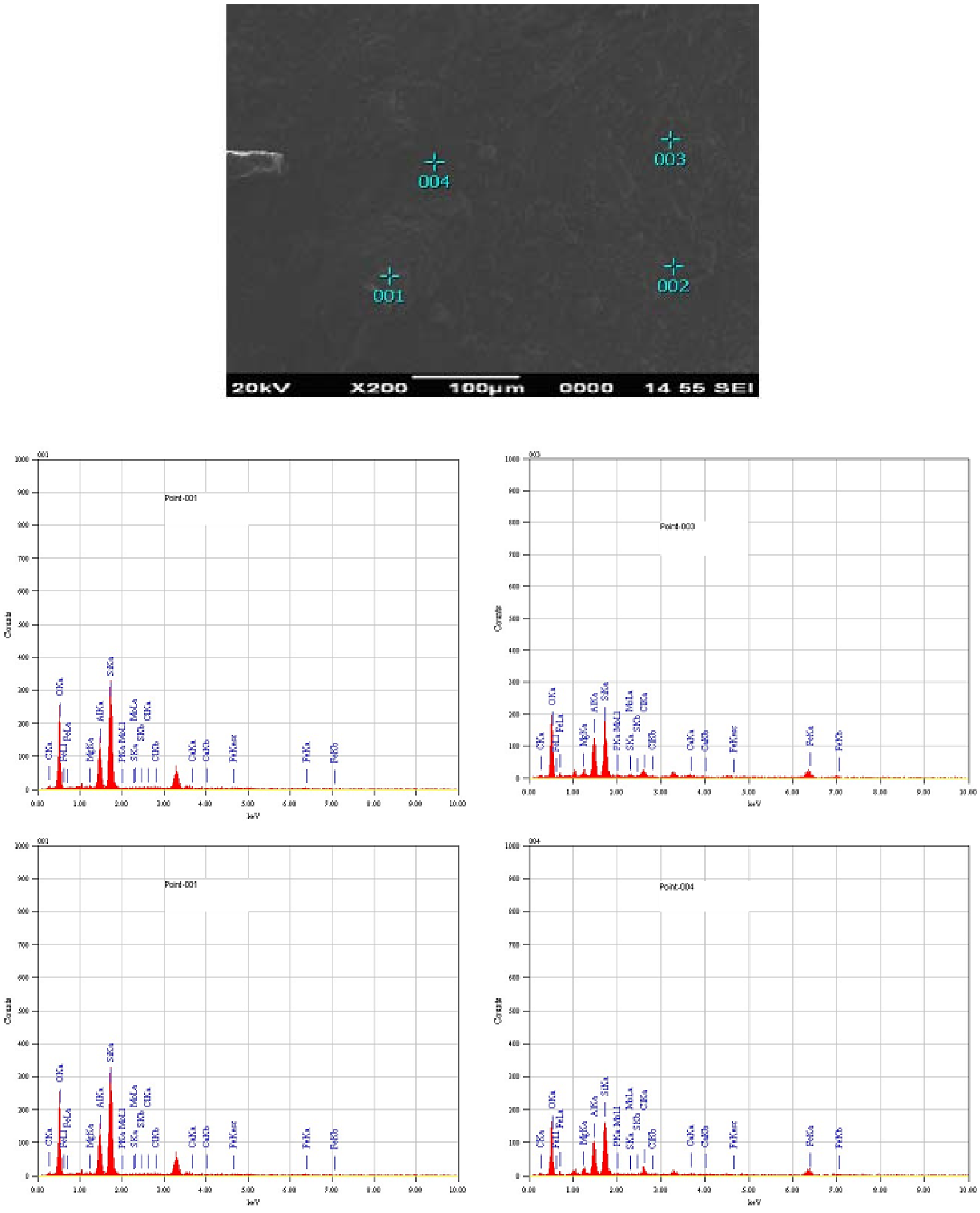

Fig. 6.14 EDS spectra of 4 spots selected from SEM image of epoxy coated brass for the month of Jul. 08

Table 6.12 Results of EDS of epoxy coated brass for Aug. 08 in Cochin estuary

Point 001

Element	Mass%	Compound	Mass%
C	31.77	C	31.77
O	30.97	-	
Mg	2.21	MgO	3.66
Al	9.1	Al_2O_3	17.2
Si	14.97	SiO_2	32.02
P	0.08	P_2O_5	0.18
S	0.56	SO_3	1.41
Cl	1.37	Cl	1.37
Ca	5.13	CaO	7.18
Fe	2.53	FeO	3.26
Mo	1.31	MoO_3	1.97
Total	100		100

Point-003

Element	**Mass%**	**Compound**	**Mass%**
C	15.61	C	15.61
O	39.94	-	-
Mg	4.75	MgO	7.87
Al	10.76	Al_2O_3	20.33
Si	22.23	SiO_2	47.56
P	0.12	P_2O_5	0.27
S	-	-	-
Cl	1.02	Cl	1.02
Ca	-	-	-
Fe	4.82	FeO	6.2
Mo	0.76	MoO_3	1.13
Total	100		100

Point-002

Element	**Mass%**	**Compound**	**Mass%**
C	36.36	C	36.36
O	22.98	-	-
Mg	1.47	MgO	2.45
Al	3.61	Al_2O_3	6.82
Si	5.69	SiO_2	12.18
P	0.14	P_2O_5	0.32
S	0.4	SO_3	1
Cl	-	-	-
Ca	27.44	CaO	38.39
Fe	1.78	FeO	2.28
Mo	0.14	MoO_3	0.21
Total	100		100

Point-004

Element	**Mass %**	**Compound**	**Mass%**
C	28.12	C	28.12
O	34.06	-	-
Mg	4.21	MgO	6.97
Al	11.13	Al_2O_3	21.04
Si	17.28	SiO_2	36.98
P	-	-	-
S	-	-	-
Cl	0.88	Cl	0.88
Ca	0.38	CaO	0.53
Fe	1.96	FeO	2.52
Mo	1.98	MoO_3	2.97
Total	100		100

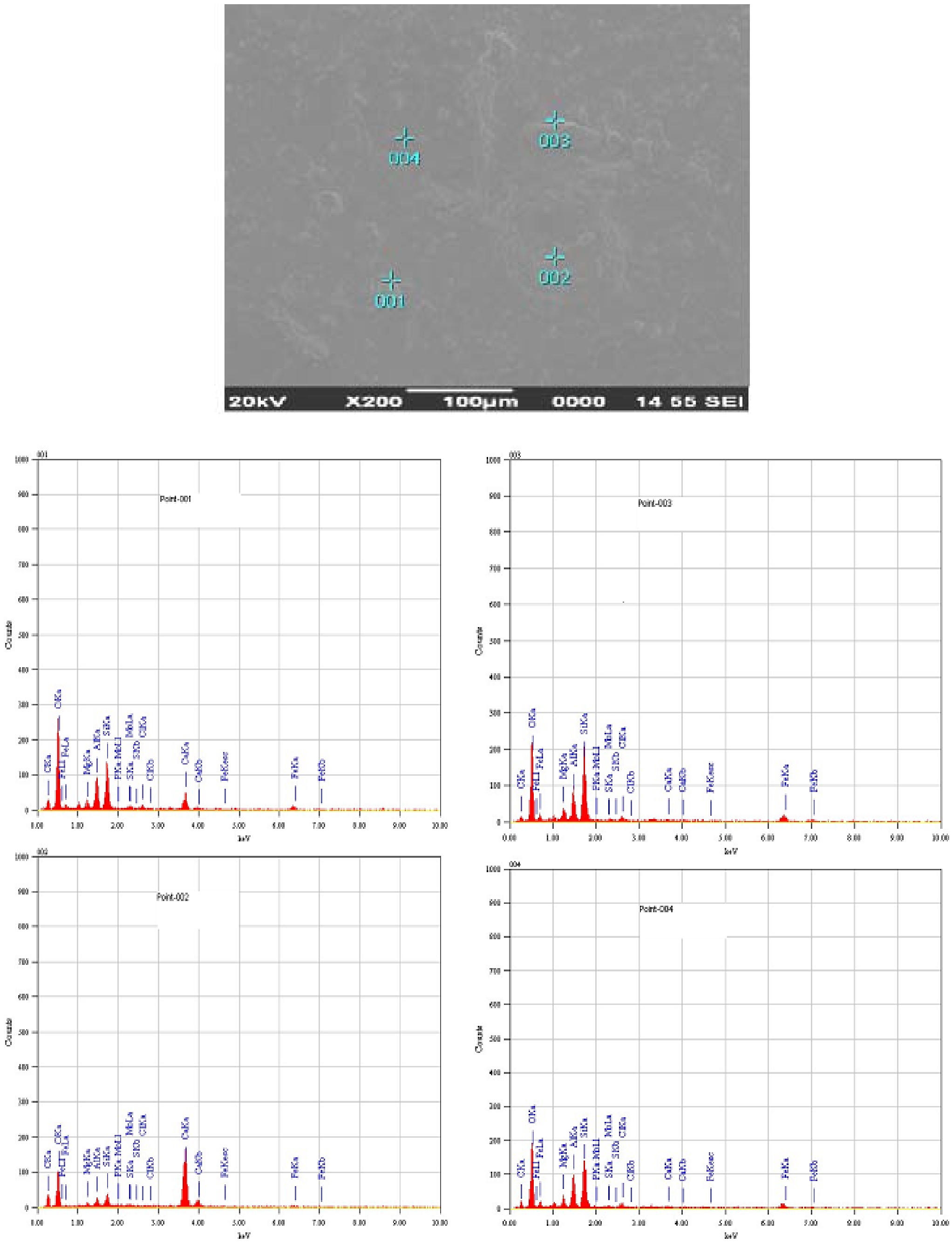

Fig. 6.15 EDS spectra of 4 spots selected from SEM image of epoxy coated brass for the month of Aug. 08

The above results suggest that there is no indication of zinc and copper on exposed panels and there is no dezincification process in all the samples exposed in Cochin estuarine water during the study period. This is due to the barrier action provided by epoxy coating. The chloride ions are not more than 8.7 % in all months and hence chloride ion does not have significant effect on epoxy coated brass. Calcium also contributes to the corrosion resistance of brass along with epoxy coating. According to Jones (1996), the deposition of $CaCO_3$ and Mg $(OH)_2$ should be able to reduce corrosion rate. The presence of carbonates of calcium, magnesium and strontium in the corrosion products of metal exposed to seawater is well known (LaQue, 1975; Schumacher, 1979). Chloride content can have harmful effects in corrosion product layers. The propagation rates of pitting decreases with decrease of chlorinity (Kota et al., 1984).

Sand, silt and other abrasive particles in suspension in seawater can aggravate deterioration of metals by removal of protective corrosion products and scale (Kuester et al., 1966). Calcium and magnesium containing deposits should be able to decrease the corrosion rate of steel (Muller et al., 2006). The composition of corrosion products and of calcareous deposits formed under cathodic polarization conditions will also influence metal corrosion (Boyd and Fink, 1978; Davis, 1987). For common steels and copper alloys, the effect of dissolved oxygen is dependent on the seawater flow velocity. The oxygen concentration has negligible effect on copper alloy corrosion rates in quiescent seawater while at seawater flow rate of 1.8 m/sec, increasing oxygen content accelerates the corrosion rate of copper(Boyd, 1978; Davis, 1987). The components such as CO_2, H_2S, NH_2, organic and inorganic acids and sulphites present in the seawater as a results of higher biological activities may also accelerate localized attack on brass (Pope et al., 1984). Organic matter and corrosion products was inversely correlated with the corrosion rate of mild steel and a metal – organic matter complex was probably involved in developing a passive film on the metal surface (Bhosle and Wagh, 1992). The increase in the concentration of organic matter by microorganisms of the corrosion products was associated with a decrease in the corrosion rate (Ford et al., 1988).

6.3 Surface compound analysis

X-ray powder pattern of the compound formed on epoxy coated brass at each exposure months in Cochin estuarine water is shown from Figs. 6.16-6.18. Various types of compounds are found on the epoxy-coated brass with different months. The surface of epoxy coated brass panels for the month of Sept. 07 and Oct. 07 are characterized by the presence of silicon oxide and strontium silicon while for Nov. 07 and Dec.07, tin oxide and aluminum phosphate are observed. Silicon nitride and silicon phosphorous are found for Jan. 08 while for Feb. 08 silicon oxide and iron oxide are noticed. Compounds identified for the month of Mar. 08 consist of silicon phosphorous, magnesium silicate and iron carbide.

The presence of phosphorous fluoride, silicon nitride and phosphorous sulfide is found on surface of epoxy coated brass in Apr. 08 while for May 08, silicon phosphorous, copper sulfate and iron silicon are observed. Phosphorous sulfide and copper sulfate are two components identified for Jun. 08 while silicon oxide, tin oxide and aluminum phosphate are seen in Jul. 08. For Aug. 08, silicon oxide, phosphorous sulfide and iron phosphate are identified. In the initial four months (Sept. 07-Dec. 07), the epoxy coated brass panels are affected by silicon, oxide, strontium silicon, tin and aluminium phosphate from the estuarine water and these months coincided with post monsoon periods. In the next four months (Jan. 08 - Apr. 08), silicon, nitride, iron, sulfide, phosphorous, silicate, carbide, oxide, magnesium and fluoride have altered the surface of epoxy coated brass and these months are pre-monsoon period without much fresh water inflow. In the last four months (May 08-Aug.08) sulfide, iron, phosphorous, tin, sulfate, silicon, oxide, aluminium and phosphate have an effect on the surface. These months are peak monsoon period.

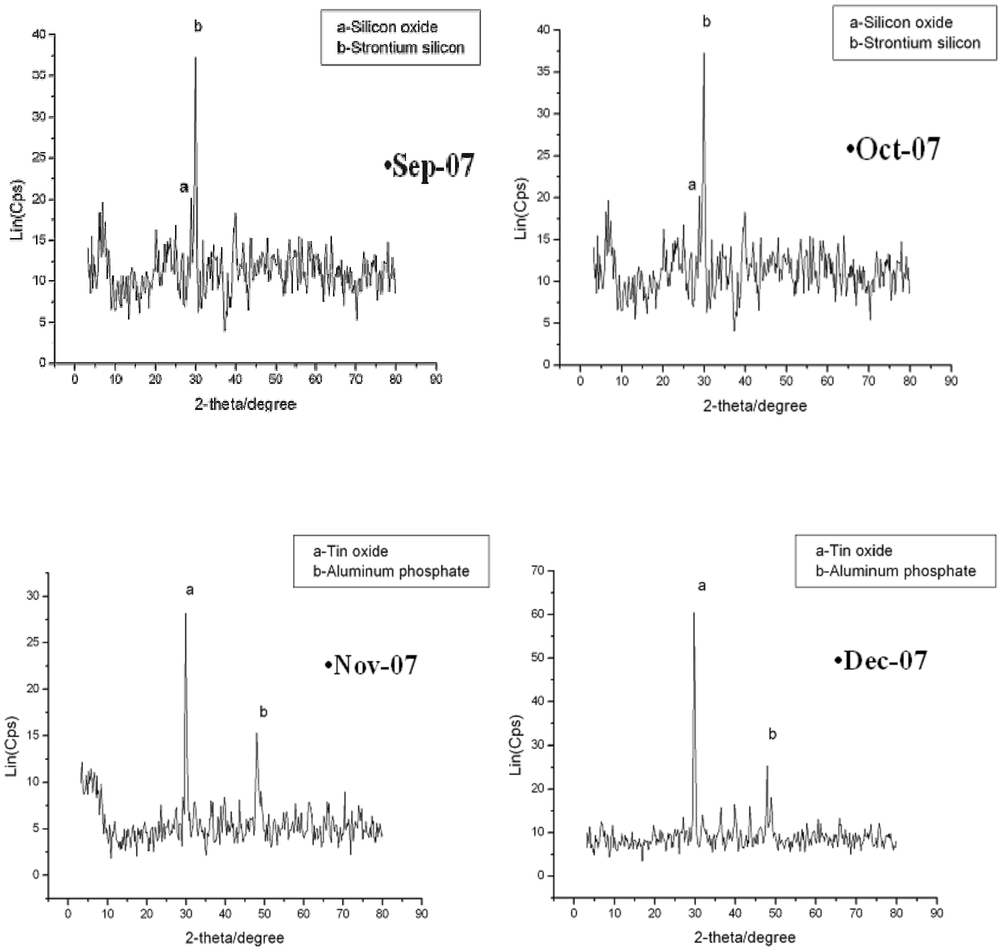

Fig. 6.16 X-ray pattern of the corrosion products on epoxy coated brass exposed to Cochin estuarine water during Sep. 07, Oct. 07, Nov. 07and Dec. 07 months

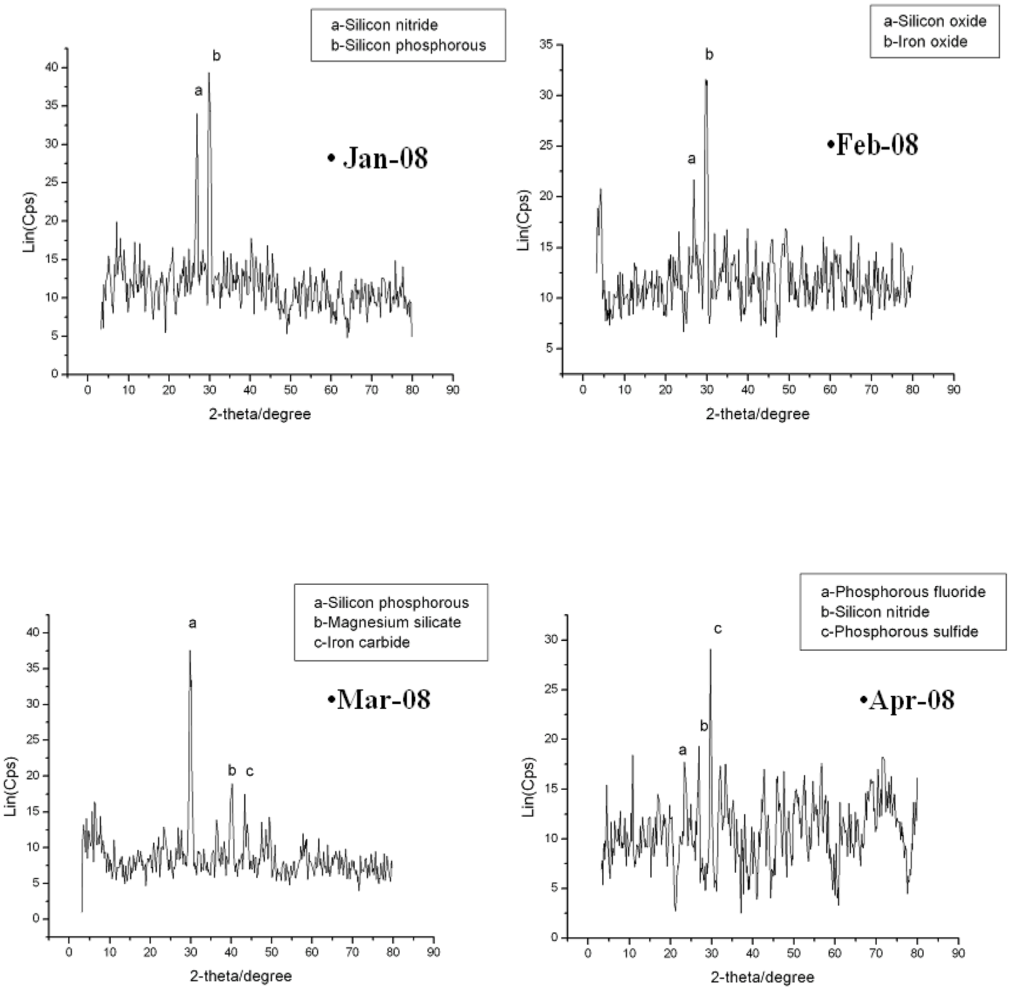

Fig. 6.17 X-ray pattern of the corrosion products on epoxy coated brass exposed to Cochin estuarine water during Jan. 08, Feb. 08, Mar. 08 and Apr. 08 months

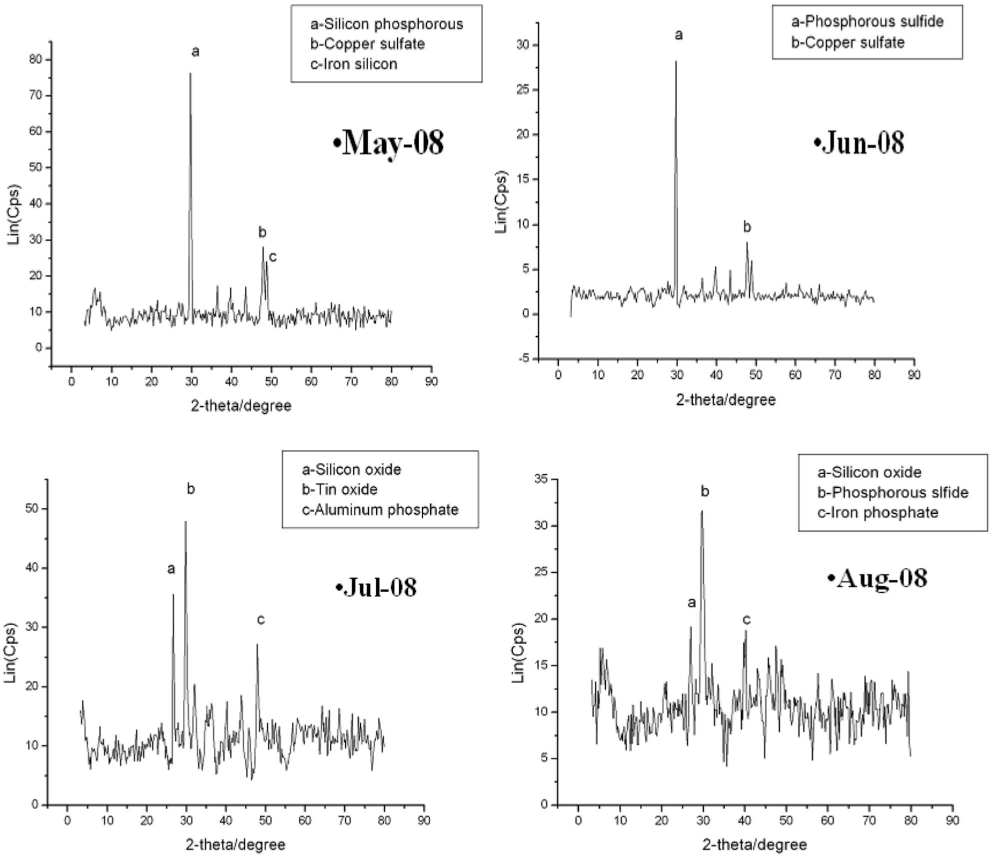

Fig. 6.18 X-ray pattern of the corrosion products on epoxy coated brass exposed to Cochin estuarine water during May 08, Jun. 08, Jul. 08 and Aug. 08

In the present study, XRD data show that the compounds formed on epoxy coated brass have no zinc compound and the epoxy coating offered protection against corrosion of brass. Several constituents of the corrosion products of copper/nickel alloys exposed to unpolluted, aerated seawater was identified but the major constituent was thought to be Cu_2O (North, 1970; Popplewell, 1973; Kato, 1980). Also varying amounts of $Cu_2 (OH)_3$ C1, $Cu(OH)_2$, CuO, $CuCl_2$, $Cu_3(OH)_2(CO_3)^2$ and $CaCO_3$ have been found in the corrosion products of these alloys (Popplewell, 1978; Mor, 1975). The longer the time the brass being exposed to highly corrosive seawater, the more severe the corrosion attack and more the corrosion products.

6.4 Surface morphology of epoxy coated brass after removal of corrosion products

Surface morphology of brass after the removal of corrosion products is shown in Figs. 6.19-6. 21. SEM images for Sep. 07 to Dec.07 in Fig. 6.19 show no cracked surface suggesting dezincification. A few scratches on epoxy coated brass indicating erosion. SEM images of Jan. 08 to Apr.08 in Fig. 6.20 shows a few white spots indicating a few remaining corrosion products and there is no indication of cracked surface attributing dezincification. SEM images for May 08 to Aug. 08 in Fig. 6.21 show little area of black spots related to pits and a few white spots indicating few remaining corrosion products.

Ritter (1982) concluded that the high pH generated under the coating was conducive for oxide growth and surface roughening of the substrate. The metabolic products and decay of sulphate reducing bacteria provide acidic conditions inside the shell facilitating the initiation of pits. Low flow may results in settling of deposits from the estuarine water with the possible consequence of local corrosion cells being set up e.g. differential aeration cell, concentration cells etc, leading to pitting while high flow rates may lead to erosion-corrosion (Shrei, 1976). Sulfide films that develop as corrosion products in polluted seawater improve resistance to impingement attack as long as they remain intact. But when they break down locally they promote severe pitting (Roger, 1948). The formation of corrosion products in a chloride environment can also deteriorate the protective properties because chloride ions can destroy the oxide layer causing pitting corrosion (Winston Revie, 2000). Syrett and Wing (1980) considered the possibility that sulfide-polluted deaerated seawater could cause accelerated attack if the flow conditions were sufficiently adverse.

Oxygen concentration cells can be created from deposits on a metal's surface or may be due to component design. Differences in oxygen content due to discrete films or deposits randomly scattered along a metal surface can cause pitting and/or crevice corrosion at these localized sites. In contrast, complete coverage of a surface by a film or a deposit can provide an effective barrier and reduce corrosion of the metal (Davis, 1987). Both macro and microfouling can have a major impact on the performance of marine components (Fontana, 1967). Macro and Microfouling organisms can break down protective paint films on a component surface. Fouling also shields the component surface from any oxygen supply thereby creating the possibilities that differential aeration cells can develop. Fouling can cause catalytic effects (Ijsseling, 1989). Plant decay or secretion products from animal life can accelerate corrosion processes. It is believed that the ability of chloride ions to penetrate and destroy passive film locally increases with temperature (Laque, 1975).

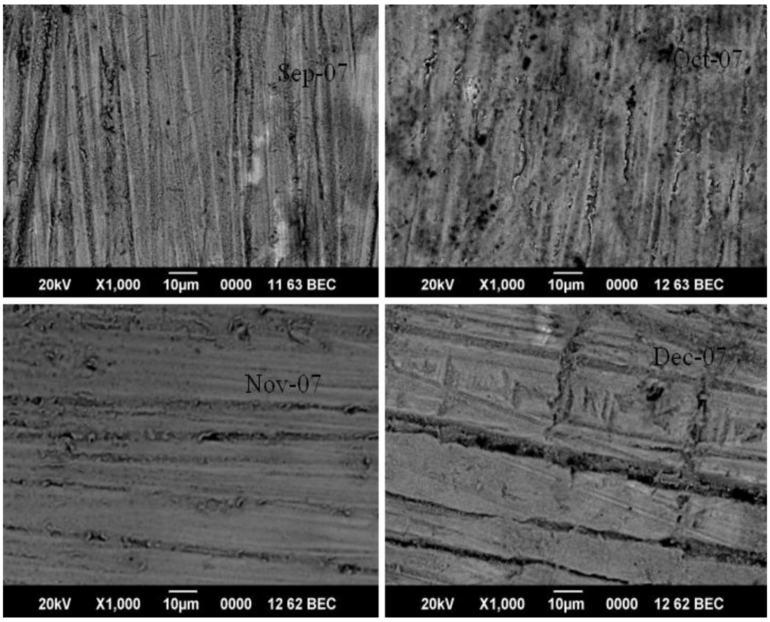

Fig. 6.19 SEM micrograph of epoxy coated brass for Sep. 07, Oct. 07, Nov. 07 and Dec. 07 months exposure in Cochin estuarine water after removal of corrosion products

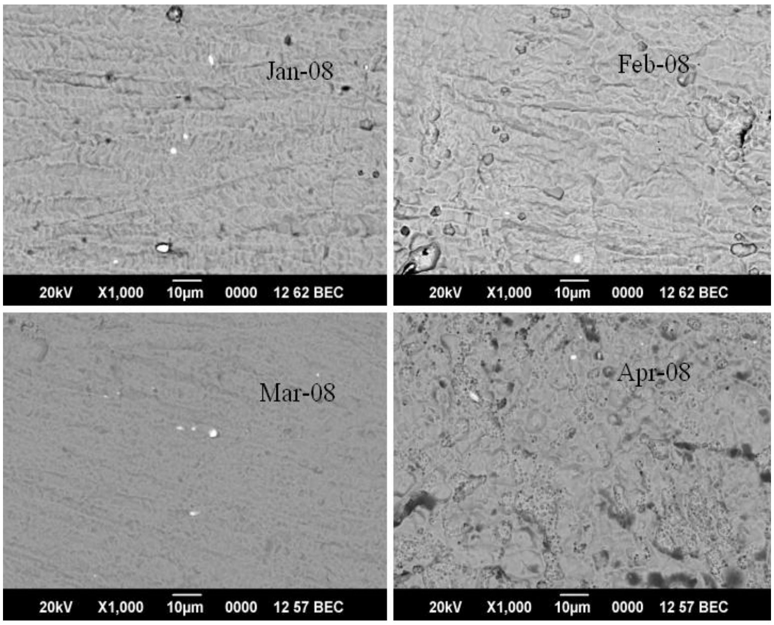

Fig. 6.20 SEM micrograph of epoxy coated brass for Jan. 08, Feb. 08, Mar. 08 and Apr. 08 months exposure in Cochin estuarine water after removal of corrosion products

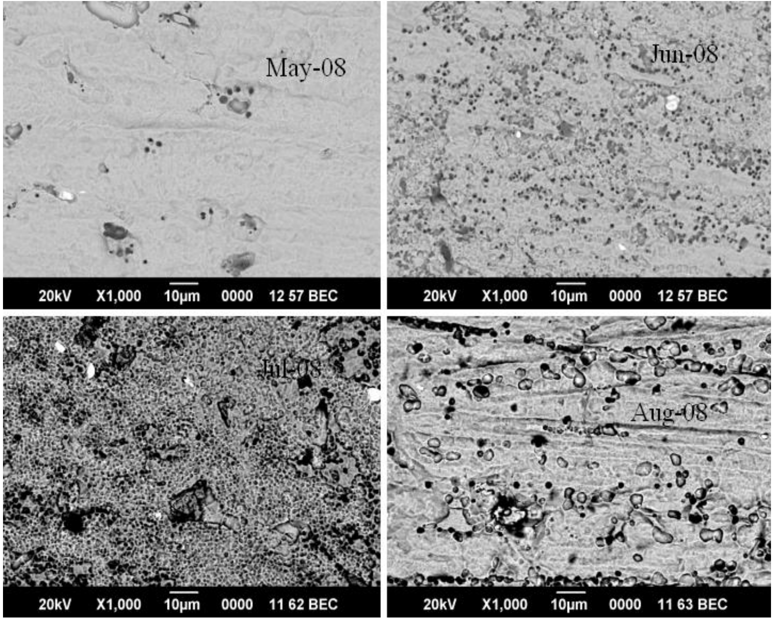

Fig. 6.21 SEM micrograph of epoxy coated brass for May 08, Jun. 08, Jul. 08 and Aug. 08 months exposure in Cochin estuarine water after removal of corrosion products

6. 5 Summary and conclusions

Visual examination of samples reveal that heavy growth of marine organisms and sediments deposits on epoxy coated brass can reduce corrosion by preventing the diffusion of oxygen to the metal surface so as to set up anaerobic conditions and can also eliminate acceleration of corrosion by a high velocity of water flow as there is no direct effect of velocity on metal surface.

From the EDS studies, it is concluded that there is no zinc and copper on the epoxy coated brass, and the absence of zinc suggest that there is no dezincification in all months and is due to the protection offered by epoxy coating. The calcium also contributes to the corrosion resistance of brass along with epoxy coating. Sand, silt and other abrasive particleswhich are rich in suspension in the estuarine water can deteriorate brass by removing the protective corrosion products, scale and epoxy coating leading to higher corrosion rate. XRD data show that the estuarine water has affected the nature of the epoxy coating on brass as many inorganic compounds mainly silicon oxide followed by tin oxide, aluminum phosphate, silicon phosphorous, phosphorous sulfide, silicon nitride, copper sulfate, strontium silicon, magnesium silicate, iron carbide, iron oxide, iron phosphate, phosphorous sulfide, iron silicon and iron phosphate are identified.

XRD data show that the absence of copper and zinc compounds on epoxy coated brass attribute the protective nature of epoxy coating. SEM surface studies reveal that there is no indication of cracked surface indicating dezincification and there are a few areas of pitting on surface. Deficiency in oxygen supply under the discontinuous deposits is responsible for the initiation of accelerated attack (pitting) in such regions due to corrosion cells formed by living marine organisms and dead organisms.

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Chapter 7

GENERAL CONCLUSION AND SCOPE OF FUTURE WORK

Monthly corrosion rates of brass in Cochin estuarine water are affected by various factors such as surface temperature, dissolved oxygen concentration, wave action, salinity, monsoon, rainfall, sediments, settlement and growth of marine organisms.

Corrosion rate of brass as assessed by weight loss method decreases significantly in Cochin estuarine water from Sep. 07 to May. 08 and this can be attributed to the protecting film formed almost completely on brass panel. Increase of corrosion rate after May 08 is related to the removal of protective film due to prolonged exposure in water. The corrosion rate of brass depends on the protective nature of corrosion products along with marine growth accumulation. The increase in biomass values after Nov. 07 implies the protective nature of the biomass over the period of exposure. Hydro chemical parameters and loss of toxic effect of brass can be the reason for the increase of bio-mass.

The sustainable noble potentials (more positive values) of -0.22 Vs. SCE between Sep. 07 and Oct.07 indicate that brass retains its normal corrosion resistance and the drops of the potential after Oct. 07 indicates the onset of pitting corrosion coupled with dezincification from Nov. 07 to Dec. 07 and then sustains at this potential up to Aug. 08 indicating the protective nature of brass.

Electrochemical studies reveal that low corrosion rate of brass is prevailed throughout the period except in Apr. 08 and May 08 during which periods the corrosion rate is high. The high values of corrosion rate of the brass in the Cochin estuary can be attributed to differential cells developed on brass by microorganisms causing microbially induced corrosion. The low corrosion rate values of brass imply the anticorrosive nature of corrosion products and biomass.

The variation in the corrosion rate values of monthly exposures determined by polarization method could be mainly attributed to the corrosion products formation and biofouling development, depending upon the local environment conditions (estuarine water chemistry in the immediate vicinity of the metal/electrolyte interface, dissolved $O_{2,}$ wave action, role of micro algae, slime forming bacteria in the bio fouling consortia) prevailed during the study period.

Dezincification factor is more than one for all months except Sep. 07 and Oct. 07, which indicate that dissolution of zinc from brass for all months except the above two months. An increase in the temperature of estuarine water makes it more corrosive even at low oxygen level and intensifies the dezincification of brass. Higher salinity can also alter the localized corrosion resistance of brass in estuarine water. There is not much variation in dissolved oxygen and pH and therefore could not be correlated with corrosion of brass. The notable decrease in mechanical properties of brass after three months period is mainly attributed to the loss in antifouling properties after three-months.

Visual observation of brass panels exposed in Cochin estuary during the study period reveals that there is no appearance of blue, pink colors on brass surface indicating zinc compound. The copper compound $CuCl_2$ or Cu_2O is possibly appearing in brownish and greenish color zone and is possibly atacamite and / or bronchantite / antlerite. The exponential decrease in the corrosion rate of brass can be attributed to the protective nature of corrosion products such as cuprous oxide and cupric hydroxy chloride, which are formed along with marine growth accumulation.

The SEM images reveal that the extent of dezincification increases up to Apr. 08 due to increases of density of crystalline grains from Nov. 07 - Apr. 08 and then reduces till Jul. 08 with slight increase for Aug. 08 as the density of crystalline grains decreases with little increase for Aug. 08. Dezincification of brass could be attributed to the role of biofilm consortia-differential aeration cells/concentration cell.

EDS studies reveal that dezincification starts from Nov. 07 since chloride ions are bound to affect the selective dissolution behavior of brass and continues till Aug. 08. However, reduction of zinc % after Apr. 08 to Jul. 08 with slight increase for Aug. 08 are observed as increase of rain fall neutralize the effect of chloride ions on brass in these months. The results are in tune with dezincification factor Z_f of respective exposure, open circuit potential and extent of loss of mechanical properties of brass.

XRD data reveal the presence of copper oxide almost in all the period of study attributing the protective nature of brass against uniform corrosion. From the results, it can be concluded that the Cochin estuarine water has affected the nature of the crystalline corrosion products, which are mainly copper oxide, silicon oxide, copper sulfide, Cu-Zn, molybdenum sulfide, copper zinc chloride hydroxide, iron sulfide, copper hydroxide phosphate and copper chloride. The products of corrosion reactions can react with compounds in estuarine water to form different compound.

SEM images of brass after removal of corrosion products show that the nature of the medium has strongly influenced the morphology of the corrosion layer as well as the size and morphology of the pits underneath the corrosion products. SEM images also reveal the localized corrosion (pitting) on selective area with preferential dissolution. The cracked area on surface during Nov. 07-Aug. 08 indicates the dezincification.

Decrease of corrosion rate determined by weight loss method after Oct. 07 is due to the accumulation of biomass on epoxy coated brass surface when uniform corrosion is considered. The corrosion rate in epoxy coated brass is much lower than the corrosion rate of brass. Increase of biomass from Sept. 07 – Mar. – 08 and from Jun. 08 – Aug. 08 is due to local drainage of coating.

The negative shifts of potential from Sep. 07 to Dec. 07 indicate that there can be localized corrosion from Sep. 07 to Dec. 07. The positive shift of potential after Dec. 07 and sustainable noble potentials (more positive values) mean that brass retains its normal corrosion resistance. Though Open Circuit Potential of brass and epoxy coated brass decreases over the period of time, the more negative potentials are noticed for uncoated brass than the epoxy-coated brass.

Electrochemical studies reveal that low corrosion rate has prevailed throughout the period except Nov. 07 to Dec. 07; Apr. 08, and Jul. 08 to Aug. 08, where high corrosion rate is noticed. The low corrosion rate values of epoxy coated brass imply an effect of barrier action of epoxy coating and fouling assemblage coupled with the adherence of sediments on epoxy-coated samples. An increase of corrosion rate is associated with local damage of epoxy coating by the turbulence and soft fouler and micro and macro algae and the results show that the corrosion rate of epoxy-coated brass is lesser than that of brass in Cochin estuarine water during the period of study.

Dezincification factor is less than one for all months, which indicates that dezincification has not occurred from the brass for all months. As there is no much variation in tensile strength, there is no much weight loss during the period of exposure. It is evident that the loss in tensile strength is directly proportional to weight loss over the period of time.

From visual examination of epoxy coated brass immersed in Cochin estuary, it is understood that heavy growth of marine organisms and sediments on epoxy coated brass can reduce corrosion by preventing the diffusion of oxygen to the metal surface so as to set up anaerobic conditions. The overcoating can also inhibit acceleration of corrosion by a high velocity of estuarine water flow as there is no direct effect of velocity on epoxy coated brass.

From the EDS studies, it is concluded that there is no zinc and copper on the epoxy coated brass, and the absence of zinc suggest that there is no dezincification in all months as the corrosion protection offered by epoxy coating. Chloride has no prominent effect on epoxy coated brass. The calcium also contributes to the corrosion resistance of brass along with epoxy coating. Sand, silt and other abrasive particles in suspended in the estuarine water can deteriorate epoxy coated brass by removing the protective layer and epoxy coating leading to higher rate of corrosion.

XRD data show that the estuarine water has affected the nature of the epoxy coating on brass as many inorganic compounds mainly silicon oxide followed by tin oxide, aluminum phosphate, silicon phosphorous, phosphorous sulfide, silicon nitride, copper sulfate, strontium silicon, magnesium silicate, iron carbide, iron oxide, iron phosphate, phosphorous sulfide, iron silicon and iron phosphate are identified. XRD data further show that the absence of zinc compounds on epoxy coated brass attributing the protective nature of epoxy coating and also absence of dezincification.

SEM surface studies reveal that there is no indication of cracked surface suggesting dezincification and there are a few areas of pitting on surface. Deficiency in oxygen supply under the discontinuous deposits is responsible for the initiation of accelerated attack (pitting) in such regions due to corrosion cells formed by living marine organisms and dead organisms. The epoxy coated brass protects brass against dezincification but not the antifouling property. Hence, epoxy coating is found to be good for preventing dezincification of brass in Cochin estuarine water if antifouling property of brass is compromised.

Scope for Future Work

The corrosion behavior of brass in presence and absence of fouling needs to be investigated to understand the mechanism.

Influence of various types of polymer coating on corrosion behavior of brass needs thorough investigation under natural and artificial conditions.

A thorough understanding of the complex phenomena of dezincification of brass in natural seawater and estuarine water can lead to development of novel alloys with high corrosion resistance and homogenized matrix.

Thorough investigation on the throwing power of copper in maintaining the antifouling property under various conditions in estuarine water will throw more light on the efficacies of leaching theory.