

Dezincification of Brass in Cochin Estuary, India

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Abstract

Corrosion characteristics of brass panels were investigated in the Cochin estuarial water of the vembanad coastal area, India at an interval of 1,3, 6, 9and 12 months. The weight gains, corrosion rates and open circuit potential of brass samples during period of one year were determined by gravimetric and digital multimeter with a saturated calomel Electrode (SCE) respectively. The concentration of Cu^{2+} and Zn^{2+} ions in solution, produced by the corrosion of brass were determined by atomic absorption spectrometry. Surface morphology of corroded surfaces, with and without the corrosion products, was analyzed by scanning electron microscopy (SEM). Energy dispersive spectroscopy (EDS) was used for the identification of the corrosion products and X-ray diffraction (XRD) was used for identification of the crystalline corrosion products. The results of the study were also discussed in the light of the sea-water characteristics.

Keywords: Brass, corrosion, estuary, Cochin

1. Introduction:

Copper and its alloys are widely used in marine environments due to their corrosion resistance, mechanical workability, excellent electrical and thermal conductivities and

good resistance to biofouling. Brass is used extensively in marine applications and in heat

exchanger tubes, for example in desalination and power generation plants, respectively.

It is well known that the aggressivity of seawater is mainly due to its chloride content.

However, other factors such as the presence of microorganisms can play an important role, since biofilms are a radically different environment in terms of pH, dissolved oxygen and other species i.e. extracellular polymeric substances (EPS). Also the dissolved organic matter and colloidal substances present in the natural sea water and polluted sea water may influence the corrosion behavior of brass. The alloys can deteriorate due to the formation of biofilms, whose polymeric structure allows local gradients of pH and O₂ to exist [1]. Although the microbiologically influenced corrosion of carbon and stainless steel has been widely studied, there has been little investigation on copper and copper alloys [2–10]. Mansfeld and Little [3] concluded that copper alloys exposed to natural seawater (NSW) were colonized by bacteria in 3 weeks and that in all cases the corrosion rates in NSW were higher than those in artificial seawater(ASW).

Kharafi et al. [7] observed selective dissolution of brass at various potentials and chloride concentrations, and concluded that chloride promotes the dissolution of copper and also of zinc. Santos CS, Mendonc et.al [9, 10] in their study on the corrosion of brass in non-deoxygenated non-buffered seawater solutions observed higher weight gains and higher corrosion rates on the brass samples immersed in NSW. Naguib and Mansfeld [11] studied the corrosion behavior of Al 2024, mild steel and cartridge brass in artificial seawater (ASW) containing a growth medium contaminated by bacteria. Under sterilized conditions they concluded that the corrosion behavior was similar to that in ASW without bacteria. Huang et al. [5] emphasized the importance of performing studies in NSW,

under anaerobic conditions. After 7 days of immersion in the SRB-containing seawater,

they noticed that the SRB attached on the alloy surface formed a biofilm and lead to intergranular corrosion. Consequently, a significant decrease in the polarization resistance was observed. Under anaerobic conditions, O₂ is not present and the cathodic reactant may be H₂O and/or organic compounds, or products from the microbial activity, particularly in NSW, or in contaminated ASW. Anaerobic bacteria may grow, and the products from their activity(EPS) may lead to significant compositional changes which modify the aggressiveness.

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 sea water conditions must be taken into account (12). Cochin estuary water is having large quantity of sediments with organic matter resulted in an anoxic condition. The main effect of estuarial water arises from a combination of low oxygen content and generally decreased PH together with the presence of sulphite ions and /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 sea water. There is inadequate data on the effect of the Cochin estuarial water on the corrosion behavior of brasses. The main objective of this work is to study the corrosion behavior of brass in estuarial water of Cochin in a period of one year and relates the effect of sea water condition on its corrosion behavior

2. Experiments:

The brass panels(65-35) of 5 cm and 4cm were polished with emery paper ,rinsed several times with distilled water, degreased with acetone, washed again with distilled water and

dried and all panels are weighed and then deployed in estuarial water at cochin, which is situated on the southwest coast of India. The panels were fixed on the fibreglass strips with PVC nuts and bolts and the panels were deployed in six replicates during beginning and retrieved at the end of each exposure period. After retrieval the panels were first rinsed gently with sterile sea water to remove any non-adhering bacteria and diatoms. The difference between initial weight prior to deployment and final weight, after corrosion products removed by standard method (13), was used for calculation of **corrosion rate** by using the following formula:

$$\text{mdd} = W/(A*T) \quad (1)$$

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

The difference between initial weight prior to deployment and final weight, before corrosion products removed, was used for calculation of **weight gain**.

The water was collected from the study area at every exposure period during the period of the study and analyzed for identifying the **environmental parameters** such as salinity, dissolved oxygen, temperature and P^H . Salinity and temperature were recorded using a salinity-temperature bridge and water sample from the study area was analyzed to estimate the dissolved oxygen content using winkle's method and a portable pH meter was used to measure the pH.

The **open circuit potentials** of brass panels immersed in estuarial water collected, at the end of each exposure period from study area, in a flask connected to the reference electrode via a KNO_3 salt bridge were measured with a digital multimeter. During the

time, the concentration of Cu²⁺ and Zn²⁺ in the solutions after each measurement was determined by atomic absorption spectrometer. Using the Cu²⁺ and Zn²⁺ concentration and Cu and Zn in brass alloy, **dezincification factor (z)** was calculated with the following equation:

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

where (Zn/Cu)_{sol} is the ratio between Cu²⁺ and Zn²⁺ ions in solution and(Cu and Zn)_{alloy} is the ratio between the two elements in the alloy.

The morphology of the surface of brass samples from immersions in estuarial water 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 5-10mins in a solution of sulphuric acid and potassium dichromate, according to (13).

Surface of corroded brass samples after 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** (Bruker AXS D8 Advance) for identifying the compounds of inorganic nature of oxides, chlorides, carbonates, hydroxides and oxychlorides of calcium, magnesium and iron.

3. Results and Discussion

3.1 Weight gain and corrosion rate

The variation of the weight gain and corrosion rate versus time is plotted in figure 1, 2. The weight gain decreases for first three months exposure and thereafter increases. Since

weight gain is low initially, one may say that the corrosion products formed in brass panel is wiped up by wave action and increases of weight gain after three months exposure attributes to increase of corrosion products on brass.

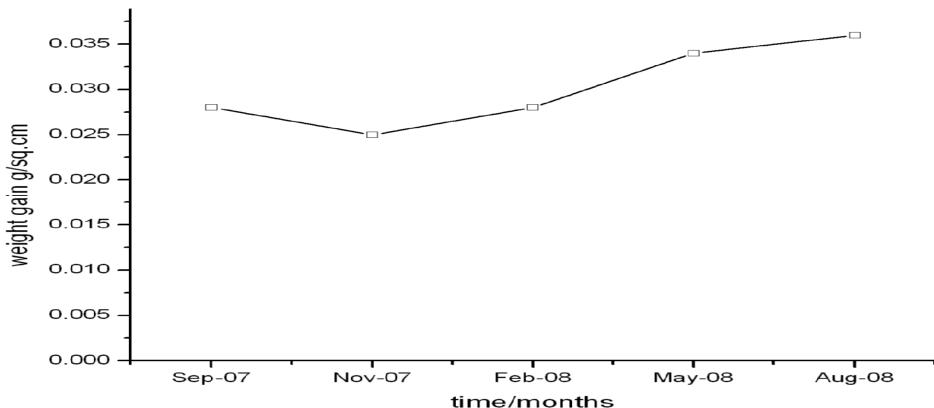


Fig. 1 Weight gains on brass sample at each exposure period in estuarial water in cochin

The corrosion rate values are decided by various factors such as surface temperature of sea water, dissolved oxygen concentration, wave action, salinity, monsoon rain and settlement and growth of marine organisms. The corrosion rates decrease significantly up to nine months exposure and low corrosion rate is related to protecting film formed almost completely on brass panel and increase of corrosion rate after nine months exposure is associated with removal of protective film due to prolonged exposure in the water. The higher values of corrosion rate experienced by the brass in the water is mainly attributed to the turbulence and soft fouler and micro and macro algae, that fouled on brass. The exponential decrease in the corrosion rate values of brass over the period of time implies the protective nature of corrosion products and biomass. It is reported that

deoxygenated water leads to significant increase in corrosion and also in the amount of precipitates (16).

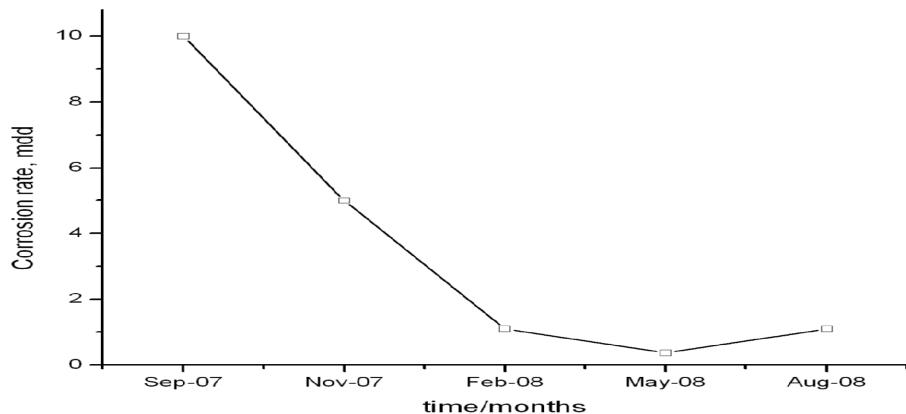


Fig. 2 Corrosion rate of brass sample immersed in estuarial water in Cochin at each exposure period

3.2 Open circuit potentials

The open circuit potential of brass panels immersed in estuarial water as a function of exposure time is given in figure 3. According to Mansfield et al(14), 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 typically of localized corrosion. The experimental results show almost constant value of -0.24 vs SCE during the first three months exposure and then decrease abruptly to a -0.31 at sixth month exposure and to -0.32 at ninth and twelfth months exposure. Santos CS, M.H. Mendonca (9) related that the negative shift of the OCP at longer time with the decrease of the O₂ in sea water.

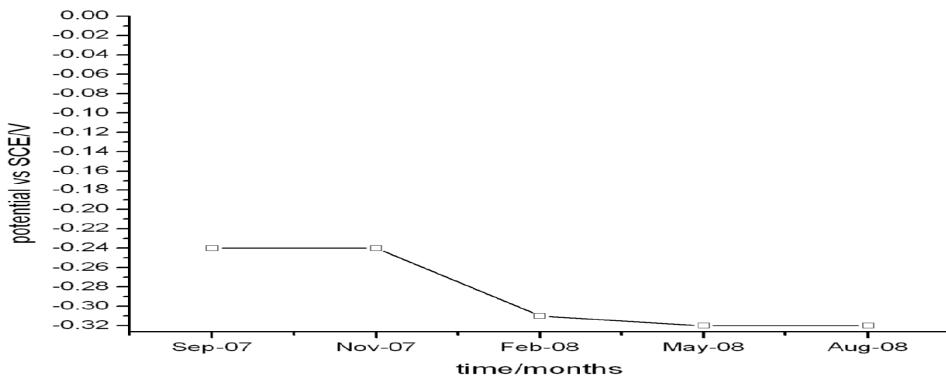


Fig. 3 Open-circuit potential curve of brass sample at each exposure period in estuarial water in cochin

Some authors (6,14,) have attributed the negative shift of the OCP to a reduction of the rate of the cathodic reaction possibly due to the decrease of the O₂ in the solution and/or to an increase of the rate of the anodic reaction. Although OCP measurement is used in electrochemical studies, it is well known fact that it provides the least amount of mechanistic information. However, many corrosion studies have used measurements of OCPs.

3.3 Dezincification factor

Figure 4 shows the dezincification factor for brass as a function of exposure time. The dezincification factor of brass was increases up to ninth month exposure and afterwards it is decreased very slowly for the remaining period. Thus a **dezincification factor higher than one means preferred dissolution of zinc**. In general leaching of zinc increases with

respect to time of exposure. The dezincification factor (Z_f) has an exponential decrease over the period of time. In all the exposures except initial period, the dezincification factor is more than one, which indicates that dissolution of zinc has occurred from the matrix of brass.

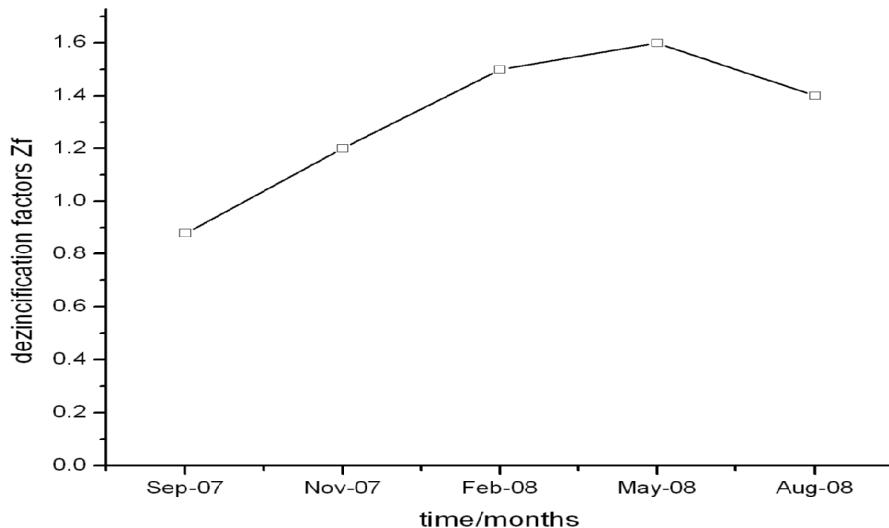


Fig. 4 Dezincification of brass sample at each exposure period in estuarial water in Cochin

Therefore dissolution of zinc occurred after first month exposure and the dissolution of Cu is predominant up to first month exposure and then there is slight dissolution of zinc for the remaining period.

3.4 Hydro chemical parameters

Variation in different parameters during the period of observation is presented in figure 5. Initially **Salinity** is found to be 11.6% on first month exposure and increases to maximum of 29.8% on third month exposure then it is reduced to 27% on sixth month exposure and

to 32.4% on ninth month exposure and afterwards it reduces to 27.4% due to fresh water

influx during the monsoon period. Salinity in marine atmospheres accelerates metallic corrosion (15). Temperature is initially 27.3 and reduces to 24 on third month exposure and then increases to maximum of and 29.5 and 31.6 on sixth and ninth month exposure respectively and after that there is a drop in the temperature to 24.5 due to influx of fresh water at the monsoon period. Dissolved oxygen was 4 ml/l at the first month exposure and remain unchanged on third month and then again it is dropped to 3.1ml/l on sixth month exposure and increases to 3.6 ml/l on ninth month exposure and afterward reduces to 3.9ml/l at the end of exposure period. PH of the water was 7.1 on exposure of sample and increases to 7.4 on third month exposure and then increases to 7.5 on sixth month exposure and reduces to 7 on ninth month exposure and after that reduces to 6.6 on twelfth month exposure. There was no much variation of dissolved oxygen and P^H of estuarial water in Cochin with regard to exposure period and therefore these data could not be correlated to corrosion of brass. It is reported that the microbial activity may contribute to lower the P^H (16). After the initial period of one month, only higher salinity and temperature were responsible for increased corrosion rate, anodic reaction and dezincification factor.

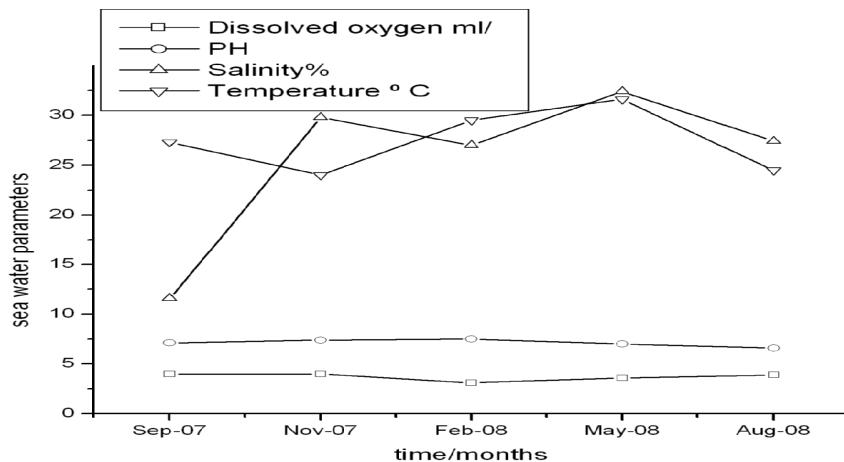
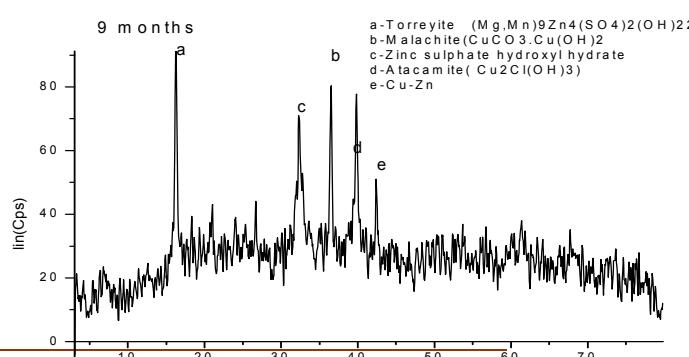
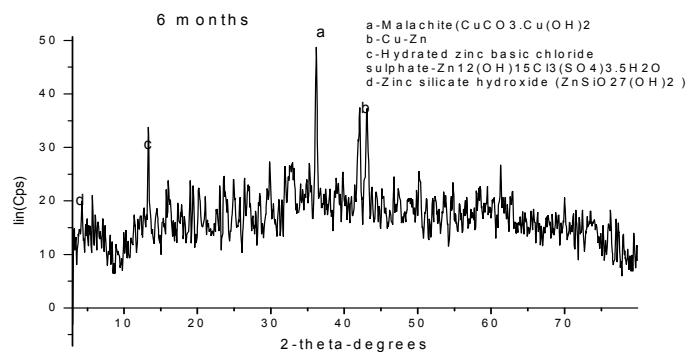
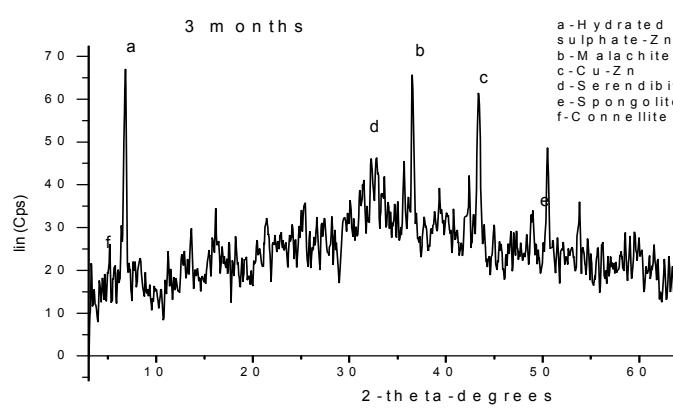
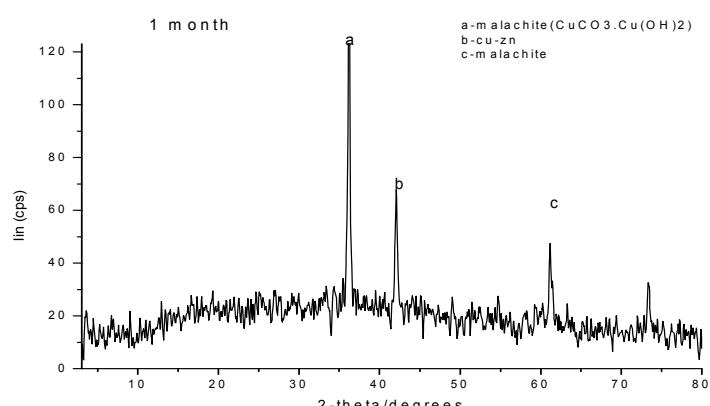


Fig. 5 Variation of dissolved oxygen, PH, salinity, temperature sample at each exposure period in estuarial water in cochin

3. 5 Surface Morphology and corrosion products

Figure 6 shows the X-ray powder pattern of the corrosion products formed on brass at each exposure months in Cochin estuarial water. The different types of compounds are found on brass exposed to Cochin water with different months. The surface of corroded brass is characterized by the presence of malachite in all five exposure period, Cu-Zn compound in all fifth exposure period except the last twelfth exposure, hydrated zinc basic chloride sulphate in third, sixth and twelfth months exposure period, zinc silicate hydroxide and zinc silicate in six and twelfth month exposure period respectively, Serendibite, Spongolite, Connellite in third month exposure period, Torreyite, Atacamite, Zinc sulphate hydroxyl hydrate in ninth exposure period



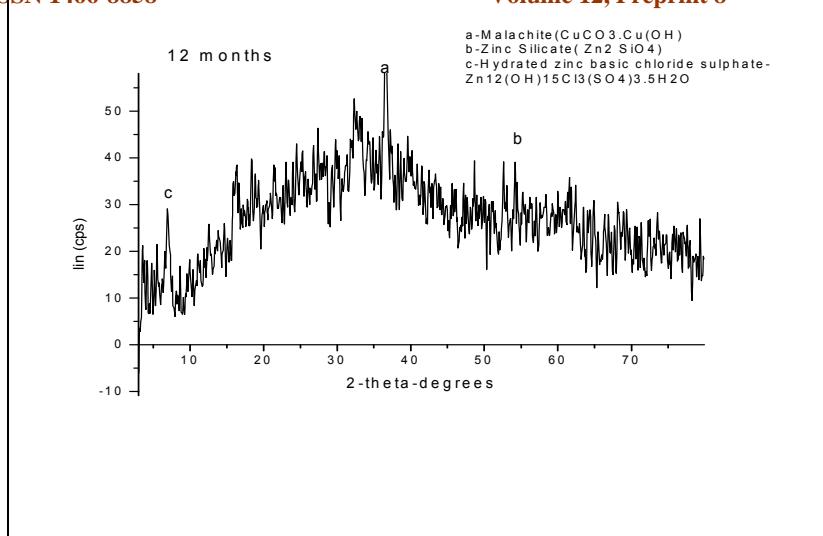


Fig. 6 X-ray pattern of the corrosion products on brass exposed to Cochin estuarial water over a period of one year

SEM micrographs and EDS spectra of brass after each exposure months in cochin estuarial water, before removal of corrosion products are given in figures 7-11. Various types of elements are found on brass exposed to the water with different months as shown in figures. 7-11. SEM image in figure.7 shows whole surface zone of 2 and 3 for which C, O, Cu, Al, Si, Mo, Mg, P, Ti, Pd are the elements identified by EDS and small dark Zone of 1,4 for which O, Fe, Mg, Al, Si are the elements identified by EDS. SEM image in figure. 8 shows small white zone of 2 and 4 for which C, O, Cu, Zn, Fe, P ,Mo, Al, Mg, Sn are the elements identified by EDS and large dark Zone of 1,3 for which where Ti, Fe, Mg, O, Al, Si,, K, C, Zn, Na, Mo, are the elements identified by EDS. SEM image in figure. 9 shows dark zone of 2 and 4 for which O, Cu, Na, S, Mo and O, Fe, Cu, Mg, Al, Si, Cl, In, S, C, Zn are the elements identified by EDS and dull white Zone of 1,3 for which O, Cu, Zn, Ti, P, S, Cl and O, Fe, Cu, Na, Mg, Al, Cl, Rb, Si , Mo, are the elements identified by EDS. SEM image in figure. 10 shows bright white

zone of 1with a crystal of 2 for which O, Fe, Cu, Al, Si, Cl, , Zn and O, Cu, Zn, Cl are

the elements identified by EDS and dull dark Zone of 3 ,4 for which Fe, O, Cu, Zn, Al,

,Mg, Si, P, Cl, Ca and C, O, Fe, Cu, Zn, ,Al, Cl,, K, are the elements identified by EDS.

SEM image in figure. 11 shows dull dark zone of 1with a crystal of 2 for which O, Fe,

Cu, Na, Al, Si, Cl, ,K, Zn and O, Si are the elements identified by EDS and dull white

Zone of 3 ,4 for which Fe, C, O, Cu, Zn, Si,, Cl, Ca and O, Fe, Cu, Zn, Si, Mo, Al,

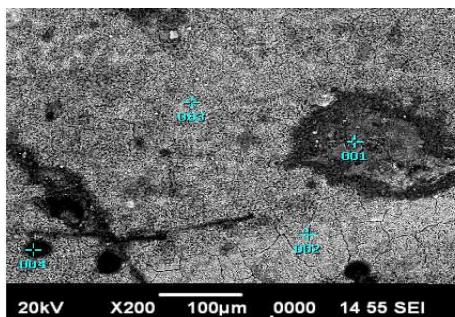
Ca,,K, are the elements identified by EDS. It should be noted that the white zone is base

material where most of the surface layer is removed and this white zone is most probably

zones where dezincification takes place and other zones are deposits/precipitates. A

porous layer is most probably related to selective dissolution of zinc, leaving almost pure

copper as reported by researchers (9).



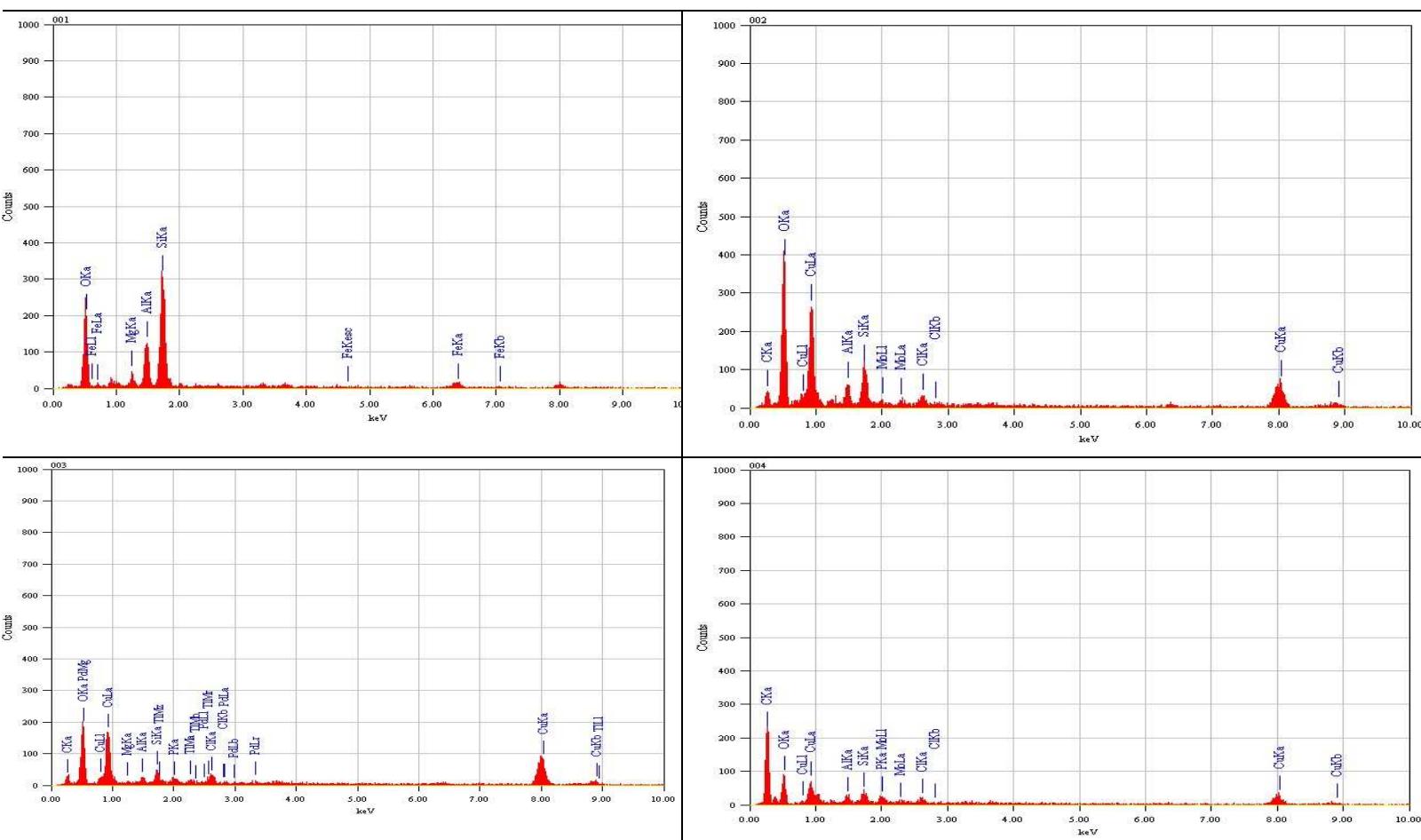


Fig. 7 SEM micrograph and EDX spectra of brass of one month exposure in estuarial water in Cochin before removal of corrosion products

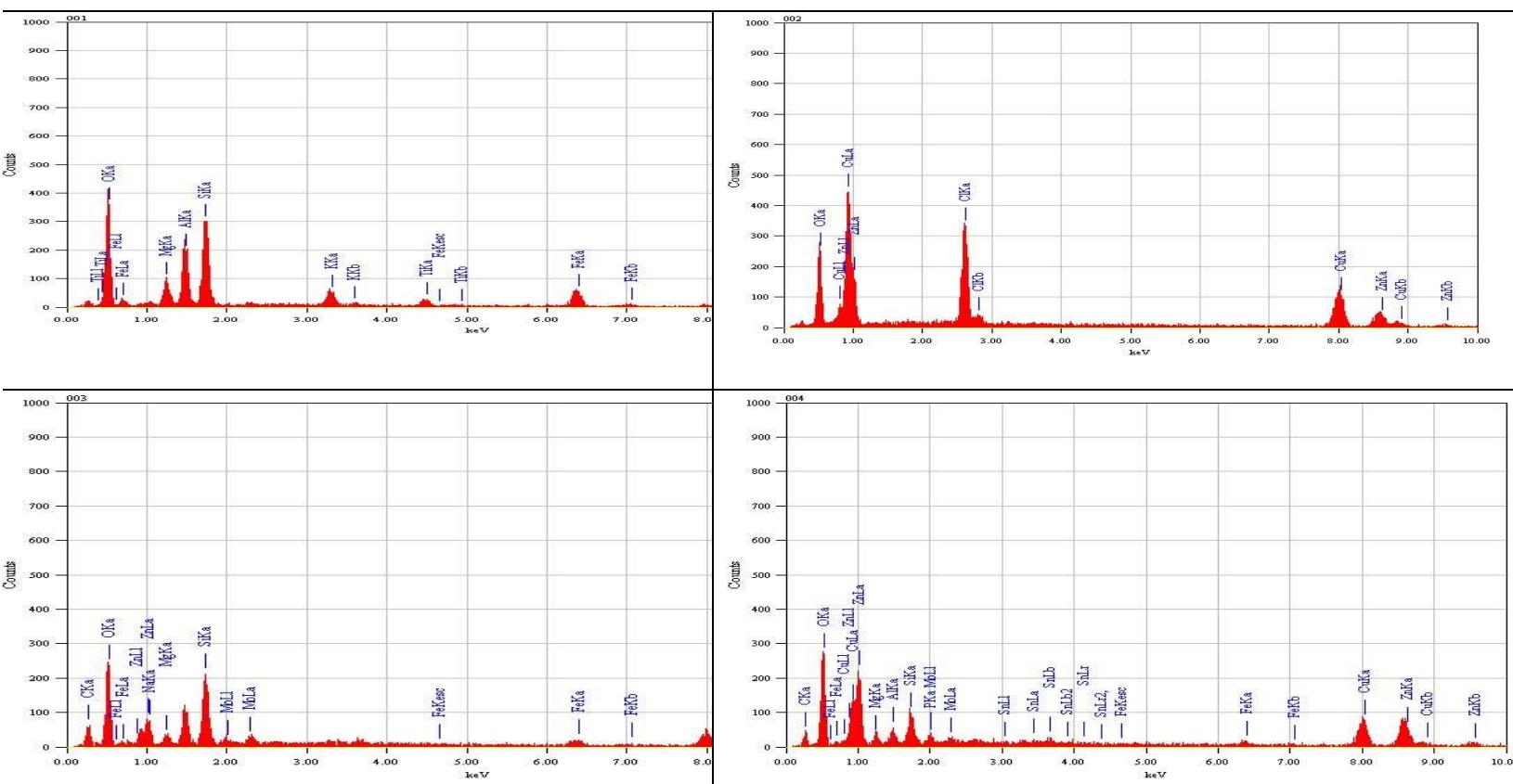
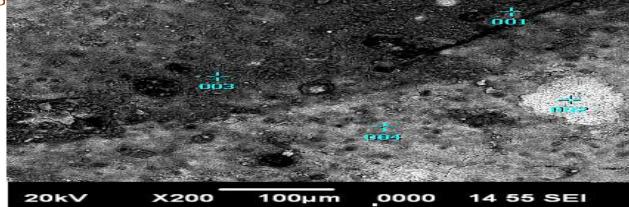


Fig. 8 SEM micrograph and EDX spectra of brass of three months exposure in estuarial water in Cochin before removal of corrosion products

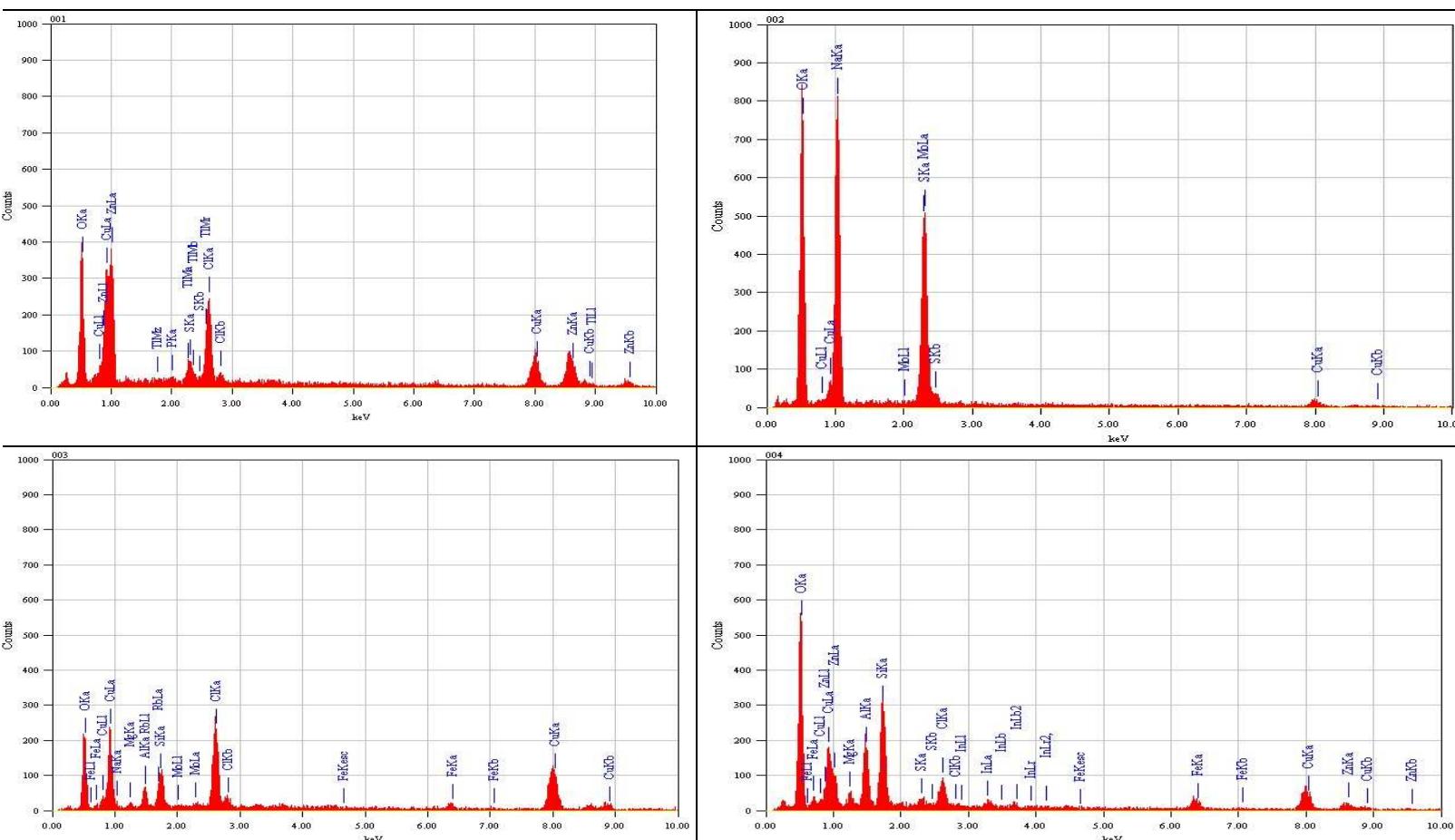
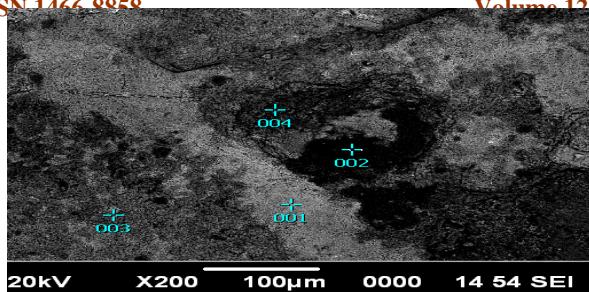


Fig. 9 SEM micrograph and EDX spectra of brass of six months exposure to brackish water before removal of corrosion products

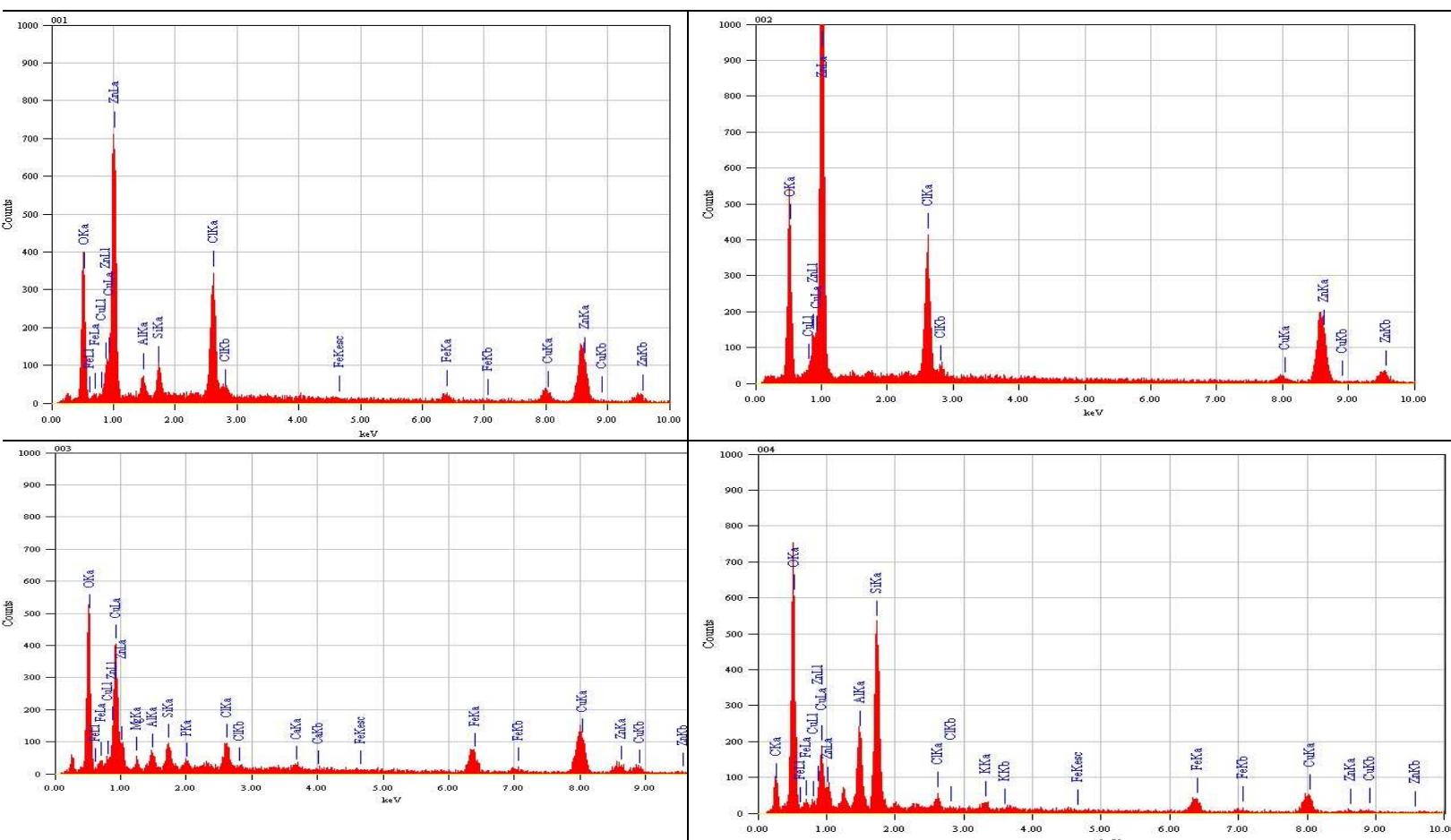
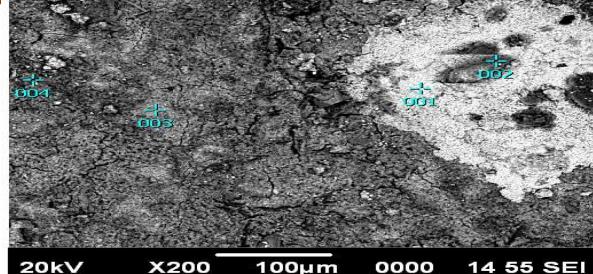


Fig. 10 SEM micrograph and EDX spectra of brass of nine months exposure to brackish water before removal of corrosion products

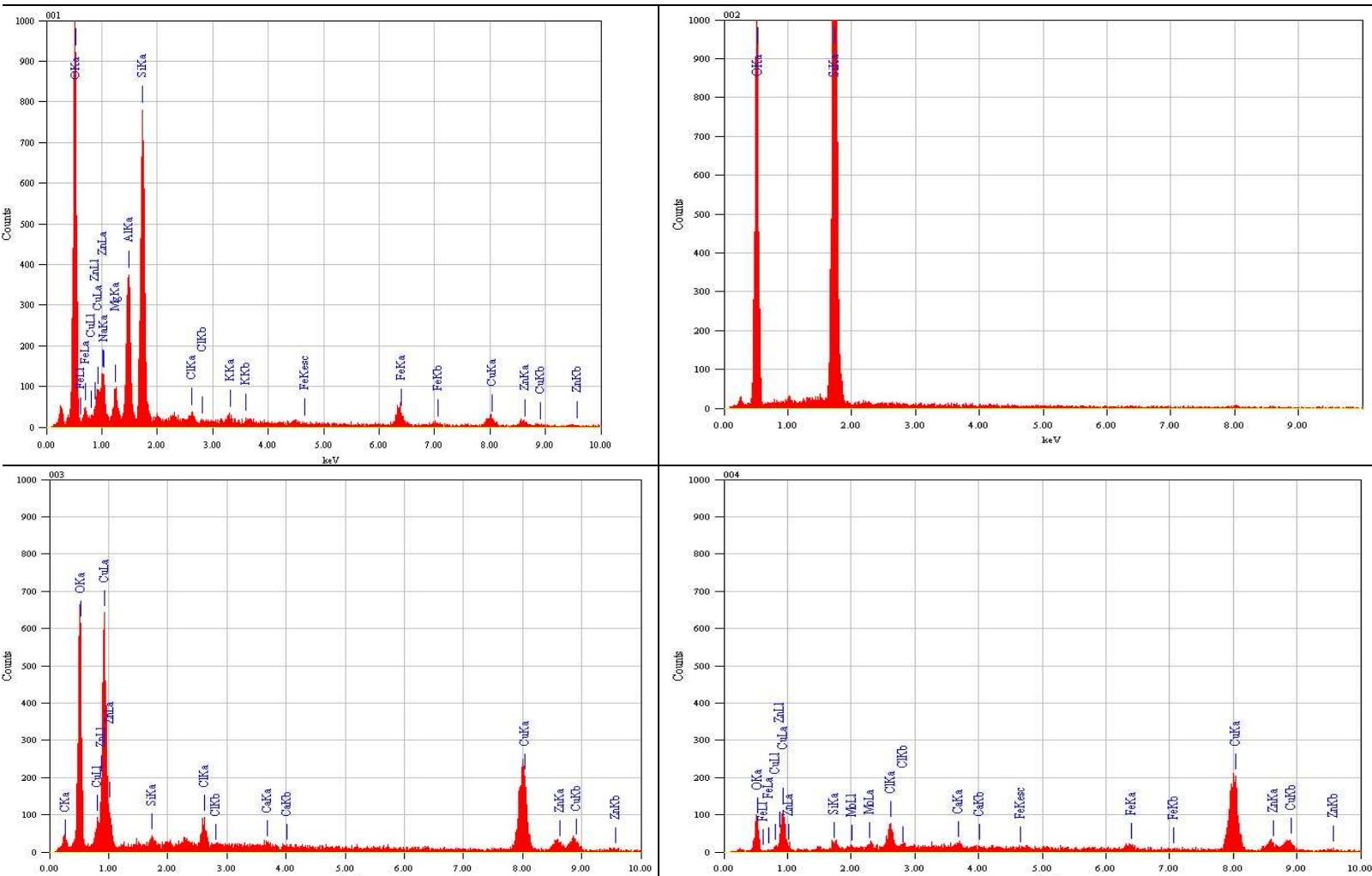
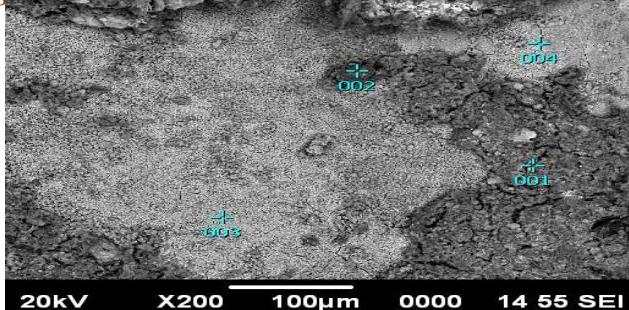


Fig. 11 SEM micrograph and EDX spectra of brass of twelve months exposure to brackish water before removal of corrosion products

SEM image in figure. 12 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 image in figure.13 shows few black spots indicating pits and a cracked area exhibiting dezincification. SEM image in figure 14 shows few cracked surface attributing dezincification and few white spots indicating few remaining corrosion products. SEM image in figure. 15 shows large area of black spots related to pits and few white spots indicating few remaining corrosion products and cracked area where dezincification has occurred. SEM image in figure. 16 shows few black spots related to pits and few white spots indicating few remaining corrosion products and there is no indication of visible cracks

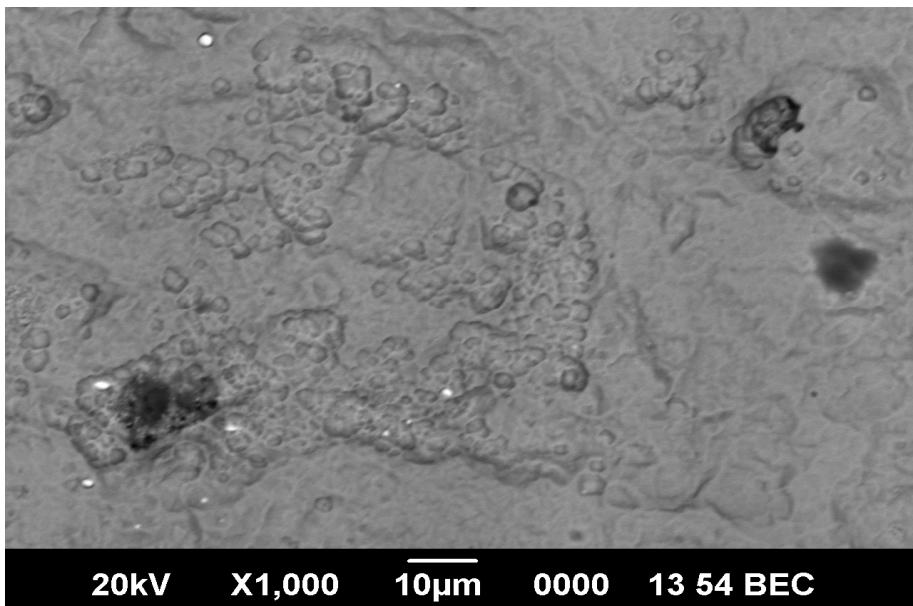


Fig. 12 SEM micrograph brass of one month exposure to brackish water after removal of corrosion products

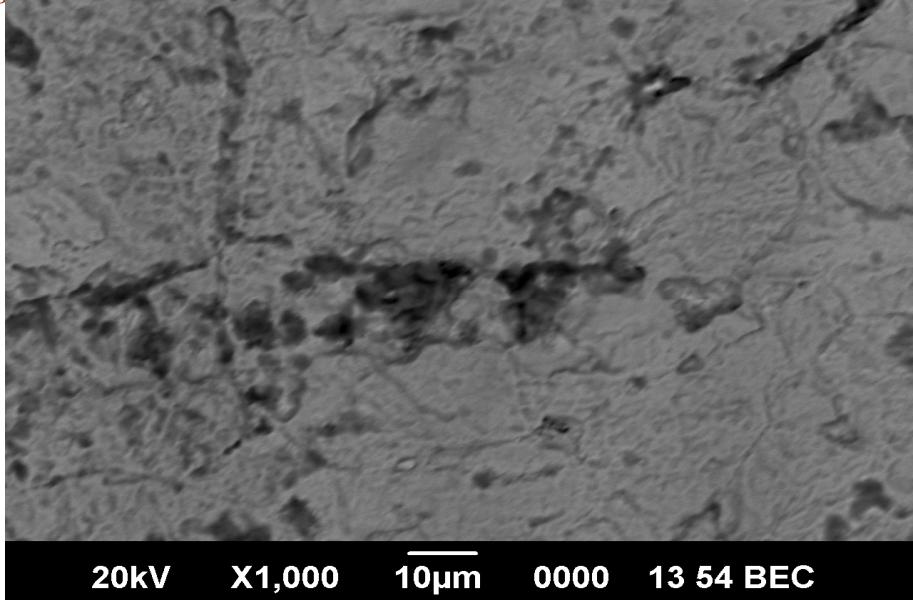


Fig. 13 SEM micrograph brass of three months exposure to brackish water after removal of corrosion products

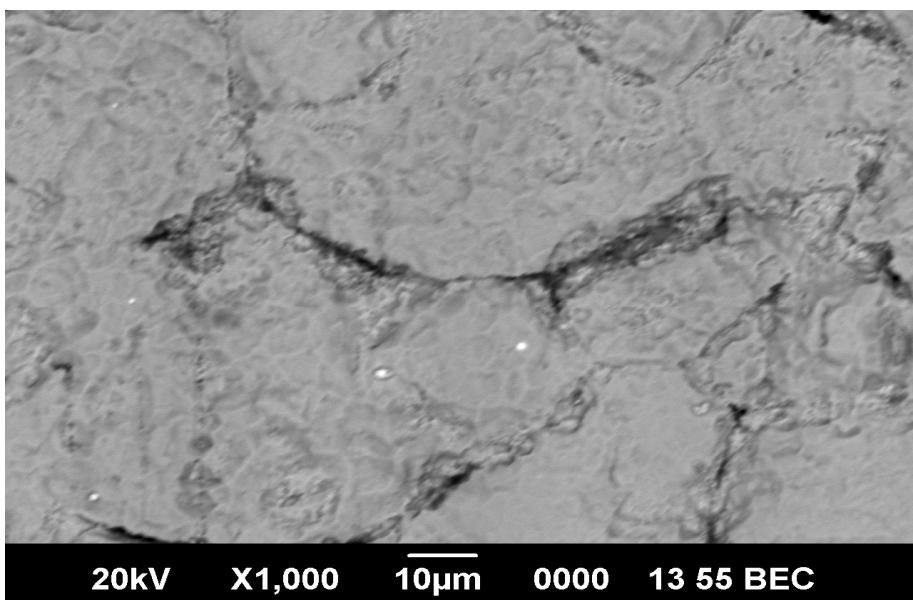


Fig. 14 SEM micrograph brass of six months exposure to brackish water after removal of corrosion products

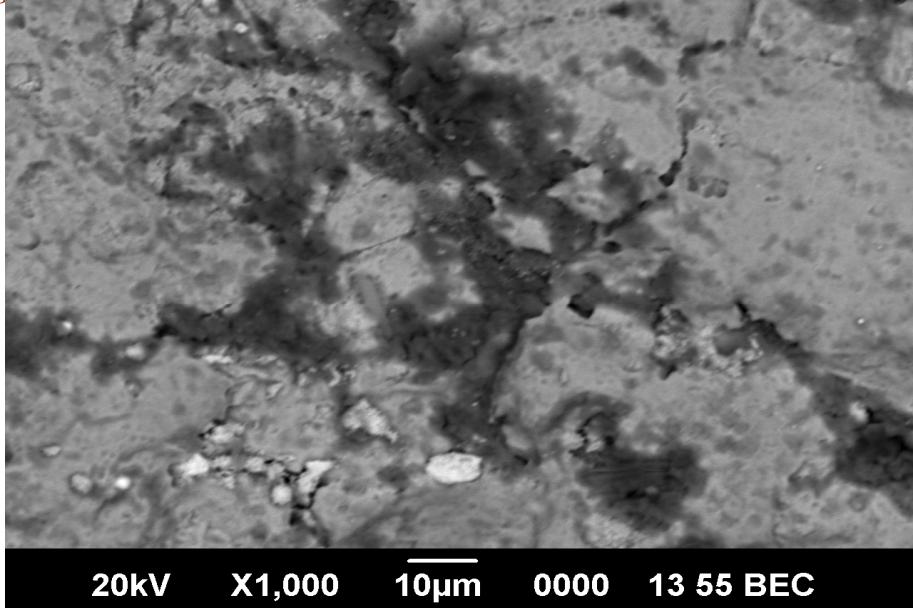


Fig. 15 SEM micrograph brass of nine months exposure to brackish water after removal of corrosion products

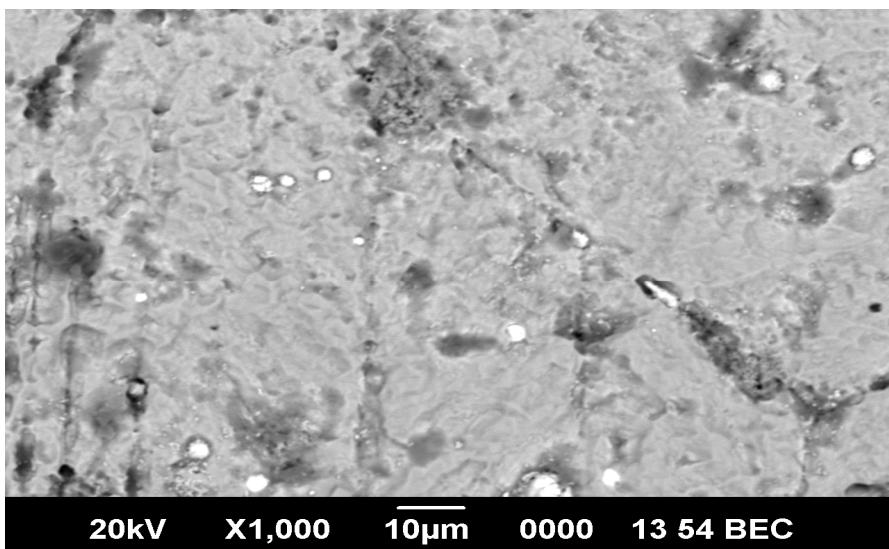


Fig. 16 SEM micrograph brass of twelve months exposure to brackish water after removal of corrosion products

4. Conclusion

The corrosion studies of brass in Cochin estuarial water have been carried out at an interval of 1, 3, 6 and 12 months. Increase of weight gain after three month exposure attributes to increase of corrosion products on brass. Decrease of corrosion rate up to six month exposure is related to protective film formed almost completely on brass. From OCP values, it is apparent that brass appears to be noble for first three months and negative shift of OCP after three months indicates localized corrosion.

Dezincification factor is found to be more than one, from the third month exposure, indicates that dissolution of zinc has occurred from the matrix of brass from the third month exposure. Therefore the dissolution of Cu has occurred predominantly up to first month exposure and then slight dissolution of zinc has occurred for the remaining period.

There has been no much variation of dissolved oxygen and P^H of estuarial water in Cochin with regard to exposure period and therefore these data could not be correlated to corrosion of brass. After the initial period of one month, only higher salinity and temperature are found to be responsible for increased corrosion rate, anodic reaction and dezincification factor.

XRD data show that the Cochin estuarial water significantly affects the nature of the crystalline corrosion products which may be responsible for the passivity of brass only during short exposure of one month. The passivity breaks down, at least on some areas, may cause higher corrosion of brass. SEM data confirms the influence of the Cochin estuarial water on the morphology of the corrosion layer as well as on both the size and morphology of the pits underneath the corrosion products.

EDX data shows presence of Zinc related to dezincification that occurred from the third

exposure period. After the removal of corrosion products, the morphology of the surfaces corresponding to all immersion periods presents a cracked surface along with boundaries except the first month of exposure and pits distributed on the whole surface of brass for all the exposure period

Studies on the electrochemical behavior of brass in Cochin estuarial water are under progress in our research group.

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