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# Corrosion Aspects Of Shipwreck Metals Of Lakshadweep Waters

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## ABSTRACT

Marine archaeological explorations revealed five shipwrecks in Lakshadweep waters. Iron, Lead and Brass metals were collected from a shipwreck off Minicoy to assess quantitatively their corrosion resistance and behaviour in sea water. Accelerated corrosion tests were carried out in the laboratory to study corrosion of shipwrecks and Cathodic-Anodic polarisation curves. The deposition layer consists of feldspar and chalcocite on brass, ferrous oxide on iron and a thick high magnesium carbonate and arganite minerals on lead shipwreck metals. The corrosion rates obtained are in the order of Iron > Lead > Brass.

## INTRODUCTION

The deterioration/corrosion of Shipwrecks in oceans is an important aspect for the marine archaeologists in recent years. When a ship is lost at sea, the shipwreck parts slowly deteriorate due to the marine environment prevailing at the site, which eventually cause the corrosion phenomena.[1]. Corrosion activity is the long lasting and most detrimental portion of the decomposition cycle for shipwreck metals [2]. The corrosion characteristic of ancient metallic materials is quite interesting since corrosion resistance is offered by them. The mechanism seems to depend primarily on the local environment and the characteristics of wreck metals. The study of the corrosion behavior of shipwrecks is an useful tool in the preservation technique and decay mechanisms. Due to the importance of concretions formed on the metal surface in both corrosion and preservation, the surface formations were analysed for their properties. Recent development of techniques for the performance of well controlled laboratory corrosion experiments provides the potential for quantitative assessment of the corrosion resistance of various metals [1].

Archaeological exploration off Lakshadweep islands, India, revealed shipwreck parts consisting of iron, brass and lead wreck metals which were retrieved from a depth of 5 to 15 mts. The representative samples of wreck metals are examined visually and it is interesting to find out their corrosion behavior in sea water. In this paper, the corrosion aspects of shipwreck metals obtained and their accelerated corrosion testing and result obtained are described.

## CORROSION AND PRESERVATION OF SHIPWRECKS

Corrosion means the destructive attack of metal by chemical or electrochemical reaction with its environment. In particular to the marine environment, corrosion is essentially an electrochemical process. The process of electrochemical reaction of metals in sea water can be given by the simple equation [1,3]. Metal → release electrons → electrolyte → electrons gained Anodic reaction Cathodic reaction.

The rate of flow of electrons depends upon various factors which include the nature of the surrounding environment and composition of metals. The cause of the deterioration of ancient metals is due to the surface effects also. The reactivity of wreck metals depends upon the variation in the degree of impurities or alloying elements present and making some regions more susceptible to corrosion. The reactivity of shipwreck metal can be assessed by electrochemical methods in-situ in the marine environment in which there is a definite correlation between the metal reactivity and the electrochemical values. There is also galvanic or bimetallic corrosion of shipwreck metals in marine environment [4]. This happens when dissimilar metals are in direct contact with each other. One metal becomes anode and corrodes more than it normally would, the other corrodes less than the normal. Since the shipwrecks are made of combination of different metals, the above process is an important aspect in the preservation of ancient shipwrecks [2]. Perhaps the most important in relation to the archaeological metals is the effect of relative areas

of metals in contact with the marine environment. The corrosion process is also influenced by the formation of the surface films and micro arid macro organisms present in the marine environment [5].

The above aspects of corrosion will be useful for archaeologists or conservators to understand the mechanisms and techniques in which archaeological wrecks are present.

### POLARISATION STUDY

To study the electrochemical corrosion behaviour of shipwreck metals of iron, brass and lead obtained from Lakshadweep waters, Polarisation studies were carried out in the laboratory. Electrochemical studies were performed using EG & G PARC model potentiostat with the software SOFTCORR to determine the corrosion current from the Tafel extrapolation method. The samples were polarised potentiodynamically at a scan rate of 0.2 mV/sec over a range of -300 to 300 mV relative to the corrosion potential in sea water. A three electrode configuration was used, consisting of test specimen, a saturated calomel electrode and platinum element as working reference and counter electrodes respectively. The corrosion current obtained for the shipwreck metals indicates the corrosion resistance and higher the value of corrosion current, lower the corrosion resistance [1].

### RESULTS AND DISCUSSIONS

The shipwreck metals obtained were examined visually in the laboratory and consists of brass, iron and lead metals. Among these shipwreck metals, brass was in good state of preservation with a thin green layer of corrosion product deposited on the surface due to the copper alloy oxidation and the presence of sulphate in seawater. This layer covering the base metal acts as a barrier between the surrounding environment and the base metal. There were no signs of any intragranular corrosion, since it was toxic to the marine life [6]. The inner brass metal was bright yellow in colour which appeared to be more noble and the metal was extremely protective due to the cover and its metallurgical characteristics. Copper alloys do not corrode much in the marine environment, unless by erosion and galvanic 'coupling' [7]. This is a very important aspect for archaeologists or conservators to notice galvanic coupling in-situ and to reduce further process of deterioration [4]. The green layer on the metal was analysed by XRD and found to consist of feldspar and chalcocite.

To know the corrosion behaviour of brass metal obtained from Lakshadweep waters in seawater, accelerated corrosion test was carried out in the laboratory. The results obtained are presented in Table 1 and figure 1. The corrosion potential for this metal varied between 200-210 mV which is in good agreement to those obtained for more noble metals. The corrosion potential is an important factor in the conservation of shipwrecks in the seawater [2,8]. The corrosion current for the brass metal was 8.82 A/sq.cm which is significantly less, indicating higher corrosion resistance of this ship wreck metal. The value of corrosion current ( $I_{corr}$ ) in turn was used to determine the rate of corrosion and to assess how much metal will be left after prolonged period of exposure. From the polarisation curve obtained for brass, it can be said that the dissolution rate of metal is very low and the metal tends to be more passive which is indicated by the cathodic curve obtained. The data will be useful in the comparison of same group of metals obtained from different shipwrecks.

The corrosion of ferrous metals depends upon their composition and the environment. The iron shipwreck metal obtained from Lakshadweep waters was found in poor state of preservation and was completely corroded with the layers of rust which is influenced by both chemical and biological activities of seawater [1,3]. Eventhough the ferrous metal was covered by calcareous deposit, due to the loose ferrous oxide product the corrosion rate was high. It was found that the metal was covered by stratified ferrous oxide product which is attached to the parent metal. This is one of the reasons for the higher corrosion of iron wrecks in Lakshadweep waters. The edges were broken due to the sediment movement and erosion. From Fig.1  $E_{corr}$  and  $I_{corr}$  values obtained for iron are -300 mV and 77 A/sq.cm respectively, which indicates poor resistance to corrosion exhibited by this shipwreck metal in the marine environment. The polarisation curve is in good agreement to those of less noble metals like wrought iron, mild steel etc [5]. The corrosion rate was nearly 9-10 times higher than that of brass metal which is an important factor to be considered in the conservation theory [2]. Lead wreck metal also suffered corrosion and a thick layer of calcareous deposit was found. The deposit was analysed and found that it consists of high magnesium carbonate and arganite minerals which may be due to the marine organisms and the site conditions. It is also possible that the deposition is due to galvanic coupling with other less noble metal. The  $I_{corr}$  and  $E_{corr}$  values obtained are 41.52  $\mu$ A/sq.cm and -295 mV respectively which

indicates higher corrosion rate than that of brass wreck metal. The corrosion activity was almost identical to that of iron and exhibits a passivity behaviour in the anodic polarisation curve [9].

**CONCLUSIONS**

1. The paper gives the information regarding the corrosion status of shipwreck metals and their behaviour in sea water and composition of deposits.

2. The iron wreck metal obtained from Lakshadweep is in poor preservation condition and corroded

**TABLE. 1 ELECTROCHEMICAL VALUES OBTAINED FOR SHIPWRECK METALS OF LAKSHADWEEP WATERS**

Metal	Ecorr [mV]	Icorr [uA/cm <sup>2</sup> ]
Iron	- 300	77.35
Lead	- 295	41.52
Brass	+ 200	8.88

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heavily with the formation of ferrous oxide layers.

3. The Brass and Lead wreck metals corroded much less compared to Iron

4. The deposition layer consists of feldspar, malachite on brass, ferrous oxide on iron and a thick layer of magnesium carbonate and arcanite minerals on lead shipwreck metals.

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