Effect of CCA treatment on corrosion and holding capacity of metallic fasteners

7.1 Introduction

Corrosion of fasteners is a universal issue that causes great economical losses in any industry. Nails or screws when used in wood, form a sandwich condition which may provide a corrosive atmosphere depending on various factors. Wood is slightly acidic when it is damp and it causes metals to corrode. This is because when a metal fastener is embedded in wet wood or when wood embedded with a fastener undergoes wetting, conditions are created that can accelerate the corrosion of the metal (Baker, 1980). The corrosion products often result in deterioration of the wood surrounding the metal gradually. When the wood is treated with an inorganic preservative like Chromated Copper Arsenate (CCA), the situation may be more conducive for corrosion or it may retard corrosion. Sometimes the presence of preservative may not influence corrosion of nails at all. All these depend on the type and quality of metal or alloy used as fastener, the wood species used, the preservative constituents and the conditions of the medium in which the nailed wood is exposed. This is especially important when it is exposed to aquatic conditions for the construction of boats, decks etc. The corrosion of iron nails used for boat building is a perennial problem faced by wooden boat builders. In the context
of treatment of wood with preservatives, there is a need to study the role of wood preservative on corrosion of fasteners used in wooden boat building.

Not many studies have been conducted regarding the role of wood preservative in corrosion of fasteners. A study by Whitney (1979) concluded that diameter loss of galvanized steel bolts may not be serious, but bolts in joints exposed to severe wetting conditions could be weakened due to rusting. For long service life under wet conditions, fasteners in contact with copper containing preservatives should be cathodic with respect to copper (Baker, 1980). Since CCA-A has higher chromium content, it is less corrosive than CCA-C. Also poles treated with CCA-A have been in service for 35 years without corrosion problems (Hartford, 1980). Aluminised iron fastenings are found more compatible with several boat building timbers and without sacrificing efficiency it can be used instead of expensive copper base alloys (Ravindran et al., 1985).

7.2 Nail and screw holding capacity of CCA treated wood

Wood is considered as a structural material also because it has got good nail and screw holding capacity. The resistance of a nail for withdrawal from a piece of wood depends on the density of the wood, diameter of the nail and depth of penetration. The surface condition of the nail at the time of driving also influences the initial withdrawal resistance.

The aim of the present study is to find out whether the presence of CCA in wood influences the corrosion of nails and whether the use of galvanized or
painted iron nail reduces corrosion. The study also aims at assessing the effect of preservative retention in wood on corrosion. The impact of corrosion products on the degradation of wood around the fasteners is also studied. The latter study aims at finding out the nail and screw holding capacity of rubber wood treated with CCA to different retentions.

### 7.3 Materials and methods

Eight numbers of 150 x 100 x 25 mm panels each of untreated control, CCA treated to the retentions 16 kg m\(^{-3}\), 29 kg m\(^{-3}\) and 42 kg m\(^{-3}\) were selected for the experiment. Nails of copper, iron, painted and galvanized iron, each of length 5 cm were used in the experiment. These nails are selected because iron and copper nails are used in the construction of wooden fishing canoes in India.

Five numbers of copper nails were nailed on the radial faces of the panel at a distance of 2 cm between each nail on all the four types of wood panels. Ten numbers each of iron and painted iron nails were nailed on the radial faces of all the four types of wood panels respectively with a distance of 1.2 cm between each nail. After drilling the sides of the panels to sufficient depth, the ten galvanized iron screws were screwed on both sides of all the four types of panels. Two sets of such experimental panels were prepared for laboratory as well as field exposure study in the estuary.

The salt spray experiment was patterned as per ASTM B-117-03. This method is selected because it is considered to be most useful in estimating the relative behaviour of closely related materials in marine atmospheres, since it
simulates the basic conditions with some acceleration due to either wetness or temperature or both. The nailed panels were then arranged on the fibre racks as specified in the standard. 3.5% salt solution was prepared using sodium chloride and the pH of the collected solution after atomization at 35°C was measured to be 7.1. A compressed air supply of 100 kN m⁻² was given for atomizing the salt solution. The exposure zone of the salt spray chamber was maintained at a temperature of 35°C and 95% relative humidity. The test was conducted for a period of 480 h. The experimental panels were collected from the chamber and the nails were carefully removed by cutting open the panel immediately after the experiment was completed. The X-ray photographs of the nailed panels were taken before exposing the panels in the salt spray chamber and after retrieving them, for analyzing whether there is degradation of wood around the fasteners due to the corrosion products.

The other sets of panels were exposed in the Cochin estuary for a period of 100 days (from 21st June to 29th September 2005). The nailed panels were tied on a rope and were immersed in the estuary at one meter below the tidal level at the North Oil Tanker Berth of the Cochin Port Trust. Salinity of the water sample was analyzed based on the Knudsen method. Dissolved oxygen was analyzed by titrimetry using Winkler’s method.

In Winkler’s method, water is sampled in a 300 ml Biological Oxygen Demand (BOD) amber coloured bottle without air bubble. 2 ml manganese sulphate (Winkler A) is then added immediately. Then 1 ml of Winker B (potassium iodide in potassium hydroxide) is added. The bottle is shaken well
after fixing the cap. 1 ml of concentrated sulphuric acid is then added and shake the bottle well. Titrate 200 ml of this sample with sodium thiosulphate with starch solution as indicator. The end point is the elimination of blue colour in one drop of thiosulphate. The concentration of dissolved oxygen in the sample is equivalent to the number of milliliters of titrant used in mg l⁻¹.

The hydrographic data of the exposure period is given in Table 7.2. On completion of the exposure period the panels were retrieved and the nails were removed for analysis as in the previous case. The cleaning of the nails and the calculation of the corrosion rate were done according to the ASTM standard G1-72 i.e., standard recommended for preparing, cleaning and evaluating corrosion test specimens. Copper nails were cleaned in the solution recommended for cleaning copper and copper alloys. Iron and painted iron nails were cleaned in the Clarke’s solution and galvanized iron screws were cleaned using alternative solution for stainless steel. The possible error due to loss of metal during cleaning was reduced by the method of recleaning and reweighing as suggested in the standard. The weight loss of each nail due to corrosion was measured and the corrosion rate was calculated as follows:

\[
\text{Corrosion rate (g m}^{-2}.h) = \frac{(K \times W)}{(A \times T \times D)}
\]

Where

\(K = 1 \times 10^4 \times D\) for the unit grams per square meter per hour (g m\(^{-2}\).h),

\(T = \text{time of exposure to the nearest 0.01 h,}\)

\(A = \text{area in cm}\(^2\) to the nearest 0.01 cm\(^2\),\)

\(W = \text{mass loss in grams, to the nearest 1 mg and}\)
Statistical analysis was carried out using univariate Analysis of Variance (ANOVA).

The nail and screw holding capacity of CCA treated rubber wood was analyzed by conducting the test according to test number 14 IS 1708-1969 viz Nail pulling and screw pulling tests. For this, rubber wood panels of size 150 x 50 x 50 mm size were selected.

Galvanized, bright, pointed iron nails of length 50 mm and 2.5 mm shank diameter with plain heads were used for the experiment. Screws were No.8 according to IS: 451-1961, galvanized and gimlet pointed. Nails and screw were driven in dry condition at 12% moisture content and pulled at once.

Nails were driven exactly at right angles to the face of the specimens to a total penetration of 25 mm. In the case of screws, a prebore 2.5 mm dia were made. In each piece, the nails or screws were driven in such away that there were two nails or screws on a tangential surface, two on a radial surface and one on each end. On radial and tangential surfaces, nails or screws were driven at a distance not less than 35 mm from the ends of the specimen and 15 mm from the edges. The two nails or screws on the radial or tangential face were not driven in a line parallel to the length of the specimen or less than the projected length of 50 mm apart.

The test was conducted in a Universal Testing Machine provided with a device suitable to grip the test piece to the fixed head and the nail or screw to the movable head of the machine. The equipment had suitable arrangements,
such as cushioning springs to prevent any sudden shocks to the machine. The specimen was held firmly during the test. The nail gripping device was then clamped to the nail. The load was applied continuously throughout the test so that the movable head moves at a constant rate of 2 mm per minute until the nail or screw is pulled out completely. The maximum load required to pull out the nails and screws were recorded. The readings of radial, tangential and end tests were recorded separately.

7.4 Results and Discussion

Galvanized iron nails were found more effective in resisting corrosion followed by copper nails. The trend does not vary notably in laboratory conditions as well as in the estuarine conditions.

In the case of nails exposed in the salt spray chamber in wooden panels, copper nails were found to have a corrosion rate value of 0.1581 g m$^{-2}$.h in 42 kg m$^{-3}$ panels, 0.1287 gm$^{-2}$.h in 29 kg m$^{-3}$ panels, 0.1063 g m$^{-2}$.h in 16 kg m$^{-3}$ and 0.0988 g m$^{-2}$.h in the control panel (Fig.1). Maximum corrosion rate was found for iron nails. Among the iron nailed panels, corrosion rate was maximum with a value of 0.9922 g m$^{-2}$.h for panel having retention of 42 kg m$^{-3}$. This is significantly higher than the rate of corrosion of nails in control panel, which was 0.7918 gm$^{-2}$.h. In the case of 16 kg m$^{-3}$ and 29 kg m$^{-3}$ the values were 0.8122 gm$^{-2}$.h and 0.8050 g m$^{-2}$.h respectively, which is not significantly different from the control panel. This suggests that higher retentions accelerate corrosion. Painted iron nails are found to corrode to a
lesser extent than bare iron nails. In this case also higher rate of corrosion was found for 42 kg m$^{-3}$ with a value of 0.7241 g m$^{-2}$.h. The corrosion rate of fasteners nailed to panels having 16 and 29 kg m$^{-3}$ retention were 0.5726 g m$^{-2}$.h and 0.6725 g m$^{-2}$.h respectively. Corrosion rate of 29 and 42 kg m$^{-3}$ panels were found significantly higher than the control panel which is having a value of 0.5785 g m$^{-2}$.h. In the case of galvanized iron nails corrosion rate was, 0.0521, 0.0471, 0.0426 and 0.0389 g m$^{-2}$.h for fasteners nailed to panels having retentions 42, 29, 16 kg m$^{-3}$ and control panel respectively.

In the case of panels exposed in the estuary, the corrosion rate values of copper nails were 0.1058, 0.0879, 0.0846 and 0.0716 g m$^{-2}$.h respectively in control, 16, 29 and 42 kg m$^{-3}$ retention panels (Fig. 2). Iron nails were also found to have similar values as that of control panel having a corrosion rate of 0.1959 g m$^{-2}$.h, 0.1594 g m$^{-2}$.h for 16 kg m$^{-3}$, 0.1921 g m$^{-2}$.h for 29 kg m$^{-3}$ and 0.1480 g m$^{-2}$.h for 42 kg m$^{-3}$. In the case of painted iron nails, corrosion was maximum in control panel with a value of 0.2087 g m$^{-2}$.h. Fasteners nailed to panels having 16 kg m$^{-3}$ retention also have corrosion rate of 0.2080 g m$^{-2}$.h. Corrosion rate of 0.1837 and 0.1883 g m$^{-2}$.h were estimated for panels having retentions 29 and 42 kg m$^{-3}$ respectively. For galvanized iron nails rate of corrosion was negligible with 0.0219, 0.0026, 0.0019 and 0.0016 g m$^{-2}$.h respectively for control, 16, 29 and 42 kg m$^{-3}$ retention panels. Observed data indicate that painting of iron nail did not reduce corrosion. Also the rate of corrosion was found to decrease with increase in retention. This may be due to the biodeterioration of wood treated to low preservative retentions and the
susceptibility to biodeterioration of untreated wood. It was observed that on prolonged exposure, deterioration of rubber wood in lower retentions of CCA viz. 16 and 29 kg m\(^{-3}\) was more than in wood treated to 42 kg m\(^{-3}\) due to attack by *Sphaeroma* spp. and *Teredo* spp. (Sreeja & Edwin, unpublished work). The degradation of wood by biological agencies permits increased contact with the outside environment which in turn accelerated corrosion.

Statistical analysis was carried out using ANOVA to find out the significant difference if any in rate of corrosion of fasteners exposed in laboratory and field conditions of four different types nailed in wood at four different retentions of CCA. Rate of corrosion was significantly different for all combinations of nail types and retention. Rate of corrosion in the laboratory condition was significantly higher than that in the field. The significance is valid at 1% level, \(R^2=0.985\). When Tukey’s test was conducted keeping nail type as variable, corrosion rate of each type of nail was found to differ significantly from other types of nails. When Tukey’s test was conducted keeping retention as variable, significantly high rate of corrosion was found only in case of iron nails used in 42 kg m\(^{-3}\) and painted iron nails used in 29 and 42 kg m\(^{-3}\) in the accelerated condition.

A study conducted at the National Physical Laboratory (NPL, 2003) of U. K. suggests that chromium salt constituent is supposed to have a small protective effect, and the arsenate radical a slightly corrosive one, in addition, the copper itself is potentially corrosive, for copper-based preservatives can leach soluble copper compounds to some extent and this copper can then plate
out as metal on to iron, zinc and aluminium, forming galvanic cells that accelerate the corrosion of the substrate metal. The leaching from freshly treated wood being much greater than that after a period of fixation, it is recommended that preserved wood be allowed to age for seven days before fasteners are inserted in the wood (NPL, 2003). To improve service life of nail in marine environment, galvanized nails and screws are reported to be more useful (TPAA, 2006). The present study also suggests that galvanized iron nails and screws are more effective in providing better service life to any structure surviving in vulnerable conditions.

Various factors have been identified that directly influence metal corrosion in the aquatic environment, including the hydrographical parameters of the environment like dissolved oxygen, pH, salinity, conductivity and physical factors like temperature and extent of water movement (North & MacLeod, 1987). Higher temperatures generally increase corrosion rates. However, corrosion needs a liquid phase and if drying occurs, higher temperatures may be beneficial (NPL, 2003). In this study also, high salinity of the salt spray resulted in high corrosion rate. Other factors like high temperature and humidity also accelerated the corrosion process. The average pH in the field condition was also higher than that in the salt spray. Since the experiment was conducted during the monsoon season, the salinity was very low during most part of the experiment (Table 7.1.1). The monthly average salinity (‰) and dissolved oxygen (mg L⁻¹) data of the experimental site in Cochin estuary during monsoon season for the last five years including the
experiment period is collected by this Institute (Table 7.1.2). The sudden fluctuations in the salinity value may be because of the tidal effect or heavy rain on the particular day of sample collection. The monthly average values of the data given in the experimental table also have similar values.

The possibility of establishment of electrolytic cells is present in the timber structure on exposure to relatively harsh environment of weather combined with CCA chemicals. Corrosion rates are related to electrical conductivity of the moist wood, which is influenced by the moisture level and the presence of soluble preservative byproduct salts. If the moisture content of the wood is below about 18 percent, the corrosion rate of metals will be very low. Thus, where the treated timber moisture content will climb above that level corrosive conditions can occur. In a long term study conducted by Forest Service Division of USDA (1988) on fasteners used in CCA treated wood, stainless steel nails and screws alone did not exhibit any visual signs of corrosion and the weight loss over fourteen year period was negligible. Wood always contains moisture and the acid in it, aided by salt if immersed in seawater, acts as a bulk electrolyte in which various electrochemical cells can be formed. This can be more vigorous than the micro-cells set up in atmospheric corrosion. The wood can be degraded by alkali formed at a cathode as well as by iron salts formed at a rusting iron anode. The shaft of a fastener inserted into wood lacks oxygen and becomes anodic, and the exposed head becomes cathodic. The cathodic alkali gives negligible protection to the head as it is soon washed away, but may cause alkaline degradation of the
wood at the area of emergence. Cathodic protection on wood vessels should be
done with care so that the products of the cathode reaction do not accumulate
and cause wood deterioration (Baker 1974). In this study, the detailed
examinations of the X-ray radiograph show that the wood in touch with the
fastener remains intact (Plate I & II). No gaps could be observed in any of the
panels where the fastener penetrates into the wood. The degradation of wood
may be less because of the presence of the preservative components. The cell
formation may have taken place between the nail and the preservative ions and
thus the wood cells would have escaped from degradation. This can be ensured
only after prolonged experiment in which the preservative components are
completely exploited during the service period.

The average values of force required for pulling nail and screw
from the rubber wood panels treated with different retentions of CCA is shown
in the figure 7.2.1 and 7.2.2. The figure shows that screw pulling strength is
more than nail pulling strength. Pulling nail or screw from the end is found to
need less force. CCA treatment is found to increase the strength of the wood as
the load required to pull nail and screw from all the three sides is more in the
case of treated panels but it is slightly less in the case of 26 kg m\(^{-3}\). Nail pulling
load is found highest from radial side in the case of 16 kg m\(^{-3}\).
7.5 Conclusion

CCA does not accelerate corrosion of fasteners nailed to it in 16 and 29 kg.m$^3$ retentions to a significant level, but in 42 kg m$^3$ retention, the rate of corrosion of nails is significantly high. The rate of corrosion was least in galvanized iron and painting of iron nail is found effective in reducing corrosion. The corrosion products do not found to accelerate the degradation of wood around the fasteners.

The increase in the load required for pulling of nail and screw in preservative treated wood concludes that CCA improves the strength of the wood. As retention increases, the load required for pulling of nail increases from tangential side whereas it remains same for radial side and the end.
Table 7.1.1: Hydrographical parameters of Cochin Estuary during the experiment

<table>
<thead>
<tr>
<th>Date</th>
<th>Water temperature (°C)</th>
<th>pH</th>
<th>Dissolved Oxygen (mg L⁻¹)</th>
<th>Salinity (%)</th>
<th>Turbidity NTU</th>
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<td>26</td>
<td>6.89</td>
<td>4.8</td>
<td>0.39</td>
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</tr>
<tr>
<td>07/07/05</td>
<td>27</td>
<td>6.89</td>
<td>4.6</td>
<td>0.20</td>
<td>29</td>
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<tr>
<td>19/07/05</td>
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<td>7.05</td>
<td>6.8</td>
<td>2.56</td>
<td>20.3</td>
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<tr>
<td>04/08/05</td>
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<td>7.49</td>
<td>5.4</td>
<td>0.42</td>
<td>28</td>
</tr>
<tr>
<td>24/08/05</td>
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<td>7.77</td>
<td>6.6</td>
<td>11.40</td>
<td>10</td>
</tr>
<tr>
<td>06/09/05</td>
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<td>7.52</td>
<td>3.4</td>
<td>0.57</td>
<td>16</td>
</tr>
<tr>
<td>20/09/05</td>
<td>30</td>
<td>7.52</td>
<td>6.4</td>
<td>3.73</td>
<td>11</td>
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</table>
Table 7.1.2: Salinity and dissolved oxygen value of Cochin estuary during monsoon for the last five years (2002 – 2006)

<table>
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<th>Month</th>
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<th>2005</th>
<th>2006</th>
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<td></td>
<td>D.O. (mgL⁻¹)</td>
<td>Salinity (‰)</td>
<td>D.O. (mgL⁻¹)</td>
<td>Salinity (‰)</td>
<td>D.O. (mgL⁻¹)</td>
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<td>2.45</td>
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</tr>
<tr>
<td>July</td>
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<td>6.26</td>
<td>5.7</td>
<td>1.76</td>
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</tr>
<tr>
<td>August</td>
<td>5.7</td>
<td>2.20</td>
<td>5.2</td>
<td>3.36</td>
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</tr>
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<td>16.50</td>
<td>5.4</td>
<td>12.45</td>
<td>5.4</td>
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Fig. 7.1: Corrosion rate of nails exposed in the salt spray chamber

Fig. 7.2: Corrosion rate of nails exposed in the estuary
Fig. 7.3: Nail pulling strength

![Nail pulling strength graph](image)

Fig. 7.4: Screw pulling strength

![Screw pulling strength graph](image)
Fig 7.5: Nailed, CCA treated rubber wood panels exposed in salt spray chamber for accelerated salt spray experiment

Fig. 7.6: The inner cross section of the CCA treated rubber wood panel and the iron nails removed from it after exposure in the salt spray chamber
Fig. 7.7: Galvanized iron removed from the wood panel exposed in the estuary

Fig. 7.8: Copper nails removed from the wood panel exposed in the estuary
Fig. 7.9: X-ray photographs of CCA treated rubber wood panels of untreated and of three different retentions nailed with copper, iron, painted iron and galvanized iron nails before exposure in the salt spray chamber

Fig. 7.10: X-ray photographs of CCA treated rubber wood panels of untreated and of three different retentions nailed with copper, iron, painted iron and galvanized iron nails after exposure in the salt spray chamber
Fig. 7.11: X-ray photographs of CCA treated rubber wood panels of untreated and of three different retentions nailed with copper, iron, painted iron and galvanized iron nails before exposure in the estuary.

Fig. 7.12: X-ray photographs of CCA treated rubber wood panels of untreated and of three different retentions nailed with copper, iron, painted iron and galvanized iron nails after exposure in the estuary.