ENVIRONMENTAL IMPACTS OF CHROMATED COPPER ARSENATE (CCA) TREATED RUBBER WOOD FOR AQUATIC APPLICATIONS

Thesis submitted to the
COCHIN UNIVERSITY OF SCIENCE AND TECHNOLOGY
in partial fulfillment of the requirement for the award of the degree of

DOCTOR OF PHILOSOPHY

in

ENVIRONMENTAL CHEMISTRY

by

AJITH PETER M.
(Reg. No. 2964)

Fishing Technology Division
Central Institute of Fisheries Technology
(Indian Council of Agricultural Research)
Cochin- 682 029, India

Faculty of Marine Sciences
Cochin University of Science and Technology
Cochin- 682 016, India

November 2008

CERTIFICATE

This is to certify that this thesis titled "**Environmental Impacts of Chromated Copper Arsenate (CCA) Treated Rubber Wood for Aquatic Applications**" is an authentic record of research work carried out by **Mr. Ajith Peter M. M. Sc.,** under my guidance and supervision in the Fishing Technology Division of Central Institute of Fisheries Technology, Cochin, in partial fulfillment of the requirements for the degree of **Doctor of Philosophy** (Faculty of Marine Sciences) and that no part thereof has previously formed the basis for award of any degree, diploma, associateship, fellowship or any other similar title of this or any other University or Institution.

Leela Edwin

Cochin-29
November, 2008

Dr. Leela Edwin
(Supervising Guide)
Principal Scientist
Central Institute of Fisheries Technology
Cochin – 682 029

DECLARATION

I, **Ajith Peter M.**, hereby declare that the thesis entitled **"Environmental Impacts of Chromated Copper Arsenate (CCA) Treated Rubber Wood for Aquatic Applications"**, is an authentic record of the research work carried out by me under the supervision and guidance of **Dr. Leela Edwin**, Principal Scientist, Fishing Technology Division, Central Institute of Fisheries Technology, Cochin, in partial fulfillment of the requirement for the Ph.D. degree in the Faculty of Marine Sciences and that no part thereof has previously formed the basis for the award of any degree, diploma, associateship, fellowship or any other similar title of any University or Institution.

28/11/08

Cochin-29
November, 2008

Ajith Peter M.
Central Institute of Fisheries Technology
(Indian Council of Agricultural Research)
P.O. Matsyapuri, Cochin-682 029

Acknowledgment

First of all I thank the Almighty for allowing me to take up and complete this work.

I would sincerely thank Dr. Leela Edwin, Principal Scientist, Central Institute of Fisheries Technology, Cochin, for her valuable guidance, encouragement and thought provoking advices through out the period of research.

I would like to thank Dr. K. Devadasan, former Director CIFT, for being the Chairman of the Research and Doctoral committees, for extending the facilities of the Institute for doing the research work and for his encouragement.

I thank Dr. B. Meenakumari, Director CIFT and former Head, Fishing Technology Division, for the assessment and guidance through out the research period.

I thank Dr. N. Chandramohanakumar, Registrar, Cochin University of Science and Technology and Head, Department of Chemical Oceanography, for being a member of the Doctoral Committee and for his valuable suggestions.

I sincerely thank all Scientists of the Fishing Technology Division, especially Dr. P. Muhamed Ashraf, Dr. Saly N. Thomas and Dr. M.R. Boopendranath for their help and encouragement throughout the work.

I thank Smt. Sreeja A. Senior Research Fellow and my colleague in the project for her unmatchable co-operation and help during the entire work

I thank Dr. V. Geethalakshmi and other Scientists of the Institute for the help they extended during the work. I express my sincere and loving gratitude to Shri. P.T. Sebastian, Smt. K.G. Sasikala, Shri. N. Krishnan, Shri. P. Raghavan (technical staff of the Material Science and Marine Pollution Section of the Fishing Technology Division) and all other staff of the Fishing Technology Division for their help and support during the research.

I am also thankful to all the technical, administrative and supporting staff of the Institute for their support and co-operation during the entire period of work.

I also thank Shri. Gipson Edapazham, Shri. Sabu. S, Shri. T.R. Gibinkumar, Smt. Usha Baghirathan, Baiju John and Kalidas (Former Senior Research Fellows, Fishing Technology Division) and all former Senior Research Fellows of the Institute, for their help, co-operation and critical comments.

I convey my gratitude to the Scientists and staff of Forest Research Institute, Dehradun, Institute of Wood Science and Technology (IWST), Bangalore, Marine Biodeterioration Division of IWST, Visakhapatnam, Rubber Wood Testing Laboratory, Rubber Board, Kottayam and Kerala Forest Research Institute, Peechi, for providing training and extending their library facilities.

Finally I express my sincere and loving gratitude to my mother, my wife, brother, sister and other members of my family for their prayer, support, advice, and understanding, which helped me to finish the task.

I also thank all my friends and relatives for their support and encouragement thorough out the period of work.

CONTENTS

Page No.

LIST OF TABLES

LIST OF FIGURES

Chapter I

Introduction

From prehistoric era onwards man depended on wood for his various recreational and constructional activities because of the structural, economic, environmental and aesthetic benefits of wood. Even though various other materials are currently available in the market, wood retains its position as the most accepted material in this regard because of its versatility. The increase of population and thereby the increase in the use of wood resulted in its scarcity. This resulted in the exploitation of forests by man. Deforestation brought about new environmental issues including evasion of various species of plants and animals other than the climate related problems like global warming. India has a rich biodiversity with more than four thousand wood species but around four hundred to five hundred species have timber value (Gairola & Aggarwal, 2005). Initially highly durable varieties like teak (*Tectona grandis*), aini (*Artocarpus hirsuta*) etc. were used for aquatic applications. The idea of using non-durable wood after chemical treatment with preservative came up only by the end of nineteenth century. Even then the use of non-durable wood for constructional activities was limited as wood preservatives were not commercially available and the use of preservation techniques was not familiar to the public. Its use became more common in the western countries by the middle of the twentieth century but is still limited in India. The scarcity of durable wood in the world made the use of non-durable and cheaper wood inevitable. Rubber wood (*Hevea brasiliensis*) is one naturally non-durable wood, which cannot be used effectively without preservation. The extractives in many species of wood contain components that provide resistance to decay, fungal and insect attack. These components are also responsible for the characteristic colour and odour of that species. Preservative treated rubber wood emerges as an alternative to the durable wood varieties when the service life of even the highly durable varieties of wood species is considerably affected by the severe attack of wood borers and the shortage of durable varieties for its replacement. Rubber wood is easily available in India as it is an agricultural by-product. Commercial rubber wood plantations are found in countries that are mainly confined to tropical and sub tropical regions. Malaysia, Indonesia, Thailand, Sri Lanka and India are the leading producers of rubber wood in Asia. About 5 million m^3 of total rubber wood produced is utilized by industries like packing cases, plywood, furniture, interior manufactures and the rest of which is used as firewood. Due to easy availability, low cost and good working qualities, rubber wood is gaining importance now a days even though it is highly non-durable.

Rubber wood is a by-product of plantation grown timber that is primarily used to prepare rubber latex. Rubber wood is tapped for latex when it matures in 14 -17 years. At an age of 25 to 30 years when the latex yield decreases the trees are felled. It is a light hard wood with a whitish yellow or pale cream colour when freshly cut. At 12% moisture content the density of rubber wood ranges between 450 - 626 kg m^{-3} (Edwin & Thomas, 2000). Rubber wood can be well compared with the other conventionally grown timbers due to its good mechanical properties and workability, but it is highly vulnerable to biodegradation (Shukla & Lal, 1985, Gnanaharan & Damodharan, 1992). Rubber wood is moderately refractory so it can take up preservatives easily (Shukla & Lal, 1985). Rubber wood is classified as a light to moderately heavy wood and its specific gravity was estimated to be 0.557 at 12% moisture content (Rubber Board, 2005).

The major weakness of wood is its susceptibility to attack by natural enemies- wood borers, insects and fungi. Although rubber wood has many desirable qualities to replace a durable wood in the marine condition it is highly vulnerable to biodeterioration because of the attack of these agencies of destruction. Rubber wood has relatively high content of starch and low content of lignin in the cell walls. The natural resistance of rubber wood to marine woodborers ~~has~~ was studied by Rao *et al.* (1993); Edwin & Pillai (2004). Wood can be classified into five different classes according to their durability viz. highly durable, durable, moderately durable, non-durable and perishable (Findlay, 1985). According to the studies rubber wood is found to be perishable under marine conditions. According to Findlay (1985) such wood requires rapid seasoning that considerably reduces the moisture content in the wood and increases the life. The service life of rubber wood panels exposed under the marine condition is about 4-6 months (Rao *et al*, 1993). The marine exposure trials conducted by Edwin and Pillai (2004) showed similar results where the panels were completely destroyed in 5-7 months. Preservation of rubber was studied by Hong *et al*, 1982; Gnanaharan and Mathew, 1982; Damodharan and Gnanaharan, 1994; Edwin and Pillai (2004).

1.1 Wood Preservatives

Wood preservatives are substances applied to wood to protect it from various natural enemies like wood borers, fungi, insects etc. and the deterioration due to weathering on exposure to different environmental conditions. Initially, traditional wood preservatives like neem oil, sardine oil and cashew nut shell liquid were more prominent. Later they were replaced with synthetic chemical preservatives. Over the past century a variety of wood preserving treatments have been developed that introduce a small amount of protective preservative into the wood cells. Preservatives that are widely used for pressure treatment of wood can be classified as oil borne, water borne (fixed and leachable) and solvent type. The water borne preservatives have largely replaced the oil borne preservatives like creosote for aquatic use, on environmental and human health considerations. Creosote was in use from 18th century for the protection of railway sleepers. The water borne preservatives include chromated copper arsenate (CCA), chromated copper boron (CCB), ammoniacal copper arsenate (ACA), acid copper chromate (ACC), ammoniacal copper zinc arsenate (ACZA) and ammoniacal copper quat (ACQ). Solvent type preservatives include pentacholorophenol and copper naphthanate.

The concept of using toxic metallic oxides is not new. In 1730 wood was treated by immersion in arsenic solutions to protect against insect attack. This method was not suitable for treating wood that would be submerged in water because the soluble arsenic salts would immediately leach out. In 1931, Falk and Kamesam conducted a series of experiments in which they attempted to fix the arsenic in wood by precipitating insoluble complexes. They developed a leach-resistant formula of arsenic pentoxide and sodium dichromate, and were granted a French patent in 1933. Copper sulfate was another soluble metallic salt that was known to be effective as a fungicide, so with the addition of copper sulfate to Falk and Kamesam's original formulation, the wood preservative CCA (Chromated Copper Arsenate) was produced. The preservation of wood using chemicals especially chromated copper arsenate (CCA) is a good method to give greater life to non-durable wood. CCA has proved to increase the life of less durable wood from 2-3 years to 15-30 years depending on the medium in which it is used (AWPA, 1994). Experiments have been conducted at the Central Institute of Fisheries Technology, Cochin using rubber wood for aquatic purposes especially in the construction of small fishing canoes (Edwin *et al.,* 2005). Out of the 16.7 million m^3 of wood preserved in USA in 1996, 13.2 million m^3 i.e., 79.1% were treated with water borne preservatives amounting to 1.9 million kg. The most widely used wood preservative for timbers exposed in aquatic environments is CCA. Nearly 5.8 million m^3 of preserved timber were prepared for marine construction, of which 95% was treated with CCA (AWPI, 1997). The treated wood is extensively used to build structures such as decks, fences, poles, pilings, playgrounds, and picnic tables. CCA-treated wood represents approximately 90% of the treated wood market by volume in Korea (KFRI, 2002). Minimum life spans in fresh and marine water for CCA treated panels are considered to be 30 and 15 years respectively (AWPA, 1994). In India about 208 treatment plants are there using 1500 tonnes of water borne preservatives to treat 3 million m^3 of wood annually and it is estimated that it would increase to a maximum of 10000 tonnes over the next decade (Kumar & Dev, 1993).

The components of CCA, chromium, copper and arsenic all have important roles in preservative efficacy. The primary role of chromium in CCA is fixation of its components with reduction of chromium from hexavalent to trivalent state. These reactions result in the insolubilization of CCA components in the wood so that they resist leaching and provide lengthy service. Copper and arsenic are vital to the preservative efficacy of CCA because of their toxicity to fungi and insects. Copper is an excellent fungicide and arsenic is especially effective against insects and helps to provide protection against some copper tolerant fungi. The efficacy of CCA against biodeterioration of wood exposed to the sea, soil and atmospheric condition have been studied in India. Retention levels of 16 kg m^{-3} have been found to be very effective in resisting borer attack in seawater (Kumar, 1985). Catamarans made of CCA treated logs of *Bombax ceiba* used for 15 years service at the Lawson's Bay fishing village, Visakhapatnam in India were studied for the efficacy of the preservative. Around 35% of preservative was still retained in the wood and the catamarans were still in usable condition (Kuppusamy *et al.*, 2002). The efficacy of CCA and the effect of its treatment in the physical and mechanical properties of boat building timbers have been studied at the Central Institute of Fisheries Technology, Cochin (Edwin *et al.,* 2005). The studies on the secondary species of timber have led to the adoption of preservative concentration of 7.5% for marine purposes. The strength of wood was not affected when lesser concentrations of CCA were used along with creosote (Edwin *et al.,* 1993; Thomas *et al.,* 1998). The dual preservative treatment technology involving the pressure impregnation of CCA followed by creosote, with a drying period in between was used in the study on the resistance of preservative treated rubber wood to marine borers. After an exposure of 33 months in sea, the dual treated wood showed excellent performance without biodeterioration (Edwin & Pillai, 2004).

Recent toxicity studies have suggested that leaching of preservative components from wood used in aquatic media may be harmful to the environment. The focus of much of the early work concerning leaching of CCA has been on monitoring leaching in terms of durability of wood and the ability of treated timbers to withstand biological decay, rather than quantifying its release to the environment and its after effects (Fahlstorm *et al.,* 1967; Hager, 1969; Cherian *et al.,* 1979; Johnson, 1982; Eaton, 1989; Green *et al.,* 1989). Only few among the previously conducted leaching experiments have examined the rate of release and the factors which may affect the leachability of copper, chromium and arsenic from CCA treated wood specimens (Johnson, 1977). Conflicting evidence exists about the extent of leaching of components from CCA treated wood. Examination of CCA treated products following prolonged terrestrial and marine weathering showed that CCA-C treated wood effectively retained copper, chromium and arsenic (Arsenault, 1975; Johnson, 1977). In contrast, Hegarty and Curran, (1986) showed that CCA treated beech and scots pine specimens weathered in seawater for one-year period showed measurable losses of copper, chromium and arsenic. Recent studies have also shown a similar pattern of leaching of copper, chromium and arsenic from CCA treated wood submerged in coastal water for one to four years (Archer & Preston, 1994; Hayes *et al.*, 1994). However the immersion conditions can affect the results obtained. In some situations, the leached preservative in the water may reach concentrations that inhibit further leaching (Brooks, 2002).

1.2 Characteristics of the preservative treatment that affects leaching

There are few important factors that has to be taken into account while conducting the preservative treatment of the wood. They include fixation of the preservative, formulation, the method of treatment and the retention of the preservative with in the wood. If these processes are done scientifically, the leaching of the preservative can be controlled to a certain extent.

1.2.1 Fixation of the Preservative

The term fixation refers to the series of chemical reactions that render the preservative non leachable during service. Fixation can otherwise be defined as the process that minimizes the leaching of the chemical components of the preservative when all chemical reactions are complete (Cooper & Stokes, 1993). The effect of wood species on the fixation reaction of CCA with lignin, and cellulose have been extensively investigated (Greaves, 1972; Greaves, 1973; Greaves, 1974). Pizzi (1982) has provided a comprehensive review of the chemistry and kinetic behavior of arsenic, copper and chromium during fixation of CCA in treated wood. During fixation, following impregnation of the treating solution, chromium undergoes conversion from the hexavalent state to the trivalent state. Most of the preservative (>90%) is chemically bound to the wood fibers by reaction with wood sugars to form insoluble arsenate precipitates. The length of the fixation period is temperature sensitive and can last from several hours at 45°C to two months at 5°C. Studies by Baldwin (1996) measuring the efficiency of the fixation mechanism, have shown that drying at 21°C will fix 95% of the metals within four days and 99% within five days. Improper fixation can result in significantly increased leaching of all CCA components. The fixation reactions are highly dependent on processing techniques and post treatment conditioning factors such as temperature, humidity and air-flow (Lebow, 1996). The reactions that take place in the wood during the fixation of CCA have a great influence on the metal species that are emitted from the wood, and the subsequent toxicity of the leachate. During the pressure treatment process, the pH of the working solution must be below 2.5-3.0 to allow the hexavalent chromium to be reduced to trivalent chromium. The trivalent chromium reacts with copper, arsenic, and wood carbohydrates to precipitate insoluble complexes in the wood. As this reaction proceeds, the pH in the wood increases to about 5.5, the normal pH of wood (Hartford, 1986).

In order to ensure prevention of leaching adequate time should be allowed for fixation before placing the wood in service. The time required for fixation varies with wood species, specimen size and retention, but the most important parameter is temperature. Temperature is very important in obtaining adequate and timely fixation. The formation of insoluble precipitates in treated wood depends on the presence of water as a substrate in which the soluble ions react. The fixing of copper, chromium, and arsenic in the wood is not completed during the pressure treatment process. Pressure treatment forces the compounds deeply into the wood where the reactions then take place over time. The presence of water over the time period when reactions are occurring is important for maximum fixation. Oven drying of CCA pressure- treated wood can drive off critical moisture and hasten the reactions to a different end point, rather than the desired insoluble precipitates (Arsenault, 1975). Drying the wood too quickly may not allow the wood to equilibrate at a higher pH, thus increasing the rate of leaching (Arsenault, 1975). Much work has been done to develop methods of high temperature fixation such as kiln drying, steam baths or water baths (Peek Willeitner, 1981). Peek and Willeitner pioneered earlier works in the field of accelerated fixation. Rapid drying may cause redistribution of chemicals between lignin and cellulose leading to higher proportions of CCA products in the cell lumens, where again they may be more accessible to leaching (Lee *et al.,* 1993; Cooper *et al.,* 1997).

1.2.2 Formulation

The ratio of components in CCA formulations is crucial to allow rapid and complete fixation which finally decides leaching. Hager et al., 1969 experimented with ten formulations of CCA to find which combination of components provided the most leach resistant formula. They found when the arsenic pentoxide (As_2O_5) content was more than two-thirds of the chromic oxide (CrO_3) content, the excess arsenic pentoxide was wasted through leaching. They also found that if the chromic oxide content was more than twice the arsenic pentoxide content, the excess chromic oxide did not contribute additional permanence. In a similar series of experiments, Häger (1969) found that copper from copper sulfate could be fixed in sawdust even without a fixing agent. Häger (1969) also found that the addition of chromium does improve the fixation of copper. The most leach resistant formulation of CCA was reported to be a mixture of chromic oxide 50%, copper oxide 17%, and arsenic pentoxide 33%. In a similar experiment, Fahlstrom *et al.* (1967) found the most leach resistant formula from their series to be a ratio of chromic oxide 49.1%, copper oxide 17.2%, and arsenic pentoxide 33.7%.

1.2.3 Preservative treatment method

The main objective of all treatment process is to get adequate quantity and uniform distribution of the preservative inside the timber in order to obtain desired service life. There are mainly three methods of application of the preservative. Surface application- this includes painting and spraying. The second one is dipping, steeping and diffusion. The last and most effective method is pressure treatment process. In this method the wood to be treated is kept in a pressure impregnation chamber and preservative is applied in high pressure with the application of vacuum before and after applying pressure. Physical parameters of the preservative treatment process such as magnitude and duration of vacuum and pressure cycles may influence penetration and retention of preservatives.

1.2.4 Retention of the preservative

The exact relationship between preservative loading or retention and leaching is not understood, even though preservative loading is known to affect the absolute concentration of elements leached (Cooper, 1994; Albuquerque & Cragg, 1995a; 1995b; 1996). Fahlstrom *et al.,* 1967 suggested the effect of retention on leaching was dependent on preservative composition with percentage leaching decreasing with increasing retention in arsenic rich formulations. In chromium rich formulations, leaching increased with retention. Proportional losses have been found to decrease at increased loadings (Archer & Preston, 1994; Hayes *et al.*, 1994). Following 85 months exposure in the marine environment, percentage losses were 52 and 44 from pine treated to retentions of 24 and 48 kg m^{-3} respectively. The reduced leaching was supposed to be due to increased total Cr concentrations in the system available to fix the remaining metal elements (Archer & Preston, 1994). At the same time other researchers have shown increased leaching with increasing retentions (Albuquerque *et al.,* 1996; Irvine *et al.,* 1972). Long term copper and chromium leaching rates were highest in CCA treated wood with retention levels >35 kg m^{-3}, whereas long term As leaching rates were increased in wood with retention levels <35kg m^{-3} (Breslin & Alder-Ivanbrook, 1998).

1.3 Characteristics of the media that affects leaching

Many features of the leaching media are important in determining leaching rates, particularly salinity, pH, wood: water volume, rate of water movement around the specimen, temperature, orientation of wood grain etc. Leaching medium is an important factor affecting release of preservative components from treated wood because physical and chemical characteristics of medium increase or decrease the solubility of fixed preservative components (Kartal *et al.,* 2004).

1.3.1 Salinity

Standard leaching test methods for preservative leaching from treated wood usually requires distilled or de-ionized water (Kartal *et al.,* 2004; Kartal & Imamura, 2005). Water is a key factor for release of preservative components from treated wood. A study by Kartal *et al.,* 2004 showed that sea water and tap water containing higher ion concentrations than distilled water resulted in less leaching of wood preserving and calcium precipitating agent, N,N-hydroxynapthalimide (NHA) from treated wood specimens. It has been suggested that at low salinities sodium chloride has a coagulating effect on the crystalline copper fixation complexes increasing surface area and decreasing solubility, and at salinities above 24 ppt the increased formation of complexes between chloride and copper may explain the increased leaching (Irvine & Dalgren, 1976). The characteristics of the leaching water can also influence leaching of preservatives. The presence of some types of inorganic ions in water has been reported to increase leaching from CCA treated wood (Irvine *et al.,* 1972; Ruddick *et al.,* 1993).

1.3.2 pH

The effects of the pH of solution on preservative loss were investigated by conducting studies using water buffered with NaOH and citric acid. This study indicated very high leaching rates at low pHs, with losses of copper up to 100% at pH 4.5 (Warner & Solomon, 1990). Leaching in dilute sulphuric acid solutions was reduced by up to a factor of 5 and later demonstrated that the high losses were due to the use of the citric acid buffer (Cooper, 1991).

In a study, sulphuric acid/nitric acid buffers were used to investigate the effect of pH on CCA leaching from western hemlock blocks (Kim & Kim, 1993). The study showed that the leaching of copper was between 16 and 25%

at pH 3, but decreased to about 1% at pH 4. Leaching of arsenic was found less affected by pH, but was generally around 2-3% at pH 4 and above. Leaching of CCA is greatly increased when the pH of the leaching water is lowered to below 3, and the wood itself also begins to degrade (Cooper, 1991; Kim & Kim, 1993). Water pH ranges are less likely to have significant effect on leaching, although the presence of organic acids may influence leaching at moderate pH levels (Murphy & Dickinson, 1990).

1.3.3 Temperature

Leaching of copper, chromium and arsenic has been shown to be reduced at lower temperatures with leaching of chromium at 20°C reported to be 0.119 $\mu g\ m^{-2}\ s^{-1}$ compared with 0.079 $\mu g\ m^{-2}\ s^{-1}$ at 8°C (Van Eatvelde *et al.*, 1995). Copper, chromium and arsenic leaching, were approximately 1.4, 1.6 and 1.5 times greater, respectively, from wood leached at 20°C than from wood leached at 8°C. Brooks (2002) also concluded that leaching of copper from CCA treated wood could be substantially increased as water temperatures increased from 8°C to 20°C. A similar temperature effect was noted in study of release of creosote components from treated wood (Xiao *et al.,* 2002). However, temperature may not be a deciding factor in the leaching of CCA in the tropical waters because fluctuation in temperatures is not so pronounced in these regions.

1.3.4 Rate of water movement

The rate of water movements around the test specimens can also influence leaching, although this effect has not well quantified. Van Eetvelde *et al.,* (1995) reported that leaching of CCA was greater when using stirred leaching water than with static leaching trials. The AWPA standard leaching test specifies the use of a low stirring speed (a tip speed of 25 – 50 cm s^{-1}). With adequate care for the method of stirring or agitation used, the mechanical abrasion of the surface of the wood can be avoided.

1.3.5 Wood: water volume

The volume of leaching water used is an important aspect, where a high wood: water volume ratio allowed toxic concentrations of metals to build up (Weis *et al.,* 1991; Albuquerque & Cragg, 1995a). Studies have been conducted exposing marine organisms to CCA treated wood or leachate waters and deleterious effects have been shown against a range of aquatic organisms (Weis *et al.,* 1991; Weis *et al.,* 1992). Criticism of this work focused on the unrealistically high ratio between wood and water volume, which allowed metal concentrations to build up to toxic levels (Albuquerque & Cragg, 1995a; Breslin & Alder-Ivanbrook, 1998). During laboratory leaching trials, the size and dimensions of wooden blocks used were found to have major influence on the percentage of preservative leached from the wood. The relatively large surface area to volume ratio of the typical small sample blocks used in most studies allows proportionately more wood available for leaching (Cooper, 1994). Significant reductions in leaching rates of all CCA elements were observed with a decrease in surface area to volume ratio (Cooper, 1994).

1.3.6 Orientation of the wood grain

The rate of movement of liquids along the grain of wood is several orders of magnitude greater than that across the grain, and samples with a high proportion of exposed end grains will exhibit exaggerated rates of preservative leaching. Losses within 24 hours have been shown to be greatest from the radial and tangential surface, although long term leaching was greatest from end grain (Osler & Holland, 1993). End grain penetration has been shown to be 40 times greater than lateral penetration and may greatly influence leaching rates (Morgan & Purslow, 1973).

1.3.7 Surface area to volume ratio of wood

It has been shown that the rate of leaching decreases markedly with increase in the size of the piece of treated wood, and when the proportion of the end grain exposed per unit of surface area leached is reduced (Arsenault, 1975; Fahlstrom *et al.,* 1967). In commodity size timber, end-grain may represent only a small percentage of exposed surfaces, but may form a significant portion of the standard test blocks. This leads to laboratory studies grossly over estimating leaching rates (Archer & Preston, 1994; Cooper, 1994; Albuquerque & Cragg, 1995a). The shape, size, volume and proportion of end grain in the wood are of prime importance in determining the potential for leaching

(Cooper, 1994). Hayes *et al.,* (1994) found a considerable reduction in the amount of metal lost with increasing block size.

The period between treatment and immersion in water greatly influences the magnitude of initial CCA release. Significant differences were observed in leaching of chromium and arsenic between wood dried for one and four weeks. Increased time allows greater reaction between preservative and wood components to occur, reducing the leachable component. CCA treated timber intended for marine use should be treated with the most leach resistant formulation available provided that such a formulation also provides adequate protection from borers. Particular care should be taken to ensure that post-treatment fixation is properly conducted.

1.4 Scope of the study

Even though CCA has been in use for several years, its impact on the aquatic environment has not been studied in detail. The focus of much of the early work concerning leaching of CCA has been on monitoring the leaching of CCA components to study the durability of wood and the ability of treated timbers to withstand biological decay, rather than quantifying its release to the environment and its after effects (Hager, 1969; Cherian *et al.,* 1979; Johnson1982; Edwin & Pillai, 2004). CCA is categorized under non-leachable preservative, but the possibility of leaching of the preservative into the surrounding medium cannot be ignored. The recent studies stressing the environmental impacts of leaching of CCA were done mainly by Hingston *et* al. (2000), Townsend *et al.* (2001). Although the earlier studies are useful as comparative tools, they are not intended to demonstrate the amount of leaching that may occur in service conditions. In this context, there is a need identify the effect of preservative retention, leaching of the preservative components in tropical aquatic conditions, accumulation in the sediment, speciation of preservative components in the water and the methods to control the leaching.

1.5 Objectives of the study

The present study aims at estimating the impact of the use of rubber wood treated with CCA for boat building and other constructional activities in the aquatic condition.

The main objectives of the study are

- to find out the rate of leaching of Copper, Chromium and Arsenic from the CCA treated rubber wood into the aquatic environment
- to find out the effect of retention of the preservative and surface area of wood on leaching of CCA constituents
- to identify the influence of the nature of media on leaching of CCA
- to identify the speciation of CCA in water
- to understand the nature of accumulation of CCA components in the sediment
- to study the effect of multiple treatment and physical barriers on controlling leaching

- to investigate the effect of the CCA treatment on corrosion of nails used for boat building and
- to estimate the nail and screw holding capacity of CCA treated rubber wood

Chapter II

Materials and Methods

The studies on the environmental impact of using chromated copper arsenate (CCA) treated wood preservative for aquatic applications were carried out mainly under two heads. Leaching studies and the corrosion studies. The leaching studies were further categorized into the effect of retention, the influence of leaching media and the control of leaching. The importance of wood sample size in leaching is also experimented. These experiments were conducted both in the laboratory and field conditions. In the laboratory, preservative treated wood panels were kept in water under accelerated condition (using magnetic stirrers) and in stagnant condition by immersing in aquaria. In the field this experiment was conducted by exposing the treated wood panels in the estuary. For this, wood was treated with CCA into different retentions and the effect of retention in leaching of CCA was experimented. The influence of leaching media in controlling the rate of leaching was experimented by exposing the treated wood panels in water of varying salinity and pH. The role of exposed surface area in leaching of preservative components was also experimented in both these methods by using two different sizes of wood panels. The experiment to identify methods to control the leaching of CCA from preservative treated panels was conducted by using multiple treatments like dual preservative treatment, by using physical barriers like FRP sheathing and by painting after CCA treatment. The accumulation pattern of CCA components in the sediment near the exposure site was also experimented in the laboratory by exposing preservative treated wood of different retentions in the vicinity of sediment collected from the field. The speciation of CCA in the water where treated wood was exposed was also studied by analyzing the species of preservative components leached into the water in the laboratory experiment.

The corrosion studies were categorized into two. The effect of CCA retention on corrosion of nails and screws used for boat building and the nail and screw holding capacity of wood panels treated to different CCA retentions. The first experiment was conducted by exposing preservative treated wood nailed with different types of nails and screws in the salt spray chamber in the laboratory and by immersing in the estuary for field experiment. The latter experiment was done by conducting the nail and screw holding capacity experiment of wood (IS 1708-1969) after nailing the preservative treated wood with nail and screw.

2.1. Materials

2.1.1. Rubber wood

Rubber wood is a light hard wood of density 450-626 kg m^{-3} having characteristic strength properties comparable to that of any commercially accepted durable wood species. Rubber wood does not offer much resistance to the penetration of wood preservatives and because of the above-mentioned qualities rubber wood is selected for the study.

The freshly felled plantation-grown rubber wood tree samples were collected from local suppliers at Cochin area. The tree was of 30 years of age. The portions of the tree free from knots, without visible evidence of infection from mould, stains or decay fungi, were used for the preparation of panels. The rubber wood panels of size 150 x 100 x 25 mm were cut and the edges of the panels were smoothened using a planer. Immediately after collecting the panels, they were immersed in 2% CCA solution to prevent the fungal attack.

Air seasoning of the panels was carried out for a period of 4 weeks promptly after immersion in 2% CCA. After the seasoning period, moisture content of the wooden panels were determined by oven dry method. In this method, representative samples of size 25 x 50 x 50 mm were weighed and dried at 102 ± 1 °C and allowed to attain a constant dry weight. The moisture content of the samples were calculated using the formula

$$\text{Moisture content} = \frac{\text{Wet weight} - \text{Oven-dry weight}}{\text{Oven-dry weight}} \quad \text{X } 100$$

The panels below 25% moisture content and devoid of any cracks were selected for the study.

2.1.2. Marine plywood

Marine plywood has been extensively used for marine construction especially for boat building due to high economical viability and relatively low damage in aquatic conditions. Marine grade plywood comprises as much as 80% of the material of any plywood vessel. To improve the quality of the plywood CCA treatment is usually employed because of greater penetration and fixation of CCA into the veneers. Marine plywood sample from Greenply manufacturers was purchased from the local market in 203.2 x 101.6 x 19mm size. Panels of size 150 x 100 x 19 mm were cut and used for the experiment. Analysis of representative plywood samples in Inductively Coupled Plasma Atomic Emission Spectrophotometer (ICP-AES) showed retention of 4.05 kg m^{-3} of CCA.

2.1.3. Preservative solutions

CCA: The commercially available CCA manufactured by ASCU was taken for the study. CCA is prepared according to Indian Standard 10013-1981. The formulation is given in the Table 2.1. The 7.5 % (w/v) of CCA solution was prepared by dissolving CCA in water by gradual increase in temperature up to 45°C. The precipitate was removed and the supernatant solution was cooled and used for preservative treatment.

Creosote: Commercially available light creosote oil with a specific gravity 1.03 was purchased and used for the experiment.

2.1.4. Paint

Coal tar epoxy finish paint (Asian paints) was purchased commercially and used for the experiments. A total of twenty-five panels were coated of coal tar epoxy paint. The base and hardener was mixed together in a ratio 4:1 as specified by the manufacturer. Two coats of the paint were given with an intermittent drying period.

2.1.5. Fibreglass Reinforced Plastic (FRP)

The FRP sheathing was done using Chopped Strand Mat (CSM) of weight 450 g m^{-2} used for boat building purposes. The resin used for reinforcement was general-purpose polyester resin. Twenty-five numbers of panels were given two layers of resin coating. The panels after proper curing were used for the experiment.

2.2. Methods

2.2.1. Preservative Impregnation Procedure

The selected panels were treated with 7.5% (w/v) CCA solution to get retentions of 16 kg m^{-3}, 29 kg m^{-3} and 42 kg m^{-3}. The above-mentioned retentions were selected in such a way that they cover the minimum (16 kg m^{-3}) and maximum (32 kg m^{-3}) retentions (Findlay, 1985) recommended by AWPA for aquatic purposes. The wet weight retention of the preservative in the panel was calculated as per ASTM D2481-81. After air seasoning for a period of two weeks, 25 panels were selected and pressure treated with creosote (dual treatment).

Preservative treatment was done by Full Cell or Bethell process according to IS–401:1960. The process called pressure impregnation was carried out in vacuum pressure impregnation chamber of 400 l capacity which is fixed vertically. The impregnation chamber was connected to a supplementary tank for storing the preservative. The panels were loaded in the treatment chamber and screwed airtight. A vacuum of 56 cm of Hg was applied for 30 minutes with a vacuum pump in order to remove the air and moisture present in the wood cells. The preservative solution from the supplementary tank was passed into the treatment chamber under vacuum. When the chamber was filled with the preservative solution the vacuum was released. The valves were closed and pressure was applied, so that preservative solution gets imbibed into the wood cells. The conditions provided in the preservative chamber to get retentions of 16 kg m^{-3}, 29 kg m^{-3} and 42 kg m^{-3} of CCA and retention of 150 kg m^{-3} for dual preservative are given in the Table 2.2. The time and amount of pressure applied varies according to the required net wet weight retention. A final vacuum of 38 cm of Hg for 15 min was applied to drain the excess of preservative from the panels and to facilitate drying.

The retention of the preservative in the panels on wet weight basis was calculated as per ASTM D2481- 81.

$$\text{Retention, kg m}^{-3} = \frac{1000\,GC}{V}$$

where, $G = T_2 - T_1$, weight in grams of the treating solution absorbed by the wood.

C = Grams of preservative in 100 grams of treating solution.

V = Volume of the block in cm^3.

The qualitative estimation of preservative penetration in wooden panels was conducted to confirm the extent of penetration of CCA into the panels. In this method, a piece of preservative treated wood sample is sprayed with a solution freshly prepared by dissolving 0.5 g of diphenyl carbazide in 50 ml isopropyl alcohol and made up to 100 ml (IS: 2753, 1991). The reagent treated surface was examined after 15 minutes. The purple coloration indicated the area where the preservative solution has penetrated. The panels selected for the studies are given in plate 2.2.

2.3 Experimental Procedures

The factors influencing the leaching of the preservative into the aquatic environment were first studied in the laboratory condition. The important factors like retention of the preservative, the influence of leaching media and the methods to control leaching were done under this category. Detailed procedure is described in the corresponding chapters.

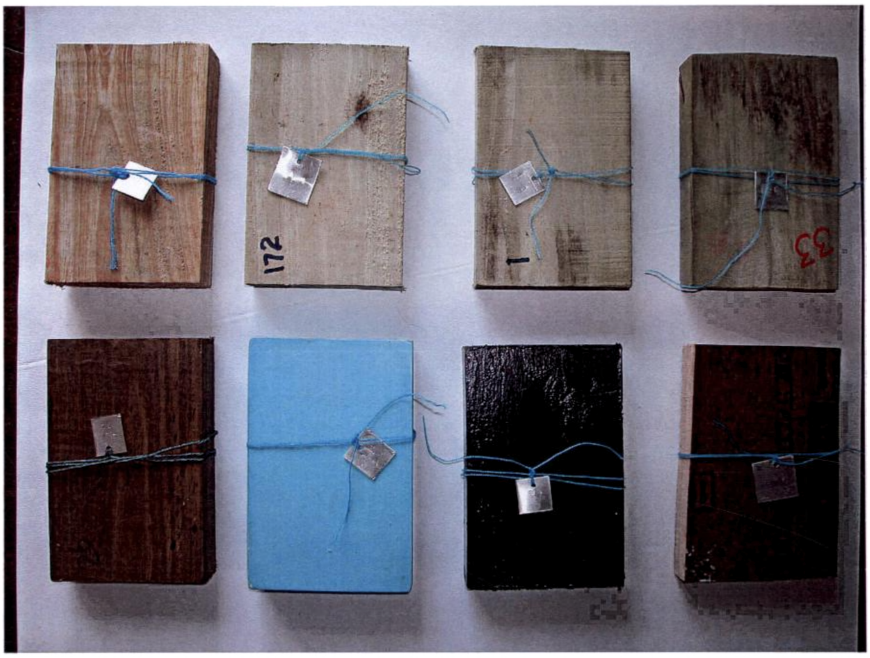
Table 2.1: **Formulation of CCA according to Indian Standard**

Element	Compound	Proportion (%)
Copper	$CuSO_4.5H_2O$	37.5
Chromium	$K_2Cr_2O_7$	50
Arsenic	$As_2O_5.2H_2O$	12.5

Table 2.2: **Conditions of Vacuum- Pressure Impregnation**

Retention (kg m^{-3})		Initial vacuum (cm of Hg)	Time (min)	Pres-sure (kPa)	Time (min)	Final vacuum (cm of Hg)	Time (min)
CCA	16	56	30	172.37	15	38	15
	29	56	30	448.16	30	38	15
	42	56	30	517.11	90	38	15
Creosote	150	56	30	344.74	45	38	15

Fig. 2.1: **Rubber wood panels selected for the study**



* Clock wise from top-Untreated, treated with CCA to 16 kg m^{-3}, treated to 29 kg m^{-3}, treated to 42 kg m^{-3}, marine plywood, painted after treatment with CCA to 16 kg m^{-3}, FRP sheathed after CCA treatment to 16 kg m^{-3} and dual treated with creosote after CCA treatment to 16 kg m^{-3}

Chapter III

Effect of CCA Retention on leaching

3.1 Introduction

Retention is a measure of the amount of treatment chemical present in the portion of wood called the assay zone. It is measured in pcf – pounds of preservative per cubic foot – or kg m^{-3} of the assay zone. The various factors that affect the leaching of the preservative are its formulation, physical parameters of the preservative treatment like vacuum pressure cycles, drying time and temperature, preservative retention and concentration of CCA solution (Fahlstrom *et al.,* 1967; Wilson, 1971; Lee *et al.,* 1993; Cooper, 1994). Among these, retention of the preservative is the most important factor that decides leaching. Even though preservative retention is known to affect the absolute concentration of elements leached, the exact relationship between preservative retention and leaching is not clear (Cooper, 1994; Albuquerque & Cragg, 1995a, b; Albuquerque, 1996). During the treatment process, copper, chromium and arsenic form insoluble complexes within the wood. The metals are unlikely to leach much because of this insoluble nature of the complex precipitates. However in the initial hours of water immersion the rate of leaching is found to be high and it reduces as time proceeds. For aquatic life, the amount of copper and arsenic leached from the wood may not be harmful (Townsend, 2001). The effect of retention on leaching of CCA into water was studied in water under accelerated condition, under stagnant condition and in the natural estuarine condition.

3.1.1 Leaching studies in water under accelerated condition

The rate of water movement around the wood specimen can influence the leaching of preservative components. The unfixed and improperly fixed preservative components will leach immediately when exposed to water especially in the accelerated condition. Flowing water is found to increase the rate of leaching as this may flush the unfixed CCA components in the wood samples. The objectives of this study are to find out the role of CCA retention in the leaching of its components, to estimate the rate of leaching of CCA components in water under accelerated condition and to identify the role of sample size in determining leaching.

3.1.2 Leaching of CCA Treated Panels Exposed in Stagnant Water

The rate of water movement around the test specimens can also influence leaching, although this effect has not been quantified (Van Eetvelde *et al.,* 1995). It is also reported that leaching of CCA was greater when using stirred leaching water than with static leaching trials. In natural environment, treated wood is supposed to be used in moving water in most circumstances. When examining the laboratory leaching experiments, the volume of water around the wood panel should be taken in to consideration. Leaching experiment in stagnant water along with accelerated condition may be useful in assessing the effect of water movement in increasing the leaching.

This experiment aims to estimate leaching of preservative components from CCA treated rubber wood panels in a stagnant aquatic media using an aquaria system, to compare the difference in the rate of leaching of CCA between accelerated and stagnant conditions and to estimate the role of multiple treatment and physical barriers in controlling leaching under stagnant condition.

3.1.3 Leaching of CCA from wood under Estuarine Condition

The conditions prevailing in the field is different from that of the laboratory. There are many factors that are uncontrollable for an experimenter that may influence leaching. Various water parameters like pH, salinity, dissolved oxygen, turbidity, temperature etc. are found to influence the leaching of CCA components from treated wood. These factors are uncontrollable and vary according to the location of the experiment and the climatic conditions. In long term marine field trials, CCA treated pine leached as much as 25% of total active ingredients within six months, with total losses rising to 52% after 85 months (Hegarty & Curran, 1986). Hayes *et al.,* 1994 also observed losses of Cu from pine submerged in coastal waters occurred most within the first 12 weeks of a 72 week leaching trial. Field trials testing the durability of different CCA treated timbers indicated that the average leaching rates of CCA were 1.8-17.3% and that those with highest leaching rates had the minimum life span (Cherian *et al.,* 1979). This suggests the need to conduct field studies along with laboratory experiments. Therefore laboratory and field studies are conducted simultaneously.

3.2 Materials and Methods

Rubber wood panels of size 150 x 100 x 25 mm prepared as mentioned in the chapter II were selected for the experiment. After six weeks of seasoning, few panels were cut into the 19 x 19 x 19 mm size (Type 1). They were then kept for the leaching experiment. The leaching experiment was patterned as per AWPA E-11, 97, The American Wood Preservers' Association Standard i.e., Standard Method for Determining the Leachability of Wood Preservatives. According to this method, six blocks were selected from each retention level having above-mentioned retentions. The six blocks were then immersed in 300 ml of de-ionized water with a wood to water volume ratio of 1:7 for 30 minutes. The panels were then leached in accelerated condition using magnetic stirrers (at a stirring speed of 25-50 cm s^{-1}) with the same type of magnetic stir bar for each leaching flask. Samples of leachates were then collected and the whole solution is replaced with fresh de-ionized water. This is done after 6, 24, 48, 96, 144, 192, 240, 288 and 336 h. The time of removal and quantities of leachates were recorded for analysis. Each leachate sample was then analysed for Cu, Cr and As in ICP-AES (Perkin Elmer-Optima 2000 DV). Another experiment was simultaneously conducted keeping the same ratio of wood to water volume in 2750 ml water using panels having 150 x 100 x 25 mm size Type 2). The results were analysed based on the concentration of the constituent elements of the preservative leached into the medium. This is done by analyzing the leachate solution and by estimating the amount of elements lost from the wood after digesting a replica of the wood sample before leaching and the original sample after the leaching, in a microwave digestion instrument and then analyzing in ICP-AES. The quantities of constituent elements leached out in different durations were analyzed with respect to surface area of panels (Table 3.2 and 3.3).

Leaching experiment was also conducted in stagnant condition in aquaria using Type 2 panels. For this, a system consisting of five aquaria tanks of 80 L capacity were constructed. Rubber wood panels, which are FRP sheathed, painted, dual treated after CCA treatment, marine plywood and panels treated with CCA alone were kept immersed in tap water by using sinkers. The hydrographical parameters of the tap water including pH, temperature, salinity, dissolved oxygen and turbidity were analyzed initially and at an interval of one month each from each tank till the experiment concluded after 12 months. This is done to identify the parameters of water that may influence the leaching of the preservative. The parameters were found not to vary much during the experiment. Water samples were also analyzed for preservative constituents in the leachate solution during the same intervals using ICP-AES. The quantity of copper, chromium and arsenic leached into the water in the aquaria from the beginning till the completion of twelve months are shown in Fig.3.

Rubber wood panels (Type 2), treated to 16, 29 and 42 kgm^{-3} retentions were selected for the experiment in the estuarine condition. Four sets of such panels along with untreated panels were taken for this purpose. One set was kept aside as unexposed sample. The remaining three sets were then tied on an iron rack taking into consideration of the statistical arrangement and kept immersed in the North Oil Tanker Berth of Cochin Port. One set panels were retrieved after six months. Another such set was retrieved after 12 months and the remaining one set after eighteen months. The foulers and borers attached to the panels were removed and the preservative components left in the panels were analyzed in ICP AES. For preparing the sample, the panels were powdered in the wood pulveriser (FRITSCH Pulverisette 14) and digested them using nitric acid and hydrogen peroxide in microwave digestion system (Ethos Plus- High Performance Microwave Labstation). The preservative components in the unexposed samples were also analyzed and percentage loss of preservative components during each interval was recorded separately. The hydrographical parameters were analyzed in every fortnight. The influence of the change in water parameters in various seasons was compared with the leaching of preservatives.

3.2.1 Hydrographical conditions of the test site

The hydrographical parameters of the test site were monitored during the entire period of the study. Atmospheric temperature and water temperature were measured in the field using centigrade thermometer corrected to ± 1°C.

Water samples were brought to the laboratory for further analysis of Dissolved Oxygen (DO), Biological Oxygen Demand (BOD), salinity, as per standard methods Strickland and Parsons (1970). The pH was determined using pH Tester (Eutech Instruments PC 510) calibrated to pH 4, 7 and 10 using NIST standard buffer solutions. The turbidity was measured using Nephelo-turbidity meter 131 (Systronics). Nitrate content of the water was estimated by colorimetric method as outlined in Strickland and Parsons (1970).

3.2.2 Arrangement of the panels and sampling strategy

Six sets of panels each set carrying six replica of six different treatment types were tied onto two iron racks and immersed at the test site 1m below in such a way that the panels are not exposed during the low tide. Panels were arranged on the rack in statistically approved Completely Randomized Design (CRD). The racks carrying the experimental panels were immersed in test site located in the North Oil Tanker Berth, Cochin. This site is situated in Ernakulam channel, which is a part of Cochin backwater system. The depth of water ranges between 6-12 meter and the tides and currents have pronounced influence on the water characteristics of the site. Six replica of each of these six types of panels were tied using polyethylene ropes of 2 mm diameter onto two different iron racks of size1.5 x 0.4 m.

The panels selected for the study included rubber wood panels treated with CCA to retention of 16 kg m^{-3}, 29 kg $m^{-3}$and 42 kg m^{-3}, CCA treated panels coated with epoxy paint, sheathed with FRP and untreated rubber wood panels as control. Two sets of panels each were considered as series I, II and III in which each set included panels of six treatment types. The racks containing the panels were immersed in the test site in June 2005. Each set of these panels was retrieved periodically over 6 months, 12 months and 18 months. The retrieved panels were brought to the laboratory and were assessed quantitatively for the preservative components. The sample digestion was carried out in Microwave Digestion system. The digested samples were analyzed for the amount of copper, chromium and arsenic.

3.3 Results and Discussion

The rate of leaching of the constituents of CCA in to the solution is graphically represented below (Fig. 3.1-3.6). The percentage loss of constituent elements from wood surfaces used for experiment was also analyzed (Table 3.1 and 3.2).

The effect of retention on rate of leaching of copper showed variation with increase in the duration of experiment. In the case of type 1 panels having 16 kg m^{-3}, leaching increased up to 48 hours and then gradually decreased as the experiment proceeded towards completion at 336 h (Fig. 3.1). In the case of 29 kg m^{-3}, leaching first increased up to 24 h then decreased till 48 h and again increased to reach the peak at 96 h and later gradually decreased by the end of 336h. In the case of 42 kg m^{-3}, the rate of release was found to be very high in the first six hours, even though the rate decreased leaching reached a maximum at 24 h and then gradually decreased. The rate was steady from 48 to 96 hours and then decreased sharply. In the case of Type 2 panels all the three retentions showed a similar pattern with very low rate of leaching in the initial hours. Later leaching increased gradually and a maximum was found at 144 h for 16 and 42 kg m^{-3} and at 192 h for 29 kg m^{-3} (Fig. 3.4). It is seen that the rate of leaching is around ten fold for Type 1 panels than the Type 2 panels. Another noticeable difference is that for Type 2 panels rate of leaching at all retentions did not decrease much and are steady even at 336 h.

In the case of Type 1 panels with retention of 16 kg m^{-3}, the rate of leaching increased up to 48 h and then gradually decreased till the end (Fig. 3.2). The case is not much different with 29 kg m^{-3}, where the only difference is that the maximum leaching is obtained at 24 h and then decreased. For 42 kg m^{-3}, the rate of leaching is highest at 24 h and then gradually decreased till the end. For Type 2 panels rate of leaching was very low compared to the type 1 panels. For 16 and 29 kg m^{-3}, the rate was still less and steady where as for 42 kg m^{-3}, rate of leaching was slightly high (Fig. 3.5).

Arsenic differs from other two metals for Type 1 panels with a low leaching rate in the first 6 hours in the case of 16 and 29 kg m^{-3} but high rate for 42 kg m^{-3} (Fig. 3.3). 16 and 29 kg m^{-3} showed a similar pattern with maximum leaching up to 96 hours and then reduced gradually till 192 h and then remained steady till the end. For 42 kg m^{-3}, steady increase is found in the rate of leaching of arsenic and reached a maximum at 24 h and again reduced gradually till 96 h. It then increased up to 144 h and then declined sharply. For Type 2 panels a typical peculiarity noted was that 42 kg m^{-3} showed a low rate of leaching than the other two and 16 kg m^{-3}showed maximum rate of leaching. Also high leaching rate was steady even at 336 h (Fig. 3.6).

The trend of greater initial release of copper in de-ionized water may be a function of different forms of copper fixation products in the wood. During the initial stage of leaching, when the release of copper was high, a variety of forms of copper are being removed from the wood. These may include copper bound to water-soluble extractives and copper precipitated with in the wood structure (Lebow *et al.*, 1999). Later this trend diminishes and the rate of leaching decreases. For the first 24 h release of copper from the samples treated to 16 and 29 kg m^{-3} shows a similar rate, then leaching increases to a maximum in the case of 16 kg m^{-3} till 48 h and shows a regular decline where as for 29 kg m^{-3} leaching reduces up to 48 hours after the initial rise, then increases and reaches the maximum at 96 h and again declines. During 48 hours the rate of leaching was found to be more in 16 kg m^{-3} than for 29 kg m^{-3}. At the same time, rate of release from 42 kg m^{-3} reaches maximum at 24 hours. For different retentions, the maximum rate of leaching of copper is found to be at different intervals. The relationship between preservative retention and rate of leaching does not follow a regular path. In a study by Archer *et al.*, (1994) a loss of 52% active ingredients from pine treated to 24 kg m^{-3} CCA and only a loss of 44% from panels treated to 48 kg m^{-3} over an exposure period of 85 months. It was suggested to be because of the increase in the availability of chromium for fixation. Contrary to that, there are researchers who found a direct increase in leaching with increase in retention (Albuquerque *et al.*, 1996).

The high rate of leaching in small panels may also be due to sizing of samples after pressure treatment. The quantity of elements leached through a centimeter square of surface shows that more than 50% of leaching has taken place in the first 48 h in the case of Type 1 panels where as for Type 2 it is distributed evenly. The rate of release of chromium is found to be higher than that of copper. The pattern of increase and decrease in the rate of leaching is almost similar for all retentions in the case of chromium. The hierarchy of leaching is generally copper, arsenic and then Chromium. The deviation found here might be due to the slight excess of chromium in the formulation (Hingston *et al.*, 2002). In wood treated with preservatives, Chromium is generally regarded as strongly fixed to the wood and leach resistant because of the formation of stable fixation products such as $CrAsO_4$ and $Cr(OH)_3$ (Pizzi, 1982b). The proportion of effectively unfixed chromium may be higher in this case, which may be remaining in the hexavalent oxidation state. The percentage of chromium in the preservative formulation is higher than copper and chromium. Therefore even when the percentage leaching of chromium is less than copper and arsenic, the rate of leaching is more in many occasions.

Lee *et al.*, 1993 studied the importance of preservative retention and fixation in leaching and found that the rate of leaching of copper increases as retention increases. They selected retentions of 3.7, 6.7, 9.3 and 39.8 kg m^{-3} for a study of 14 days in fresh water. Merkle *et al.*, 1994 recorded copper losses of

2.5 and 1 μg cm^{-2} day^{-1}, Chromium losses of 0.04 and 0.01 μg cm^{-2} day^{-1}, and arsenic losses of 2 and 0.8 μg cm^{-2} day^{-1} after 2 and 21 days of exposure respectively for each of the elements. Baldwin *et al.* (1996) recorded levels of 1.89 and 0.2 μg cm^{-2} day^{-1} for copper and arsenic respectively when average levels were taken for 28 days. Breslin and Alder-Ivanbrook (1998) recorded copper, chromium and arsenic leaching as 0.7-1.3, 0.04-0.1 and 0.08-0.2 μg cm^{-2} day^{-1} respectively. A study by Brown & Eaton (2001), also shows that rate of leaching is prominent during the initial hours. The present study also shows a similar pattern with high initial losses in all retentions for all the elements with chromium showing maximum leaching and arsenic minimum. As the number of days increases, the rate of leaching decreases in all retentions for all the constituent elements. The noticeable point is that the reduction in the rate of leaching is slow for arsenic when compared to other elements.

In the case of CCA treated rubber wood panels for stagnant water leaching studies, 2.58 ppm of arsenic was found to leach during the twelve months when cumulative leaching of copper was 1.27 ppm and that of chromium was 0.32 ppm. These values are very less when compared to leaching in accelerated condition. Rate of leaching of arsenic was found to be similar in accelerated and stagnant condition showing that movement of water around the treated wood does not influence the leaching of arsenic. Leaching rate of copper and chromium was less when compared to leaching in accelerated condition. Comparably high water temperature in the last months of exposure (Table 3.4) may be a reason for high leaching rate in the last part of the experiment (Fig. 3.7). Low salinity of the water used in the experiment (Table 3.4) may also be a reason for low leaching rate. For all the treatments, leaching was found to be least for chromium which was most in accelerated condition proving that water movement very much influences leaching of chromium. FRP sheathing and painting reduced leaching to a great extent in stagnant water with values of 0.16 ppm copper, 0.01 ppm chromium and 0.23 ppm arsenic for FRP sheathed panels and 0.24 ppm copper, 0.01 ppm chromium and 0.15 ppm arsenic for painted panels (Fig. 3.8 & 3.9). Dual treatment also reduced leaching to a considerable extend with a value of 0.46 ppm of copper, 0.15 ppm of chromium and 0.89 ppm of arsenic (Fig. 3.10). Commercial marine plywood when exposed to stagnant water found to leach 0.49 ppm of copper and 0.18 ppm of chromium and 0.16 ppm of arsenic. Here, leaching of arsenic was less than copper and chromium (Fig. 3.11).

Copper is an essential element in the normal metabolism of both plants and animals. Therefore, a significant portion of the copper found in both fresh and marine systems may be taken up by the biota. The ultimate fate of much of this copper is sedimentation. Regardless of whether the treated wood is exposed to precipitation, freshwater, seawater, sediments or soil, the movement and composition of water is the key to leaching of the preservative components from the wood (Hayes *et al.,* 1994; Albuquerque *et al.,* 1996). This experiment also proves that the movement of water is a key factor in deciding the leaching of CCA components from treated wood. Leaching is reduced considerably in stagnant water when compared to leaching under stirred or accelerated water. Differences found in the leaching rates for these elements in CCA treated wood may be a function of the rate of dissolution and transport of metal salt precipitates formed during wood treatment.

Leaching of CCA is found to be very less in the initial six months. In the case of 16 kg m^{-3} retention panel, more than 97% of the preservative was left after this period. For 29 kg m^{-3}, around 96% of preservative was left in the wood panels after this duration. For 42 kg m^{-3}, it was 94.5%. Leaching through FRP sheathed and painted panels was almost negligible as 98.8% and 99.9% of CCA were left in these panels respectively after six months of exposure in the estuary. In the following six months leaching increased only slightly. The quantity of CCA left in the wood panels after twelve months of exposure in the estuary were 92.4%, 92.1%, 92.6%, 95.5% and 96.5% for 16 kg m^{-3}, 29 kg m^{-3}, 42 kg m^{-3}, FRP sheathed and painted panels respectively. In the last six months leaching is comparably high especially from the panels treated to lower retentions. The quantity of preservative retained after eighteen months were 65.1%, 70.3, 81.4%, 84.1% and 90% for 16 kg m^{-3}, 29 kg m^{-3}, 42 kg m^{-3}, FRP sheathed and painted panels respectively. The quantity of CCA components in the 16 kg m^{-3} reduced from 6.5 to 5 kg m^{-3} during the 18 months of exposure. In the case of 29 kg m^{-3}, the initial retention of 10.7 kg m^{-3} reduced to 8 kg m^{-3}. For, the initial retention of 22.8 kg m^{-3} was reduced to 19 kg m^{-3}. The quantity of preservative initially present in the panels and the percentage of preservative retained after six, twelve and eighteen months are shown in table 3.6. The residual retention of CCA in different type of treatment is shown in figures 3.12– 3.16.

In long term marine field trials, CCA treated pine leached as much as 25% of total active ingredients within six months, with total losses rising to 52% after 85 months (Hegarty & Curran, 1986). Hayes *et al.,* 1994 also observed losses of Cu from pine submerged in coastal waters occurred most within the first 12 weeks of a 72 week leaching trial. Chemical and anatomical differences between wood species result in different rates of leaching. The chemical nature of wood affects the mode and quality of fixation (Cooper, 1994). Wood anatomy determines depth of penetration, but may also facilitate leaching. Cherian *et al.* (1979) found considerable differences in leaching rate between different species of Indian timbers exposed in Cochin Harbour, India. Marked differences in rate of seawater leaching were noted between European beech (*Fagus sylvatica*) and Scots pine (*Pinus sylvestris*) (Leightly, 1987).

Results of the study by Breslin and Alder Ivanbrook (1998) show that preservative retention and the leaching of elements from CCA-C treated lumber was highly variable. 90-day leaching rates for Cu and Cr increased as CCA retention increased whereas arsenic flux decreased with increased CCA retention. Common preservative components such as copper, chromium and arsenic are reactive with soil constituents (Lebow, 1996) and are not freely mobile in soil. Thus environmental concentrations tend to be concentrated in areas immediately adjacent to treated wood or water drips off treated wood into soil. Even when soil samples are removed from directly under the drip line of a deck, environmental concentrations of leached preservative components can vary greatly (Lebow *et al.,* 2000). A study to assess the leaching of copper, chromium and arsenic from CCA treated *Paraserianthus falcataria* panels exposed to marine conditions at Krishnapatnam harbour on the east coast of India by Tarakanadha and Rao (2006) reveals that the elemental loss was slightly higher in panels treated to lower loadings (16 kg m^{-3}) than higher loadings (32 kg m^{-3}) at initial stages for a period of 6 months. The total elements loss in panels treated to lower loadings after 36 months was 32.1%, 22% and 31.8% for copper, chromium, arsenic respectively, while in higher loadings the loss was 28.4%, 25.2% and 28.1% for copper, chromium and arsenic respectively for the same period. Among the three elements, copper and arsenic lost slightly higher levels than chromium. In this study after 18 months of exposure, total loss of CCA was 35% for the lowest retention which was 16 kg m^{-3}. For the next highest retention which was 29 kg m^{-3}, CCA loss was 30%. For the highest retention which was 42 kg m^{-3}, the percentage loss of CCA was 18.6%.

3.4 Conclusion

With increase in retention of CCA, leaching of copper, chromium and arsenic in de-ionized water increases. In the case of Type 1 panels, leaching of constituent elements is prominent in the initial hours in all the retentions, whereas for type 2 panels rate of leaching is low in the initial hours and it gradually increases. With the increase in surface area to volume ratio, leaching increased to around ten fold. The percentage loss of elements from treated wood during leaching was lowest in 29 kg m^{-3} retention. Also quantity of elements leached per centimeter square of surface is also lowest in 29 kg m^{-3}. From the above results, 29 kg m^{-3} can be taken as an optimum retention for better performance and low rate of leaching.

Leaching of CCA is very less in stagnant water when compared to leaching in accelerated condition. Rate of water movement around the specimen proved to be an important factor in deciding the rate of leaching. The water movement around the treated wood is found to influence leaching of chromium because there is no flushing of water. The unfixed chromium remains in the wood because of lack of water movement. Rate of water movement is not found to have much influence on arsenic leaching. FRP sheathing, painting and dual treatment proved effective against leaching of CCA in stagnant water. Since marine plywood leaches less quantity of chromium and arsenic it can also be used for boat building from environmental point of view.

In the first twelve months, leaching of CCA is found to be less when compared to the next six months for all retentions. The percentage of preservative retained in the wood is more for higher retentions. This shows that rubber wood panels treated with lower retentions of CCA tend to lose more preservative components when compared to their total preservative intake. This could be because after 12 months of exposure, panels treated to lower retentions may degrade to some extent leading to loss of preservative components. This suggests the usage of higher retentions in estuarine conditions. Also, painting and FRP sheathing is found effective in reducing leaching.

Table 3.1: **Percentage loss of constituent elements of CCA**

Metal	16 kg m^{-3}(%)	29 kg m^{-3}(%)	42 kg m^{-3}(%)
Copper	4.05	2.64	5.43
Chromium	3.4	2.93	3.42
Arsenic	1.84	2.37	2.61

Table 3.2: **Rate of leaching of preservative components from Type 1 panels in μg cm^{-2}**

Element	Retention (kg m^{-3})	Frequency of sampling in hours								
		6	24	48	96	144	192	240	288	336
Cu	16	2.707	7.395	9.816	7.185	3.512	1.636	0.807	0.611	0.044
	29	2.540	7.940	5.955	7.919	3.621	2.295	1.265	0.729	0.022
	42	11.87	15.62	15.14	14.69	18.22	6.401	3.214	0.829	0.087
Cr	16	10.54	14.68	16.62	12.95	7.18	4.123	2.443	1.985	0.960
	29	13.49	17.23	12.32	11.77	6.762	4.504	2.810	2.038	1.134
	42	23.15	32.20	28.10	26.65	15.40	8.317	5.785	2.627	1.352
As	16	0.333	2.050	2.988	2.869	1.985	1.156	1.003	1.374	0.873
	29	0.666	3.512	2.748	3.42	2.727	2.372	1.716	2.016	1.745
	42	3.040	7.024	6.057	6.898	7.584	4.012	3.733	2.082	1.745

Table 3.3: **Rate of leaching of preservative components from Type 2 panels in μg cm^{-2}**

Element	Retention (kg m^{-3})	Frequency of sampling in hours								
		6	24	48	96	144	192	240	288	336
Cu	16	0.152	0.457	0.944	0.400	1.738	1.607	1.227	1.491	1.591
	29	0.970	1.457	1.544	1.358	2.137	2.263	1.963	1.466	1.656
	42	0.590	1.340	2.438	1.199	2.613	2.269	1.995	2.175	2.078
Cr	16	1.662	0.309	2.444	0.950	2.525	2.678	2.406	2.627	2.596
	29	1.965	2.597	2.030	1.012	1.634	1.852	1.588	2.701	1.362
	42	3.054	5.373	7.068	2.897	5.491	4.686	4.519	4.509	4.409
As	16	0.526	0.519	1.017	0.825	2.319	2.386	2.298	2.053	2.368
	29	0.315	0.443	0.884	0.858	1.257	1.181	1.350	2.456	1.116
	42	0.218	0.683	1.268	0.855	5.171	1.570	1.712	1.674	1.800

Table 3.4: **Hydrographical parameters of water in the aquaria**

Months	pH	Water temperature (°C)	Dissolved Oxygen (mg L^{-1})	Salinity (‰)	Turbidity (NTU)
Initial	7.79	29.4	5.4	0.583	2
1	7.75	28	5.6	0.398	0
2	7.53	29	6.2	0.039	3
3	7.19	28.3	5.4	0.048	5
4	7.27	28.8	5.6	0.048	9
5	7.17	28.3	5.4	0.086	10
6	7.47	29	5.8	0.122	6
7	7.98	29.4	6.8	0.148	8
8	7.96	28.8	7	0.141	1
9	8.01	29.9	6.2	0.156	5
10	8.03	30.4	6	0.142	4
11	7.95	30.9	6.4	0.136	6
12	8.03	30.4	5.8	0.154	8

Table 3.5: **Cumulative amount of copper, chromium and arsenic leached in twelve months from various panels under stagnant water condition**

Specimen type	Cu (ppm)	Cr (ppm)	As (ppm)
CCA treated	1.270	0.322	2.575
FRP sheathed	0.156	0.013	0.234
Painted	0.239	0.014	0.150
Dual treated	0.463	0.148	0.888
Marine Plywood	0.489	0.182	0.160

Table 3.6: **Residual retention of CCA in different types of treatments after exposure in the estuary**

Theoretical retention	Dry salt retention (kg m^{-3})	After 6 months (%)	After 12 months (%)	After 18 months (%)
16 kg m^{-3}	6.5	97.26	92.38	65.07
29 kg m^{-3}	10.69	95.9	92.08	70.29
42 kg m^{-3}	22.8	94.39	92.63	81.42
FRP	6.5	98.78	95.53	84.05
Paint	6.5	99.88	96.48	89.97

Fig. 3.1: **Rate of leaching of copper from Type 1 panels**

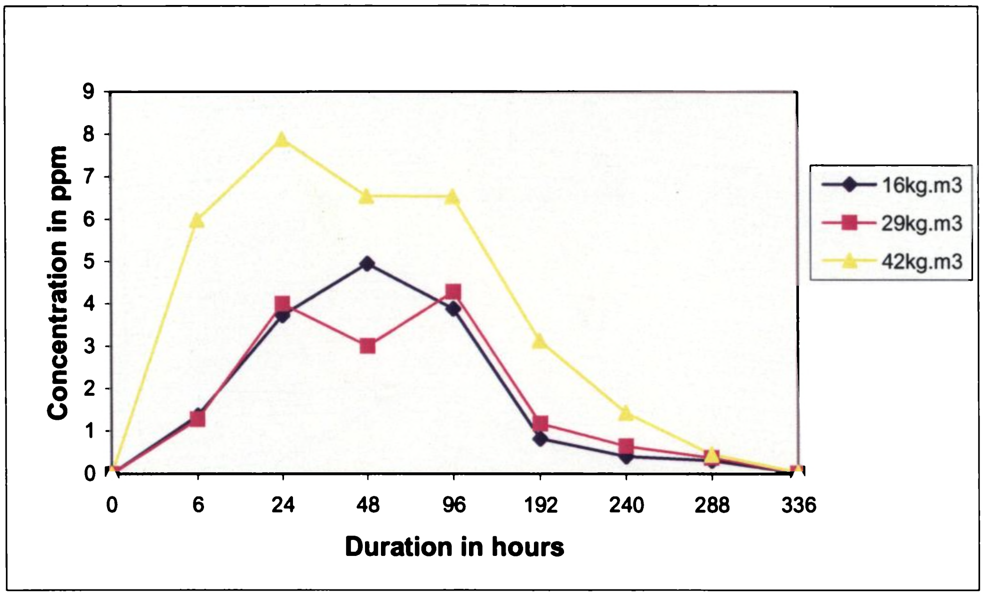


Fig. 3.2: **Rate of leaching of chromium from Type 1 panels**

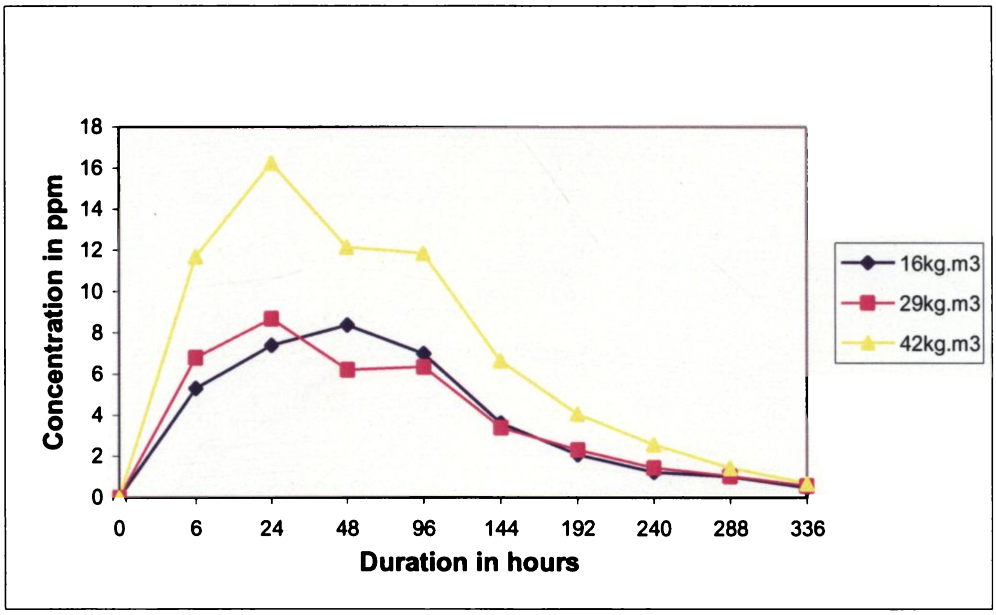


Fig. 3.3: **Rate of leaching of arsenic from Type 1 panels**

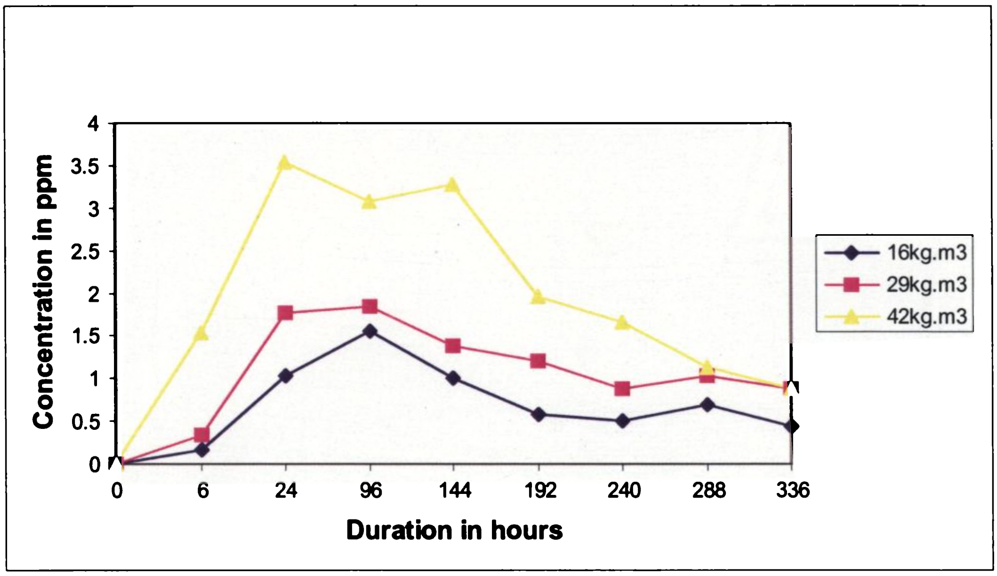


Fig. 3.4: **Rate of leaching of copper from Type 2 panels**

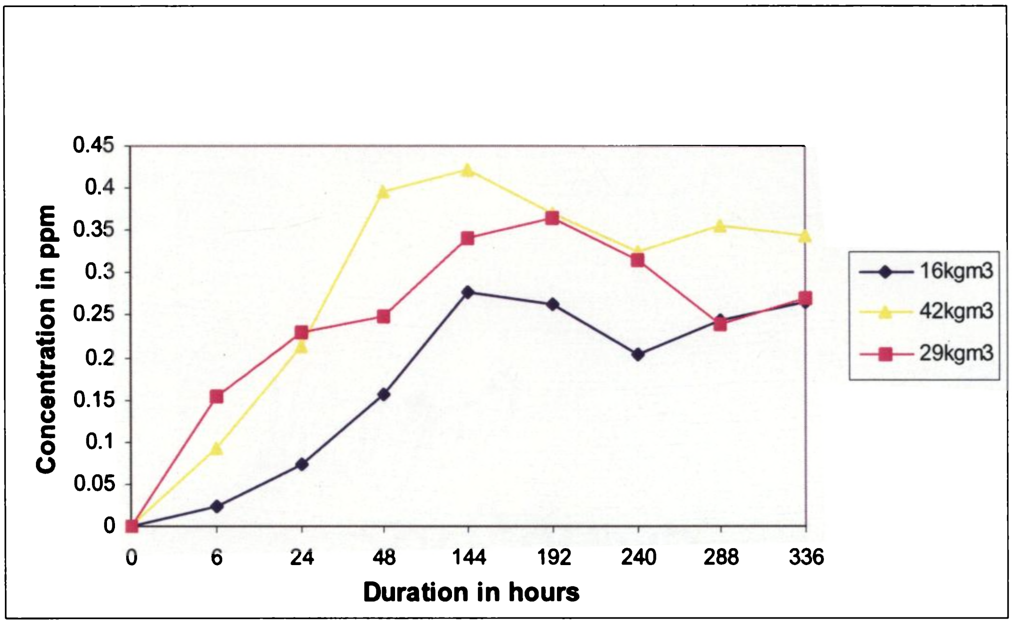


Fig. 3.5: **Rate of leaching of chromium from Type 2 panels**

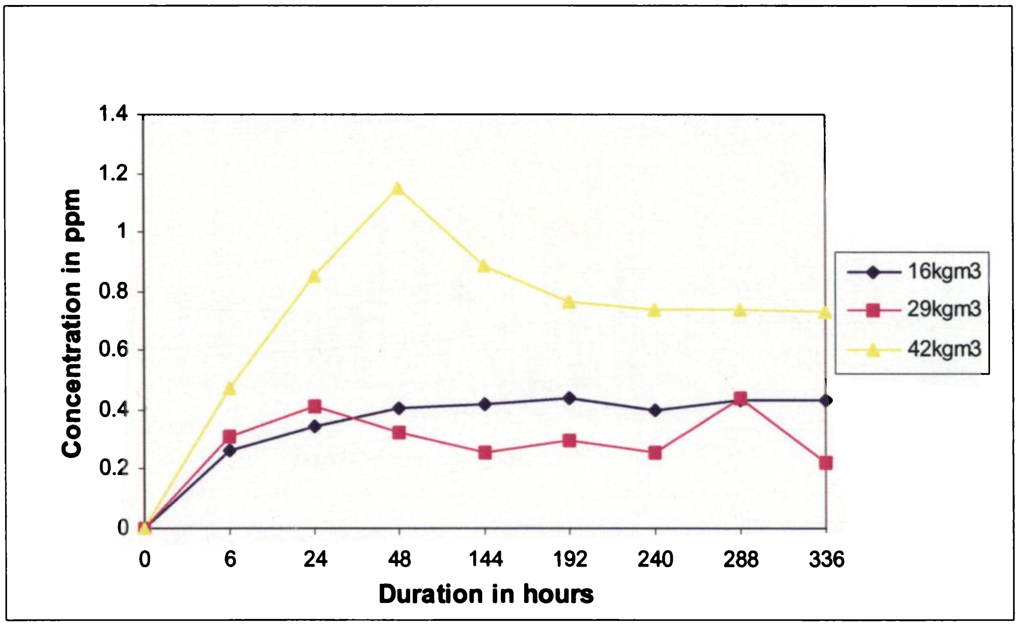


Fig. 3.6: **Rate of leaching of arsenic from Type 2 panels**

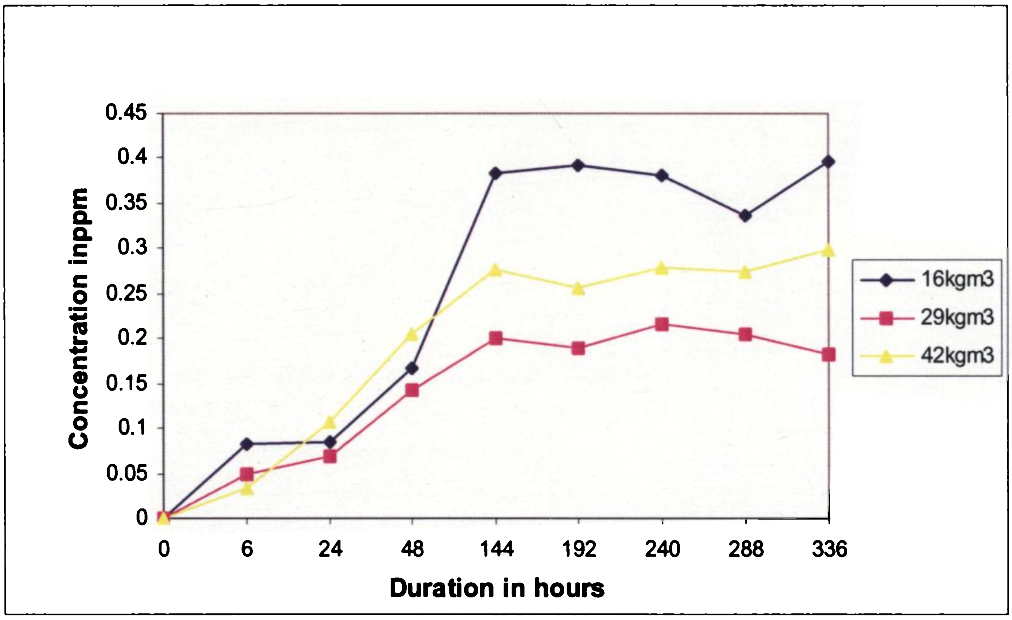


Fig. 3.7: **Leaching of Cu, Cr & As from CCA treated panel**

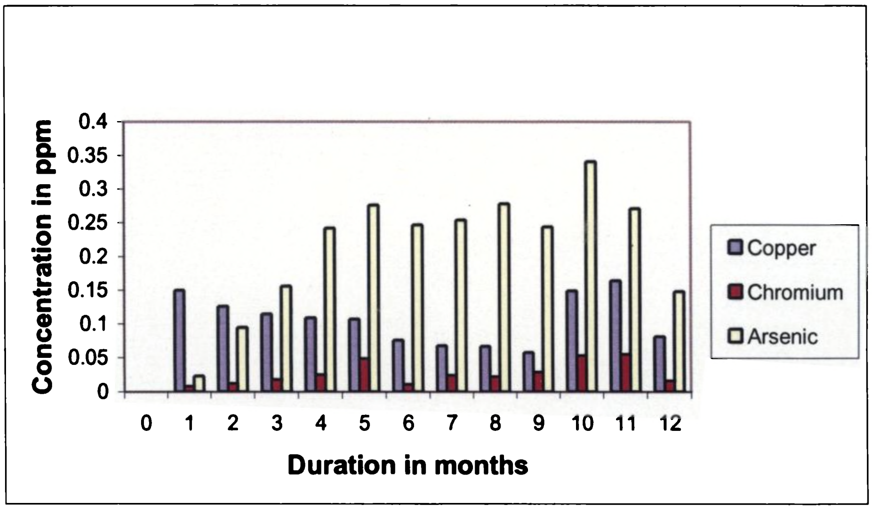


Fig. 3.8: **Leaching of Cu, Cr & As from CCA treated panel sheathed with FRP**

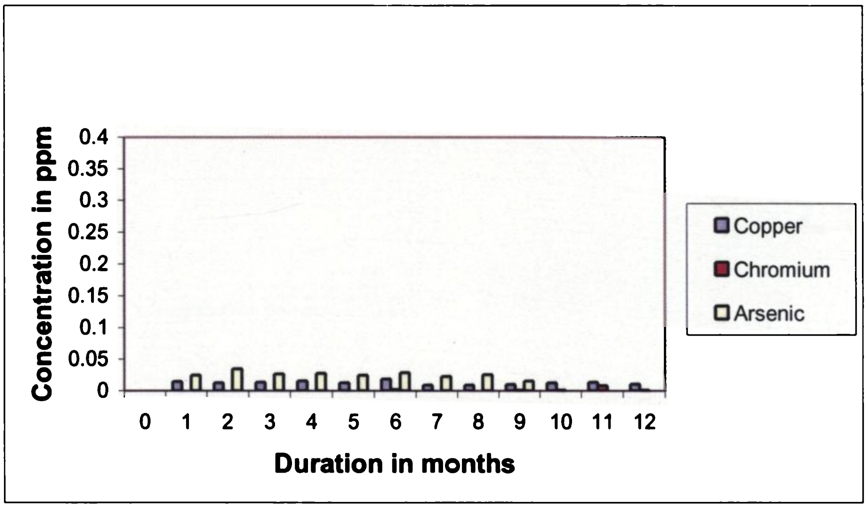


Fig. 3.9: **Leaching of Cu, Cr & As from panel painted after CCA treatment**

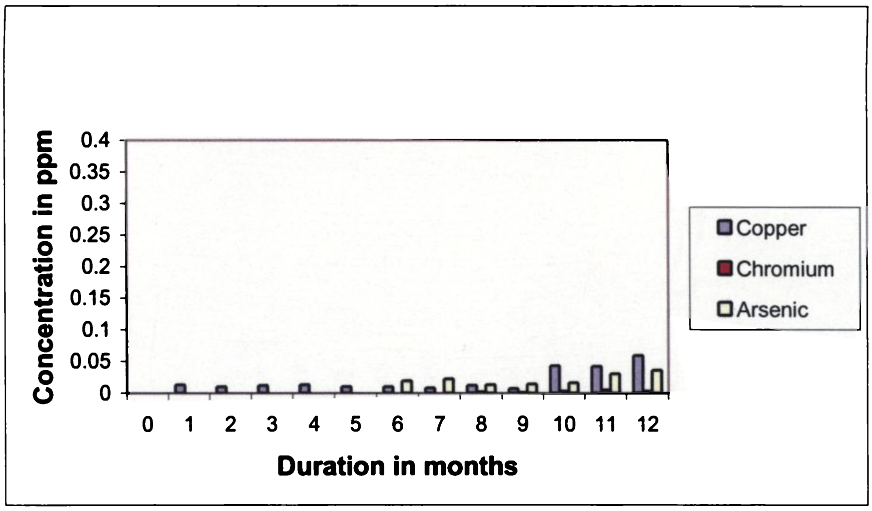


Fig. 3.10: **Leaching of Cu, Cr & As from dual treated panel**

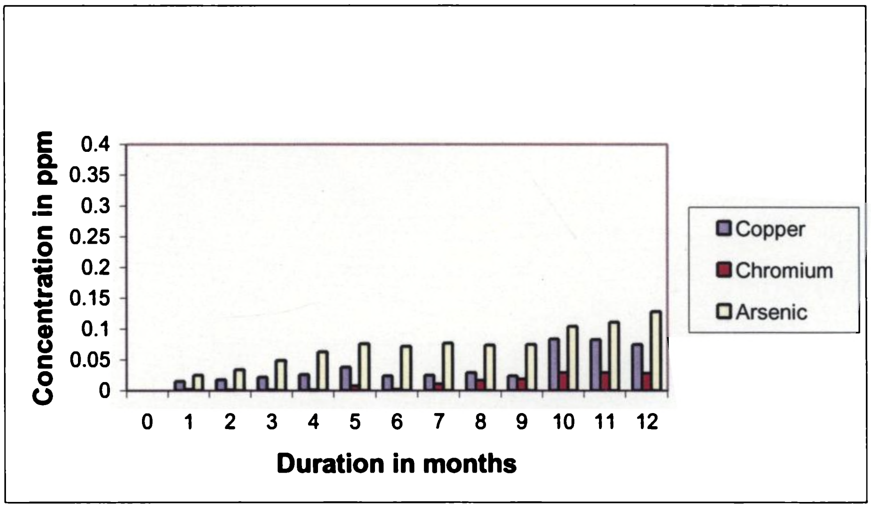


Fig. 3.11: **Leaching of Cu, Cr & As from marine plywood**

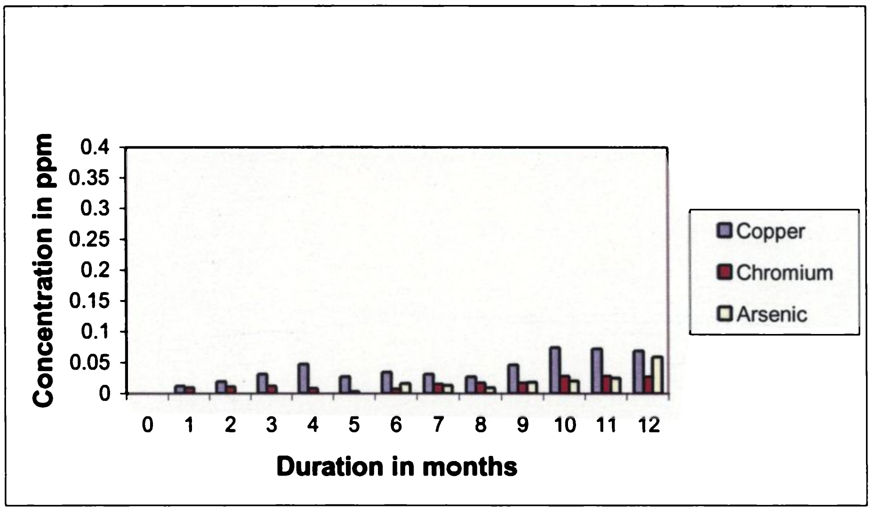


Fig. 3.12: **Residual retention of CCA in 16 kg m^{-3} treated panel**

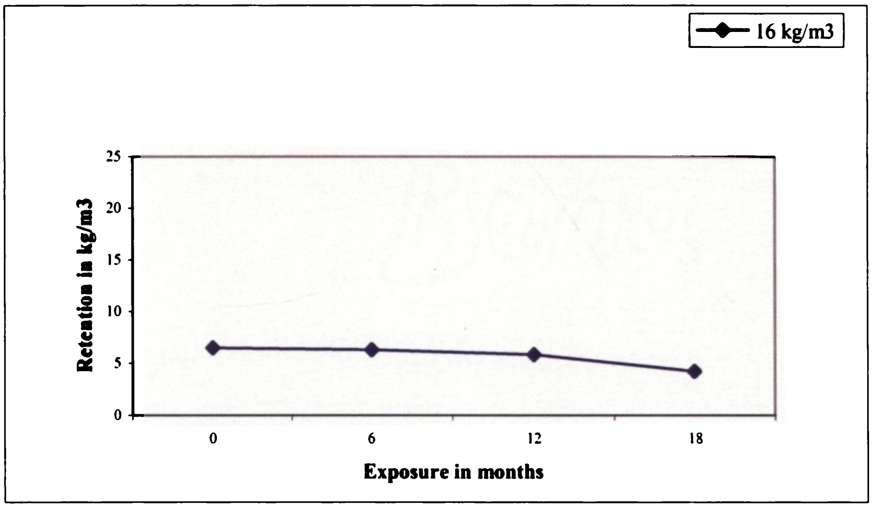


Fig. 3.13: **Residual retention of CCA in 29 kg m^{-3} treated panel**

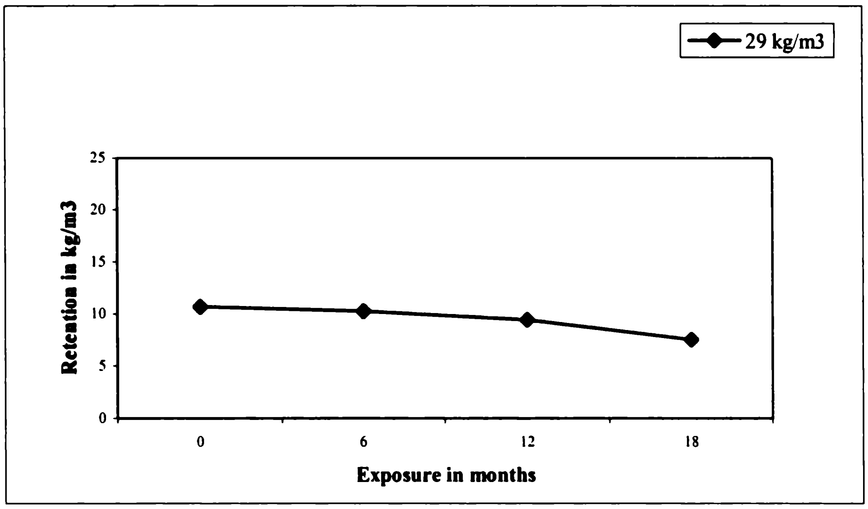


Fig. 3.14: **Residual retention of CCA in 42 kg m^{-3} treated panel**

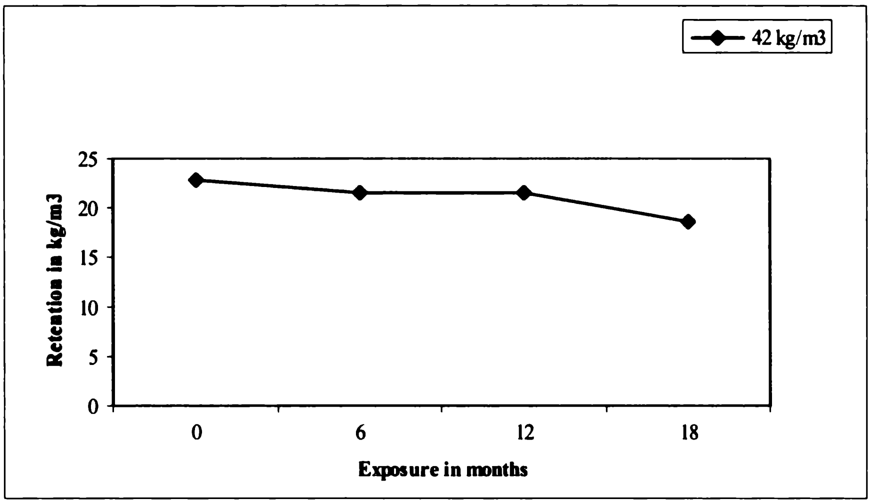


Fig. 3.15: **Residual retention of CCA in 16 kg m^{-3} treated panel sheathed with FRP**

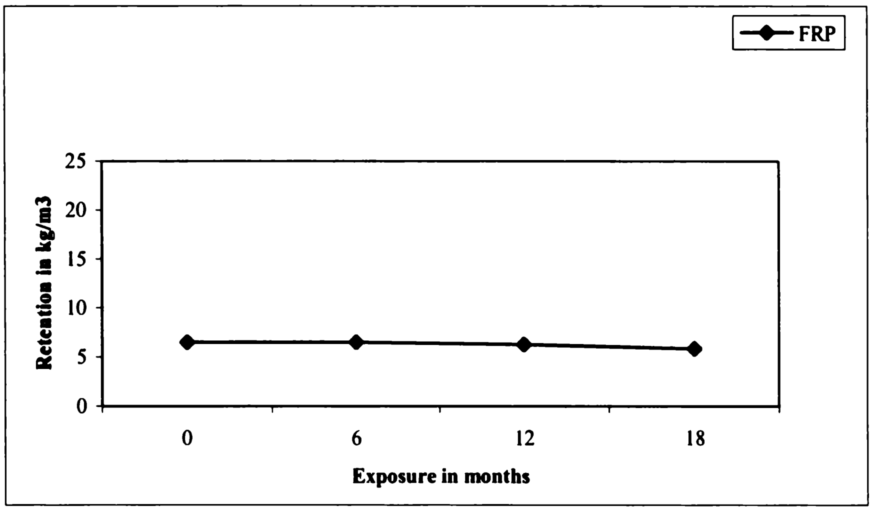


Fig. 3.16: **Residual retention of CCA in 16 kg m^{-3} panel painted after treatment**

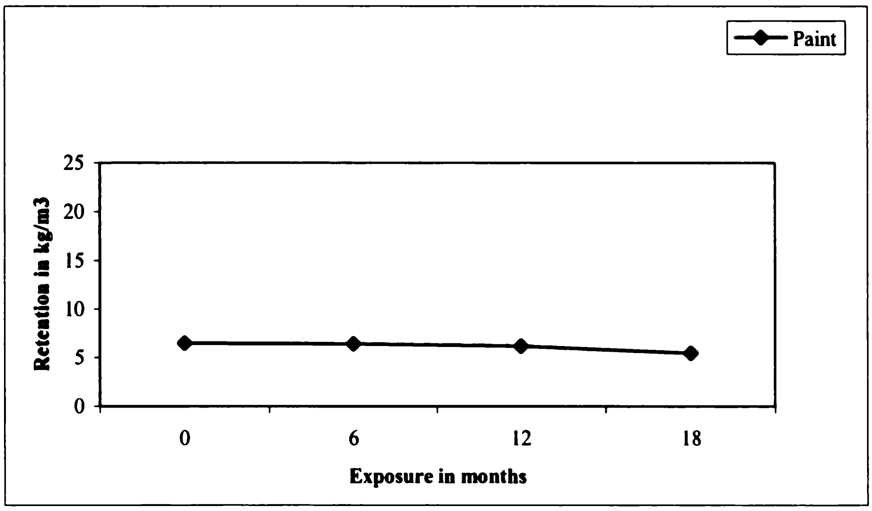


Fig. 3.17: **Laboratory experimental set up of accelerated leaching studies**

Fig. 3.17: **Laboratory set up of stagnant leaching studies**

,

Fig. 3.18: **Panels arranged and kept ready on iron rack for immersion in the estuary**

Chapter IV

Influence of the nature of media on leaching of CCA constituents

4.1 Introduction

Preservative treatment is given to wood in order to obtain protection from the environment in which wood is exposed. Even when there is no attack from the natural destroying organisms like insects or fungi, deterioration can occur due to weathering in the natural environment. These forces can act by increasing the leaching of the preservative in which the wood is treated. Otherwise, the nature of the media in which the preservative treated wood is exposed can influence leaching of CCA. The nature of media is influenced by various factors. These factors include the pH, salinity, water temperature and movement of water around the exposed specimen. This study deals with the most important factors, pH and salinity.

4.1.1 Influence of pH

pH of the medium in which the preservative treated wood is exposed is an important factor which determines the rate of leaching. In normal conditions pH of the water bodies will be in the range of 6.5 to 8. In certain circumstances there can be a reduction or increment in the pH that may influence the rate of leaching. This could be because of the formation of complexes. Van Eetvelde *et.al.,* 1995 observed maximum leaching of chromium and arsenic under neutral conditions. At the same time, initial losses of copper increased with decrease in pH. The increase of leaching on increase of acidity is said to be due the additional hydrogen ions acting in the acid-ion exchange reactions on wood cell walls. Dahlgren (1975) examined the relative leaching of copper as a function of pH and found that leaching rates exceeding 9% at pH 4.0 were reduced to very low values (<0.5%) at pH 6.8. Cooper (1990, 1991) also examined pH effects on the leaching of CCA treated wood. He cautions that when treated wood is exposed to acidified water, maintained at a low pH, the CCA losses are increased compared to neutral water.

4.1.2 Influence of salinity

Preservative treated wood is being utilized for construction purposes especially in the aquatic medium. The salinity of the water in which preservative treated wood is exposed can be a factor determining the leaching of the preservative components. Scots pine and beach sap wood blocks treated with CCA were exposed in cooling towers receiving water from fresh water, sewage effluent and marine sources with results indicating increased loss of copper and chromium with increasing conductivity of the surrounding waters (Irvine *et al.,* 1972). Solutions of higher ionic strength have been shown to leach higher concentrations of CCA, even when no increase in copper loss was observed in the salinity range from 0 to 24 ppt. Certain preservative components may leach out easily in the presence of some salt contents in the saline water because of the possibility of complex formation. Pine sapwood treated with CCA and leached in salt solutions of varying strength resulted in increased copper leaching compared to de-ionized control water and leaching rates increased with salt solution concentration (Placket, 1984).

The present study aims at estimating the influence of acidic, neutral, alkaline conditions and salinity of the aquatic medium on leaching of CCA components from treated rubber wood.

4.2 Materials and methods

Rubber wood panels (Type 1), treated to 16 and 42 kg m^{-3} retentions were selected for this experiment. This is because they cover both the minimum and maximum retentions of CCA treatment recommended for fresh water and saline water conditions. The selected pH includes 2.5, 4.5, 7 and 8.5. The solutions required for leaching experiment was prepared using de-ionized water. The water was acidified using hydrochloric acid. Alkaline solution was prepared using ammonium hydroxide. The panels were immersed in 2750 ml water having the above mentioned pH and the beakers were placed on the magnetic stirrer. The stirring speed was standardized to 25-50 cm s^{-1}. The leachates were collected and the whole solution is replaced at 6, 24, 48, 96, 144, 192, 240, 288 and 336 h. The samples were then analyzed in ICP AES and the results of each sampling were recorded.

This experiment was conducted to identify the influence of salinity of the media on leaching of the preservative constituents. The rubber wood panels of size 150 x 100 x 25 mm, treated to 16 and 42 kg m^{-3} retentions were selected for this experiment. This is because they cover both the minimum and maximum retentions recommended for saline water. The selected panels were then immersed in artificial seawater prepared according to IS 8770-1978 for 35 ppt. Another saline solution of 23 ppt was also prepared. The leaching experiment was then conducted simultaneously in 35 ppt, 23 ppt and de-ionized water. The panels were immersed in 2750 ml water and beakers were placed on the magnetic stirrer. The stirring speed was standardized to 25-50 cm s^{-1}. The leachates were collected and the whole solution is replaced at 6, 24, 48, 96, 144, 192, 240, 288 and 336 h. The samples were then analyzed in 797 VA Computrace ion analyzer (Voltammeter). The results of each sampling were recorded for analysis.

4.3 Results and Discussion

Analysis of the treated wood panels before exposure to leaching shows that 16 kg m^{-3} treated wood contained 559.25 mg copper, 949.52 mg chromium and 386.71 mg arsenic. In the case of panels exposed to 4.5 pH solution, 3.31 mg of copper, 6.87 mg of chromium and 5.98 mg of arsenic was leached into the solution during 336 h of the experiment. At the same time panels exposed to 2.5 pH solution showed a high leaching. Here, 248.5mg of copper, 115.87 mg of chromium and 45.17 mg of arsenic were leached.

The analysis of the panel having 42 kgm^{-3} initial retention showed that it contained 1287 mg copper, 2567.4 mg chromium and 991.65 mg arsenic. These panels when exposed to 4.5 pH solution for 336 h, 7.99 mg of copper, 10.23 mg of chromium and 5.86 mg of arsenic were leached. Similarly, when these panels were exposed to a solution having 2.5 pH, 243.28 mg of copper, 111.12 mg of chromium and 33.54 mg of arsenic were found leached.

Another set of panels exposed in the neutral and alkaline pH also initially contained the same quantity of copper, chromium and arsenic. The panels having 16 kg m^{-3} retention, when exposed to a solution having pH 7, 3.1 mg of copper, 5.25 mg of chromium and 4.1 mg of arsenic were leached. Another such panel when exposed to a solution of pH 8.5, the quantity of preservative components leached out slightly reduced to 2.11 mg of copper, 4.54 mg of chromium and 3.57 mg of arsenic. 42 kg m^{-3} retention panel when exposed to solution of pH 7, 14.55 mg of copper, 20.96 mg of chromium and 8.28 mg of arsenic were leached. Similarly another set of panels when exposed to solution of pH 8.5, 7.04 mg of copper, 15.35 mg of chromium and 4.99 mg of arsenic were leached. The results are shown in graph (Fig. 4.1.1- 4.1.6).

Experiments were conducted to investigate the effect of addition of humic acids to artificial seawater. The addition of humid acid was reported to cause increase in the loss of copper and arsenic. This may be explained by the relative tendency of copper to bind to a range of organic matters (Beacher *et al.,* 1983; Fleming & Trevos, 1989; Livens, 1991). In the absence of humic acids, leaching was dominated by chromium. The citric acid buffer system used by Warner and Solomon (1990) caused excessive metal losses not solely associated with low pH. Cooper (1990) acknowledges that it is possible for some naturally occurring complex organic acids to accelerate leaching of CCA components, by an undetermined amount, at pH values < 4.5. The previous experiments in this regard suggest that more copper and chromium will be leached from CCA treated wood at low pH. In this study also copper is found to leach in much higher quantities than chromium and arsenic at high acidic pH where as chromium is found to leach more in all other pH conditions. Arsenic leaching does not appear to be as sensitive to pH. The data suggest that normal pH values (>4.5) expected in open aquatic environments do not influence leaching rates. The literature clearly demonstrates increased copper losses from CCA treated wood at very low pH values (<4.5). This study also proved the same conclusion.

In the case of 16 kg m^{-3} panels exposed to 34 ppt solution, 2.84 ppm of copper, 1.39 ppm of chromium and 0.007 ppm of arsenic were leached into the solution during 336 h of the experiment. At the same time panels exposed to 23 ppt solution showed a high leaching. Here, 3.72 ppm of copper, 1.28 ppm of chromium and 0.007 ppm of arsenic were leached.

Analysis of the leachate solution of 42 kg m^{-3} treated panels when exposed to 34 ppt solution for 336 h showed 1.38 ppm of copper and 1.49 ppm of chromium. Arsenic was not present in detectable quantities. Similarly, when these panels were exposed to a solution having 23 ppt, 1.86 ppm of copper and

1.55 ppm of chromium were detected. Here also, arsenic was not found in detectable quantities.

The results of the studies conducted by Lebow *et al.,* 2000, comparing leaching in de-ionized water and seawater are worth noting. In comparison to copper, chromium release rates were much lower and relatively insensitive to the seawater concentration of the leaching solutions. Arsenic release tended to be greater in the de-ionized water than seawater solution. Unlike chromium, the greater release in de-ionized water did not appear to decrease over time. The effect of salinity on the rate of copper release changed with time. For the first month the rate of release of copper in de-ionized water was greater than or equal to that in seawater whereas in the remaining months copper release in the seawater was significantly greater than the release in de-ionized water and when leaching rates stabilized after 10 to 15 months, the rate of copper release in seawater was 8 to 25 times greater than that in de-ionized water.

Irvine *et al.*(1972) examined the retention of CCA in small wood blocks exposed to seawater from cooling towers. They found that metals leached more readily in cooling tower water than in conventional laboratory leach tests. Irvine and Dahlgren (1976) investigated the effects of salts on the leaching of CCA components and developed a theoretical mechanism to explain the increased leaching rates of CCA components exposed to marine environments. They concluded that at low salinity, sodium chloride has a coagulating effect on the copper, reducing its rate of leaching. At higher salinity, complexation of copper and chromium with chlorine and sodium ions results in increased leaching of these metals. At high CCA retentions, loss of arsenic is shown to lag behind that of chromium and copper due to complexation of the liberated copper and chromium ions. At lower retentions (<1.8 lbs/cf.) this trend is reversed and arsenic is more easily leached than copper. The most complete analysis of salinity effects was found in study conducted by Irvine and Dahlgren (1976). In the lower term (20 weeks in test), they report relatively low levels of copper loss at salinities less than 10 ppt. There is a significant increase to approximately twice this loss at 22 ppt. Above 22 ppt, losses increase slightly as salinity increases to 35 ppt. Most of the leaching data for CCA has been developed in salt water (30 ppt). Irvine and Dahlgren (1976) did not find significant differences in loss rates at salinities between 0.0 and 25 ppt after 40 weeks of leaching. However, they observed an increase of approximately 50% in copper losses at salinities greater than 25 ppt in the long term (40 weeks).

4.4 Conclusion

pH is found to have much influence on leaching. Similar quantities of copper, chromium and arsenic were found to leach from both 16 and 42 kg m^{-3} panels exposed to a highly acidic pH of 2.5. Therefore the percentage leaching is more from 16 kg m^{-3}. This shows that, retention has got no influence on leaching in highly acidic conditions. At the same time leaching reduced to around 1% at a pH of 4.5. Also retention was found to influence leaching in neutral and alkaline pH. Lowest leaching was found at pH 8.5 in the case of 16 kg m^{-3} retention and at pH 4.5 in the case of 42 kg m^{-3}.

Leaching of copper is more prominent than chromium and arsenic in saline media. Arsenic leaching is found to reduce considerably in saline water. Also rubber wood treated to lower retentions is found to leach more than higher retentions in saline water. Higher retentions of preservative treatment are found more suitable in higher salinities.

Fig. 4.1: **Rate of leaching of copper on varying retention at acidic pH**

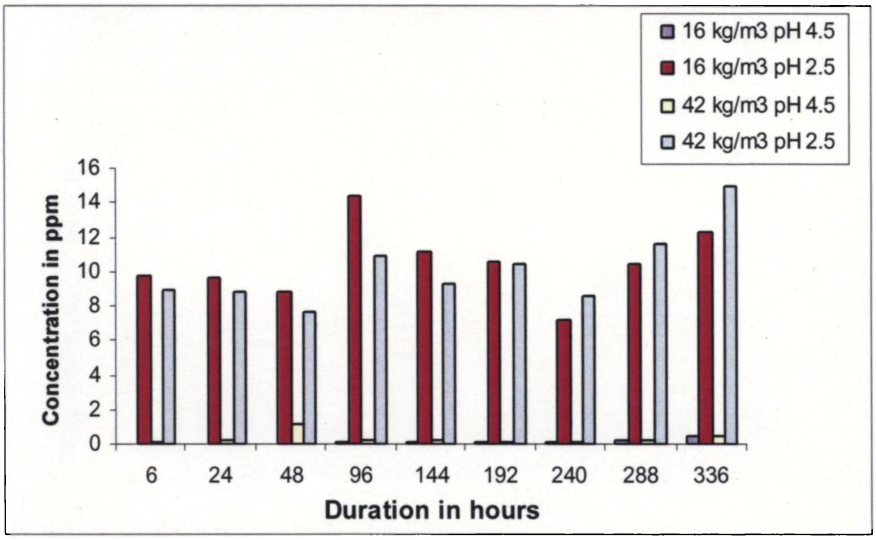


Fig. 4.2: **Rate of leaching of chromium on varying retention at acidic pH**

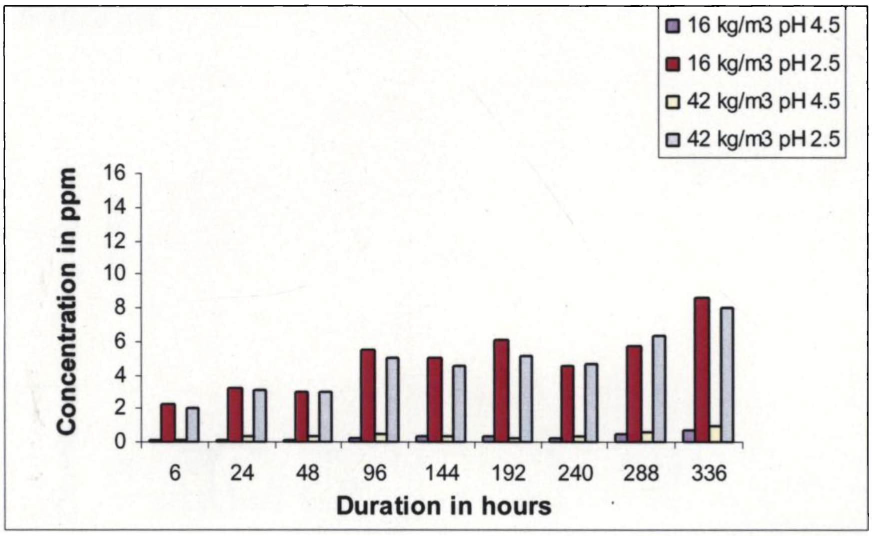


Fig. 4.3: **Rate of leaching of arsenic on varying retention at acidic pH**

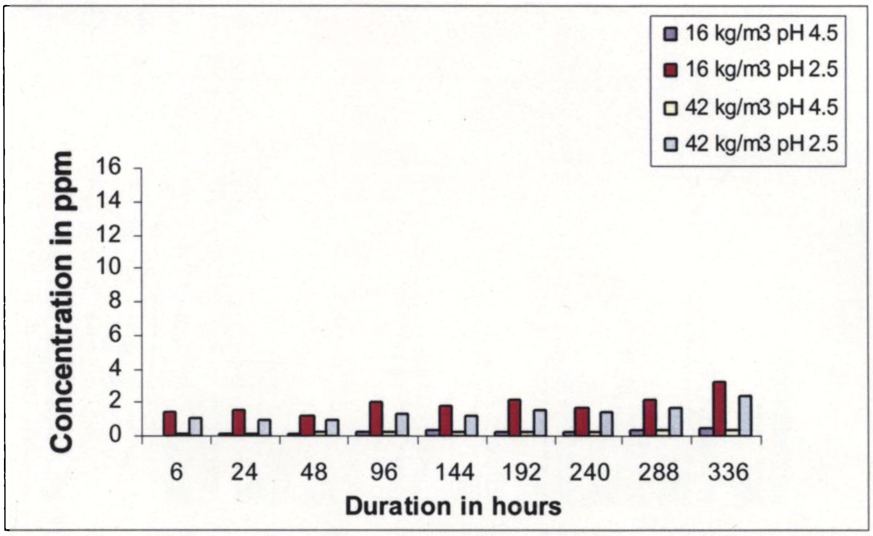


Fig. 4.4: **Rate of leaching of copper on varying retention at neutral and alkaline pH**

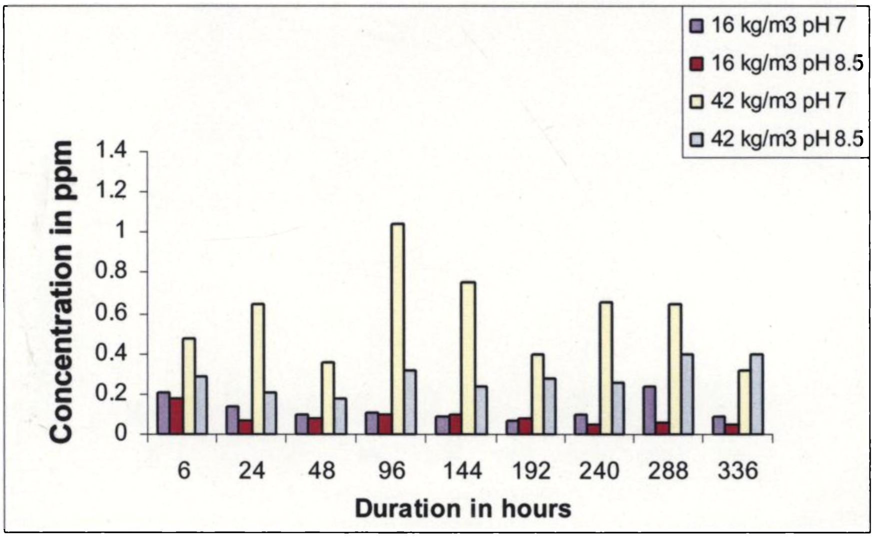


Fig. 4.5: **Rate of leaching of chromium on varying retention at neutral and alkaline pH**

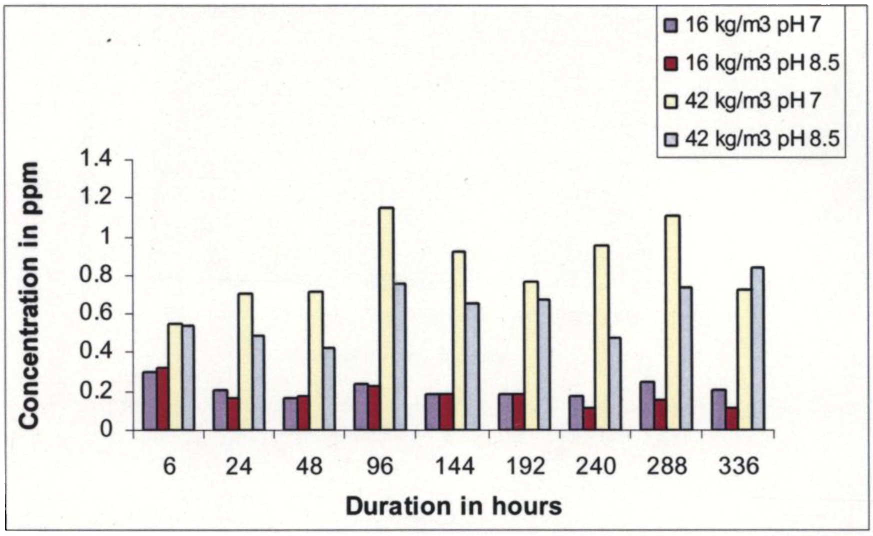


Fig. 4.6: **Rate of leaching of arsenic on varying retention at neutral and alkaline pH**

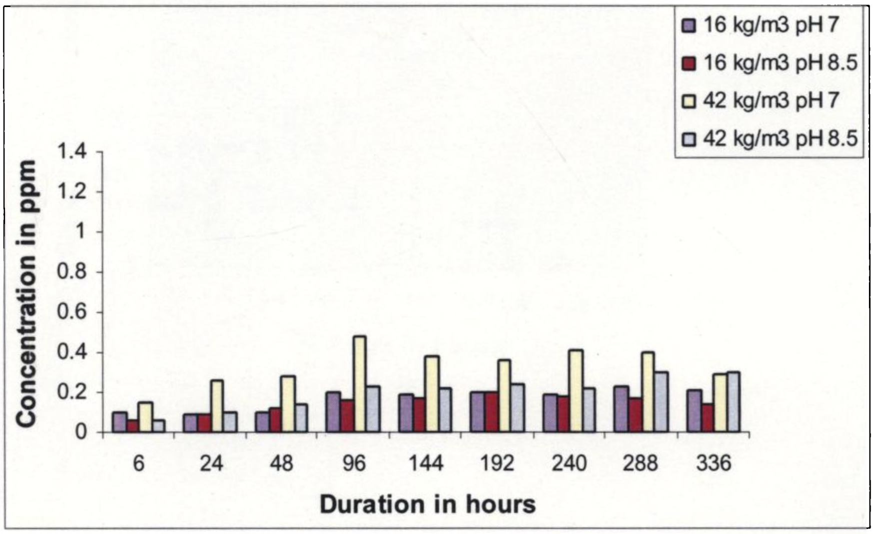


Fig. 4.7: **Leaching of copper on varying salinity**

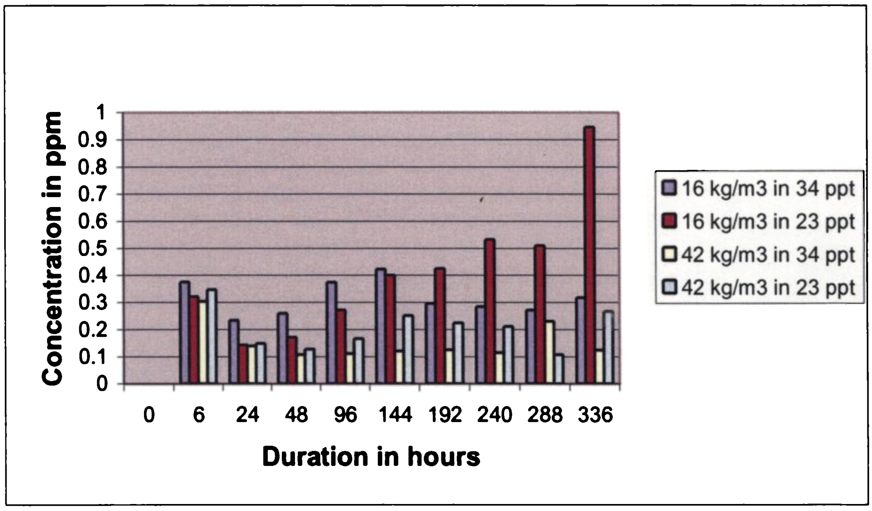


Fig. 4.8: **Leaching of chromium on varying salinity**

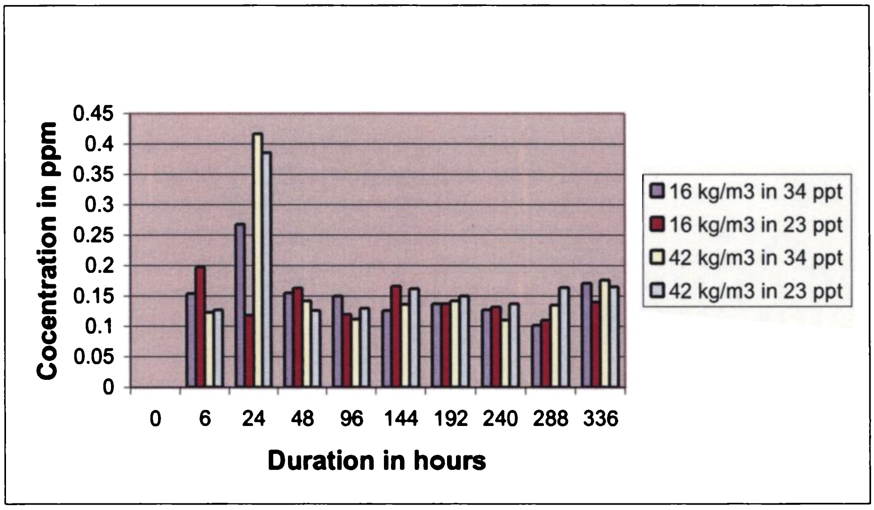
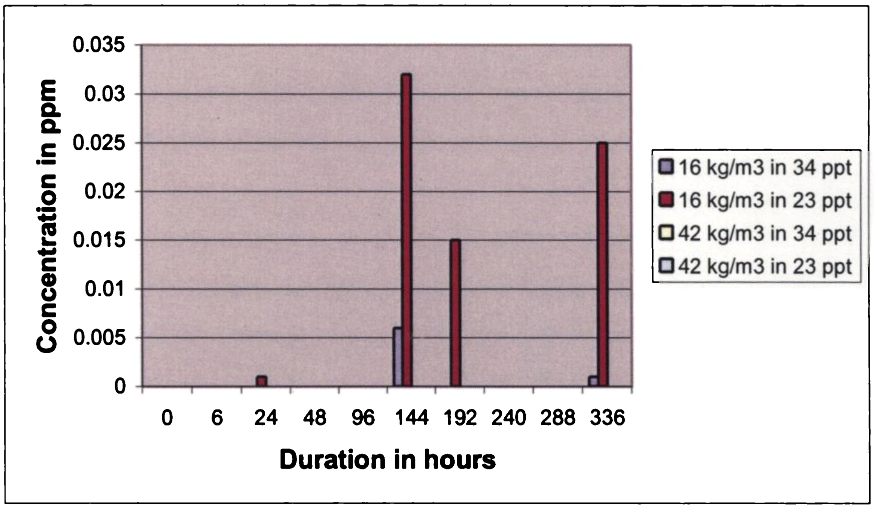


Fig. 4.9: **Leaching of arsenic on varying salinity**



Speciation and accumulation of CCA

5.1 Speciation of CCA in Water

5.1.1 Introduction

Speciation is comparably a new branch of analytical chemistry. It describes the main properties of a compound in terms of chemical bonding between its atoms or molecules and is useful for the understanding of transport behaviour, toxicity and contamination. Earlier, most chemical analyses used to determine the total metal content whereas nowadays the determination of organic molecules is carried out by examining both structure and behaviour in reactivity. In the absence of organic compounds, hexavalent chromium is the most stable form of chromium in equilibrium with atmospheric oxygen. The degree of toxicity of leachate depends upon the chemical speciation of the components of CCA that are released when treated wood is placed in seawater. Although significant information exists on speciation of the individual elements in CCA, there are very less research specific to CCA leachates (Albuquerque & Cragg, 1995a). The form of the metals that are leaching is not exactly known, weather as individual elements, as copper or chromium arsenates, as inorganic complexes or possibly even as organo-metallic complexes bound to water-soluble extractives (Lebow, 1996). In seawater metals can exist as free metal ion, or combine with anionic or naturally derived organic ligands to form complexes. Free metal ions are usually present at a relatively low percentage of total dissolved metal in seawater (Bruland, 1983). The percentage of free metal ions is known to vary depending on pH, but it is generally assumed that seawater has a sufficient buffering capacity to resist major pH changes (Langston, 1990). Becher *et al.*, 1983 found that copper complexes with humic acids found in seawater. Arsenic has two main oxidation states, As (V) and As (III), the former is less toxic form and is predominant in seawater (Sanders & Windom, 1980). As (V) occurs almost entirely as $HAsO_4^-$ ions in the arsenate form. In this form it bears a similarity to phosphate hence is readily taken up by phytoplankton (Sanders & Windom, 1980). As (III) occurs mainly (87%) as $As(OH)_3$. Sanders and Windom (1980) estimate that as much as 15-20% of total arsenic is reduced by phytoplankton during the spring and blooms on the continental shelves. In the present context, speciation studies are conducted in order to understand the form in which the components of CCA leach into the aquatic environment and to quantify it.

5.1.2 Materials and Methods

The speciation of CCA was studied in artificial seawater prepared in the laboratory. The artificial seawater was prepared according to the Indian Standard (IS 8770-1978) For this experiment, rubber wood panels of size 150 x 100 x 25 mm, treated to 16 and 42 kg m^{-3} retentions were selected. They were then made to leach in accelerated condition in the laboratory according to AWPA standard E-11, 97. The collected leachates were analyzed in 797 VA computrace ion analyzer (Voltammetry). Copper was analyzed for oxidation state II alone. Chromium was analyzed for the oxidation state Cr III and VI. The leachate solution was sampled for experimenting the speciation of CCA into water. For this, copper, chromium and arsenic were analysed in their present oxidation state in voltammeter. Later the samples were oxidized using potassium permanganate and sulphuric acid as per the method and then analyzed again. Copper was analysed on the Hanging Mercury Drop Electrode (HMDE) by means of Anodic Stripping Voltammetry (ASV). Chromium was analysed Static Mercury Drop Electrode (SMDE) by the method called voltammetric determination of chromium in small quantities. Determination of arsenic was done by ASV at the Rotating Gold Electrode (RDE). In the initial analysis chromium only in the (VI) oxidation state was analysed and after oxidation, chromium in the fixed and reduced state viz, (III) oxidation state was also analyzed. The difference between the final and initial values shows chromium in the (III) oxidation state. If the fixation reaction is properly done, chromium in the (VI) oxidation state will be less.

Similarly, arsenic in the (III) oxidation state is analysed in the first set. This is done by lowering the potential to –200 V. In the next stage, the potential is increased to –1200 V. At this high potential the whole arsenic gets analyzed and the difference gives the arsenic component in the (III) oxidation state by calculating the difference between them. Thus the quantity of copper, chromium and arsenic leached in various species can be quantified.

5.1.3 Results and Discussion

The degree of toxicity of leachate depends upon the chemical speciation of the components of CCA that are released when treated wood is placed in seawater. Leaching of chromium in the (VI) oxidation state, which is the form of chromium in the preservative, is found to be less in the leachate when compared to total chromium leached. This proves that during fixation of the preservative, chromium (VI) reduces to other species especially chromium (III). Former fixation studies also supports this observation. Arsenic also does not found to leach in the (III) oxidation state. Arsenic is found to leach in the (V) oxidation state, which is the original form in the preservative. This could be because there is no change in the oxidation state of arsenic during fixation. Arsenic is found to leach only in small quantities when analyzed for total arsenic in the leachate. Fig 5.1.1 shows the quantity of copper, chromium and arsenic that leached into saline water in the form of species in witch it is present in the preservative and Fig 5.1.2 shows the total quantity of copper, chromium and arsenic that leached from rubber wood treated with CCA to different retentions. It is also seen that leaching is more prominent in lower salinity (23 ppt) than higher salinity (34 ppt).

Copper occurs in natural waters primarily as the divalent cupric ion. It may be found as a free ion or complexed with humic acids, carbonate, and other inorganic and organic molecules. Baldwin *et al.,* 1996 studied partitioning of metals to sediment during laboratory leaching trials with marine piles, and found that copper bound to both low and high organic carbon sediment in the same degree and did not desorbs to the overlying waters. Chromium exhibited minimal adsorption to high organic carbon sediment only and arsenic is found in all cases in the interstitial or overlying waters. Speciation into different oxidation states was not possible due to low concentrations. The toxicity of copper, chromium and arsenic is highly dependent on the specific form in which it is present.

Two species of chromium are prevalent. Chromium (III) is less toxic than chromium (VI). Interaction of chromium (VI) molecules with organic compounds can result in reduction to a comparatively less toxic trivalent form. However, in aerobic marine environments, chromium (VI) is the more abundant species. Chromate and dichromate are soluble in water and are therefore mobile in aquatic environments. Chromium in the (VI) oxidation state is known to be carcinogenic and mutagenic, but if reduced to Cr (III), as during the CCA fixation process, it may be significantly less harmful (Sanders & Reidel, 1987). Arsenic may also be carcinogenic and mutagenic and of the predominant oxidation states, As (V) is thought to be the more prevalent and less toxic form than As (III). Also inorganic arsenic and hexavalent chromium Cr (VI) originates from leached CCA chemicals causes health problems in human (Townsend *et al.*, 2001; Hingston *et al.*, 2000).

Many analytical procedures can only measure the total metal concentration, sometimes with the ability to distinguish between oxidation states. Few techniques are able to provide information concerning complexation. Fractions of organically associated copper exceeding 98% have been reported in Atlantic waters (Buckley, 1986; Kramer, 1986). The presence of organic ligands in seawater suggests that a high proportion could become bound to organic material and thus less toxic to biota. The possible species that may be subject to leaching from treated wood are copper hydroxide ions, CrO_3, $HCrO_4^-$ or $CrAsO_4$ (Hayes *et al.,* 1994). Of the forms of copper present in CCA treated wood, $CuSO_4$ physically adsorbed by the various wood constituents was the likely leachate component (Pizzi, 1982b).

In a study by Lebow *et al.;* (1999) comparing the release of copper, chromium and arsenic into seawater and deionized water from CCA treated wood, the following results were found. During the initial stage of leaching, when the release of copper is high in solution a variety of forms of copper are being removed from the wood. These might include copper bound to water-soluble extractives, copper adsorbed to particulate matter and copper precipitated within the wood structure. It is known that seawater cations such as Ca^{2+} and Mg^{2+} compete with metals for ion exchange sites on organic matter (Salomons & Forstner, 1984). Although copper may form stronger complexes with organics than does Ca^{2+} or Mg^{2+}, the high concentrations of these ions in seawater can decrease copper complexation with organic ligands (Bodek *et al.,* 1988). The relatively low initial release rate in seawater may have been caused by precipitation of chromium in colloidal form. Chromium is likely to form complexes with polyflavanoid tannin extractives and these complexes may have been precipitated by seawater metals but remained soluble in deionized water leachate (Ryan, & Plackatt, 1987). It has also been reported that the presence of metal cations (such as Na^+, Mg^{2+}, K^+, and Ca^{2+} in seawater) could result in the immobilization of soluble arsenic through the precipitation of metal arsenates (Bodek *et al.,* 1988). Chromium is present in seawater as the more toxic Cr (VI) form rather than Cr (III). This is because of the high pH of seawater (Ahrland, 1975). It is readily taken by phytoplankton as the soluble chromate ion, CrO_4^{2-} (Baldwin *et al.,* 1996). This is comparable in size and charge to the sulphate ion (Ahrland, 1975). The chromate ion does not form complexes with anions but acts as a potential metal coordinating ligand itself.

The chemistry of arsenic in water is complex and the form present in solution is dependent on such environmental parameters as pH, organic content, suspended solids and sediment characteristics. Thermodynamic considerations predict that at neutral pH, and relatively high levels of dissolved oxygen, most arsenic should be oxidized to arsenate. However, Penrose (1974) notes that most inorganic arsenic in the sea is in the form of arsenite. The study also found that marine bacteria could reduce arsenate to arsenite. This biological transformation may be responsible for the 2:1 ratio of arsenite to arsenate observed in some marine water. In contrast, Andreae (1978) reports that arsenic III (arsenite) represents only about 20% of the total arsenic found in seawater. Andreae (1978) found significantly more reduced arsenic (arsenite) than would be expected in highly oxygenated water where chemical equilibrium models suggest that most of the arsenic should be in the less toxic arsenate form. The ratio of arsenite to arsenate is correlated with chlorophyll production suggesting that the speciation of arsenic in natural waters is highly influenced by biological activity. The relatively high level of arsenic found in sediments, compared to the water column suggests that the ultimate fate of arsenic in aquatic environments is incorporation into sediments.

5.1.5 Conclusion

Lower content of Cr (VI) in the leachate shows that, fixation of the preservative has taken place properly. Total chromium leaching is increasing with increase in retention in saline conditions where as leaching of copper is higher in lower retentions. Another noticeable point is that leaching of copper is higher in lower salinities. In the case of Cr (VI), higher leaching was in higher salinities whereas for total chromium, leaching pattern is similar in both salinities. Arsenic leaching is present only in negligible quantities.

Fig. 5.1.1: **Speciation of copper, chromium and arsenic**

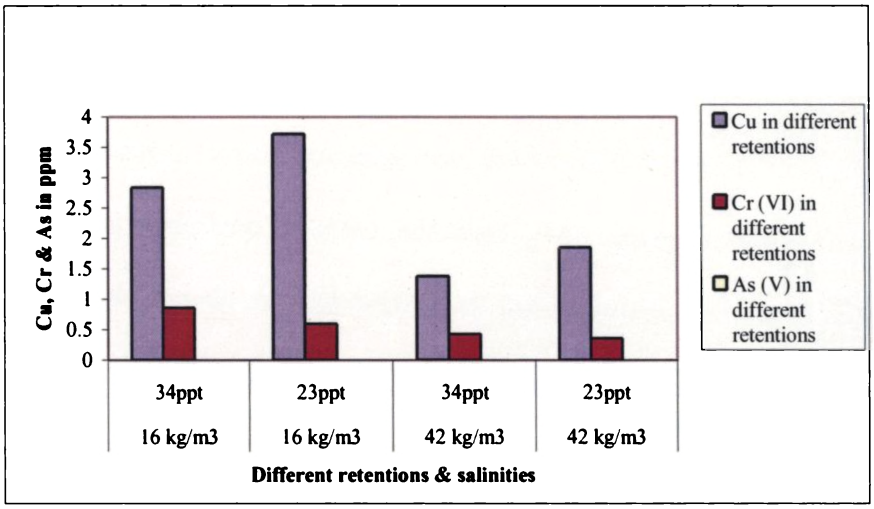
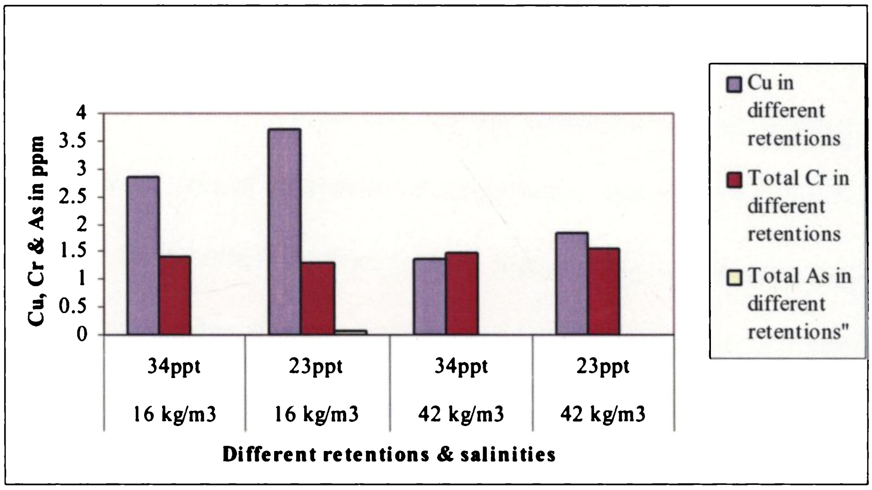


Fig. 5.1.2: **Total copper, chromium and arsenic leaching**



5.2 Accumulation of CCA Components in the Sediment

5.2.1 Introduction

When CCA treated wood is exposed in an estuary, the preservative components that are leaching from the wood diffuse into the water and a part of it gets adsorbed into the sediment. The adsorption of these components depends mainly on the texture of the sediment and the content of organic matter present. Among CCA components, chromium is found to have more mobility, though its mobility depends highly on the oxidation state. Trivalent chromium is highly reactive with organics and quickly fixes to soil or sediments and hexavalent chromium is more soluble, less likely to be adsorbed and has been reported to move through soil at the same rate as groundwater. The accumulation of these elements in the sediments, water column and biota would be expected to be highest for recently constructed large structures built in poorly flushed systems and less for smaller structures built in well flushed systems. Levels of preservative components detected in the sediments did not appear to adversely affect either the abundance or diversity of aquatic invertebrates. No significant difference was found in invertebrate populations before and after the experiment when CCA treated wood was used for construction in aquatic environment. Also elevated environmental concentrations of preservative components were found only in close proximity to the treated wood (Lebow *et al.,* 2002). This is because the leached preservative components either have low water solubility or reaction with components of the sediment. The poor environmental mobility of the preservative components has the positive aspect of limiting the range of any environmental contamination. However, over time it can also lead to gradual increases in soil levels of these components immediately adjacent to treated structures.

Since the sediment collected from the test site in the estuary is found highly contaminated with the components of CCA, the experiment was conducted in the laboratory condition using sediment collected from another site.

5.2.2 Materials and methods

The accumulation studies of CCA components in the sediment were conducted by exposing treated panels of various retentions to the sediment collected from site uncontaminated with CCA components. The panels of untreated rubber wood and panels treated to retentions 16, 29 and 42 kg m^{-3} were immersed in 2750 ml de-ionized water containing 50 g sediment. The initial pH of the sediment was six. The organic content of the sediment was analyzed before exposing it into the treated wood. The sediment texture being very important in determining the adsorption properties of the sediment was also analyzed before exposing to preservative treated wood (Table 5.2.1). Copper, chromium and arsenic content of the sediment were analyzed before introducing the sediment into water. The experimental set up was kept undisturbed for a period of one month. Later the preservative components in the sediment were analyzed after the experiment is over (Table 5.2.2).

5.2.3 Results and Discussion

Copper is found to adsorb in the sediment more than chromium and arsenic (Fig 5.2.1-5.2.3). Fig. 5.2.1 shows the quantity of copper that accumulated in the sediment from rubber wood panels treated with CCA to different retentions. Here it can be seen that more copper is found in the sediment exposed to 29 kg m^{-3}. This could be because of the high leaching of copper in that particular retention. 155.4 ppm of copper is found to accumulate in the sediment from panel treated to 29 kg m^{-3}, 127.8 ppm of copper from 16 kg m^{-3} and 132.4 ppm from 42 kg m^{-3}. Similarly, Fig. 7.2 and Fig. 7.3 respectively shows the quantity of chromium and arsenic that accumulated in the sediment from rubber wood panels treated with CCA to different retentions. 131.2 ppm of chromium was found to accumulate from 16 kg m^{-3}, 117 ppm from 29 kg m^{-3} and 104 ppm from 42 kg m^{-3}. In the case of arsenic, 22.6 ppm from 16 kg m^{-3} and 11.6 ppm from 29 kg m^{-3} and 11 ppm from 42 kg m^{-3}. Chromium and arsenic were found more in sediment exposed to 16 kg m^{-3}. The sediment used in the experiment is found to be of sandy silt type and it contained 2.19% of organic matter.

The ultimate fate of chromium VI appears to be incorporation into fine grained sediments with high organic and iron content. Chromium III forms stable complexes with negatively charged inorganic and organic compounds.

Precipitated chromium hydroxides remain in the sediments under aerobic conditions. With low pH and anoxic conditions, chromium III hydroxides may solubilize as ionic chromium III. However, Lu & Chen (1976) found that chromium was not significantly released from sediments into seawater under either oxidizing or reducing conditions.

The impacts due to the release of elements from CCA pressure treated wood depend on many factors: the amount of treated wood present, treatment level, age of the wood and the movement of water surrounding the structure. The accumulation of these elements in the sediments, water column and biota would be expected to be highest for recently constructed large structures built in poorly flushed systems and less for smaller structures built in well flushed systems. Brooks (1996) developed a model based on the Putt (1993) leaching data to estimate the impacts of copper leaching on the water column and sediments surrounding CCA-C pressure treated bulkheads and pilings. The initial (<7day) copper leaching rates found in the Brooks model and those measured in a study conducted by Breslin and Alder-Ivanbrook (1998) are similar. The summary of the detailed study recently conducted (Brooks, 2002) on the environmental suitability of CCA-treated marine piling is against any suggestions that treated piling is harmful to sediment-dwelling life. Measured amounts of copper, chromium and arsenic in naturally occurring water, sediment and in the leachate and treated sediments established that some variability occurred between measured amounts due to the behavior of the three metals in natural environmental conditions (e.g., seawater, sediment and wood). Analyses for arsenic demonstrated that approximately 59.5 mg arsenic/m^2 of treated wood surface area leached from the treated pilings. Arsenic did not appear to adsorb on sediment of either type and, in almost all cases, was not observed in interstitial or overlying water.

5.2.4 Conclusion

Copper is found to adsorb in the sediment more than chromium and arsenic. Also more copper is found in the sediment exposed to 29 kg m^{-3}. Chromium and arsenic were found more in sediment exposed to 16 kg m^{-3}. Considering accumulation of all the three elements, 42 kg m^{-3} retention is found to be more effective in reducing accumulation of CCA components in sediment.

Table 5.2.1: **Texture of the sediment used in the study**

Type of sediment	Content (%)
Sand	33.52
Silt	45.48
Clay	21.00

Table 5.2.2: **Initial and final concentration of copper, chromium and arsenic in the sediment**

Sample name	Cu (ppm)	Cr (ppm)	As (ppm)
Unexposed	16.8	30.8	10.4
Control	25.8	63.8	2.2
CCA 16 kg m^{-3}	127.8	131.2	22.6
CCA 29 kg m^{-3}	155.4	117	11.6
CCA 42 kg m^{-3}	132.4	104	11

Fig. 5.2.1: **Leaching of copper into sediment**

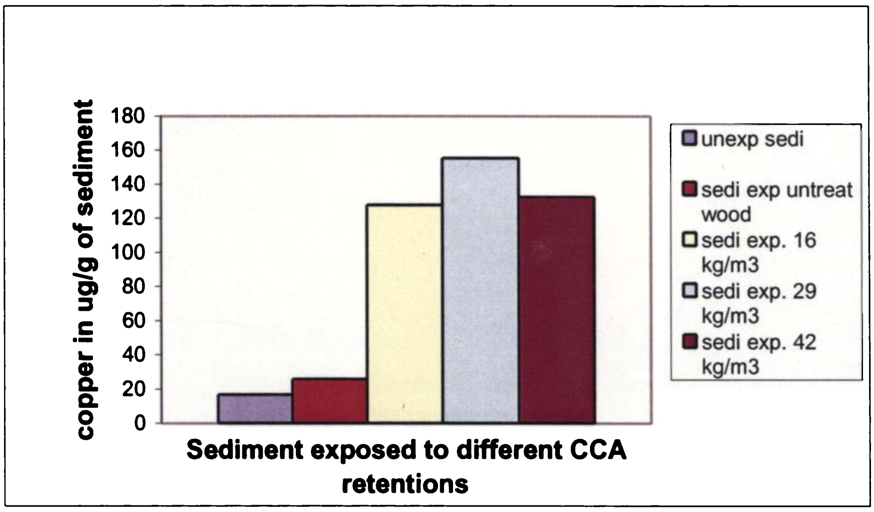


Fig. 5.2.2: **Leaching of chromium into sediment**

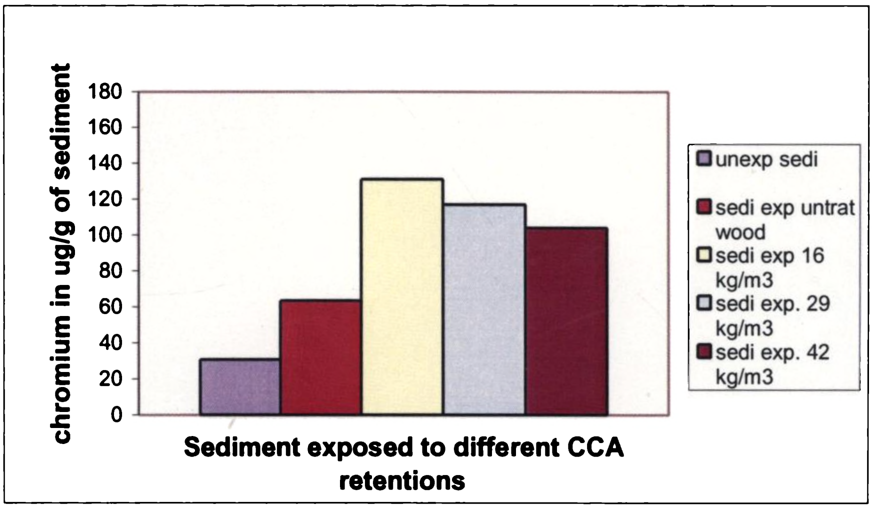
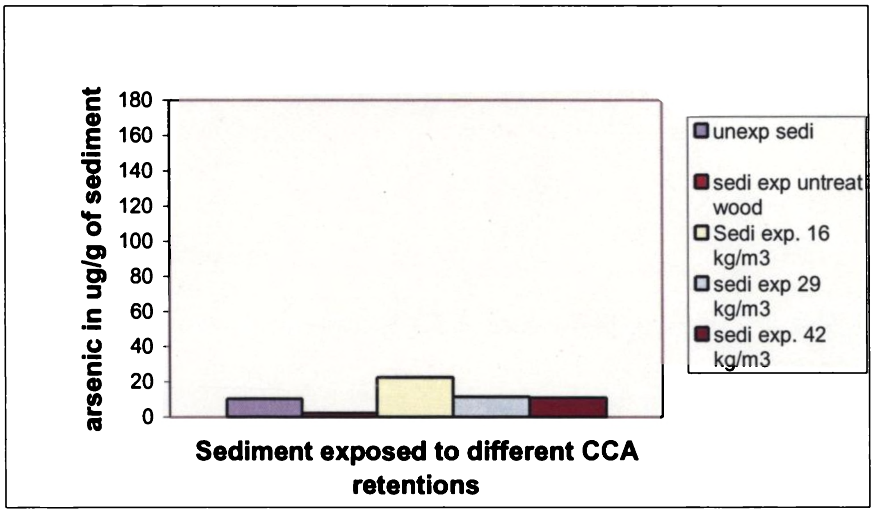


Fig. 5.2.3: **Leaching of arsenic into sediment**



Control of CCA leaching from treated rubber wood panels

6.1 Introduction

Even though the use of CCA as a wood preservative improves the life of non-durable wood, the slow diffusion of the preservative into the aquatic environment through leaching, weathering, decay or erosion of the treated wood can be a threat to aquatic life (Lebow, 1996). In this context it would be appropriate to discuss methods to prevent the leaching of the preservative components into the aquatic medium. Physical barriers like sheathing the treated wood with materials like Fibreglass Reinforced Plastic (FRP), coating the treated wood with paint, sealants or water repellents are some of the methods. Stilwell (1998) studied the ability of boards with polyurethane, latex/acrylic, oil stain and spar varnish coatings and they were found to be very effective in reducing dislodgeable CCA chemicals for at least one year after they are applied. The ability of coatings to reduce the leachability of arsenic from CCA treated wood was studied by Cooper *et al.*, (1997) which showed that a water seal applied after CCA treatment, significantly reduced the quantity of arsenic leaching for a period of two years after its application. Edwin *et al.*, (unpublished) carried out studies by sheathing CCA treated rubber wood with FRP and found that it is resistant to rots and attack by borers.

Therefore it can be used for fishing boat construction. Experiments have been conducted at the Central Institute of Fisheries Technology, Cochin using rubber wood for aquatic purposes especially in the construction of small fishing canoes (Edwin *et al.,* 2005). The present study evaluates the effectiveness of sheathing with FRP, painting and pressure treatment with creosote after treating with CCA in prevention of leaching of CCA components from treated wood into water under laboratory condition. The study also aims at evaluating the effect of increase in volume to exposed surface area ratio of wood panels on leaching.

6.2 Materials and Methods

Two types of panels were selected for the experiment based on their size. The first type referred to as Type 1, have 19 x 19 x 19 mm size and the second one have 150 x 100 x 25 mm size (Type 2). Type 1 panels were classified into four types according to treatment given and Type 2 panels were classified into six types according to the treatment.

Type1

- CCA treated
- FRP sheathed after CCA treatment
- Paint coated after CCA treatment
- Treated with creosote after CCA treatment (dual treatment)

Type 2

- Untreated panel sheathed with FRP
- Untreated panels coated with paint
- CCA treated
- FRP sheathed after CCA treatment
- Paint coated after CCA treatment
- Dual treatment

Type 1 panels were sized from type 2 after the CCA and dual treatment. Painting of the panels was done with two coats of epoxy finish paint which is used to protect wood, steel, concrete etc from harsh climates, pollution, salt spray, acids oils and solvents. Dual treated panels were prepared by pressure treating CCA treated panels with creosote to obtain retention of 150 kg m^{-3} In order to obtain this retention, a pressure of 414 kPa was applied along with an initial vacuum of 56 cm of mercury for 30 min and a final vacuum of 38 cm of mercury for 15 min. An intermittent drying period of four weeks was given after each treatment. Six panels each were selected from all categories for the leaching experiment.

FRP sheathed, painted, dual treated and CCA treated panels of types 1 and 2 were made to undergo accelerated leaching in the laboratory. The leaching experiment was patterned as per AWPA E-11, 97. Type 1 panels were kept immersed in 300 ml of de-ionized water for 30 minutes with a wood: water volume ratio of 1:7. The water in the beakers containing the panels was then constantly stirred using magnetic stirrers (at a speed of 25-50 cm s^{-1}) with the same type of magnetic stir bar for each leaching flask. Samples of leachates were then collected and the whole solution is replaced with fresh de-ionized water. This is done after 6, 24, 48, 96, 144, 192, 240, 288 and 336 h. The quantities of leachates at the time of sampling were recorded for analysis. Leaching experiment was similarly conducted in 2750 ml water for type 2 panels also keeping the same ratio of wood: water volume. Each leachate sample was then analysed for Cu, Cr and As in ICP-AES (Perkin Elmer-Optima 2000 DV) using NIST standards. The quantity of preservative components present in the wood before exposure to water was also analyzed in ICP-AES after digesting the wood sample in microwave digestion system (Ethos Plus- High Performance Microwave Labstation). The quantities of copper, chromium and arsenic leached out into the water were analyzed with reference to the type of treatment given and the size of panels. Statistical analysis was carried out using Multivariate Analysis of Variance (MANOVA).

6.3 Results and Discussion

Type 1 panels initially contained 77.01 mg of copper, 130.76 mg of chromium and 53.25 mg of arsenic. In the case of copper 5.1 mg was found to leach from the control panel during 336 h of the experiment. 0.007 mg of copper leached from FRP sheathed panel, 0.003 mg from painted panel and 1.71 mg from dual treated panel. In the case of chromium, it was 10.81 mg from control panel, 0.033 mg from FRP, not detectable from paint and 4.379

mg from dual. For arsenic, it was 2.213 mg from control panel, 0.86 mg from FRP, 0.087 mg from painted panel and 3.997 mg from dual treated panel.

Type 2 panels initially contained 559.25 mg of copper, 949.52 mg of chromium and 386.71 mg of arsenic. In the case of copper 4.088 mg leached from the control panel. 0.016 mg from FRP sheathed panel, 0.005 mg from painted panel and 1.72 mg from dual treated panel. In the case of chromium, it was 7.74 mg from control panel, non detectable from FRP, paint and 4.184 mg from dual. For arsenic, it was 6.09 mg from control panel, 0.879 mg from FRP, 0.423 mg from painted panel and 4.997 mg from dual treated panel. The cumulative loss of the metal constituents expressed in percentage is shown table 1. The trend of leaching of copper, chromium and arsenic is shown in figure 1-6.

MANOVA of copper, chromium and arsenic concentrations pertaining to type 1 and type 2 at four levels of treatment combinations were observed at different intervals. Metal concentrations were significantly different for all the combinations of treatment and size at different time intervals. Copper, chromium and arsenic leached in significantly high quantities from type 1 panels than from type 2 panels. The significance is valid at 1% level, $R^2 = 0.99$.

Control panels showed maximum leaching followed by dual treatment. FRP and paint coating had least leaching. When Tukey's test was performed for the type 1 panels keeping treatment type as variable, it was found that leaching of copper was not significantly different between FRP sheathing and painting where as all other treatments were found to differ significantly with each other. The leaching of chromium and arsenic was significantly different between all the treatments.

When Tukey's test was performed for type 2 panels keeping treatment as variable, it was found that leaching of copper and chromium through FRP sheathed and painted panels was not significantly different where as for all other treatments leaching were found to differ significantly with each other. Leaching of arsenic from all the treatments was found to differ significantly.

When Tukey's test was performed keeping the interval of water replaçement as variable and all treatments as constants, leaching was found to differ significantly between intervals for both type 1 as well as type 2 panels.

Type 1 panels leached more than type 2 panels for all types of treatments especially control and dual. This is attributed to the difference in volume to surface area ratio of type 1 and type 2 panels. The volume: surface area ratio for type 2 panels is 1: 1.13 whereas it is 1:3.16 for type 1 panels. Another noticeable difference is that leaching of arsenic is more from dual treated panels in the case of type 1 panels where as it is more from CCA treated control panel in the case of type 2 panels. Also arsenic is found to leach more than copper and chromium from FRP sheathed and painted panels in both type of panels. The absence of copper, chromium and arsenic in the leachate solutions of untreated panels sheathed with FRP and paint suggests that neither untreated wood nor FRP (paint also) does not contain any CCA constituent. Therefore the quantity of arsenic leached belongs to the preservative alone. This may be because when water penetrates the surface of the wood, it lifts the arsenic up to the surface (Williams, 2002). According to Stilwell, (1998) opaque polyurethane and acrylic finishes have the ability to protect the wood surface from ultraviolet radiation as well as water penetration. Therefore they form the most durable coatings as far as prevention of leaching is concerned. Coatings are readily accepted by CCA, which is helpful even in increasing the service life of the finishes and thereby the wood lasts long. Also painting reduces the damage and weathering due to the effects of water, sunlight, temperature variation and mildew (Ross *et al.,* 1992). However, according to studies conducted by the U.S.D.A. Forest Products Laboratory, paint products typically do not penetrate the wood but form a film on its surface which may crack, peel, or chip (Williams & Feist, 1993; Lebow, 2002). Commonly used commercial coatings such as latex paint, penetrating deck stains and oil-based paint will reduce the leaching of chemicals from the wood (Lebow, 2002). A properly applied paint system is efficient in providing protection to wood surface from UV radiation. The paint film reduces water absorption and pigments in the paint block UV radiation thus preventing photo degradation (Williams, 2005). Results of the present study also show that painted panels are most efficient in reducing leaching.

A sheath improves appearance of any material and protects it. Also it diminishes decay and the attack from marine organisms, chemicals and the service life will be extended (Schindler, 1999). The physical properties such as water absorption, glass content, abrasion resistance and mechanical properties like static bending strength and compression parallel to grain strength of FRP sheathed rubber wood panels have been studied in this laboratory (Edwin *et al.*, unpublished).

It is observed from the results of leaching of painted panels that the epoxy paint is impervious to movement of copper and chromium ions across it. However arsenic is observed to leach in negligible quantities. Even though coatings have no effect on the amount of swelling and shrinking, there is pronounced effect on the rate of exchange of water vapour between the wood and the surrounding atmosphere (Schniewind & Arganbright, 1984). All known coatings are impervious to water vapour to some extent and does not adhere to wood. Coatings protect wood from the external factors that may accelerate leaching of the preservative components. The migration of arsenic from wood into the surrounding soil has been reduced in a period of one year by 80-100% when opaque coatings formulated using acrylics or polyurethane was applied to CCA treated wood (Stilwell & Musante, 2004). In the present study also quantity of copper and chromium leached through FRP sheathed and painted panels were less than 1% of that leached through control panels. For arsenic it was in the range of 10 to 20%.

Studies have been conducted on the efficacy of dual preservative treatment against biodeterioration and also its impact on mechanical properties of wood (Edwin *et al.*, 1993, Edwin & Thomas, 2000). However, no studies have been conducted on ability of dual treatment to reduce leaching.

6.4 Conclusion

FRP and Epoxy finish paint is found to be very effective in reducing leaching. The leaching through FRP sheathed and painted panel is negligible when compared to dual treated panel. Even though dual treatment with creosote also reduces leaching of CCA, FRP sheathing and painting are more successful in this regard. Also the rate of leaching increases with increase in volume to surface area ratio.

Table 6.1. **Cumulative loss of copper, chromium and arsenic from Type 1 and Type 2 panels**

Sheathing/ Coating	Type 1 panels			Type 2 panels		
	Cu %	Cr %	As %	Cu %	Cr %	As %
Control	6.62	8.27	4.16	0.731	0.815	1.575
FRP	0.0084	0.025	1.61	0.0029	0	0.227
Paint	0.0041	0	0.163	0.001	0	0.109
Dual	2.22	3.35	7.51	0.307	0.441	1.292

Annexure 1: **Multivariate Analysis of Variance (MANOVA)**

Tests of Between-Subjects

Source	Dependent	Type III of	df	Mean	F	Sig.
Corrected	cu	165.83 [a]	71	2.336	918.54	.000
	cr	617.75 [b]	71	8.701	136184	.000
	as	66.05 [b]	71	.930	12402.23	.000
Intercep	cu	27.09	1	27.09	10654.64	.000
	cr	127.79	1	127.79	2.0E+0	.000
	as	28.56	1	28.56	380790.	.000
type	cu	17.03	1	17.03	6699.56	.000
	cr	90.28	1	90.28	1.4E+0	.000
	as	12.52	1	12.52	166991.	.000
trt	cu	40.31	3	13.44	5285.31	.000
	cr	173.68	3	57.89	906188	.000
	as	24.11	3	8.040	107174.	.000
time	cu	11.95	8	1.495	587.73	.000
	cr	31.00	8	3.876	606687.	.000
	as	1.063	8	.133	1771.82	.000
type *	cu	26.50	3	8.834	3474.14	.000
	cr	124.78	3	41.59	651052	.000
	as	14.40	3	4.801	64007.85	.000
type *	cu	12.12	8	1.515	595.95	.000
	cr	33.65	8	4.207	658500.	.000
	as	.752	8	.094	1252.79	.000
trt *	cu	27.87	24	1.161	456.72	.000
	cr	76.83	24	3.201	501084.	.000
	as	6.055	24	.252	3363.10	.000
type * trt *	cu	30.02	24	1.251	491.98	.000
	cr	87.49	24	3.646	570607.	.000
	as	7.134	24	.297	3962.80	.000
Error	cu	.366	144	.003		
	cr	.001	144	6.389E-		
	as	.011	144	7.501E-		
Total	cu	193.29	216			
	cr	745.54	216			
	as	94.62	216			
Corrected	cu	166.20	215			
	cr	617.75	215			
	as	66.06	215			

a. R Squared = .998 (Adjusted R Squared

b. R Squared = 1.000 (Adjusted R Squared =

Fig. 6.1: **Leaching of copper from type 1 panel**

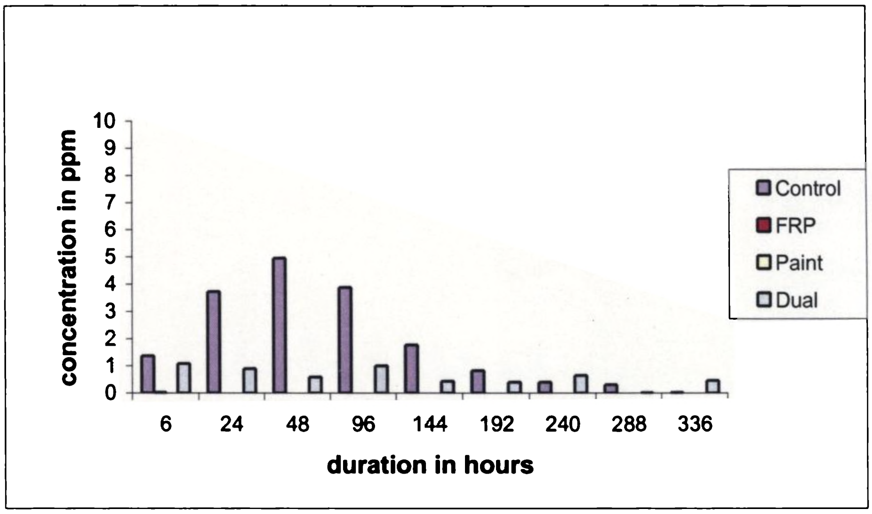


Fig. 6.2: **Leaching of chromium from type 1 panel**

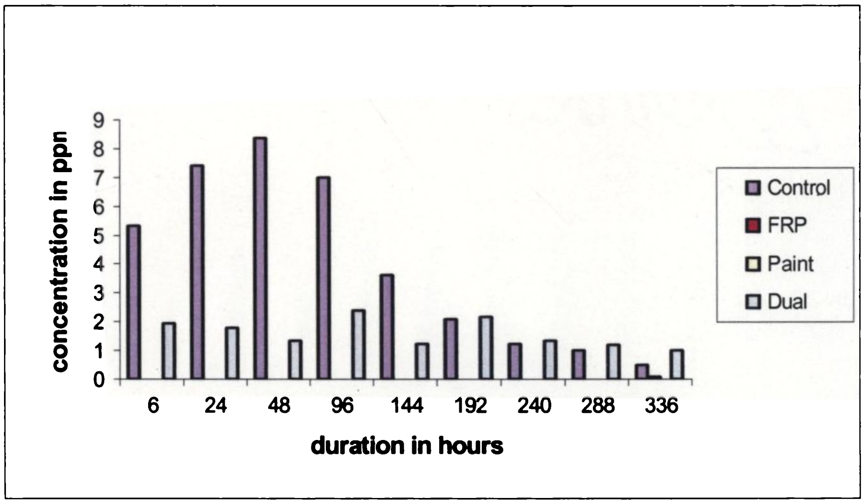


Fig. 6.3: **Leaching of arsenic from type 1 panel**

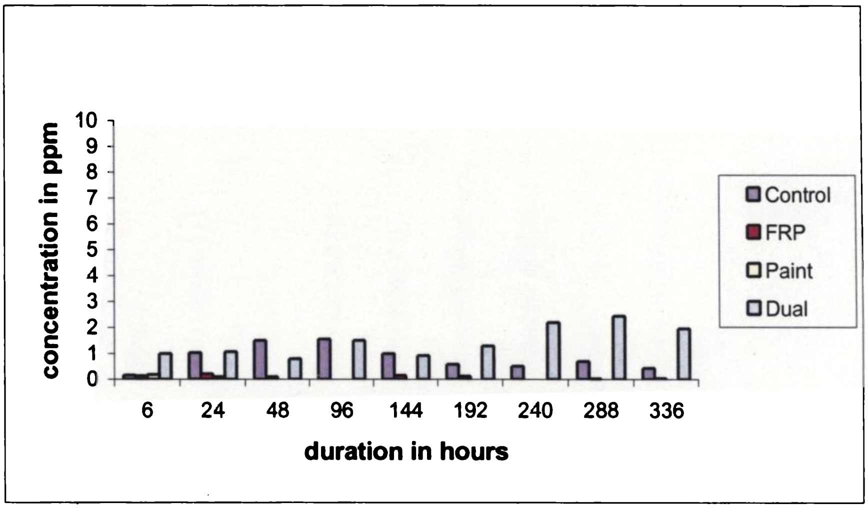


Fig. 6.4: **Leaching of copper from type 2 panel**

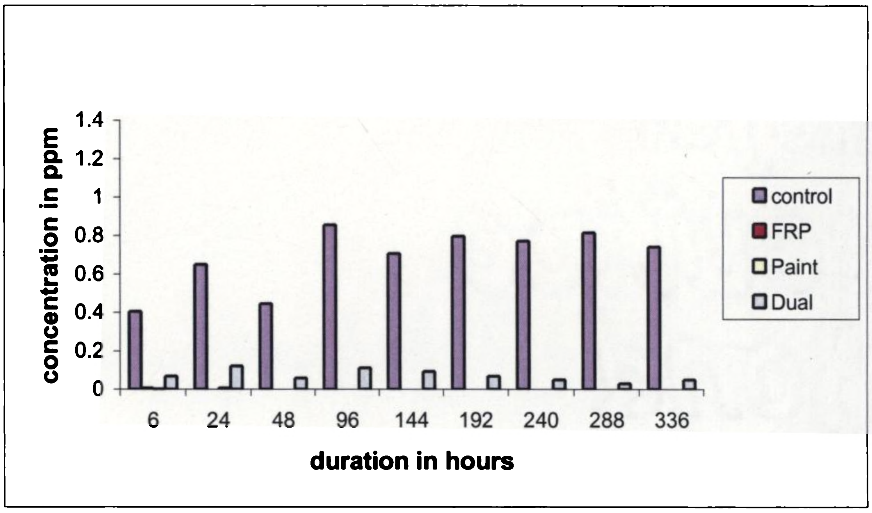


Fig. 6.5: **Leaching of chromium from type 2 panel**

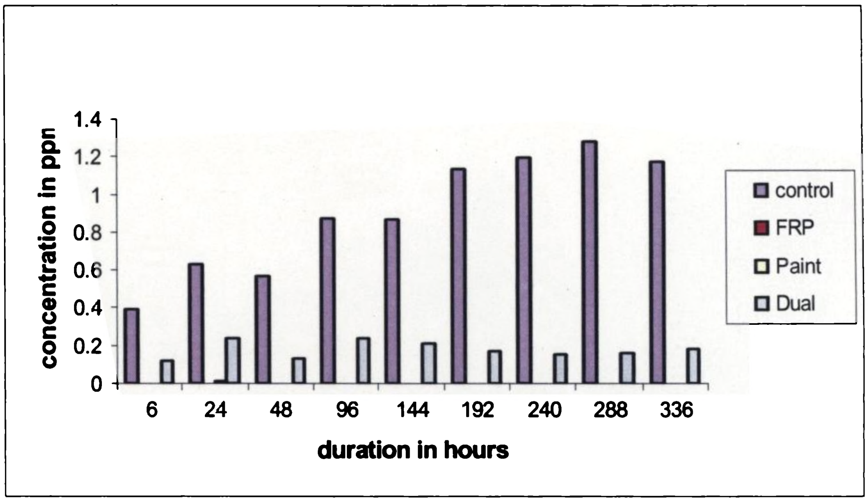


Fig. 6.6: **Leaching of arsenic from type 2 panel**

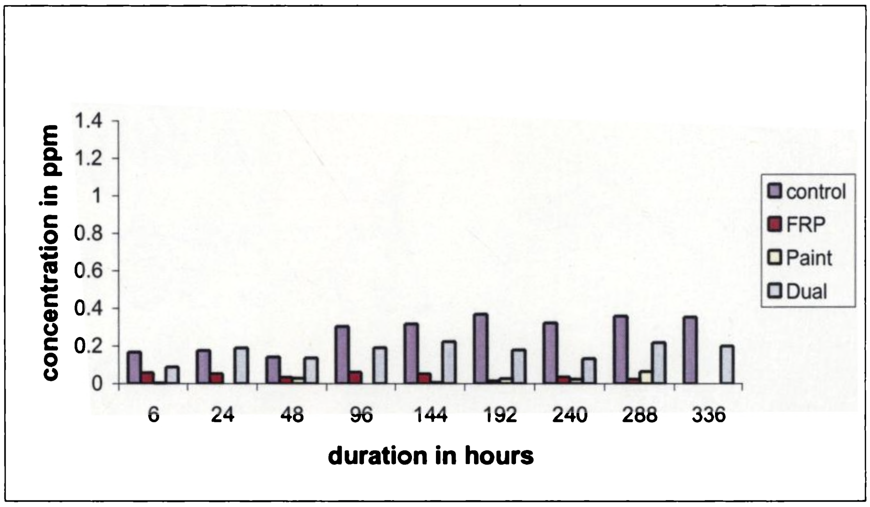
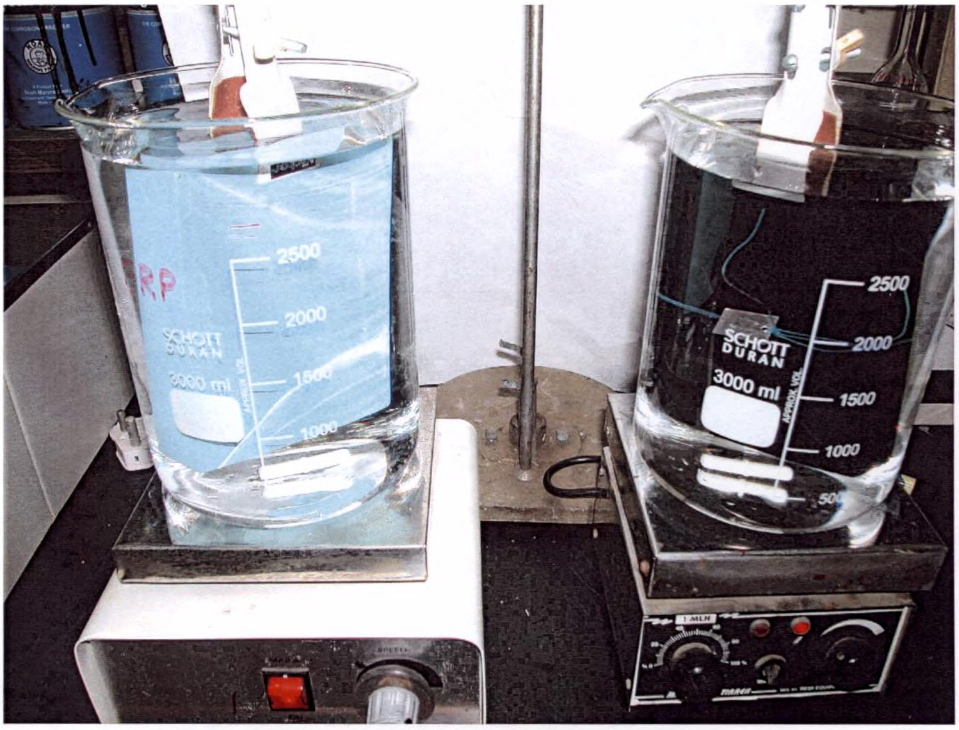


Fig. 6.7: **Experimental set up of studies for control of leaching in the accelerated condition**

Fig. 6.8: **FRP sheathed and painted panels exposed to accelerated conditions using magnetic stirrers**



Chapter VII

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 thiosulphte 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:

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

Where

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

T = time of exposure to the nearest 0.01 h,

A = area in cm^2 to the nearest 0.01 cm^2,

W = mass loss in grams, to the nearest 1 mg and

D = density in g cm^{-3}

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 having16 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**

Date	Water temperature (^{0}C)	pH	Dissolved Oxygen (mg L^{-1})	Salinity (‰)	Turbidity NTU
21/06/05	26	6.89	4.8	0.39	32
07/07/05	27	6.89	4.6	0.20	29
19/07/05	25	7.05	6.8	2.56	20.3
04/08/05	25	7.49	5.4	0.42	28
24/08/05	28	7.77	6.6	11.40	10
06/09/05	27	7.52	3.4	0.57	16
20/09/05	30	7.52	6.4	3.73	11

Table 7.1.2: **Salinity and dissolved oxygen value of Cochin estuary during monsoon for the last five years (2002 – 2006)**

Month	2002		2003		2004		2005		2006	
	D.O. (mgL^{-1})	Salinity (‰)	D.O. (mgL^{-1})	Salinity (‰)	D.O. (mgL^{-1})	Salinity (‰)	D.O. (mgL^{-1})	Salinity (‰)	D.O. (mgL^{-1})	Salinity (‰)
June	5.4	2.45	5.2	18.58	5.0	5.75	4.9	4.66	5.7	4.62
July	5.5	6.26	5.7	1.76	5.9	1.96	5.9	1.29	5.7	1.41
August	5.7	2.20	5.2	3.36	6.6	3.46	5.9	3.88	6.2	6.68
September	5.5	16.50	5.4	12.45	5.4	11.85	5.1	2.15	6.1	3.30

Fig. 7.1: **Corrosion rate of nails exposed in the salt spray chamber**

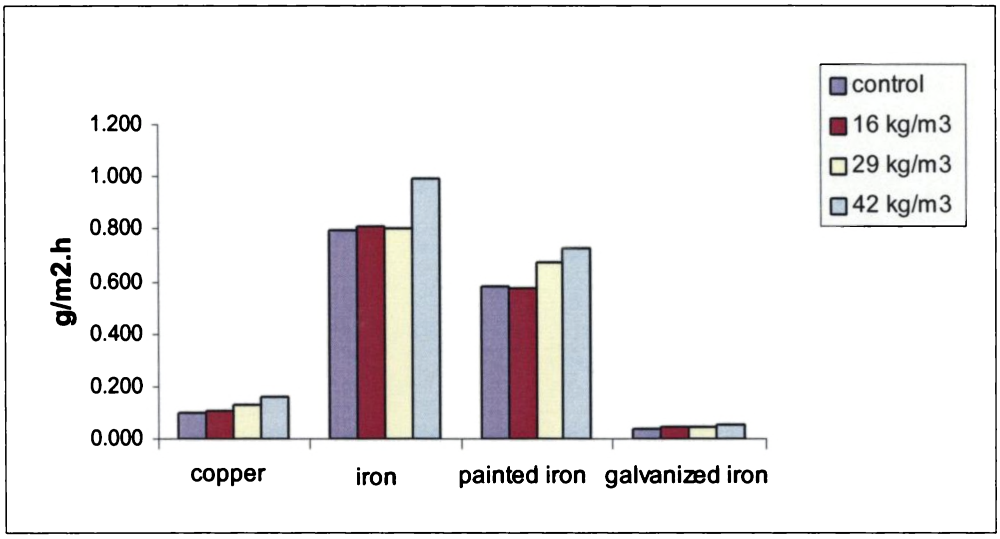


Fig. 7.2: **Corrosion rate of nails exposed in the estuary**

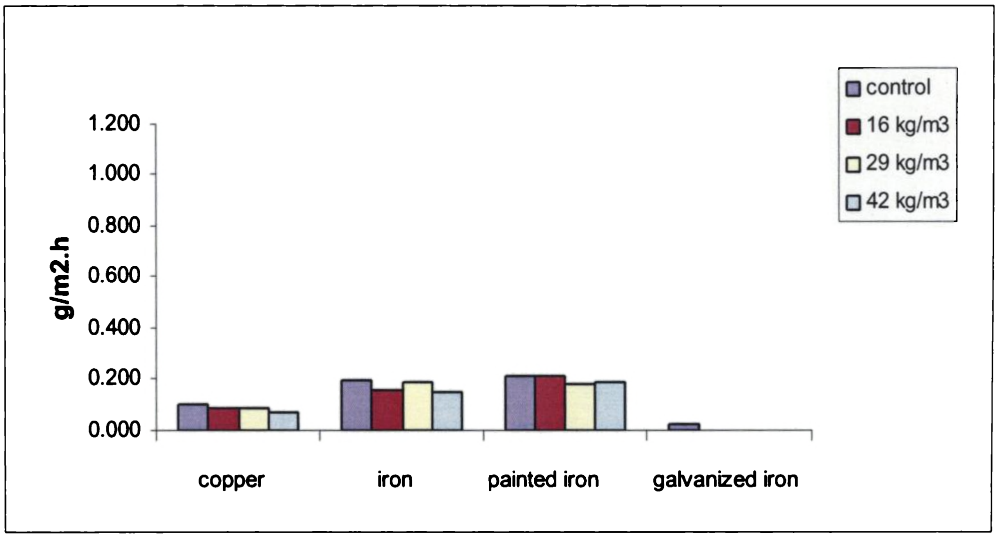


Fig. 7.3: **Nail pulling strength**

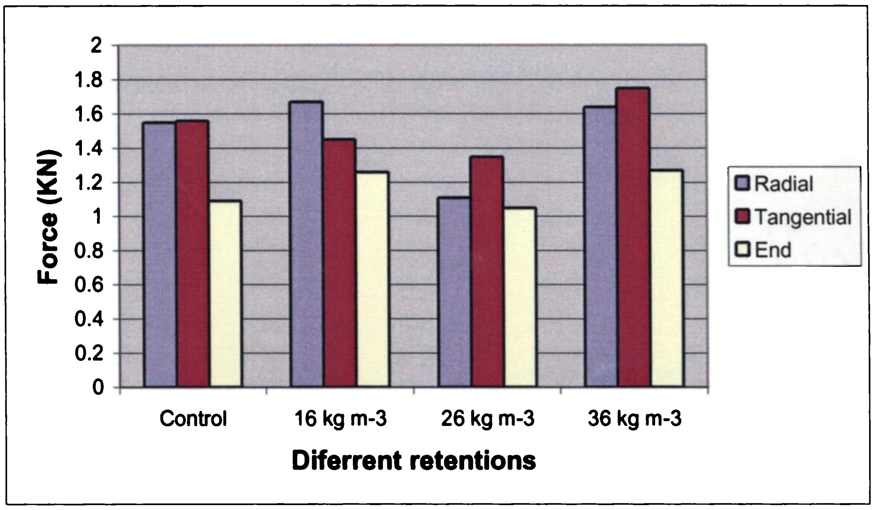


Fig. 7.4: **Screw pulling strength**

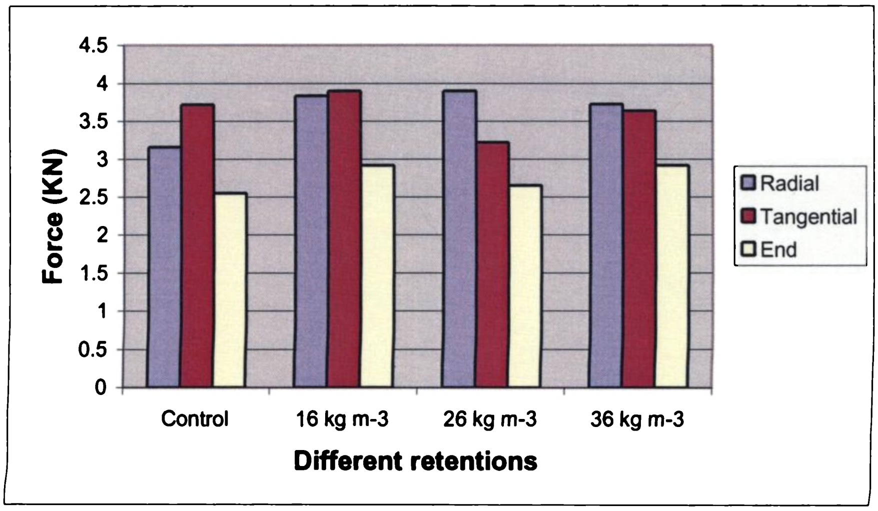


Fig 7.5: **Nailed, CCA treated rubber wood panels exposed in salt spray chamber for accelerated salt spray experiment**

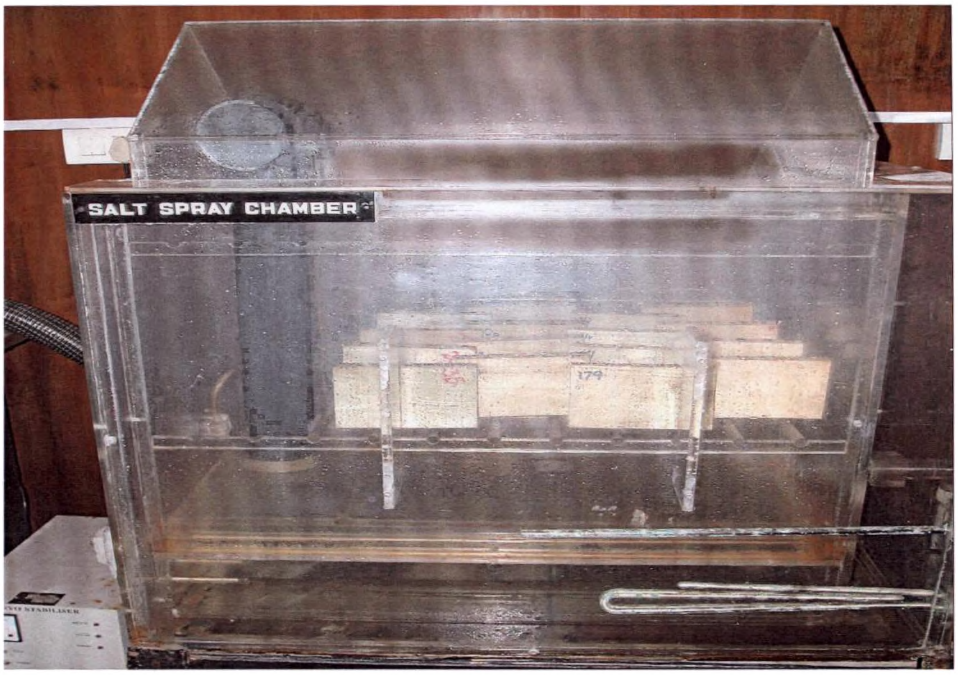


Fig. 7.6: **The inner cross section of the CCA treated rubber wood panel and the iron nails removed from it after exposure in the salt spray chamber**

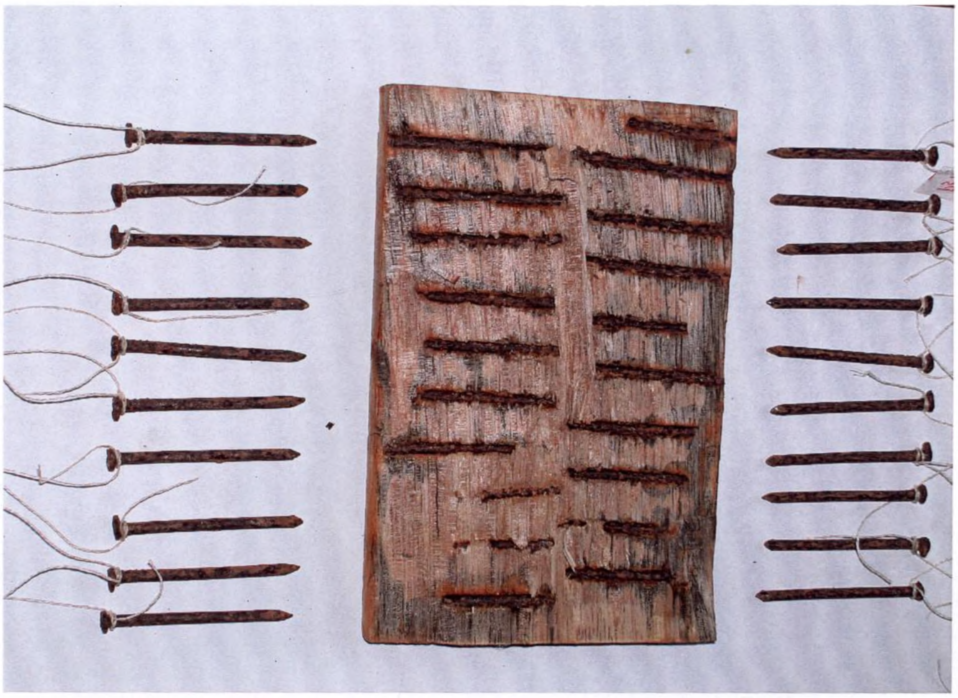


Fig. 7.7: **Galvanized iron removed from the wood panel exposed in the estuary**

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**

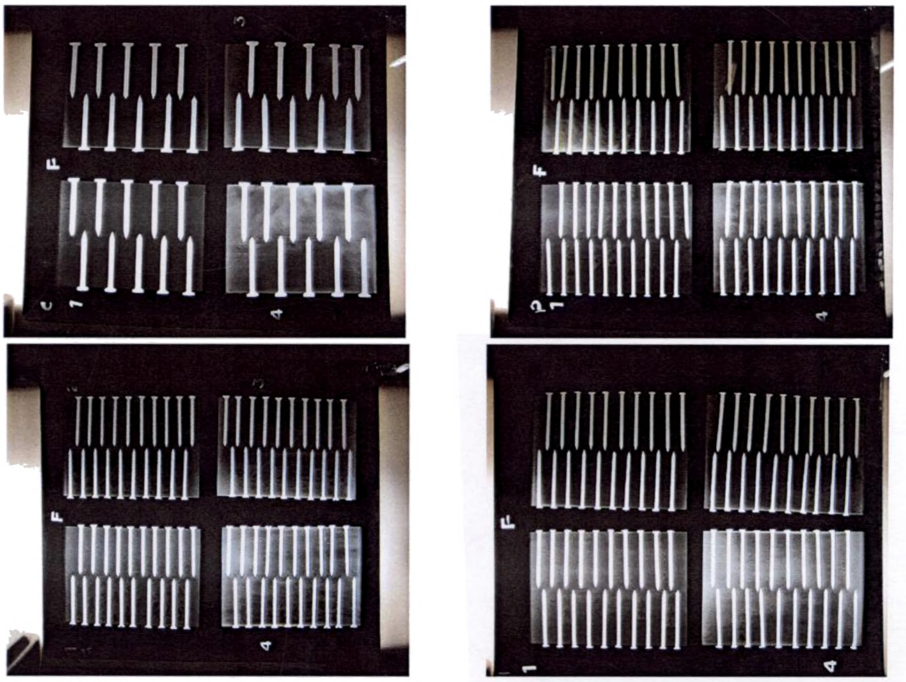


Fig. 7.11: **X-ray photographs of CCA treated rubber wood panels of untreated and of three different retentions nailed with copper, iron, painted iron and galvanized iron nails before exposure in the estuary**

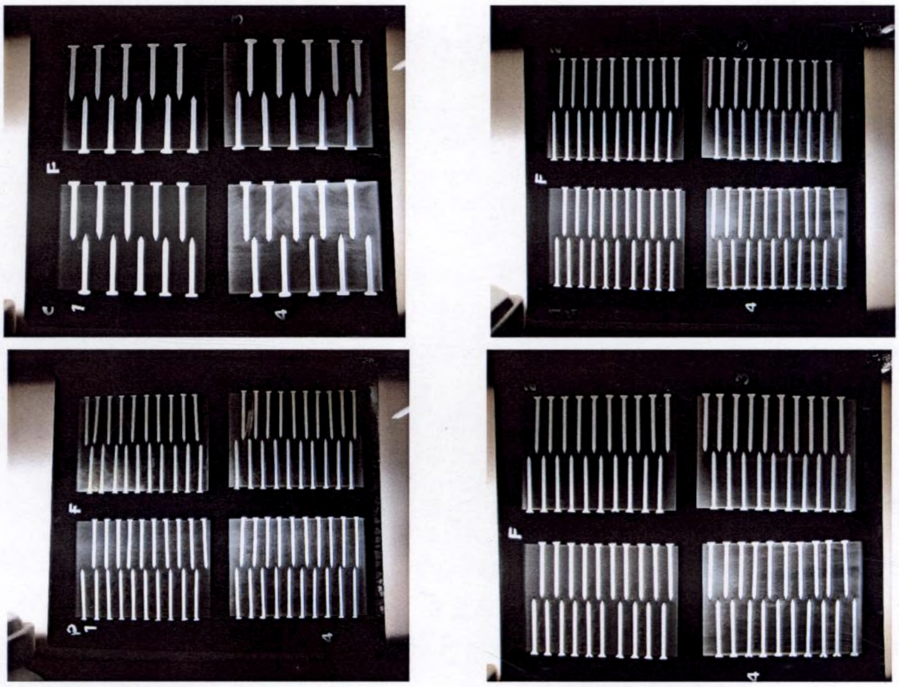
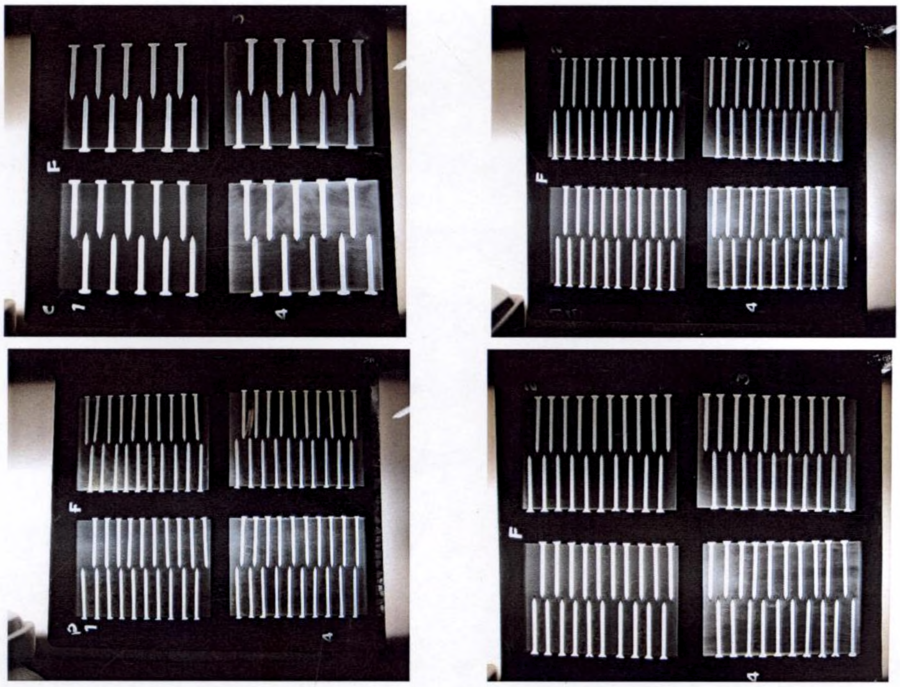


Fig. 7.12: **X-ray photographs of CCA treated rubber wood panels of untreated and of three different retentions nailed with copper, iron, painted iron and galvanized iron nails after exposure in the estuary**



Chapter VIII

Summary and Conclusions

The studies on the environmental impacts of chromated copper arsenate (CCA) treated rubber wood for aquatic applications concentrated mainly on the leaching of CCA under different conditions. Leaching was studied with respect to the effect of preservative retention, the influence of leaching media and the methods of controlling leaching. Also the speciation and the accumulation pattern of the leachate components were also studied. These experiments were conducted both in the laboratory and field conditions. In the laboratory, this study was conducted by keeping preservative treated wood panels in water stirred as well as in stagnant condition by immersing in aquaria. In the natural conditions, this experiment was conducted by exposing the treated wood panels in the estuary. The influence of the nature of leaching media in controlling the rate of leaching was experimented by exposing the treated wood panels in water of varying salinity and pH. The experiment to identify methods to control the leaching of CCA from preservative treated panels was conducted by using multiple treatments using creosote and CCA, by using physical barriers like Fibreglass Reinforced Plastic (FRP) sheathing and by painting after CCA treatment.

The commercially available CCA wood preservative manufactured by Ascu Arch Timber Protection Ltd., Kolkata was taken for the study. CCA is prepared according to Indian Standard 10013-1981. Since the treated wood is put to aquatic applications, retentions above and below 32 kg m^{-3} which is generally prescribed for protection of wood at sea was selected. The selected panels were treated with 7.5% (w/v) CCA solution to get retentions of 16 kg m^{-3}, 29 and 42 kg m^{-3}.

In the accelerated condition, leaching rate of panels was higher in the initial hours and decreased gradually in the later hours. The maximum leaching rate was found for chromium, then for copper and the least for arsenic. For 150 x 100 x 25 mm panels leaching rate was reduced to 10% compared to 19 x 19 x 19 mm panels. 42 kg m^{-3} retention panel was found to leach more in the case of chromium, but for copper and arsenic similar leaching pattern was found for all the three retentions. Also leaching though not prominent in the initial hours, increased gradually and found to continue the same pattern till the end of 336 hours.

In the case of stagnant water, arsenic was found to leach more than copper and chromium, and the rate of leaching of arsenic was similar in accelerated and stagnant conditions. In the case of CCA treated and dual treated panels arsenic is found to leach more than copper and chromium. The pattern of leaching of arsenic was similar in accelerated and stagnant condition. Leaching rate of copper and chromium was less when compared to leaching in accelerated condition.

In the estuarine condition leaching of CCA is found to be very low in the initial six months, the following six months leaching increased slightly. In the last six months leaching is comparably high. This is found to be because of the degradation of panels treated to lower retentions that led to exposure of a greater surface area. In the case of 16 kg m^{-3} only 65% of the CCA components were retained after 18 months of exposure where as for 29 kg m^{-3} and 42 kg m^{-3} 75 and 80% of components were retained respectively after the same period. In the case of FRP sheathed and painted panels more than 85% of the preservative was retained after 18 months of exposure.

In the experiment to identify the influence of the nature of media in leaching of CCA, 16 kg m^{-3} panels exposed to 2.5 pH solution were found to leach 80% more copper, 20% more chromium and 10% more arsenic than panels exposed to 4.5 pH solution for 336 h and for 42 kg m^{-3} panels when exposed to 2.5 pH solution found to leach 30% more copper, 10% more chromium and 5% more arsenic than panels exposed to 4.5 pH solution for 336 h. The panels having 16 kg m^{-3} retention, when exposed to a solution having pH 7 leaching was found to be slightly higher than that exposed to solution of pH 8.5. Similarly, the leaching from 42 kg m^{-3} retention panels when exposed to solution of pH 7 was double than that exposed to 8.5 pH solution.

In the experiment to identify methods to control leaching, FRP sheathed panels and painted panels leached negligible quantities of copper, chromium and arsenic when compared to unsheathed panels and dual treated panels also reduced leaching to 10% of that leached from unsheathed panel.

The results of the corrosion studies conducted in the laboratory show that rate of corrosion of copper nails increase with increase in retention of the CCA treated panel. The highest corrosion rate was found for copper nails used in 42 kg.m^{-3} panels and the lowest in the control panel. Also, corrosion rate was maximum for iron nails driven into panels having retention of 42 kg m^{-3}. This is significantly higher than the rate of corrosion of nails driven in control panels. In the case of 16 kg m^{-3} and 29 kg m^{-3} the values were not significantly different from nails driven into the control panel. This suggests that higher retentions of preservative accelerate corrosion of iron nails. 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 nails driven into 42 kg m^{-3}. In the case of galvanized iron nails corrosion rate was in the descending order 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 found to decrease from control panel to 42 kg m^{-3} retention panel. Iron nails were also found to have a decrease in corrosion rate for nails used in control panel to that nailed in 42 kg m^{-3}. In the case of painted iron nails, corrosion rate was similar in nails driven into control and 16 kg m^{-3} retention panels. Corrosion rate was found to decrease for nails driven into panels having retentions 29 and 42 kg m^{-3} respectively. For galvanized iron nails rate of corrosion was negligible for all the four types of panels. The nail pulling force was maximum for tangential side for the retention 36 kg m^{-3}. The lowest value was reported for the end surface for the control panel. Radial face also has values near to tangential face. Screw pulling force is found to be more than nail pulling force. In the case of screw pulling, highest value was reported for tangential side in the case of 16 kg m^{-3} and that from radial side for 26 kg m^{-3}. Lowest value was for end surface for control panel.

Recommendations

- Optimum retentions of CCA around 29 kg m^{-3} are more preferable for aquatic applications in order to ensure optimum durability coupled with minimum environmental contamination through leaching.
- The application of finishes like FRP sheathing and painting with coal tar epoxy of CCA treated rubber wood is found effective for reducing leaching as they retained more than 85% of the preservative after 18 months of exposure. Hence CCA treatment can be effectively used in combination with sheathings.
- Copper or galvanized iron nails are better choice compared to iron and painted iron nails for application in CCA treated wood for use in aquatic environment.
- The increase in the load required for pulling of nail and screw in preservative treated wood concludes that CCA does not affect the strength of the wood.
- Further studies in this regard should focus on alternative wood preservatives in which arsenic is replaced with some other elements having preservative properties since arsenic in the (III) state is carcinogenic.

References

Ahrland, S. (1975) Metal Complexes Present in Seawater. In: Dahlem Workshop on the Nature of Seawater. (Ed. Goldberg, E.D.) Physical and Chemical Sciences Research Report1.

Albuquerque, R.M. & Cragg, S.M. (1995a) Evaluation of impact of CCA-Treated Wood on the Marine Environment (IRG/WP 95-50040, The International Research Group on Wood Preservation, Stockholm).

Albuquerque, R.M. & Cragg, S.M. (1995b) Fouling organisms as the indicators of the Environmental Impact of Marine Preservative Treated Wood (IRG/WP 95-50063, The International Research Group on Wood Preservation, Stockholm).

Albuquerque, R.M., Cragg, S.M. & Icely, J.D. (1996) Leaching of CCA Treated Wood Submerged in Seawater: Effects of High Loadings, and a comparison between Laboratory and Marine Conditions (IRG/WP 96-50080, The International Research Group on Wood Preservation, Stockholm).

Andreae, M.O., 1978. Distribution and speciation of arsenic in natural waters and some marine algae. *Deep-Sea Research*, Vol. 25, 391-402.

Archer, K. & Preston, A. (1994) Depletion of wood preservatives after four years' marine Exposure in Mt. Maunganui Harbour, NZ. IRG/WP 94-50036, The International Research Group on Wood Preservation, Stockholm.

Arsenault, R.D. (1975) CCA-treated foundations-a study of permanence, effectiveness, durability and environmental considerations. In: proceedings, American Wood Preservers' Association, Washington, DC.

AWPA, (1994) *Book of Standards*. Woodstock, MD. American Wood Preservers' Association, Washington, DC, USA.

AWPA, (1997) Standard method of determining leachability of wood preservatives E11. Book of Standards. p 5 (Granbury, TX: American Wood Preservers' Association, Washington, DC).

AWPI, (1997) The 1996 Wood Preserving Industry Production Statistical Report. American Wood Preservers Institute, Virginia.

Baker, A. J. (1974) Degradation of wood by products of metal corrosion. Forest Products Laboratory, Forest Service, United States Department of Agriculture, Madison.

Baker, A. J., (1980) Corrosion of metal in wood products. In: Durability of Building Materials and Components. ASTM STP 691. P. J. Sereda and G. G. Litram, Eds., American Society of Testing and Materials, pp. 981-993.

Baldwin, W.J., Pasek, E.A. & Osborne, P.D. (1996) Sediment toxicity study of CCA-C treated marine piles. *Forest Products Journal,* 46, pp 42-50.

Becher, G., Oestvold, G., Paus, P. & Seip, H.M. (1983) Complexation of copper by aquatic humic matter studied by reversed phase liquid chromatography and atomic absorption spectroscopy. *Chemosphere,* 12 (9-1), 1209-1215.

Bodek, L., Lyman, W.J., Reehl, W.F. & Rosenblatt, D.H. (1988) (Eds) Arsenic, Chapter 7.2, Environmental Inorganic Chemistry Properties, Processes and Estimation Methods (SETAC special publications service). (Pergamon Press, New York). pp.1-10.

Breslin, V.T. & Alder-Ivanbrook, L. (1998) Release of copper, chromium and arsenic from CCA-C treated lumber in estuaries. *Estuarine and Coastal Shelf Science*, 46, pp 111-125.

Brooks, K.M. (1996) Evaluating the environmental risks associated with the use of chromated copper arsenate-treated wood products in aquatic environments. *Estuaries,* 19, pp 296-305.

Brooks, K.M. (2002) Charactering the environmental response to pressure treated wood. In proceedings. Enhancing the durability of lumber and engineering wood products, Forest Products Society , Madison, WI, pp 59-71.

Brown, C.J., Eaton, R.A. (2001) Toxicity of chromated copper arsenate (CCA) treated wood to non-target marine fouling communities in Langstone Harbour, Portsmouth, UK. *Marine Pollution Bulletin* 42, pp 310-318.

Bruland, K.W., (1983) Trace elements in seawater. In: Chemical Oceanography. (Riley, J.P., Chester, R., eds, Academic Press, London) 8, pp157-220.

Buckley, P.J.M., van den Berg C.M.G. (1986) Copper complexation profiles in the Atlantic Ocean. A comparative study using electrochemical and ion exchange techniques. *Marine Chemistry* 19, pp 281.

Cherian, P.V., Sharma, M.N.& Cherian, C.J., (1979) A study on the leaching of copper-chrome-arsenic (CCA) from some common Indian timbers tested in Cochin harbour waters. *Journal of the Indian Academy of Wood Science*, 10, pp 31-34.

Cooper, P.A., (1991) Leaching CCA from treated wood: pH effects. *Forest Products Journal,* 41, pp 30-32.

Cooper, P.A., Stokes, D. (1993) Leaching characteristics and fixation of copper diethyldithiocarbomate treated wood. In proceedings, (American Wood Preservers' Association, Washington, DC) 89, pp192-203.

Cooper, P.A. (1994) Leaching of CCA: Is it a problem? In: Environmental considerations in the manufacture, use and disposal of Pressure treated Wood. (Forest Products Society, Madison, WI, USA).

Cooper, P.A., Ung, Y.T. & Kamden, P.D. (1997) Fixation and leaching of red maple treated with CCA-C. *Forest Products Journal,* 47, pp 70-74.

Dahlgren, S.E. 1975. Kinetics and mechanism of fixation of Cu-Cr-As wood preservatives. Part5. Effect of wood species and preservative composition on leaching during storage. Holzforschung. 29, pp 84-95.

Damodaran, T.K., Gnanaharan, R. (1994) Upgreadation of rubber wood. KFRI Research Report No. 93. Kerala Forest Research Institute, Peechi.

Eaton, R.A. (1989) An international collaborative marine trial to investigate the effect of timber substrate on the efficacy of CCA and CCB wood preservatives. *Material and Organismen,* 24, pp 51.

Edwin, L., Saly N. Thomas, N. Unnikrishnan Nair and K. Ravindran (1993) Dual preservative treatment for small fishing vessels-Observations on the mango wood. Low energy Fishing, *Fishery Technology (Spl. Issue)* Society of Fisheries Technologists (India), Cochin, pp 98-102.

Edwin, L., Thomas, S.N. (2000) Effect of creosote and copper-chrome-arsenic treatments on the compressive strength of Haldu wood (*Adina cordifolia* Benth & Hook). *Fishery Technology,* Society of Fisheries Technologists (India), Cochin, 37 (1), pp 1-4.

Edwin, L., Gopalakrishna Pillai, A.G. (2004) Resistance of preservative treated rubber wood to (*Hevea brasiliensis*) marine borers *Holz Roh Werkst,* 62, pp 303-306.

Edwin, L., Thomas, S.N., Meenakumari, B. (2005) Utilization of Rubber Wood for Fishing Canoe Construction. *Fishery Technology* Society of Fisheries Technologists (India), Cochin, 42 (1), pp 47-54.

Fahlstrom, G.B., Gunning, P.E. & Carlson, J.A. (1967) Copper-Chrome-Arsenate wood preservatives: a study of the influence of composition on leachability. *Forest Products Journal* 17, pp17-22.

Findlay, W.P.K. (1985) Preservative Methods. In: Findlay, W.P.K. (Ed), Preservation of Timber in the Tropics, Martinus Nijhoff/ Dr. W. Junk Publishers, Dordrecht, pp 141-157.

Fleming, C.A., Trevos, J.T., (1989) Copper toxicity and chemistry in the environment: review. *Watrer, Air and Soil Pollution* 44, pp 143-158.

Gairola, S., Aggarwal, P. (2005) Status of wood preservation in India. (IRG/WP 05-30386, The International Research Group on Wood Protection, Stockholm).

Gnanaharan, R., Mathew, G. (1982) Preservative treatment of rubber wood (Hevea brasiliensis). KFRI Research Report: 15. Kerala Forest Research Institute, Peechi.

Gnanaharan, R., Damodharan, T. K. (1992) Mechanical properties of rubber wood from 35-year old plantation in central Kerala, India. *Journal of Tropical Forest Science* 6, pp 12-16.

Greaves, H. (1972) Structural distribution of chemical components in preservative treated wood by energy dispersion X-ray analysis. *Material and Organismen* 7 (4), pp 277-286.

Greaves, H. (1973) *X-ray analysis of selected anatomical structures in copper chrome arsenate treated wood* (IRG/WP 320, The International Research Group on Wood Preservation, Stockholm).

Greaves, H. (1974) The micro distribution of copper chrome arsenic in preservative treated sap woods using X-ray micro analysis in scanning electron microscopy. *Holzforschung,* 28 (6), pp 193-200.

Green, C.A. Smith, G.M. & King, B. (1989) The effects of aqueous leaching on the moisture uptake and decay of CCA-treated wood exposed to soil burial. *Material and Organismen,* 24, pp 193-205.

Hager, B. (1969) Leaching tests on copper-chromium-arsenic preservatives. *Forest Prod J,* 19, pp 21-26.

Hartford, W. H., (1980) An attempt to summarize pertinent technical and economical facts relating to the CCA treatment of poles. Report submitted to AWPA T4/P4 Ad Hoc committee on conductivity and corrosion.

Hayes, C., Curran, P.M.T. & Hynes, M.J. (1994) Preservative leaching from softwood submerged in Irish coastal waters as measured by atomic absorption spectrometry. *Holzforschung,* 48, pp 463-473.

Hegarty, B.M. & Curran, P.M.T. (1986) Biodeterioration and micro distribution of copper chrome arsenic (CCA) in wood submerged in Irish coastal waters. *Journal of International Wood Science,* 10, pp 245-253.

Hingston, J.A., Collins, C.D., Murphy, R.J. & Lester, J.N. (2000) Leaching of chromated copper arsenate wood preservatives: a review. *Environmental Pollution* 111, pp 53-66.

Hingston, J.A., Moore, J., Bacon, A., Lester, J.N., Murphy, R.J., Collins, C.D. (2002) The importance of short term leaching dynamics of wood preservatives. *Chemosphere 47*, pp 517-523.

Hong, L.T., Seyain, M.A., Goh, T.A., Daljeet Singh, K.D. (1982) Preservation and protection of rubber wood against biodeteriorating organisms for more efficient utilization. *The Malaysian Forester* 45, pp 299-315.

Irvine, J., Eaton, R.A. & Jones, E.B.G. (1972) The effect of water of different ionic composition on the leaching of water-borne preservative from timber placed in cooling towers and in the sea. *Material and Organismen*, 7, pp 45-71.

Irvine, J., Dalgren, S.E. (1976) The mechanism of leaching of copper-chrome-arsenic preservatives in saline waters. *Holzforschung,* 30, pp 44-50.

Johnson, B.R. (1977) Performance of single panel and dual treated panels in a semi-tropical harbour. In: Proceedings of the American Wood Preservers' Association, Washington, DC, pp73.

Johnson, B.R. (1982) A look at creosote versus chromated copper arsenate salts as wood preservatives for the marine environment. *Ind Eng Chem Prod,* 21 pp704-705.

Kartal, S.N., Won-Joung Hwang. & Yuji Imamura. (2004) Effects of hard water, sea water and humic acid on the release of CCA components from treated wood. (IRG/WP 05-50228, The International Research Group on Wood Protection, Stockholm).

Kartal S. N. & Imamura Y (2005) Effects of N'-N-(1, 8-Naphthalyl) hydroxylamine (NHA-Na) and hydroxynaphthalimide (NHA-H) on boron leachability and biological degradation of wood. *Holz als Roh und Werkstoff* 62 (5), pp 378-385.

KFRI, (2002) Preservative Treatment of Exterior Woods for Landscape Architecture, Proceedings of 3rd Wood Preservation Symposium, Korea Forest Research Institute, Seoul, Korea.

Kim,J.J., Kim, G.H. (1993) Leaching of CCA Components from treated wood under acidic conditions. (IRG/WP 93-50004, The International Research Group on Wood Preservation, Stockholm).

Kramer, C.J.M. (1986) Apparent copper complexation capacity and conditional stabilty constants in North Atlantic waters. *Marine Chemistry* 18, pp 335-345

Kumar, S., 1985. Wood preservation practices for marine application. In: Harvest and Post- harvest technology of Fish. (Ravindran, K., Nair, U.N.,Perigreen, P.A., Madhavan, P., Pillai, A. G. G., Panicker, P.A., and Thomas, M., Eds), Society of Fisheries Technologists (India), Cochin.

Kumar S., Dev, I. (1993) Wood preservation in India. Indian Council of Forestry Research and Education, Dehradun pp 263.

Kuppusami, V., Balaji, M., Rao, M.V., and Rao, S. (2002) Leaching of CCA From Bombax ceiba Catamarans in operation for 15 yeas. Institute of Wood Science and Technology, Bangalore. (IRG/WP 02-50191, The International Research Group on Wood Preservation, Stockholm).

Langston, W.J. (1990) Toxic Effects of Metals in the Incidence of Metal Pollution in Marine Ecosystems. In: Heavy Metals in the Marine Environment. (CRC press, Boca Raton, Florida).

Lebow, S.T., (1996) Leaching of Wood Preservative Components and their Mobility in the Environment. Summary of Pertinent Literature.

(United States Department of Agriculture, Forest Service, Forest Products Laboratory, Madison, WI).

Lebow, S.T., D.O. Foster & Lebow P.K. (1999) Release of copper chromium and arsenic from treated southern pine exposed in seawater and freshwater. *Forest Products Journal,* 49 (7/8), 80-89.

Lebow, S.T., P.K. Lebow. & D.O. Foster. (2000) Environmental Impact of preservative treated wood in a wetland boardwalk. Part1. Leaching and Environmental accumulation of preservative elements. (FPL- RP-582. Madison, WI: U.S. Dept. of Agriculture, Forest Service, Forest Products Laboratory) pp126.

Lebow, S.T., 2002. Coatings Minimize Leaching from Treated Wood. Forest Products Laboratory Madison, WI: United States Department of Agriculture, Forest Service.

Lebow, S.T., Brooks, K.M. & Simonsen, J. (2002) Environmental Impact of treated wood in service. In: Proc. Enhancing the durability of lumber and engineered wood products, Kissimmee, FL. (Forest Products Society, Madison, WI), pp 205-215.

Lee, A.W.C., Grafton, J.C. & Tainter, F.H. (1993) Effect of rapid redrying shortly after treatment on leachability of CCA-treated southern pine. *Forest Products Journal,* 43, pp37-40.

Leightly, L.E. (1987) Chemical analysis of IRG/ COIPM international marine test samples. (IRG/WP 4114 The International Research Group on Wood Preservation, Stockholm).

Livens, F.R. (1991) Chemical reactions of metals with humic material. *Environmental Pollution* 70, pp 183-208.

Lu, J.C.S., Chen, K.Y. (1976) Migration of trace metals in interfaces of seawater and polluted surficial sediments. *Environmental Science and Technology.* 11: pp 174-182.

Morgan, J.W.W., Purslow, D.F. (1973) Physical and chemical aspects of preservative treatment by non-pressure methods. *Holzforschung,* 27, pp 153-159.

Murphy, R.J., Dickinson, D.J. (1990) *The effect of acid rain on timber.* (IRG/WP 3579, The International Research Group on Wood Preservation, Stockholm).

National Physical Laboratory, 2003. www.npl.co.uk/lmm/docs/corrosion_checklist.pdf viewed on 24-11-06

National Physical Laboratory, 2003. www.npl.co.uk/lmm/docs/corrosion_of_metals_by_wood.pdf viewed on 24-11-06

North and MacLeod, 1987. http://www.pastfoundation.org/Arizona/Rationale_3.htm viewed on 23-11-06.

Orsler, R.J., Holland, G.E. (1993) Assessment of Losses of Wood Preservatives from Treated Wood by Leaching into the Environment.

2nd International Symposium on Wood Preservation, (Cannes-Mandelieu, France).

Peek, R.D. & Willeitner, H. (1981) Fundamentals of Steam Fixation of Chromated Wood Preservatives (IRG/WP 3483, The International Research Group on Wood Preservation, Stockholm).

Penrose, W.R., (1974) Arsenic in the Marine and Aquatic Environments: Analysis, Occurrence and Significance. CRC Critical Reviews in Environmental Control. 465-482

Pizzi, A. (1982b) The chemistry and kinetic behaviour of CCA/B wood preservatives III Fixation of a Cr/As system on wood. *Journal of polymer science and Polymer Chemistry* 20, pp 725-738.

Placket, D.V., (1984) Leaching tests on CCA treated wood using inorganic salt solution (IRG/WP 3310). The International Research Group on Wood Preservation, Stockholm.

Putt, A.F. (1993) Sediment bound CCA-C leachate 10 day repeated exposure toxicity to Amplisca abditta Under Static conditions. (Springborn Laboratories Inc, Wareham, MA, USA).

Rao, K.S., Santhakumaran, L.N., Balaji, M., Srinivasan, V.V. (1993) Natural Resistance of rubber wood to marine borers and preliminary note on the effects of the preservative treatment. *Indian Journal of Natural Rubber Research* 6, pp 71-74.

Ravindran, K. Gopalakrishna Pillai, A. G. & Balasubramanyan, R. (1985) Corrosion behaviour of metallic fastenings in contact with wood.

Ross, A.S., Bussajaeger, S., Carlson, R. and Feist. W.C., (1992) Professional Finishing of Pressure Treated Wood. American Painting Contractor, 69 (7): 107-114.

Rubber Board (2005) Rubber board, Ministry of Commerce and Industry, Government of India, http://rubberboard.org.in/rubberstatisticsdisplaypage.asp

Ruddick, J.N.R., Yamamoto, K., Wong, P.C. & Mitchell, K.A.R. (1993) X-ray photoelectron spectroscopic analysis of CCA-treated wood. *Holzforschung*, 47, pp 458-464.

Ryan, K.G., Plackatt, D.V. (1987) The interaction of polyflavinoid tannins with CCA in *Pinus radiata.* IRG/WP/3422. (IRG secretariat, Stockholm, Sweden).

Salomons, W.& U. Forstner (1984) Metals in the Hydrocycle. (Springer-Verlag, Berlin) pp 349.

Sanders, J.G., Windom, H.L. (1980) The uptake reduction of arsenic species by marine algae. *Estuarine and Coasalt Marine Science,* 10, pp 555-567.

Sanders, J.G., Reidel, G.F., (1987) Control of trace element toxicity by phytoplankton. In: Phytochemical Effects of Environmental Compounds edited by Saunders, J.A., Kosak-Channing, L., Conn, E.E., (Plennum Press, New York), pp 131-149.

Schindler, D.E. (1999) Sheathing wood with FRP. http://www.practicalsailor.com/newspics/charts/876sheathingwood.pdf viewed on 09-06-06.

Schniewind, A.P. and Arganbright, D.G., (1984) Coatings and their effect on dimensional stability of wood. Waac Newsletter, 6 (2): 2-5.

Shukla, S., Lal, M. (1985) Physical and mechanical properties of *Hevea brasiliensis* (Rubber wood) from Kerala. *Journal of Timber Development Association (India)*, 31, pp 29-30.

Stilwell, D.E., (1998) Arsenic from CCA treated wood can reduced by coating. Frontier Plant Science. 51(1) pp 6-8.

Stilwell, D.E. and Musante, C.L., (2004) Effect of coatings on CCA leaching from wood treated in a soil environment. In: Environmental impacts of preservative treated wood, pre conference proceedings, 8-11 February, 2004 Orlando, Florida, USA, pp 113.

Tarakanadha, B. & Rao, K.S. (2006) Leaching of CCA from *Paraserianthus falcataria* panels exposed to field conditions at Krishnapatnam harbour, Andhra Pradesh. (IRG/WP 06-50241 The International Research Group on Wood Protection, Stockholm).

Thomas, S.N., Edwin, L & Ravindran, K. (1998) Effect of single and dual preservative treatments on the strength of boat building timbers. In: Advances and Priorities in Fisheries Technology (Balachandran, K.K., Iyer, T.S.G., Madhavan, P., Joseph, J., Perigreen, P.A., Raghunath, M.R., and Varghese, M.D. Eds.) Society of Fisheries Technologists (India), Cochin, 117-120.

Timber Preserver's Association of Australia, (2006) http://www.tpaa.com.au/fastenerscca.htm viewed on 30-11-06

Townsend, T., Stook, K., Tolaymat, T., Song, J.K., Solo-Gabriele, H.M., Hosein, N., Khan, B. (2001) New lines of CCA –treated wood research: In service and disposal issues. (Florida Center for Hazardous Waste Management, Gainesville).

Van Eatvelde, G., Homan, W.J., Militz, H. & Stevens, M., (1995) Effect of Leaching Temperature and Water Acidity on the Loss of Metal Elements from CCA Treated Wood in Aquatic Applications. Part1. Laboratory Scale Investigation (IRG/WP 95-50046, The International Research Group on Wood Preservation, Stockholm).

Warner, J.E., Solomon, K.R. (1990) Acidity as a factor in leaching of copper, Chromium and arsenic from CCA-treated dimension lumber. *Environmental Toxicology and Chemistry,* 9, pp 1331-1337.

Weis, P., Weis, J.S. & Coohil, L. (1991) Toxicity to estuarine organisms of leachates from chromated copper arsenate treated wood. *Archives of Environmental Contamination and Toxicology,* 20, pp 188-194.

Weis, P., Weis, J.S., Greenberg, A., Nosker, T.J. (1992) Toxicity of construction materials in the marine environment: A comparison of

CCA-treated wood and recycled plastic. *Archieves of Environmental Contamination and Toxicology* 22, pp 99-106.

Whitney, R. S., ·(1979) Timber fasteners and potential problems of corrosion. Building Research Association of New Zealand, BRANZ Reprint No. 10, 25 pp.

Williams, R.S. and Fiest, W.C., (1993) Durability of paint or solid-colour stain applied to pre weathered wood. *Forest Products Journal* 43(1): 8-14.

Williams, L., 2002. http://www.wral.com/money/1620661/detail.html viewed on 12-07-06.

Williams, R.S., 2005. Weathering of wood. In: Roger M. Rowell (Eds.). Handbook of wood chemistry and wood composites. Tylor & Francis, New York, pp. 139-186.

Wilson, A. (1971). The effects of temperature, solution strength and timber species on the rate of fixation of a copper-chrome-arsenate wood preservative. Institute of Wood Science 5(6): pp 36-40.

Xiao, Y., Simonson, J., Morrel, J.J. (2002) Effects of water flow rate and temperature on leaching from creosote treated wood. Research Note (FPL-RN-0286. Madison, WI: U.S.D.A., Forest Service, Forest Products Laboratory).