CORROSION BEHAVIOUR OF ZINC AND ZINC ALLOY COATED STEEL FASTENERS IN TIMBER

CHUNXIAN ZOU

Master of Philosophy

THE UNIVERSITY OF ASTON IN BIRMINGHAM

October 1993

THE UNIVERSITY OF ASTON IN BIRMINGHAM

The Corrosion Behaviour of Zinc and Zinc Alloy Coated Steel Fasteners in Timber

Chunxian Zou

Submitted for the Degree of Master of Philosophy 1993

Summary

The corrosion behaviour of a wide range of zinc and zinc alloy coated steels (hot-dip galvanised and electrodeposited), with or without a conversion coating treatment, in timber environments has been investigated using electrochemical measurement and SEM/EDXA analysis.

The corrosion tests were carried out on specimens immersed in copper/chromium/arsenic (CCA) "salt" and "oxide" formulated solutions for rapid preliminary evaluation of corrosion performance. The polarisation resistance was measured in CCA "salt" solution as a function of time, while the corrosion behaviour in CCA "oxide" solution was determined by potentiodynamic scan.

A corrosion sensor was devised to assess the corrosion performance of coated steels in CCA treated timber by measuring corrosion potential and polarisation resistance. The effect of moisture content of timber on the corrosion of zinc coated steels was also carried out using the sensor. It was found that the sensor worked well, even at low moisture content. The sensor is simple, easy to construct and has the potential to be used in field studies.

The ranking of corrosion tendency of zinc and zinc alloy coated steels in CCA solution and CCA treated timber has been given based on electrochemical measurements and SEM/EDAX analysis. It was found that the corrosion resistance of zinc coated steels is significantly improved by the addition of alloying element and conversion coating. The Zn-55%Al and Zn-12.5%Ni coated steels were found to give the best corrosion performance.

Surface observation and analysis of the wood and coated steel samples were conducted using SEM/EDAX. Evidence of cracking and pits were observed on a number of coated steels and general corrosion products found were $Zn(OH)_2$ and $ZnSO_4$. The corrosion mechanism and service life prediction have been discussed.

Keywords: Corrosion, Polarisation resistance, Timber, CCA preservatives, Zinc alloy, Coated steel, Conversion coatings, Electrochemical sensor, Moisture content.

DEDICATION

FOR SHENGQI AND YAO

ACKNOWLEDGEMENTS

I am sincerely indebted to Dr. N. R. Short for his invaluable supervision, continual interest and encouragement, and arrangement of financial support.

I am also grateful to Dr. J. K. Dennis for his guidance and valuable suggestion.

I also thank:

Colleagues in the Laboratory for their help and stimulating discussion;

The technical staff of the Department;

My husband, parents and whole family for their constant support, patient and long-suffering.

CONTENT

Figure List

Table List

Chapter 1

Introduction and Aims of the Investigations

Timber has been used in a variety of applications ranging from engineering materials to a source of energy, and is one of the oldest and most widely used construction materials. Although many new materials have been introduced, timber, today, is still valuable as an engineering material because of its inherent structure, properties and renewable nature. For example, timber is widely used for frames and trussed rafter roofs in the U.K., cladding and weather board in North America and foundations for commercial buildings in New Zealand.

Metal fasteners are widely used for joining timber. The efficiency and success of timber as a construction material depend on the integrity of wood-metal joints. Under dry conditions, wood and metal are usually compatible, conversely, under damp conditions, wood needs to be treated with chemical preservatives to allow its use in wet conditions. The most commonly used chemical preservatives for construction timber are oxide and salt formulated copper/chromium/arsenic (CCA) water-borne solutions. Treated timber in a high humidity environment can be a very corrosive medium for metal fasteners, with subsequent deterioration of joint strength and hence structural integrity. Under harsh environmental conditions, the selection of fastener materials must be carefully considered to avoid or reduce the corrosion risk.

Pure zinc coatings continue to be used widely for the protection of steel from corrosion, since the general corrosion rate of zinc is much less than that of steel and the zinc sacrificially protects exposed steel substrata at e.g. cut edges and accidental damage. Consequently zinc coated steel has found use in a wide range of construction application[1,2]. In particular it is used for timber fasteners such as metal plates, joist hangers, nails etc.

Considerable efforts are being made to improve the corrosion resistance of zinc coatings for use in harsher environments, longer service life, or reduced coating thickness for a given service life. Attempts at improvement have concentrated on: alloying the zinc with elements such as aluminium[3], iron[4,5], nickel[4,6] or cobalt[4,7]; developing new conversion coating treatments; or painting/power coating. It has recently become evident that there is a considerable synergistic effect between improvements in general corrosion resistance found by addition of alloying elements to the zinc and improvements found by the use of compatible conversion coating treatment, resulting in coatings with a much greater potential for use in construction applications[8-15]. However, two problems may arise, either the degree of sacrificial protection is reduced or the coating may be more susceptible to failure by pitting. Whilst the corrosion behaviour of these new coating systems has been studied for other applications such as automotive industry, no investigations have been made for their use in chemical preservative treated timber.

This present work is aimed at carrying out a fundamental investigation to assess the corrosion performance of passivated zinc and zinc alloy coated steel when used in contact with preservative treated timber.

These investigations should provide:

(i) Data for service life prediction of a series of passivated and unpassivated zinc and zinc alloy coated steel in contact with water saturated CCA treated timber.

(ii) A fundamental understanding of the corrosion mechanism of these materials in CCA treated timber.

(iii) A simple electrochemical sensor which would be useful for evaluating and monitoring the behaviour of the new coating systems in extended field studies.

Investigations were carried out as follows:

(a) A wide range of commercial zinc and zinc alloy coated steel, with or without conversion coatings, were characterised with regard to composition and structure.

(b) Oxide and salt formulated CCA solutions were used to simulate a preservative treated timber environment for rapid preliminary evaluation of the corrosion performance of zinc and zinc alloy coated steels and the characterisation of corrosion products. Techniques used included linear polarisation and potentiodynamic polarisation scans.

(c) The development of a simple electrochemical sensor to aid in the evaluation of corrosion behaviour in treated timber.

Chapter 2

Literature Review

2.1 Structure, Properties and Use of Timber

2.1.1 Timber Structure and Chemistry

Timbers are classified as hardwoods and softwoods. Hardwoods are produced from broad leaf trees and mainly employed for decorative purposes such as flooring and furniture, but they are playing an increased structural role with the aid of new designs and synthetic resin glues. The structure of hardwoods is more complex than that of softwoods and the elements that compose the wood are more varied. A pictorial diagram of a typical hardwood, greatly enlarged, is shown in Figure 2.1[16]. Softwoods are produced from needle leaf trees and provide most of the timber used in building today. It is particularly suitable for external use such as windows and doors and internally for rafters etc. It is durable, fairly strong and easily worked by machines and hand tools because of its softness and straight grain. The structure of softwoods is simpler than that of hardwoods. A pictorial diagram of a typical softwood, greatly enlarged, is shown in Figure 2.2[16]. The softwood cell wall accounts for 98% of the wood material. The cell walls are of layered structure composed of polymeric compounds, primarily cellulose fibrills interspersed with hemi-cellulose and lignin which surround the lumen. The lumen forms the main channels for flow of sap or preservative solution through the timber. Flow of materials between adjacent cells occurs via openings in the cell wall known as pits. Between the cells is the middle lamella. The microstructure of wood and the molecular structure of a cell wall are shown in Figure 2.3 and Figure 2.4 respectively[17]. This is amorphous and contains a high concentration of lignin. A typical chemical analysis for scots pine is 52% cellulose, 22% hemicellulose, 26% lignin. Linear cellulose chains are aligned and stiffened by the formation of intra and inter molecular hydrogen bonds to form the fibrils which make up the cell wall layers. Hemicelluloses are polysaccharides composed of various sugar units, with shorter molecular chains than cellulose and branching of the chains. The hemicelluloses do not pack as well as cellulose polymers. Lignin is a polyphenolic branched polymer which fills the spaces between the polysaccharide fibrillar elements of the cell wall. Coniferyl alcohol is the predominant precursor of the softwood lignin.

In both softwood and hardwood there is an annular band of wood nearest to the bark, called the "sapwood". The central core of the wood inside this wood is known as the "heartwood". The function of the sapwood is to transport the sap from the roots up the trunk to the leaves. The heartwood does not carry out this function, but gives mechanical support to the trunk. Only minor changes occur in the anatomical structure of the wood when sapwood changes into heartwood. A feature of this change is the entry of air into the tracheids and vessels, replacing the sap. As a result of this, the cells in the wood parenchyma and in the rays die and no longer store reserve food materials. It is well known that heartwood is more resistant to decay.

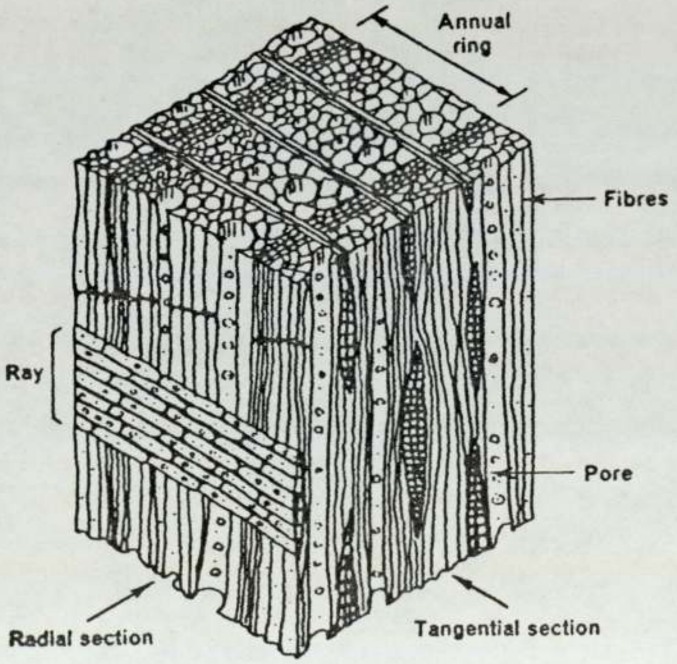


Figure 2.1 Small piece of hardwood greatly enlarged[16]

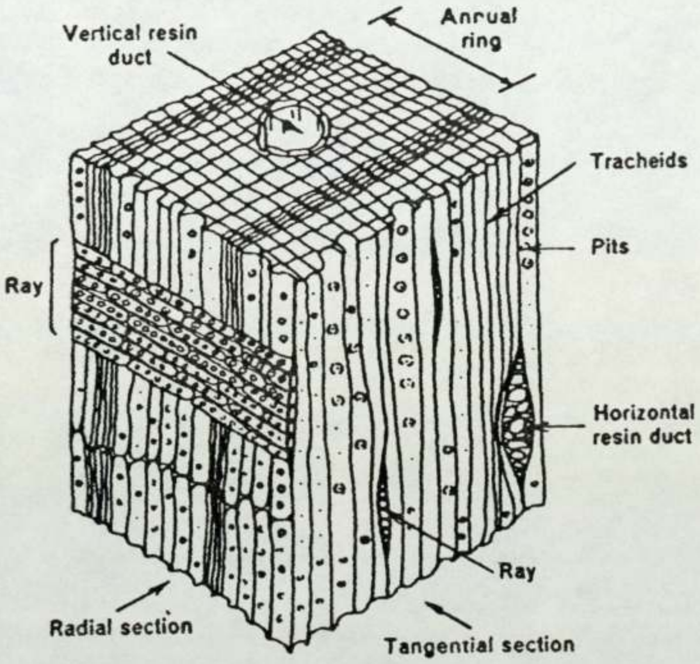


Figure 2.2 Small piece of softwood greatly enlarged[16]

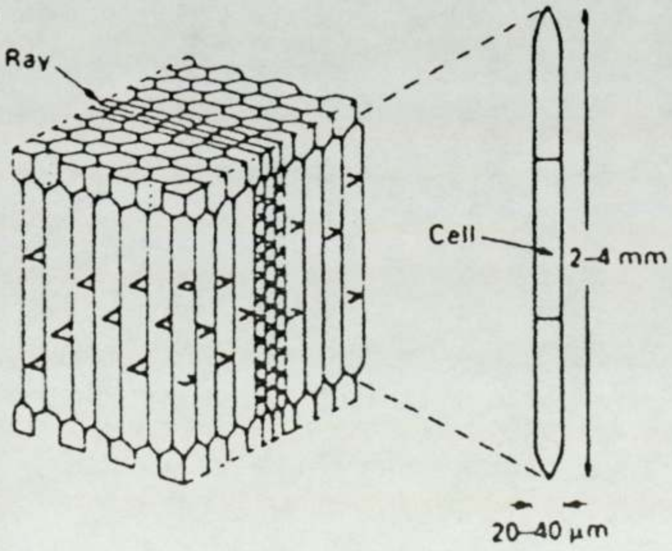


Figure 2.3 The microstructure of wood[17]

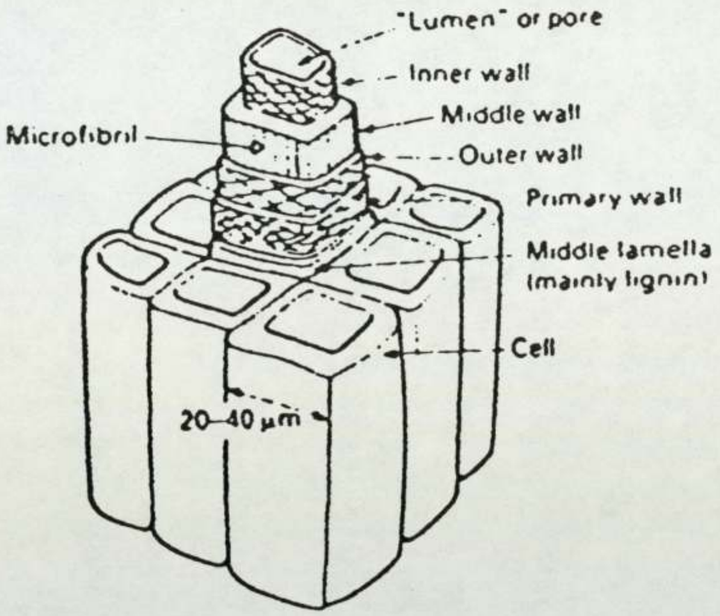


Figure 2.4 The molecular structure of a cell wall[17]

2.1.2 Moisture Content

Timber is a hygroscopic material and so its moisture content changes when the RH of its environment changes until equilibrium is achieved. When it has a relatively higher moisture content than the surrounding air, it will dry out and shrink, whilst when these condition are reversed it will absorb moisture and swell. Green wood contains moisture which saturates most of the cell wall and fills or partly fills many of cell pores in the sapwood. During drying the "free" moisture is first lost from the cell space and this involves little change in properties except a change in density. Eventually drying will result in the wood reaching the fibre saturation point, normally at a moisture content of 25-30 per cent, where further drying results in the loss of "bound" moisture of the cell wall. The loss of bound water typically results in shrinkage and progressive change in physical properties, for example, the effect of drying on compressive strength for pine samples is shown in Figure 2.5[18]. Moisture is a very important factor and effects the behaviour of timber in a number of very critical ways. Untreated timber must remain at moisture content below about 18 per cent to avoid timber decay.

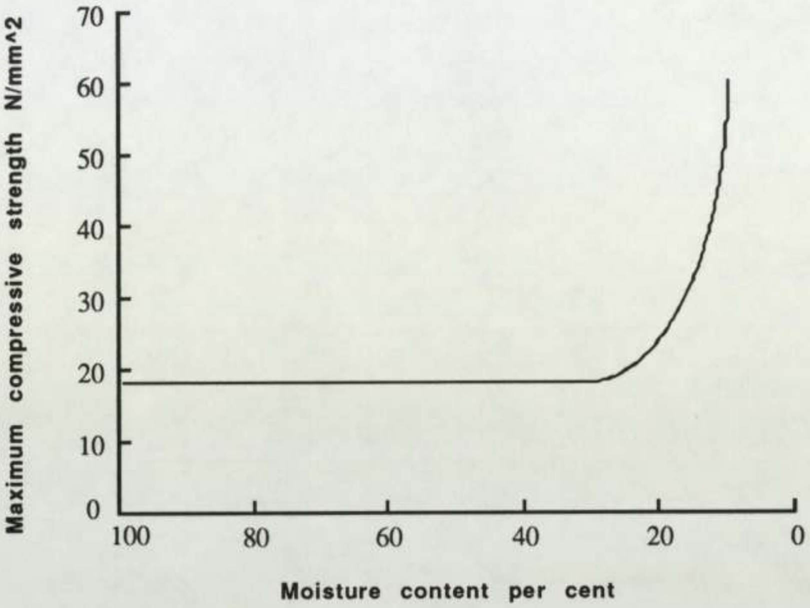


Figure 2.5 Effect of drying on compression strength on pine sample[18]

2.1.3 Properties and Use of Timber

As a result of its cellulose structure timber is the only natural material which combines the advantages of being strong in tension and reasonably strong in compression. It is a light material with a high bending strength. Its strength to weight ratio is excellent and this character makes timber an appropriate for spanning large open spaces without resorting to the cumbersome business of stone vaulting. Dry timber is a poor conductor of heat and electricity, since it contains a considerable volume of air enclosed in the cells. This excellent insulating property of timber makes it a particularly suitable material for walls of buildings in cool climates. The lower thermal conductivity renders it suitable for the construction of fire resistant doors. Moreover, timber has good resistance to alkalis and weak acid, so it is also very suitable for the construction of buildings in which chemical processes releasing acidic vapours may be carried out. Last, but not least, another major use of timber is the timber trussed rafter roof, that will be described in 2.4. Timber has always been a useful, economical and durable material, provided that the right kind and correct grades are chosen and that it is seasoned to the correct moisture content and is used in a suitable environment.

2.2 Timber Preservation

When timber is being used as a structural material, its durability is a matter of the utmost concern. No timber is immune to deterioration if exposed for a sufficiently long period to the natural environment. The serviceable life of timber depends on the species concerned, the amount of sapwood present, the use to which the timber is put and the situation and environmental conditions. It may include resistance to fungi decay, insect attack and mechanical wear, and different timbers vary enormously in their resistance to degradation. No species is completely and permanently resistant to all forms of decay. When suitable physical and chemical preservative treatments are used for timber, its serviceable life will be increased significantly .

2.2.1 Deterioration and Preservation of Timber

Timber is a material which is composed almost entirely of organic matter and deterioration is mainly by fungi and wood boring insects. They destroy the wood substance so that the whole loses strength and form. Like other living plants fungi need suitable conditions for germination and development[16,19]. Firstly, wood destroying fungi and insects need a food supply in order to live, their food being the wood. Secondly, sufficient moisture must be present in timber for decay to occur. The moisture content of timber is usually the most critical factor in the establishment and continuation of decay of timber, and at least 20 per cent moisture content is necessary for any fungi to develop. While under very dry conditions, below 10-12 per cent, even the most hardy insects can not breed. Thirdly, fungi require oxygen for growth and respiration, if air is excluded, fungi will be killed. Finally, fungi growth needs a suitable temperature, the overall limits of fungi growth are up to blood heat and down to the freezing point of water, at low temperature growth slows or may cease altogether. However many fungi can survive exposure to low temperature for long periods. High temperatures in excess of 38°C destroy fungi and the most favourable temperature for fungi rapid growth is about 23°C. In brief, the risk of attack by fungi will be eliminated if any factor which is described above is removed. However, sometimes, timber has to be used in damp or wet situations, such as in contact with the ground, or in a humid atmosphere where condensation is prevalent, such as trussed rafter roofs. Under such conditions its moisture content may rise above 20 per cent, timber may need to be protected by chemical means which involves treatment of the timber with certain chemicals that are poisonous to the fungi and insects that attack it. Such a process in usually described as wood preservation.

2.2.2 Chemical Wood Preservation

The modern industrial wood preservation industry began in the early 19th century, though the use of inorganic chemicals can be traced back to the Egyptians, who preserved their rulers by mummification which involved steeping the body in Natrum, a mixture of various sodium salts for seventy days and then in an oily or bituminous substance for a similar time. The Egyptian mummies are now at least four thousand years old. The Chinese, 2000 years ago, immersed their wood in sea water or the water of a salt lake prior to using it as a building material. The preservation of timber has developed considerably during the past 30 years and has become an important requirement of good building practice. The wood preservatives in general use are sufficiently toxic to wood destroying-fungi and wood-boring insects.

There is no wood preservative which is ideal for all purposes as wood in different situations requires varying degrees of protection depending on the hazard to which it will be exposed. Any good preservative should meet the following requirements:

(i) The product must be sufficiently toxic at a convenient concentration to render the wood immune to the attack of the organisms to which the treated wood is likely to be exposed.

(ii) The preservative must persist in the wood for many years in an active form.

(iii) It must not be corrosive to metal, or cause deterioration to the wood , which suggests that no product that is strongly acidic or alkaline in reaction can be safely used.

(iv) The product must not endanger the health of operators applying it, nor should it render the wood poisonous to those handling it, or coming into contact with it in service.

(v) It must not increase significantly the flammability of the wood.

(vi) It must be reasonably inexpensive for bulk users.

Commercial wood preservatives available today can be divided into three main types:

(1) Tar oil: These are essentially distillates of coal-tar, known under the general name of coal tar creosote. It is a complex mixture of organic compounds distilled from coal tar with a distillation range of 200-400^{o}C. The properties and performance of coal-tar creosote as a preservative have been described in a series of publications, see for e. g. reference 20-22.

(2) Organic solvent: An organic solvent wood preservative is one in which wood preserving chemicals are dissolved in a nonpolar organic solvent. The solvent is usually volatile and when it evaporates the active ingredient is left in the wood and is resistant to leaching by water. It is the active ingredient which is toxic to fungi and insects. Active ingredients are normally copper and zinc naphthenate, pentachlorophenol and tributyltin

oxide. Organic solvent preservatives have been used for 80 years, industrial and remedial use have been extensive for 30 years. Potentially they cause no swelling or distortion of seasoned wood. This makes them particularly suitable for joinery, and once the solvent has dried off the treated wood can be painted. They penetrate readily without detrimental effect. If correctly formulated, they are effective in any situation and can be applied by both simple and sophisticated techniques and are clean. However, they have got some disadvantages, e.g. high cost, they are a health hazard and the solvents are generally flammable. These preservatives have been discussed in detail in several publications[18,23].

(3) Water-borne: These are aqueous solutions of one or more chemicals which are fungicidal and insecticidal. Whilst there are many hundreds of water soluble preservatives they can be divided into two main groups:

(a) leachable water-borne preservatives: These preservatives do not become "fixed" in the wood and can give adequate protection against insect attack and fungi decay induced by damp conditions. They are normally for internal use, where the timber is not in contact with the soil or exposed to leaching. Preservatives based on fluorides and biflourides are still used for this purpose particularly in Germany, but in the U.K. and New Zealand, boron compounds are preferred. The boron preservative (disodium octaborate tetrahydrate) is normally applied only to freshly sawn timber at the sawmill.

(b) Highly -fixed water-borne preservatives: These are aqueous solutions of one or more chemicals. These preservatives owe their performance to a reaction that takes place between their components after contact with the wood, causing the active ingredients to form precipitates which are virtually insoluble in water and therefore permanently incorporated in the wood. Thus this type of formulation can be for external use. Among formulations most used are copper/chromium/arsenic (CCA) compositions. CCA preservatives will be separately reviewed in section 2.3, owing to their relevance in the present work.

Having decided on the type preservative, efficiency depends mainly on the method of applying the preservative. The methods of application (in decreasing order of effectiveness) are as follows:

(1) Pressure processes: There are two principal types of pressure treatment: the "full-cell" and the "empty-cell" methods.

In the full-cell process the wood is placed in a pressure cylinder and a vacuum is applied. The cylinder is then filled with the preservative and when it is full to capacity hydraulic pressure is applied for a period long enough to give the requisite treatment. After emptying the preservative a final vacuum is generally given to clean the surface of the charge for handling. The full-cell process is normally used with the water-borne preservatives.

In the empty-cell process a preliminary vacuum is not used and, as a result of air remaining in the cells, the timber is relieved of its surplus preservative and cell cavities of wood are left only partially filled. These methods are normally restricted to treatments with creosote or similar preservative oils. They can give adequate retention and yet minimise the risk of subsequent "bleeding" of the preservative from the timber during use.

Pressure treatment is the most effective treatment for timber to be used under adverse conditions since it ensures a deeper penetration and a higher loading of preservative. The relevant British Standards are BS 144: part 2 1990 [24] and BS 4072: 1974[25].

(2) Double vacuum process: This is suitable for treating external joinery with an organic solvent type of preservative. Timber is placed in a vessel and subjected to a vacuum. This is maintained for a short period so that, on filling the vessel and releasing the vacuum, controlled penetration in the sapwood is obtained. The amount of organic solvent preservative used and consequent penetration obtained depends on the actual treatment cycle, but by

employing a second vacuum immediately after treatment whilst the timber is still in the vessel, sufficient control over absorption is possible to ensure that the retention of the relatively high cost preservative is adequate but not excessive. In general, satisfactory painting and gluing can be obtained with treated timber provided that a sufficient drying time is allowed after treatment for the preservative solvent to evaporate from the wood.

(3) Diffusion of green timber: In this process, freshly sawn unseasoned timber is dipped, at the sawmill, in a concentrated solution of water-borne boron preservative and then close-stacked under restricted drying conditions to allow the boron to diffuse into the timber. After drying, the then seasoned and treated timber is penetrated throughout with preservative.

(4) Immersion/Deluging: There are simple methods of preservation whereby timber is submerged in cold preservative for a period which can very from a few seconds to several days. The process is generally referred to as a dipping treatment when the period of immersion is up to about 10-15 minutes, and a steeping treatment, when immersion is over several hours or days. Although all types of preservative can be applied by immersion treatments, the preference is usually for the low viscosity organic solvent type as these generally give a deeper penetration than the other types.

There are other methods of treating timber, but some of these have only limited application and are rarely applicable to timber used in the constructional field. Therefore, they are not reviewed here.

2.3 Copper/Chromium/Arsenic (CCA) Wood Preservatives

CCA water-borne preservatives applied using vacuum/pressure treatments can provide an effective protection for wood. It has become an important requirement of good building practice and widespread as a major method of wood treatment because of the ease of application, low cost, good penetration and non-staining properties. The treated timber is used in a wide variety of situations. Treatment of structural timber for buildings is widely specified, with the emphasis being placed on the use of these materials in roof spaces.

2.3.1 Composition of CCA

Since the first copper, chromium, arsenic (CCA) formulation was invented in 1933 by an Indian Government Research Worker in the form of copper sulphate ($CuSO_4.5H_2O$), potassium dichromate ($K_2Cr_2O_7$) and arsenic pentoxide ($As_2O_5.2H_2O$), CCA has grown to become the dominant wood preservative world wide in terms of volume of wood treatment[26]. While initially this growth was slow, in the past thirty years the use of CCA has grown rapidly. There are now many CCA wood preservatives in the world, but they all originate from the three active ingredients: copper, chromium and arsenic. Within the CCA group the copper, chromium and arsenic components are present in varying proportions and incorporated variously as oxide or salts. BS 4072[25] was first published in 1966. It specified the two CCA's commercially available in Great Britain, Type 1 and Type 2, as shown in Table 2.1. For many years American Wood Preservers Association (AWPA) specification defined CCA wood preservatives in terms of their equivalent salt contents, just as BS 4072, but this practice was abandoned in 1969 and preservatives have been defined in terms of the equivalent active oxide system as shown in Table 2.2. The five CCA's may be conveniently compared by expressing the formulation as metal oxide although commercial products use salts and /or oxide as raw material. They are listed in Table 2.3.

In CCA wood preservatives, the copper acts as a fungicide by causing precipitation of proteins within the fungi and by interference with enzyme reactions. However certain fungi are relatively tolerant to copper and arsenic is present both to protect timber from decay by copper tolerant fungi and to act as an insecticide. The presence of chromium improves the fixation and leach resistance of the treatment.

Table 2.1 The Compositions of two types of CCA (BS 4072)[25]

Ingredient	Type 1		Type 2	
	Nominal	Minimum	Nominal	Minimum
Copper (expressed as $CuSO_4.5H_2O$) % (m/m)	32.6	29.5	35.0	31.5
Chromium (expressed as $Na_2Cr_2O_7.2H_2O$) % (m/m)	41.0	37.0	45.0	40.5
Arsenic (expressed as $As_2O_5.2H_2O$) % (m/m)	26.4	23.5	20.0	18.0

Table 2.2 The Compositions of three types of CCA (AWPA)

Ingredient	Type A	Type B	Type C
Copper (as CuO) % (m/m)	18.1	19.6	18.5
Chromium (as CrO_3) % (m/m)	65.5	35.5	47.5
Arsenic (as As_2O_5) % (m/m)	16.4	45.1	34.0

Table 2.3 The Compositions of five typical commercial CCAs

Product	Standard	CrO_3	CuO	As_2O_5
CELCURE A	BS 4072 (Type 1)	46	17	37
TANALITH C	BS 4072 (Type 2)	52	19	29
ASCU	AWPA (Type A)	65	18	17
K33	AWPA (Type B)	35	20	45
WOLMAN CCA	AWPA (Type C)	47.5	18.5	34

2.3.2 Fixation of CCA

Owing to the commercial importance of CCA many studies have been carried out to explain the fixation mechanism. Different methods have been employed by various workers. Dahlgre[27-29] measured change in pH on reaction of CCA with wood floor and tested leachability of chromium during the course of fixation to determine rate constants for the various reactions. Pizzi[30-32] analysed insoluble reaction products formed during the reaction of CCA with simple model compounds selected to represent the building block of cellulose and lignin. Both the work of Dahlgren and of Pizzi has shown that chromium arsenate was one of the main reaction products. It was found by Pizzi that the chromium (VI) could be reduced both in the presence of cellulose and lignin like model compounds, but that the chromium arsenate formed interacted more strongly with lignin like compounds. The principle fungicidal element, copper, is present in more than one form, the balance between the various forms depending on the exact CCA composition and timber species. The fixation mechanism for a substantial proportion of copper was proposed to be by ion exchange. Simple copper salts such as copper sulphate are also believed to undergo ion exchange in the timber, and formation of insoluble copper arsenate will also contribute to copper fixation. Richardson[33] explained the fixation of CCA preservatives in pine. It is probable that some of the copper reacts with water in soluble wood components, probably forming a copper and cellulose complex. The remaining copper reacts with dichromate to produce mixed copper chromates. The remaining dichromate is reduced from the hexavalent to trivalent state and then reacts with any arsenic present or, if arsenic is absent, is absorbed onto the wood. Arsenic is fixed principally by trivalent chromium, probably as $CrAsO_4$, although some arsenic may be absorbed by the wood elements. At high arsenic concentration some may be precipitated as copper arsenate. At low solution concentrations absorption by the wood elements may be the major fixation process. The ratio of CrO_3 to As_2O_5 should be at least 1.5 in order to ensure arsenic fixation. The ratio of CrO_3 to CuO should be at least 2, in order to ensure maximum fixation of the toxic elements. In more recent work Henshaw[34]studied the fixation of CCA wood preservative in soft wood and hard wood. He found that the course of fixation appears to be similar in both softwood and hardwood. Water is necessary for fixation reactions to proceed to completion in pine sapwood. Fixation is virtually complete after two weeks at 20°C in moist conditions (83% RH). It proceeds less rapidly with decreasing temperature, hence treated wood can not be dry too quickly. Although there have been various explanations of fixation of CCA , the following factors are most important during the fixation of CCA treated wood:

(i) The redox reaction between Cr^{6+} and wood consumes H^+ thereby increasing pH and is the essential component of fixation since it causes the inorganic metallic arsenates to become insoluble.

(ii) Inorganic metallic arsenate precipitation forms the largest proportion of reaction products .

(iii)The chemical components of wood are modified by CCA particularly in the lignin regions thus enabling copper to be more effectively bound to the wood.

(iv) Wood/metal/arsenate complexes assist in binding the metals more effectively.

2.4 Timber Trussed Rafter Roofs

The timber trussed rafter roof is a major use of timber as a constructional material. Trussed rafters have been in use in the United Kingdom since the latter half of the 1960s. They have been used mainly for roofs of domestic building but are being increasingly utilised for larger buildings such as schools, institutional buildings and industrial premises. As a result of survey during the winter of 1979/80[35], it was estimated that there were approaching two million trussed rafter roofs in the U.K., excluding Northern Ireland. At the time this total was increasing at a rate equivalent to approximately 200000 per year. A code of practice for trussed rafters was established in 1973[36]. The survey showed that about 20 per cent private sites used CCA treated trussed rafters[35]. Less than 10 per cent local authority sites used CCA treated trussed rafters. It is known that CCA wood preservatives treatment will enhance the corrosion rate of metal fasteners in contact with the timber. To understand the corrosion behaviour of metal fasteners in trussed rafter roofs, it is necessary to consider first the microclimate found in roof spaces and then the potential corrosion process of different metal embedded in timber.

2.4.1 Microclimate of Roof Space

(i) Moisture content: The moisture content of timber used for roof trusses in Britain has usually been 10-18 per cent in service. In some cases, The moisture content of the trussed rafter roof timber could be higher, e.g. between 17 and 22 per cent. This results from penetration of rain or snow through a poor building structure, or because of condensation of water vapour from inside the house resulting from poor ventilation or insufficient use of insulation materials at ceiling level. In rare cases, the moisture content of the trussed rafters has been higher than 33 per cent[35]. Some trussed rafters stored on site have been found to exceed 22 per cent. A survey of the moisture content of trussed rafter roofs timber in service and in site are shown in Figure 2.6 and 2.7.

(ii) Ventilation: It is essential that cold roof spaces are effectively ventilated to the outside to prevent condensation. In addition, to minimise ingress of water vapour into the roof space from the room below. The location and size of ventilation openings should be determined by the building designer. Some further information is published in BS 5268[36]. Less than half the trussed rafter roofs in Britain had some degree of ventilation although it was not always sufficient, but about half of roofs had not got any kind of ventilation.

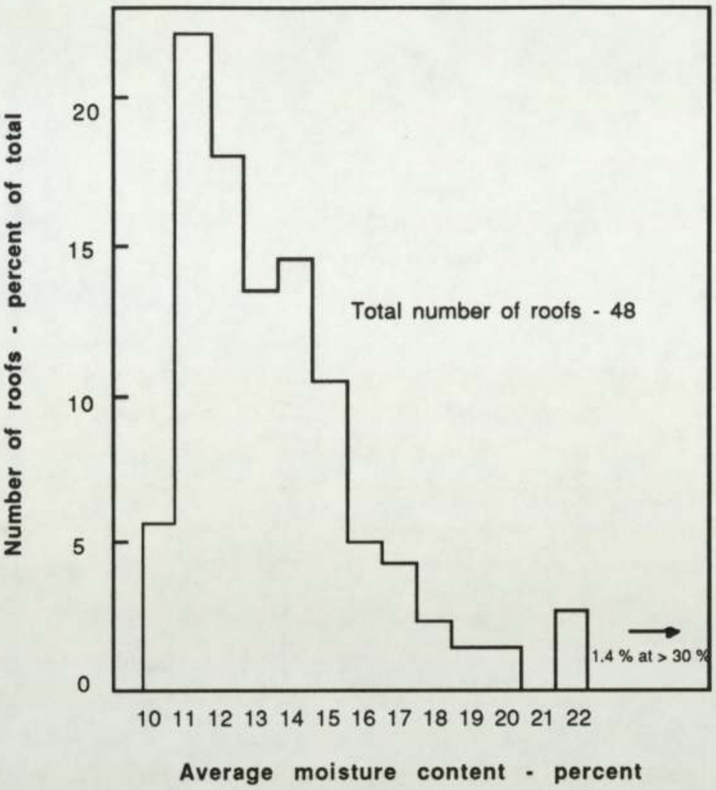


Figure 2.6 Average moisture content in the roofs surveyed[35]

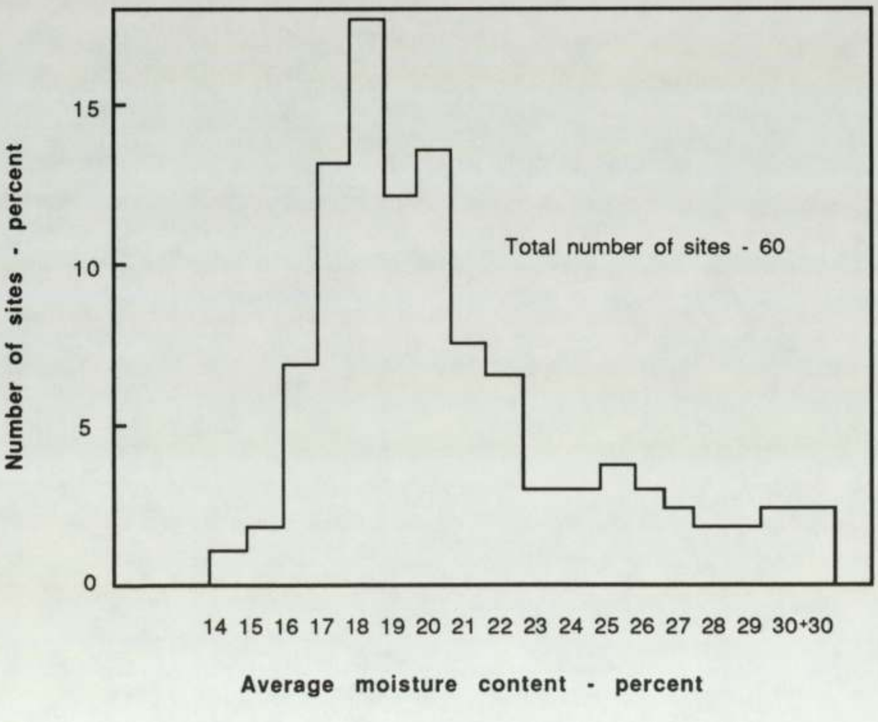


Figure 2.7 Moisture content of trussed rafters at 60 sites surveyed[35]

(iii) Roof insulation: In the majority of trussed rafter roofs, the insulation required to comply with the statutory regulation for thermal transmittable is provided by placing the insulating material between the ceiling tie members on top of the ceiling board. Placing the insulation at this level results in a cold roof space. Alternatively, the insulating material may be placed at rafter level which will result in a warm roof space. The survey in Britain in 1980 shown that more than 70 per cent of new roofs had ceiling level insulation of 75 mm or thicker,[33] whereas only 21 per cent of roofs in service were insulated to this standard. The thickness of insulation material at ceiling level is summarised in Figure 2.8.

(iv) Condensation: For the trussed rafter roofs, if the thickness of insulation material at ceiling level was more than 75 mm and the ventilation was not sufficient, some condensation may take place, which will cause the roof timber to be damp.

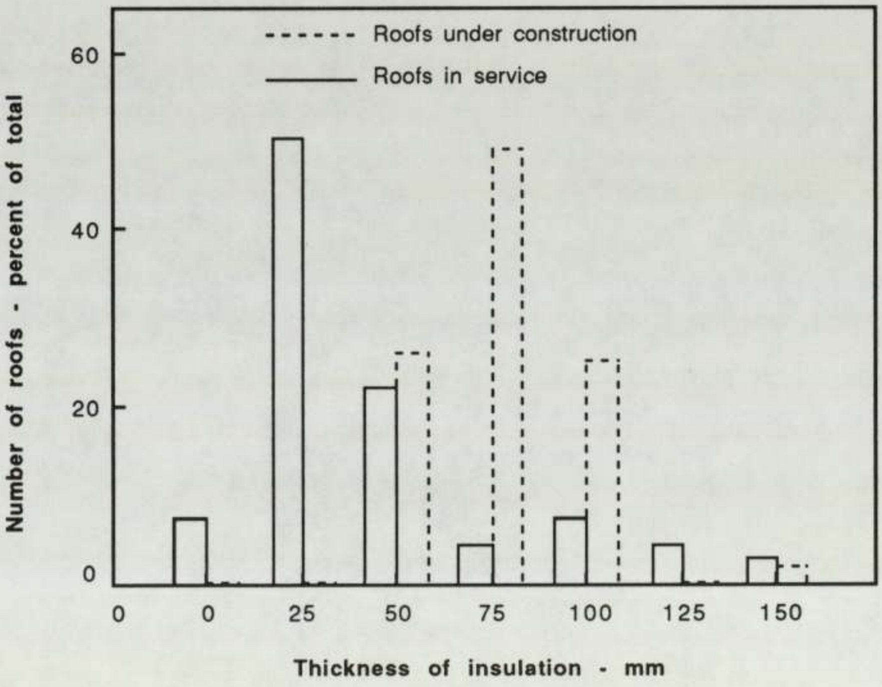


Figure 2.8 Thickness of insulation in trussed rafter roofs surveyed[35]

2.4.2 Species of Timber for Trussed Rafter Roofs

The species of timber used in the fabrication of trussed rafter roofs should comply with BS 5268 part 3 1985[36]. Some of the species of timber suitable for trussed rafter construction are listed in Table 2.4.

Table 2.4 The Species of timber for trussed rafter roofs [36]

Origin	Europe	Canada	USA	Britain
Standard name	White wood Red wood	Southern Pine Hem-fir Douglas fir-larch	Spruce pine fir Hem-fir Douglas fir-larch	Scots Pine Corsican pine

2.4.3 Fasteners for Timber Trussed Rafter Roofs

Metal fasteners are widely used for joining timber and there are many shapes and varieties of material. Material selection is based on the type of wood being supported and the environment to which it is exposed. However, mild steel and galvanised mild steel are the most common materials for timber work.

For exterior use or in damp or corrosive environments, fasteners should be of rust resistant materials or coated to inhibit corrosion. The choice of material will depend upon the degree of hazard coupled with the expected life of the structure. For trussed rafter roofs, punched metal plate fasteners with either integral teeth or holes, through which separate nails are driven, should be manufactured from hot-dip galvanised plain sheet or coil in accordance with grade Z2 of BS 2989 1982[37]. Alternatively, where a greater resistance to corrosion is required, austenitic stainless steel of a grade defined in BS 1449 part 2 1983 [38] may be used. On the other hand, when timber has been treated with water-borne wood preservative salts a stabilisation period of about 14 days should be allowed to elapse between the treatment and the introduction of metal work. All fasteners used in roof construction, including those used with galvanised punched metal plate fasteners or plywood gussets, should be coated protectively by hot-dip galvanising, sherardizing or other suitable treatment against corrosion.

2.5 Corrosion of Metal Fasteners in Timber

During the last 20 years or so various warnings have been issued concerning the possibility of enhanced corrosion of metal fasteners in timber treated with CCA products. A survey about corrosion of metal fasteners in trussed rafter roof timber in Britain in 1982 showed that the corrosion of nail plates was more advanced in CCA treated timber than in untreated timber[39]. A series of studies about metal corrosion in CCA treated wood have been carried out by various workers using different methods. The literature on wood-metal corrosion has been reviewed carefully by Graham[40].

2.5.1 Corrosion of Metal in Untreated Wood

Damp wood will corrode metals. There are two different forms of metal corrosion in untreated wood

(i) Crevice corrosion

(ii) Galvanic corrosion

For a single isolated metal fasteners in damp timber, its corrosion can be explained in terms of crevice corrosion. A crevice corrosion cell is set up on any metal surface in contact with an electrolyte when oxygen access to that surface is not uniform. Thus for a fastener in damp wood, a more oxygenated environment exists at the head than on the shank, thus causing the exposed head to become a cathode and the shank to become an anode of a crevice corrosion cell. the mechanism of metal corrosion is described in Figure 2.9. Note that the metal dissolves at the anode, and metal atom release electrons. These electrons flow through the metal to adjacent areas and enter into cathodic reactions.

The principal reactions that may occur are:

At the anode: $M = M^{n+} + ne$

At the cathode: $2H^+ + 2e = H_2$

or $O_2 + 2H_2O + 4e = 4OH^-$

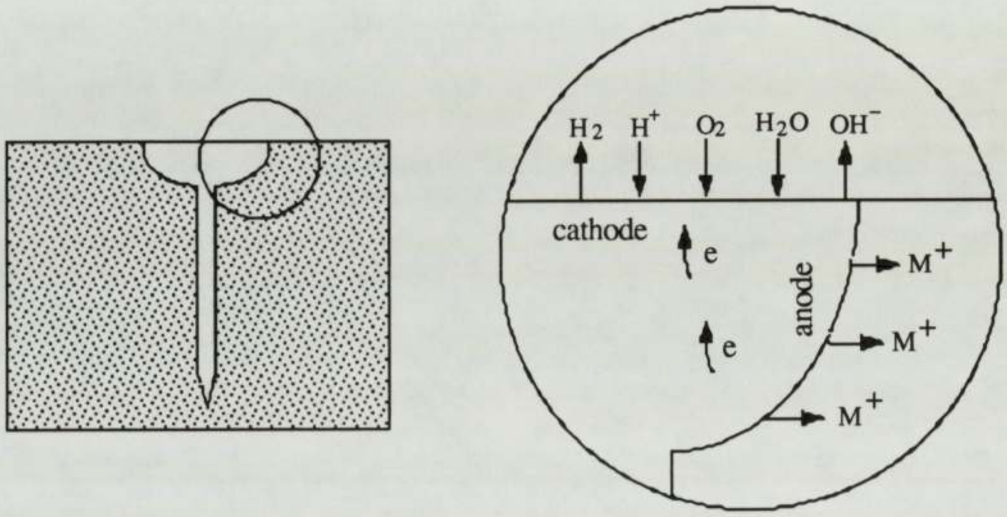


Figure 2.9 The mechanism of crevice corrosion of fastener in timber

Anodic reactions are usually quite straightforward. They include the dissolution of the metal, that is the change of metal to metal ion, which then oxidises to higher states. Iron ions are active catalysts in that they may promote chemical reaction in cellulose that in turn causes a loss of strength of the wood[41,42].

The two cathodic reactions illustrated show that concentration of hydrogen ions and oxygen are key factors in the corrosion process. A source of H^+ ions in wood is acetic acid which is formed by hydrolysis of acetylated polysaccharides present in wood[43,44]. The pH of most woods is in the range 3.0-5.0. Some woods are more aggressive than others. Farmer[45] considers that the pH value, resulting from aqueous extracts, gives some measure of the aggressiveness of wood. In general, a strongly acidic wood with a pH less than 4.0 will cause metal corrosion, while a less acid wood, with pH greater than 5.0, may be relatively safe. Variations in pH can exist within a particular species, e. g. the pH of beech varies from 4.5-5.9 and this can present difficulties in assessing the corrosion risk.

Water is the most critical component for crevice corrosion, as above reactions are electrochemical processes and require a medium in which ions can diffuse in the electrolyte portion of electrochemical cell. But dry wood has a low ionic conductivity, so the water in wood provides the electrolyte for the corrosion of metal in contact with wood. For any timber, crevice corrosion can not occur when the moisture content of timber less than 20 per cent. In an uncontaminated environment, reduction of relative humidity to less than 75 per cent will almost stop the corrosion of metals.

Dissimilar metals in contact with one another in damp timber will form a galvanic corrosion cell that results in accelerated corrosion of the less corrosion resistant metal and very little attack of the more corrosion resistant metal. Reactions are such that, it is possible that acid could accumulate adjacent to the anode and also, if the anode is iron, then the ferrous ions can initiate degradation of wood. At the cathode, the reaction will depend on the pH, and in neutral solution, the reaction is:

$$O_2 + 2H_2O + 4e = 4OH^-$$

whilst under acid condition, the reaction is:

$O_2 + 4H^+ + 4e = 2H_2O$

This explains the frequent finding of alkaline conditions around a metal cathode embedded in wood. After a number of years, the accumulation of alkali can weaken the wood. Thus in practice, it is important that dissimilar metal fasteners are not used in timber. For hot-dip Zinc coated steel fasteners, coating damage must be limited otherwise the zinc coating will corrode quickly.

2.5.2 Corrosion of Metal in Treated Wood

Where long service life in wet conditions is required, wood should be treated with preservatives. The oil type preservatives may not create highly corrosive condition in the timber. However water-borne preservatives, e, g. CCA will enhance the corrosion risk to fasteners in timber.

This increase of corrosion risk may be as a result of the following. Firstly, CCA preservatives contain copper. If the treated timber is allowed to dry out too quickly, copper fixing will not go to completion. Even if it is fully fixed, there is still about 1-5 per cent soluble copper and some of this free copper migrates to the fasteners and is deposited by displacement of copper ions by metal from fasteners[45]. This sets up a bimetallic cell, which will cause the fastener to corrode rapidly . Secondly, in treated timber, crevice corrosion can still occur although the critical moisture content necessary may be lowered slightly. The presence of salts will increase the ionic conductivity of the moist timber, so that a lower moisture content might produce the same ionic conductivity. The critical moisture content for metal corrosion in CCA salt formulated treated timber may be about 16 per cent, but the CCA oxide formulations do not create the same problem. Taylor[46] has compared the difference in conductivity and corrosivity between CCA oxide and CCA salt treated wood. Finally, the greatest impact of preservatives on use of timber is to allow them to be used in wetter conditions. Untreated timber must remain at moisture contents below about 18 per cent to avoid timber decay. Corrosion of metal is negligible in this relatively dry state, because the critical moisture content for corrosion of metal is about 20 per cent. However, preservative treatments allow the timber to be used at high moisture contents and under such conditions, corrosion of metal will be initiated. Crevice corrosion usually requires an incubation period to develop but once started, it proceeds at an ever-increasing rate[47].

2.5.3 The Method of Assessing Corrosion of Metal in Contact with Timber

The traditional method of assessing corrosion of metals in contact with timber is long-term exposure in the appropriate environment. Such tests have generally required many years which is unacceptably long in terms of assessing the likely hazard to one type of fastener in a particular timber medium. In much of this work results are reported as weight loss of the fasteners after a certain period of time. The exposure conditions include indoor, outdoor, ground and laboratory.

The International Research Group on wood preservation investigated the corrosion of fastener in western red cedar with treated CCA[48]. In outdoor exposure tests in British Columbia for nine years, the results would suggest the use of stainless steel or silicon bronze nails but not galvanised steel to fasten water-borne preservative-treated shingles or shakes as a roof. These nails are proven to be corrosion resistant. The Swedish Wood Preservation Institute reported work on sixteen years old railway sleepers and indicated that mild steel fasteners corroded at two to five times the rate of galvanised steel fasteners[49]. A significant difference was noted between the salt and the oxide formulations, the latter being much less corrosive. Other exposure tests were carried out in outdoor (85-95 per cent RH) and indoor conditions (35-65 per cent RH) over an eight year period[50]. Two conclusions drawn were (a) at timber moisture contents below 15 per cent no corrosion will occur, and (b) at moisture content above 15 per cent, mild steel and zinc electroplated steel will corrode significantly.

Both conclusions apply to treated and untreated wood.

Laboratory investigations attempt to accelerate corrosion behaviour by increasing temperature or relative humidity. Most laboratory tests are usually carried out in high humidity environments or partially or even fully immersed. One example of this type of work has been conducted by Wallin[51]. He maintained his specimens at 100 per cent humidity and 20°C temperature for one year to determine the corrosion rate of some metals and alloys in untreated wood and CCA treated wood. It was shown that ordinary steel corrodes faster than other common fastener metals such as copper, brass, aluminium and stainless steel. Zinc coatings will prevent the steel corrosion provided that the coatings are sufficiently thick. The hot-dip galvanising of steel is far better than electroplated zinc coating. Simm[52] investigated the corrosion behaviour of several metals in CCA treated timber, the samples were placed at 100 per cent relative humidity and 25°C for 30 months. The results showed that the corrosion loss of mild steel, bright zinc-plated mild steel and aluminium-alloy fasteners in damp wood have been increased by CCA treatment. The Scandinavian Lead zinc Association[53] indicated that the corrosion of rates of bare steel, galvanised steel, copper and brass were some 20-30 per cent greater in treated than in untreated timber at 100 per cent RH and 20°C. However Associated Lead Manufacturers Ltd[54] gave different results: in saturated conditions galvanised nails and sherardised screws showed greater corrosion in treated than in untreated timber, stainless steels, aluminium, brass and copper showing no effect. In conditions of 100% RH, aluminium as well as the zinc-coated steel showed enhanced corrosion by a factor of about three over untreated timber. Among the information reported by manufacturers of fasteners is that from the GKN Fasteners Corrosion Laboratory[55]. From exposure tests carried out at 50°C, 95% RH for 42 weeks, zinc-plated screws in treated wood showed corrosion rates approximately twice those in untreated wood, thus suggesting that high humidity laboratory exposure tests are rather more severe than outdoor exposure. For stainless steel, silicon bronze and brass no differences in corrosion rates were found between treated and untreated timber. Another important paper originates from the Princes Risborough Laboratory[56]. Laidlaw and Cox have published the results of work carried out to determine the effect that the corrosion of galvanised nail plates may have on joint strength, with particular reference to trussed rafter roofs. Exposure of nail plates embedded in pinus sylvestris at 87% RH, 27°C conditions led to the conclusion that the presence of "salt" formulation CCA increased the corrosion of the plates and caused a reduction in static strength of the joints. The bulk moisture content of wood specimens was reported to be 22-24 per cent after 12 months, with the surface of the timber in contact with the nail plate being wetter than this. It was pointed out that the degree of corrosion experienced by the nail plates in these tests was greatly in excess of that observed in buildings in U.K. Thus it is not expected that loss in joint static tensile strength due to corrosion would occur during normal service. However, Preliminary fatigue strength tests suggest that loss of fatigue strength of joints can occur before the joint loses static strength. It was emphasised that a very considerable amount of further work is necessary to validate these preliminary fatigue results and to provide a firm basis on which to interpret their implications for the durability of rafters in service. The potential efficiency of plastic coating for the protection of galvanised plates under severe exposure conditions has been demonstrated.

Electrochemical techniques have been used for corrosion rate determination of metal fasteners in contact with timber since the 1980s. These techniques can rapidly measure the corrosion rate and are especially useful when combined with surface analysis techniques. When the moisture content of the timber was in the range generally found in buildings, the electrical conductivity of timber is too low to use conventional corrosion measurement and monitoring techniques. Electrochemical noise and impedance techniques are applicable to low conductivity media. A method was devised by Duncan in 1981[57] which uses agar gel or starch gel loaded with the chemical expected to occur as treatment residues. The polarisation resistance of metal in this model "wood" can be measured. The effect of copper, chromium and arsenic residues in concentrations comparable to the free concentration in treated wood were tested on stainless steel, mild steel , galvanised steel, brass and aluminium. The general trend of results was as might have been anticipated from aqueous corrosion. Cu^{2+} promotes corrosion, Cr^{6+} provided its concentration exceed a value somewhere between 0.0025 and 0.00025M, inhibits corrosion. The presence of As^{5+}in the starch gel promoted corrosion of brass and galvanised steel, but had no effect on mild steel or aluminium in starch, nor on any of the metals in the agar gel. Stainless steel had an immeasurably small corrosion rate in these gels, and might be predicted from this to have a negligible corrosion rate even in wet CCA treated timber. Cox and Laidlaw[58] measured potentiodynamic polarisation curves for zinc in CCA oxide and CCA salt solutions, which are shown in Figure 2.10 and Figure 2.11 respectively. Figure 2.10 showed a plateau (A-B) at low current density, indicating the presence of a very thin passive film, with a comparatively high electrical resistance, on the zinc surface. Entirely different results were produced on testing the "salt " formulation which exhibited the typical curve of anodic dissolution of the zinc (Figure 11) and showed no evidence of passivation. These results were confirmed by corrosion product analysis. X-ray diffraction analysis showed that the zinc corrosion product obtained in the "salt" series was a mixture of zinc oxide and zinc hydroxide, while that on the "oxide" plates contained zinc oxide and a basic carbonate [$Zn_5(CO_3)_2(OH)_6$] Basic zinc carbonates are known to provide greater corrosion protection to underlying zinc than either oxides or hydroxides. The results from the model "wood" and from preservative solutions, however, do not reflect precisely those in the preservative treated timber, as will be discussed later in this work. On the other hand, Jack[59] used A.C. impedance, linear polarisation and weight loss measurements to study the corrosion of metals in contact with treated wood. Their results showed that:

(1) The corrosion rates of zinc and iron in contact with water-saturated wood are probably controlled by the diffusion of reactants to, or products from, the metal, if the moisture content of timber is below 22 per cent. The corrosion rate is approximately constant from 22 per cent moisture level upward and decreases with decreasing moisture content below 22 per cent.

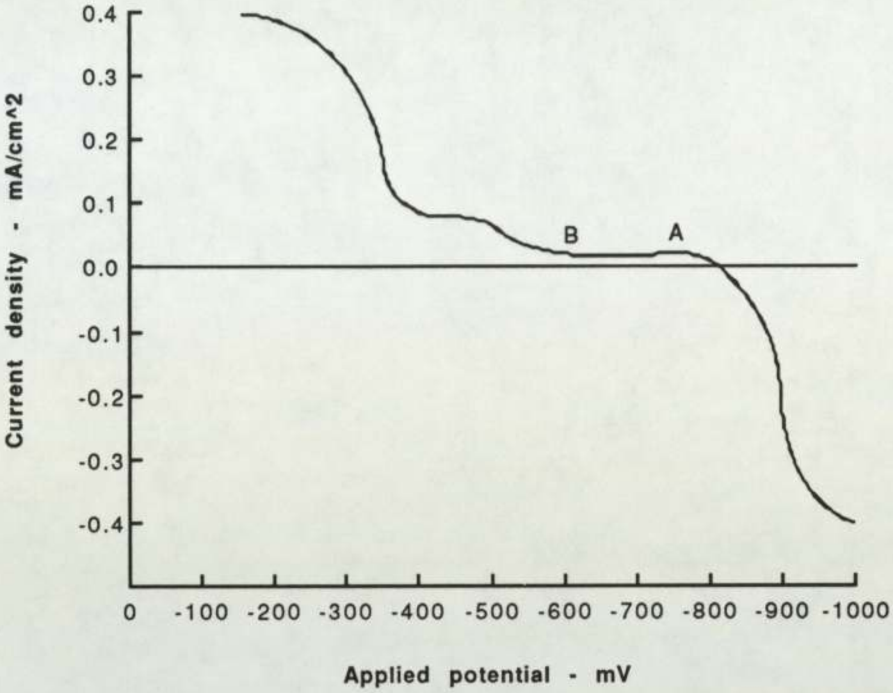


Figure 2.10 Potential scan for zinc in "oxide" CCA[59]

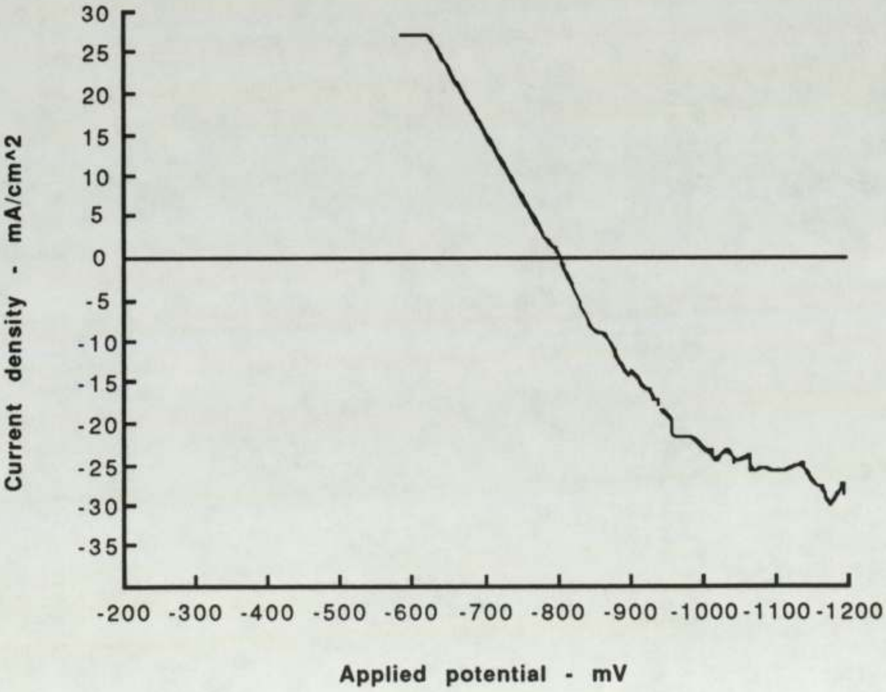


Figure 2.11 Potential scan for zinc in "salt" CCA[59]

(2) For saturated wood, the corrosion rate of metal is approximately halved when oxygen is removed from the system, which implies that in the absence of oxygen, the cathodic current is carried by H^+ in untreated timber and H^+ and Cu^{2+} in treated timber.

(3) The corrosion rate decreases with increasing time, which suggests that the process is self-limiting due to building of corrosion products at the electrode.

(4) There is probably a relationship between the corrosion rate and degree of preservative loading.

More recent work carried out at UMIST[60] has involved the development of corrosion monitoring techniques to determine corrosion rates of metals in untreated and treated timber. The monitoring techniques include A.C. impedance, zero resistance ammeter and electrochemical noise. It was claimed that this monitor can be used in roof trussed rafter roofs at typical "service" moisture content, but no detailed results had been published.

Chapter 3

Experimental Procedures

3.1 Introduction

The corrosion behaviour of metal fasteners in preservative treated timber environments has been determined using electrochemical techniques. Linear polarisation resistance measurements were made on zinc and zinc alloy coated steel, in CCA "salt" solutions and embedded in CCA treated timber. Linear polarisation resistance measurements were also conducted on zinc coated steel in timber with a series of different moisture contents. Potentiodynamic scanning curves were measured on these coated steels in CCA "oxide" solution and CCA treated timber. Tafel plots were measured on the samples embedded in treated timber. The nature and concentration of products were determined using scanning electron microscope (SEM) with energy dispersive X-ray analysis (EDXA).

3.2 Materials

All of the investigations were carried out on a series of commercially produced zinc and zinc alloy coated steels, hot-dipped galvanised and electrodeposited, with or without conversion coatings. Conversion coatings were of the chromate type and applied commercially. The details of these zinc and zinc alloy coated steels are listed in Table 3.1.

3.3 Specimen Preparation

The working electrode for all electrochemical measurements was cut from "as received" flat sheet (about 1 mm thick) in the form shown in Figure 3.1 and was spot welded to a steel bar. The welded steel bar, the cutting edges and other none working surface were painted with a Lacquer (sealac), to give a working surface area of approximately 3.0 cm^2. All specimens were degreased with methanol and acetone prior to lacquering.

Table 3.1 Details of the zinc and zinc alloy coated steel used in the investigations

Sample	Coating Composition (%)						Surface Spangle	Conversion Coating	Source
	Zn	Al	Fe	Si	Co	Ni			
G1	100						Normal	Chromated(0.05% Cr)	British Steel
G2	100						Smooth	Chromated(0.2%)	British Steel
G3	92		8.0					None	British Steel
G4	43.5	55		1.5			Normal	Chromated	British Steel
G5	43.5	55		1.5			Smooth	None	British Steel
G6		5.0						None	British Steel
E1	100							None	Canning
E2	100							Blue Passivated	Canning
E3	100							Full Passivated	Canning
E4	99				1.0			None	Canning
E5	99				1.0			Chromated	Canning
E6	87.5					12.5		None	Schloelter
E7	87.5					12.5		Chromated	Schloelter
E8	99.4		0.6					None	Schering
E9	99.4		0.6					Yellow Passivated	Schering
E10	99.4		0.6					Black Passivated	Schering

G1-G6 galvanised zinc and zinc alloy coated steel

E1-E10 electrodeposited zinc and zinc alloy coated steel

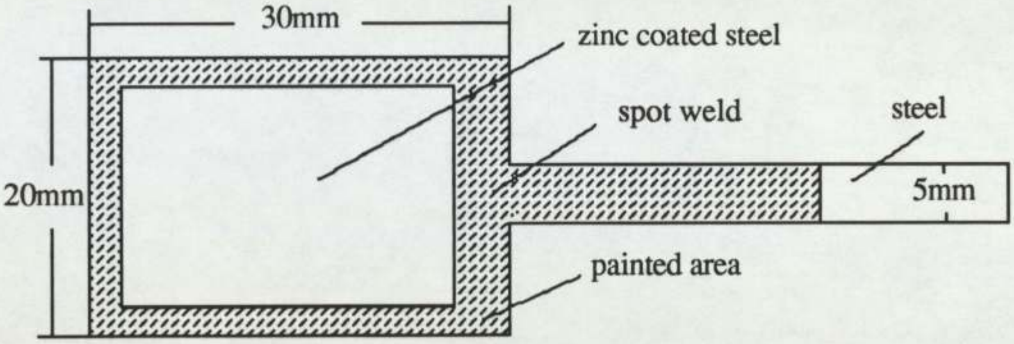


Figure 3.1 The working electrode for electrochemical measurement

A stainless steel, counter electrode was used for electrochemical measurements in timber, and had the same geometry as the working electrode.

3.4 Environment

Both CCA preservative solutions and CCA treated timber have been used for investigation of corrosion behaviour of zinc and zinc alloy coated steel.

3.4.1 CCA Wood Preservative Solutions

Two salt formulated CCA preservative solutions (Type 1 and Type 2, BS 4072: 1987) and one oxide formulated CCA preservative solution (Tanilith) have been prepared for electrochemical measurement. The compositions of these preservatives are listed in Table 3.2 and Table 3.3 respectively. The concentration of preservatives for Type 1 and Type 2 salt formulation solutions should be 2% according to BS 4027: 1987, but the actual concentrations of these solution, were 1.46% and 1.6%, due to the absence of an arsenic compound and the pH was 3.70 for both solutions. The concentration for Tanilith solution was 0.83% and the pH was 2.30. It should be noted that arsenic compounds were not used, because it was reported that it would not have significant effect on corrosion behaviour[43]. It also proved difficult to purchase arsenic compounds due to legislation regarding their sale.

Table 3.2 The composition of Type 1 and 2 CCA preservatives

Composition	Type1	Type2
$CuSO_4.5H_2O$ (% mm)	32.1	35.0
$Na_2Cr_2O_7.2H_2O$ (% mm)	41.0	45.0

Table 3.3 The active oxide content of Tanilith C

Active Oxide Content	Tanilith C
CuO (% mm)	11.1
Cr_2O_3 (% mm)	30.6

3.4.2 CCA Treated Timber

A number of CCA treated wood samples were prepared in the laboratory for the purpose of measuring corrosion rate of zinc and zinc alloy coated steel in CCA treated timber. The samples were cut from European Red Wood. Each set of specimens consisted of three pieces of wood A, B, C as shown in Figure 3.2. An inset slot was made on piece A and B with the same dimension of the working and counter electrodes, so that these electrodes could be positioned accurately. Pieces A and B were the same size and thickness, while piece C was much thinner to reduce the electrical resistance between working and counter electrodes. Piece C was put between piece A and B to make a sandwich structure as an electrochemical cell which will be further described in Section 3.5. In the case of the experiments carried out to determine the effect of moisture content of timber on polarisation resistance of coated steel test, pieces A and B were much thinner (5 mm).

Type 2 salt formulation and Tanilith C oxide formulation preservative solutions were prepared as described in 3.4.1. The wood specimens were immersed in these two solutions respectively for one week to ensure that the preservative solutions had penetrated throughout piece C. The specimens were kept in air for three hours to allow the excess of solution to drain off after taking them out of the solutions. Then they were left in a 100% RH cabinet for a two weeks fixation period before the metal samples were mounted to build an electrochemical cell.

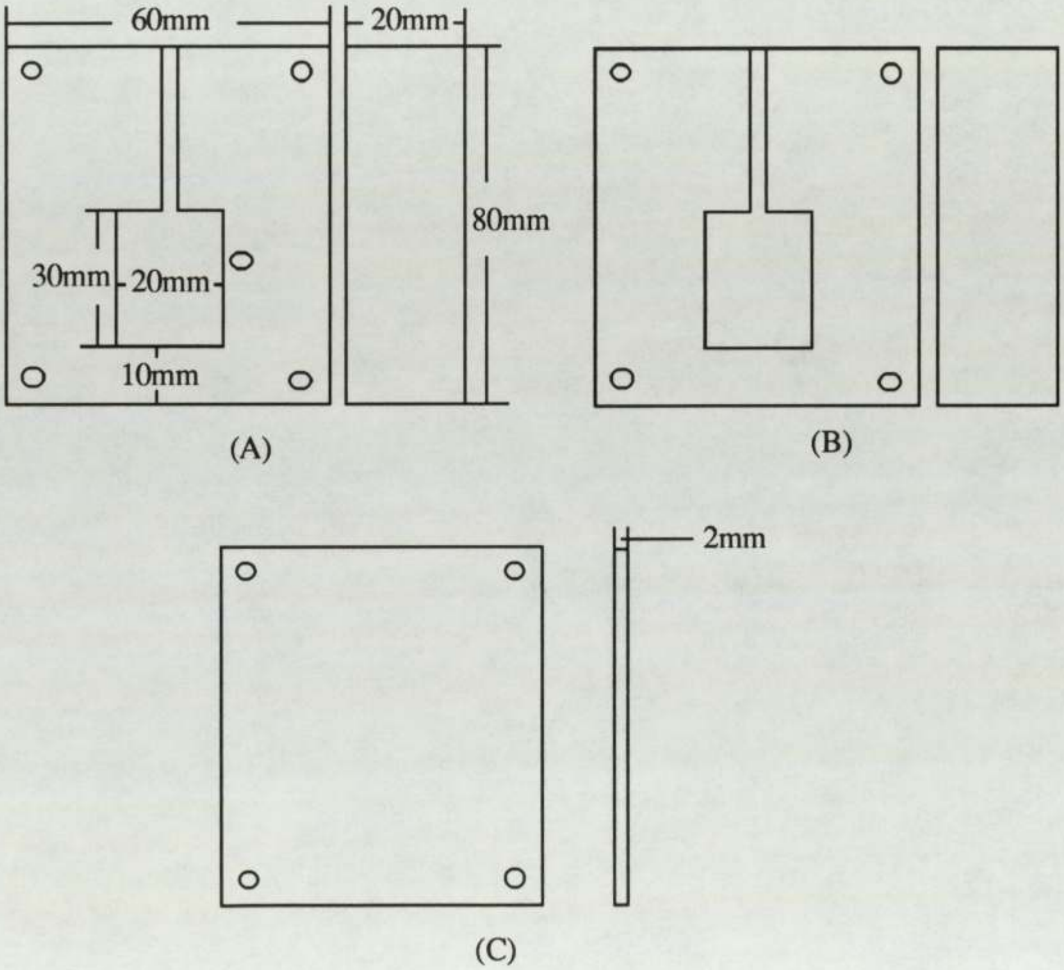


Figure 3.2 Three different pieces of each set of wood specimen

3.5 Electrochemical Measurement

All electrochemical measurements were performed using a "PARC corrosion system 432" with a model 273 potentiostat controlled by an IBM microcomputer, as schematically illustrated in Figure 3.3. IR potential compensation was made for all electrochemical measurements by using a current interruption technique which is available in this corrosion system.

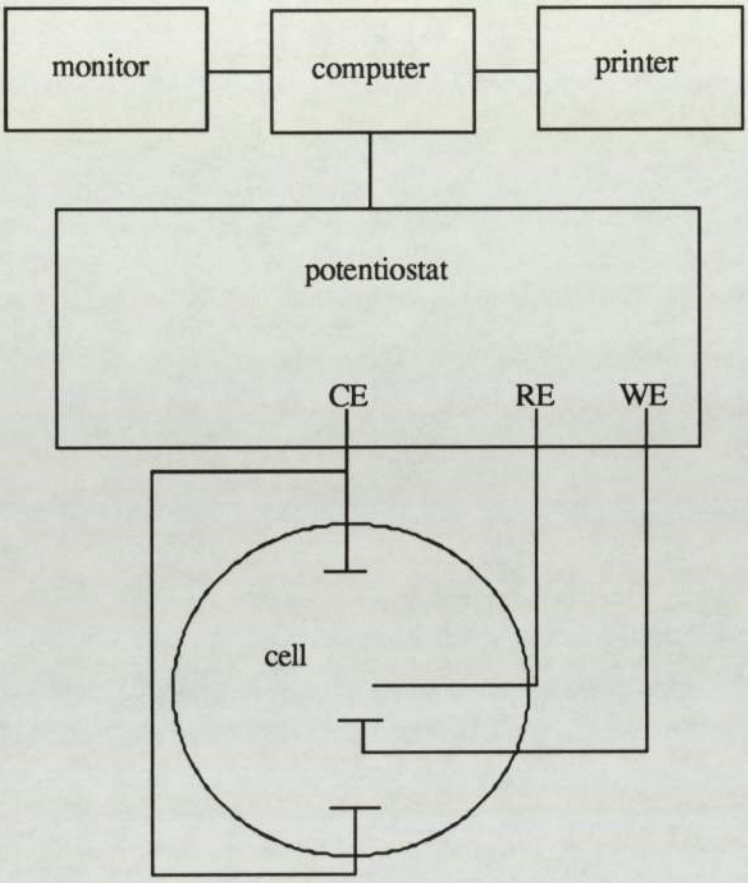


Fig 3.3 Schematic diagram of the hardware used for electrochemical measurement

In the solution test, a three electrode system was used for the corrosion cell which is shown in Figure 3.4. The test cell was a beaker which had a capacity of 400 ml. The large quantities of the solution (the ratio of volume of the solution to surface area of working electrode was larger than 100 ml/cm^2) were used to avoid or reduce change in the composition of the electrolytes during a test. A platinum electrode was used as a counter electrode. Potentials were measured against a saturated calomel electrode (sce). Linear polarisation resistance of zinc and zinc alloy coated steel in Type 1 and 2 "salt" solution and potentiodynamic scaning curves in "oxide" solution were determined using a potentiodynamic sweep method. Sweep rate was 0.5 mV/sec for both tests. Linear polarisation resistance measurement was made in the potential range of ± 25 mV at the corrosion potential, whilst potentiodynamic scanning was commenced at -1000 mV (sce.) and swept in the positive direction to the potential where transpassivation occurred.

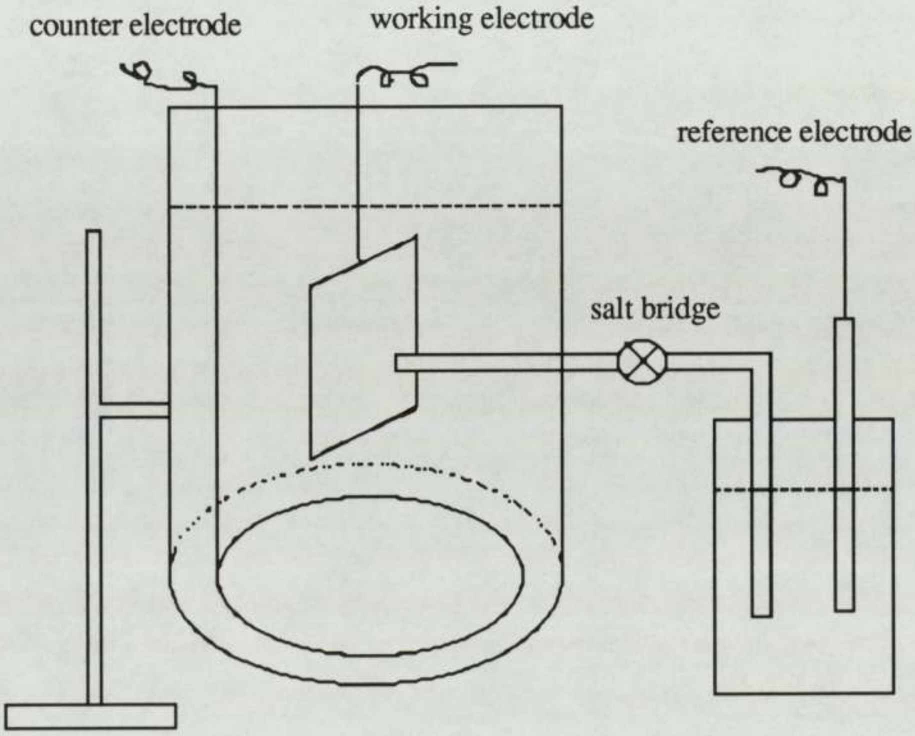


Figure 3.4 The cell for electrochemical measurement in CCA solutions

In the CCA treated timber test, a three electrode system was also used for a corrosion cell as shown in Figure 3.5. The test cell was a sandwich structure timber set. Stainless steel was used as counter electrode, potentials being measured against a saturated calomel electrode (sce). The working electrode and counter electrode were mounted in wood samples A and B respectively. Piece C was put in between piece A and B. These three pieces were then held together by plastic bolts through the four corners of the wood samples. Plastic bolts were used for holding the sample to avoid the corrosion products of metal bolts affecting the test results. Contact between the reference electrode and wood was made via a catheter filled with 13% $NaNO_3$ and 3% Agar, which was inserted into a small hole drilled into piece A. The preliminary tests have shown that this electrochemical cell can provide good electrical contact and reproducibility, when the wood had high moisture content. As in the solution work, Linear polarisation resistance, Tafel plots and potentiodynamic scanning curves were measured. Linear polarisation resistance as a function of moisture content of CCA treated timber was also measured on coated steel samples in a series of different moisture content CCA treated timber pieces.

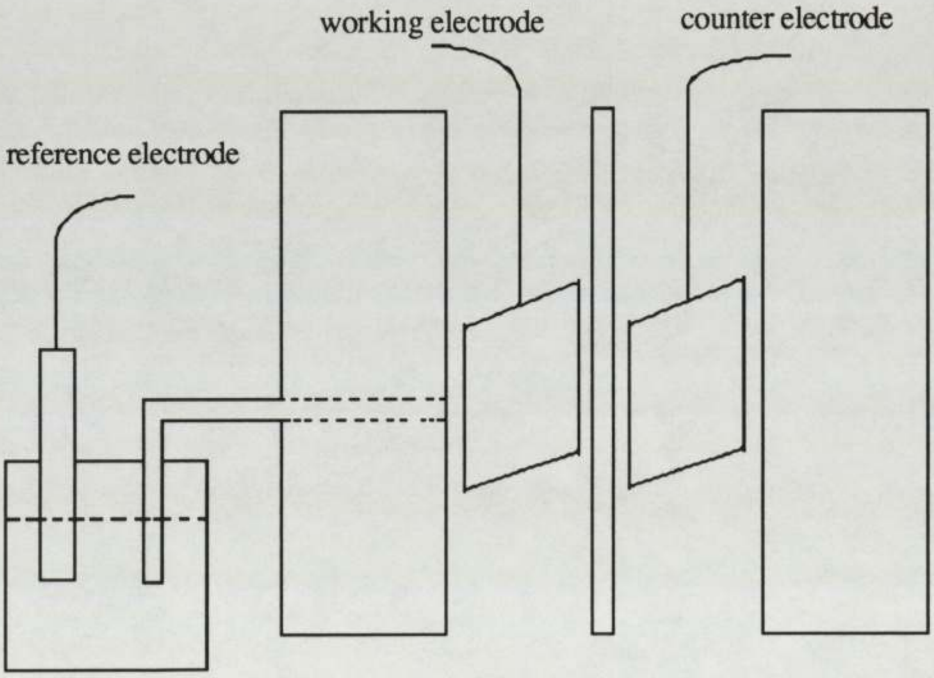


Figure 3.5 The cell for electrochemical measurement in treated timber

3.6 Surface Observation and Analysis

The as-received zinc and zinc alloy coated samples were characterised using a Cambridge Instrument Model 150 (SEM) and analysed with an energy dispersive X-ray analysis (EDXA) attachment. In addition, surface analysis was also performed on selected specimens after corrosion tests. Specimens were cleaned in deionised water and dried with acetone. Non-conducting materials such as corroded and chromated films were coated with surface active solvent and electrically connected to the SEM with colloidal silver. This avoids charging of the sample in the SEM and improves the resolution.

Chapter 4

Results and Discussion

4.1 Salt Formulated CCA Solutions

4.1.1 Linear Polarisation Resistance Measurement

The polarisation resistance technique is now familiar to those interested in corrosion rates, and was developed originally to describe the ratio between applied potential and current for an electrode. The polarisation resistance at small applied potentials is related systematically to the corrosion current density, and thus the corrosion rate. For a corrosion system if the anodic and cathodic processes are in simple electrochemical equilibrium, both processes are activation controlled, and the activation energy barrier at the electrode/solution interface is symmetrical, then under these circumstances, it was established that, close to the corrosion potential, applied potential and current density are linearly related to a close approximation. The linear polarisation resistance, R_p can be related to the corrosion current density by Stern and Geary's formula[61].

$$R_p = \frac{\Delta E}{\Delta I} = \frac{\beta a \beta c}{2.3 I_{corr}(\beta a+\beta c)} \qquad (4.1)$$

Where βa and βc are the anodic and cathodic Tafel constants. The Tafel constants are characteristic of a particular corrosion system and can be determined from a separate scan of several hundred millivolts either side of the corrosion potential (E_{corr}). When the Tafel constants for a given system are known. Stern and Geary's formula can be written:

$$R_p = \frac{B}{I_{corr}} \qquad (4.2)$$

Linear polarisation resistance measurement can be used as a rapid technique to estimate corrosion tendencies of a metal[62]. It is particularly useful for monitoring the corrosion rate over a long test period, because the polarisation is applied on a small scale and does not seriously disturb the corrosion system. It was used to evaluate the corrosion performance of zinc and zinc alloy coated steel in Type1 and 2 "salt" CCA solutions and embedded in "salt" and "oxide" timber.

4.1.2 Corrosion Performance of Zinc and Zinc Alloy Coated Steel in "salt" Solutions

Twelve types of zinc and zinc alloy coated steel samples were immersed in Type 2 "salt" solutions. The polarisation resistance (R_p) and corrosion potential (E_{corr}) were taken after the appropriate interval of time, i.e. 20 minutes, 24 hours, one week and two weeks. The immersion solution was replaced with a fresh one after every measurement, to avoid a change of solution composition that may affect the test results. Corrosion potentials were measured before linear polarisation resistance measurement. A typical linear polarisation plot of zinc coated steel (E3) is shown in Figure 4.1. The corrosion potential and polarisation resistance of samples in Type 2 "salt" solution for the different immersion times are shown in Figure 4.2 and 4.3 respectively. Figure 4.2 shows that the corrosion potential of all samples initially moved in a positive direction with immersion time but became more or less constant after one week. The polarisation resistance of most samples also approached a stable value after one week, with the exception that it increased remarkedly with time for zinc aluminium alloy coated samples, especially during the first week, and that it increased with time for zinc cobalt alloy coated steel with chromate conversion coating during first 24 hours and decreased sharply afterwards. In the case of both galvanised and electrodeposited pure zinc coatings, with and without conversion coatings, a potential value of about -950 mV was reached after one week immersion, indicating that these samples remain electrochemically active and continuous dissolution occurs from the surface. At that negative potential the Cu^{2+}

from the solution may be deposited on to the samples and form a galvanic cell that results in accelerated corrosion of zinc and the zinc alloy coated steel. This was confirmed by the surface observation that a copper deposit appeared on the surface of electrodeposited pure zinc coated samples E1, E2 and E3 after 24 hours. No further measurements were carried out after one week, since severe corrosion occurred and the zinc coatings were partially lost, this will be discussed later. Corrosion was also observed on the surface of galvanised pure zinc coated samples G1 and G2. The polarisation resistance of these pure zinc coated samples were all small, suggesting that the pure zinc coating may not provide sufficient corrosion protection in this medium. The potential of samples containing Al, Fe, Co or Ni were more positive compared with that of pure zinc coated samples and the polarisation resistance was large. In particular, for zinc aluminium and zinc nickel alloy coated samples, the polarisation resistances were much larger, indicating that the corrosion tendency of these zinc alloy coating are much less than the others in this Type 2 solution. Surface observation showed

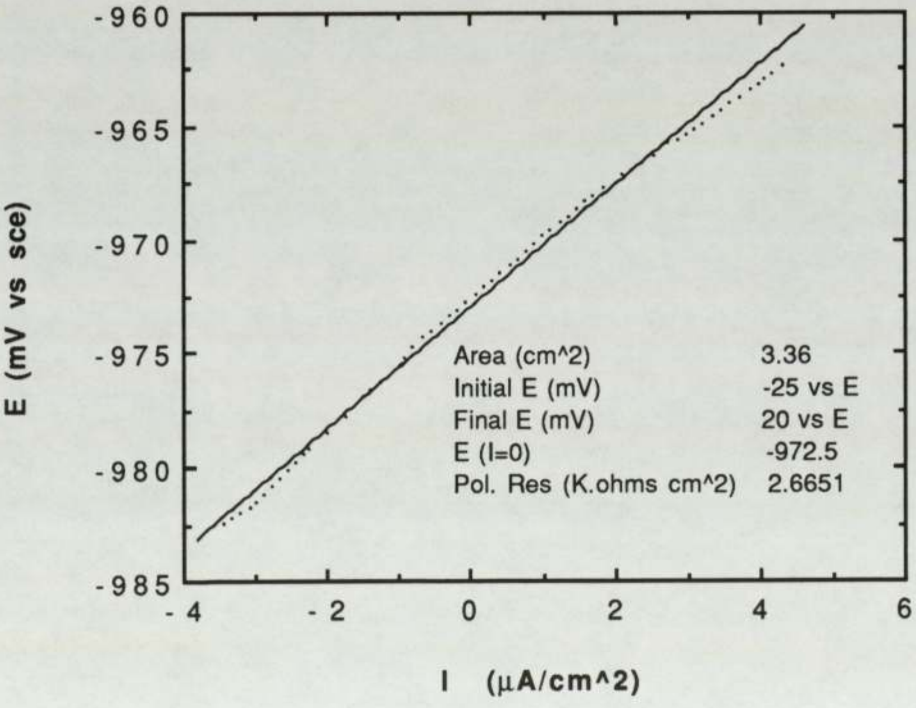


Figure 4.1 The linear polarisation plot of sample E3 in Type 2 "salt" solution after 24 hours immersion

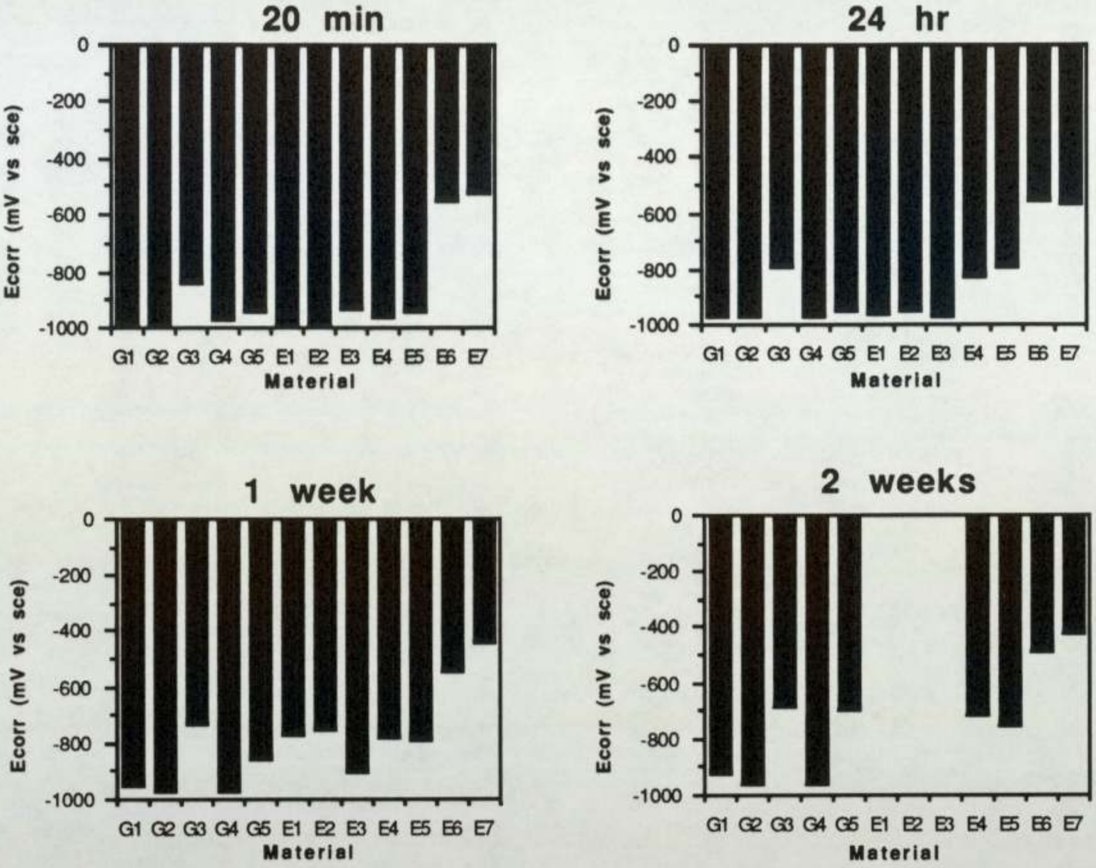


Figure 4.2 The corrosion potential of samples in Type 2 "salt" solution for different immersion times

that only zinc aluminium and zinc nickel alloy coated samples were still bright after two weeks immersion. It should be noted that zinc aluminium alloy coated samples showed no advantage during the first 24 hours immersion, but the polarisation resistance increased with time. However, for zinc cobalt alloy coated samples, a very large polarisation resistance was measured during the first 24 hours immersion, it decreased with time and pitting corrosion occurred. It may be concluded from these results that zinc aluminium and zinc nickel alloy coated steel are suitable for use in "salt" CCA treated timber environment. The polarisation resistance results also showed that the polarisation resistance of coated samples with a conversion coating was larger than that without conversion coatings during early stages, but there was no apparent difference at longer immersion times. This may suggest that the thin chromate film is readily broken down in a short time in this solution. Therefore, conversion coatings may not provide a long enough period of protection for zinc and zinc alloy coatings in this environment. However, the results from CCA preservatives solution can only be used to simulated the treated timber environment for rapid preliminary evaluation and may not exactly reflect the performance of these coated steels in treated timber, as will be discussed later.

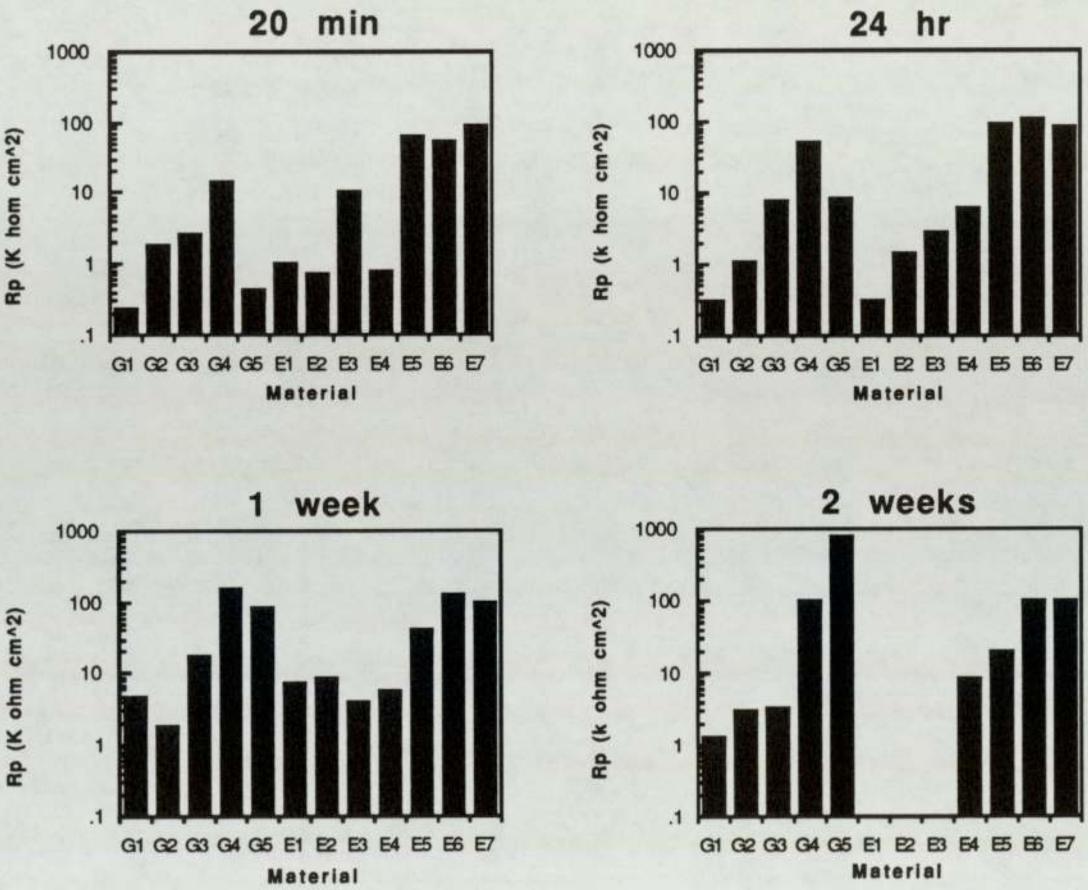


Figure 4.3 The polarisation resistance of samples in Type 2 "salt" solution for different immersion times

The corrosion potential and polarisation resistance measurements on these coated steel were also carried out in Type 1 "salt" solution and the results are shown in Figure 4.4. The results obtained in Type 1 "salt" solution are similar to those obtained in Type 2 "salt" solution. They suggest that the variation of CCA composition within the limits set by BS 4072[25] may not significantly affect the corrosion performance of zinc and zinc alloy coated steels. The tests were only performed for 24 hours and then the samples were taken out from solution, and cleaned and dried for SEM/EDAX analysis.

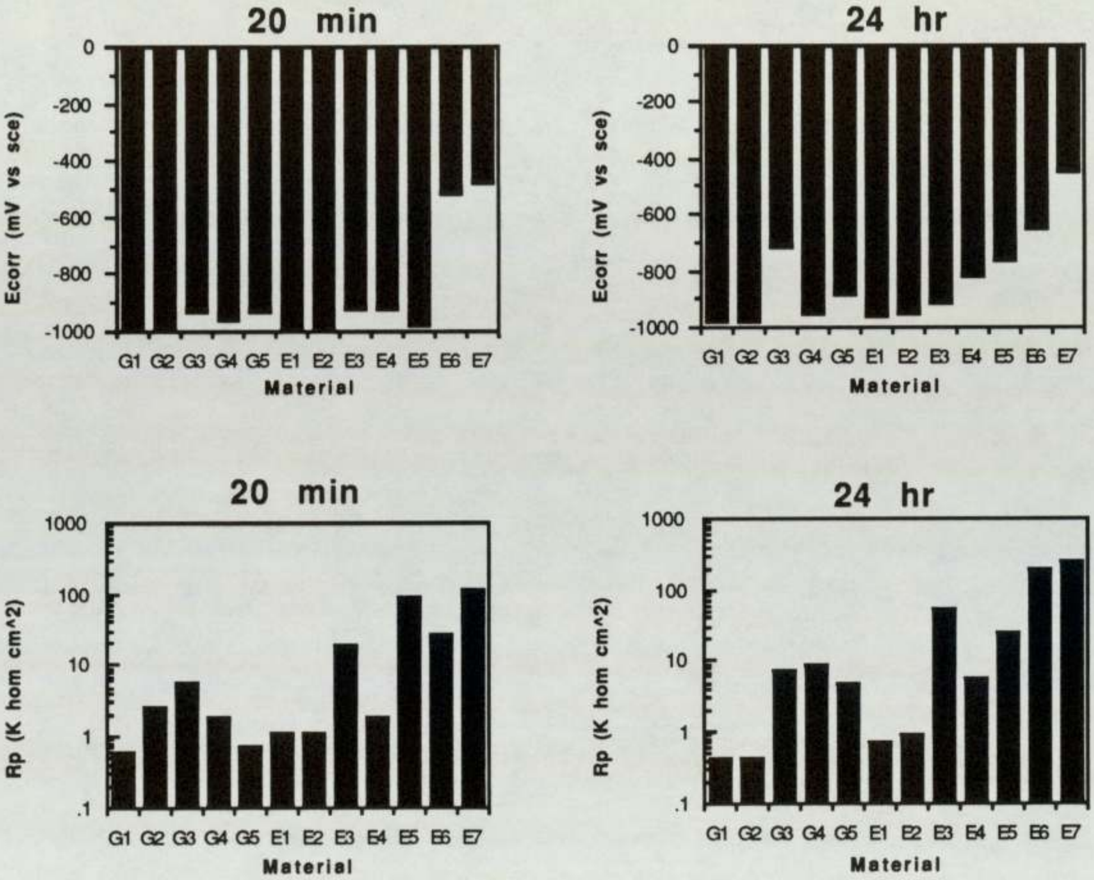


Figure 4.4 The corrosion potential and polarisation resistance of samples in Type 1 "salt" solution during 24 hours immersion

4.2 Oxide Formulated CCA Solutions

4.2.1 Passivation of a Corrosion System

A metal surface is said to be "passive" when, although it is exposed to an environment under conditions such that reaction of the metal with the environment ought to occur with decrease in the thermodynamic free energy of the system, it remains visibly unchanged for an indefinite period[63]. Figure 4.5 illustrates a typical potentiodynamical anodic polarisation curve for a metal electrode which shows passivation . In the first part (A-B), the electrode is in active dissolution state. As the potential rises, the anodic dissolution current increases following a Tafel relationship between potential and current. At B there is a departure from linearity that becomes more pronounced as the potential is increased. In the region B-C, a pre-passive film forms on the surface for some electrodes. The anodic current decreases dramatically as the potential rises from C and reaches a very small value at D. The current density and the potential at C where transition occurs are referred to as the critical current density, i_{crit}, and the passivation potential, E_{pp}, respectively. In the passive region D-E, the current remains reasonably constant, independent or slightly dependent on the potential and is called the passivation current density, i_p. As the potential increases above E, the current starts to increase along curve E-F, which is referred to as the transpassive region. Depending on the nature of the passivation system and the potential, the transpassive region may be associated with gas evolution or further oxidation of the metal. In many passivation systems, the increase of the current appears at a much more negative potential than E, associated with pitting corrosion and/or passive film breakdown. It should be noted that some passivation systems may not exhibit the complete curve of Figure 4.5 and only part of it may be obtained. A passivation state can be achieved by pushing the potential of the metal into the passive region, alternatively, the metal is in a "self- passivation" state, if the corrosion potential falls in the passsive region D-E. E_p and i_{crit} reflect the energy barrier when a transition process occurs. The more negative the passivation potential and the lower the critical current, the more easily passivation is achieved. ip is associated with an electrode process, either the dissolution of the passivation film or the transfer of ions through a passive layer. It may represent the nature and property of a passive surface.

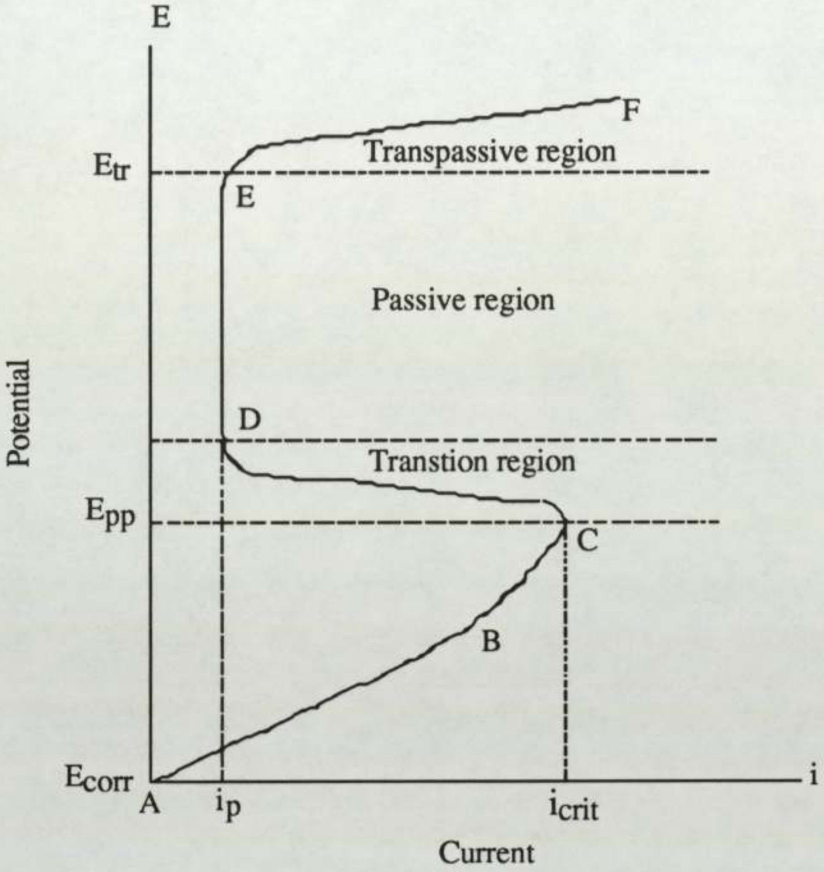


Figure 4.5 Schematic anodic polarisation curve of a metal electrode which shows passivation

4.2.2 Passivation Behaviour of Zinc and Zinc Alloy Coated Steels in "Oxide" Solutions

The zinc and zinc alloy coated samples were immersed in "oxide" solutions so that corrosion potential, E_{corr}, could be measured at the appropriate intervals of the time, i. e. 20 minutes, 24 hours, one week and two weeks. The results are shown in Figure 4.6. The polarisation resistance is extremely difficult to measure in this solution because the corrosion current is very low and the corrosion potential is very unstable. The polarisation resistance was therefore not determined in "oxide" solution, but instead potentiodynamic scan curves were measured at 24 hours and one week after immersion. A typical potentiodynamic scan curve of zinc and zinc alloy coated samples is shown in Figure 4.7, where it can be seen that the sample is passive in the potential region -800 mV to +300 mV. The potentiodynamic scan curves of samples for 24 hours immersion were similar to those for one week, so the passive film may be formed on the sample surface in a short period. The E_{pp}, i_{crit}, E_{tr} and i_p from these potentiodynamic scan curves after one week immersion are listed in Table 4.1. Figure 4.6 shows that the potential of samples in "oxide" solutions were much more positive than in

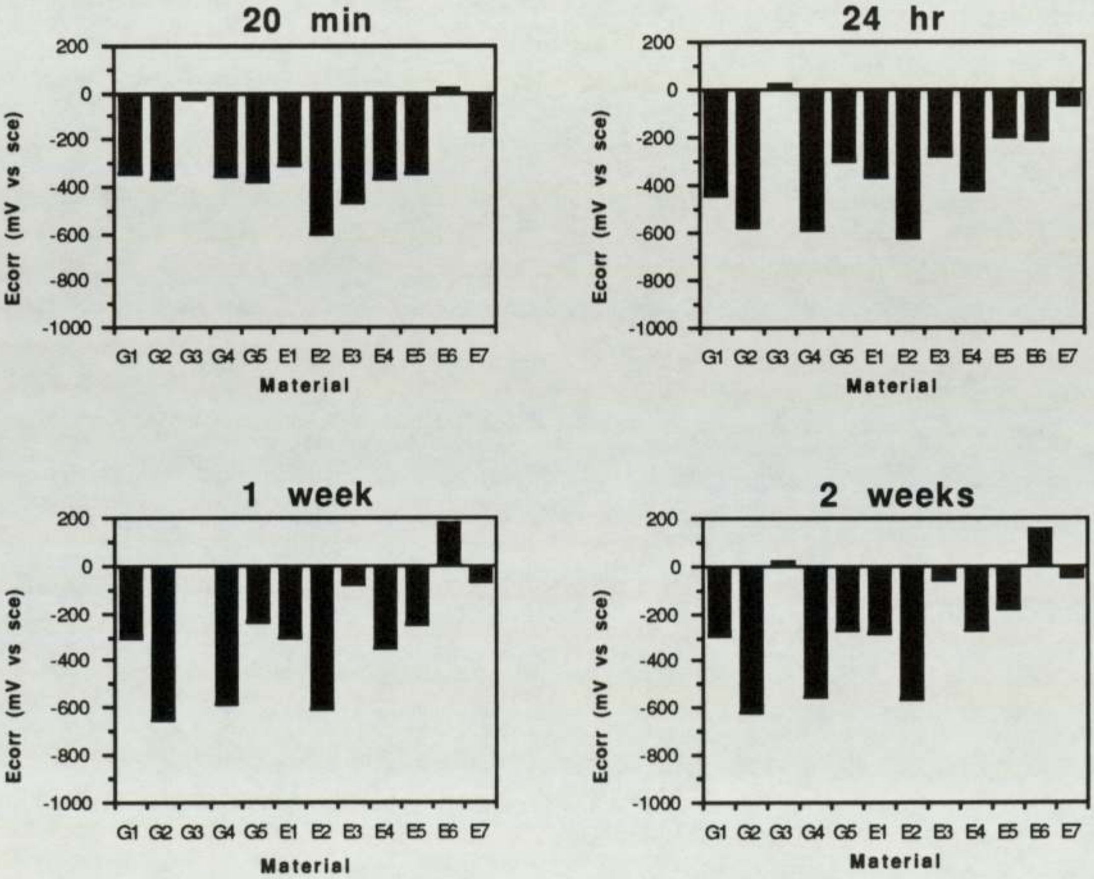


Figure 4.6 The corrosion potential of samples in "oxide" solution for various immersion times

"salt" solution. The potentials were not stable during the testing period, but all fall in the passive region (E_{pp} - E_{tr}), indicating that the pure zinc and zinc alloy coated steel are self-passivated in this solution, This may suggest that passive films formed on the specimen surfaces in "oxide" solution provide greater corrosion protection to zinc and zinc alloy compared to films formed in "salt" solution. Visual surface observation suggested that no corrosion was found on the surfaces of any samples after two weeks immersion. It should be stressed that since all samples are in a "self-passive" state, E_{pp} and i_{crit} will not appear in the polarisation curves if the potentiodynamic sweep commences from the corrosion potential. In the present work, the sweep was made to start at a very negative potential (-1000 mV vs sce), the surface of the sample was somewhat activated. E_{pp} and i_{crit} corresponds to the passivation potential and the critical current density respectively, when the transition from active to passive occurs in this condition. The passivation curves of G5 to G4 samples in the Table 4.1, even though, do not exhibit E_{pp} and i_{crit} and show that these samples directly enter the passive state without an energy barrier. It can be seen from Table 4.1 that the

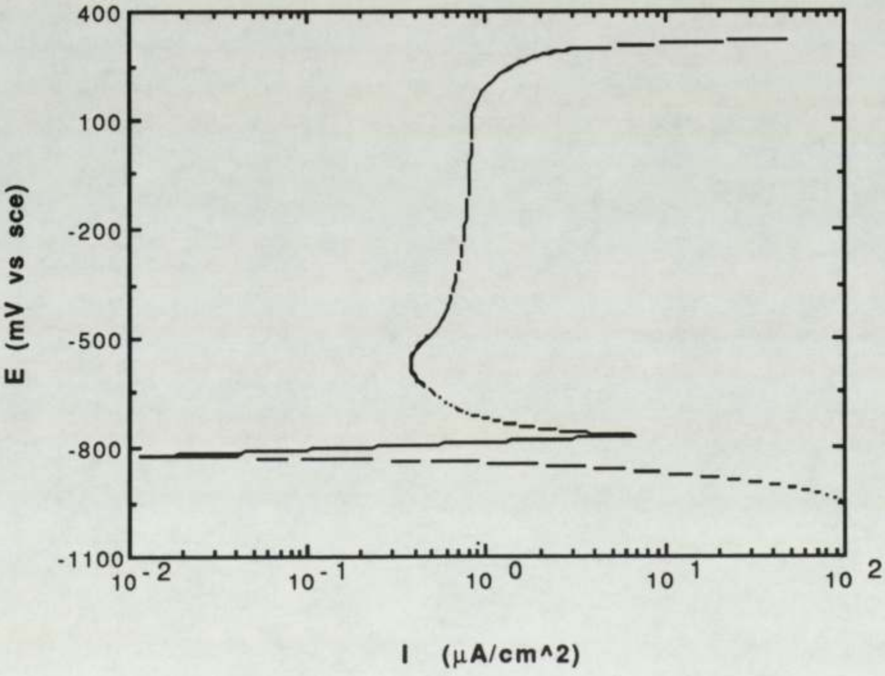


Figure 4.7 The potentiodynamic scan curve of pure zinc coated steel sample, E3, in "oxide" solution after one week immersion

Table 4.1 Epp, icrit, Etr and ip obtained from potentiodynamic scan curves in "oxide" solutions after one week immersion

Specimen	E_{pp} (mV)	i_{crit} (μA/cm2)	E_{tr} (mv)	i_p (μA/cm2)
G5			334	0.0041
E7			190	0.014
E6			188	0.016
E3			104	0.056
G4			188	0.074
E5	-780	0.18	-74	0.089
G2	-776	2.2	162	0.47
E1	-776	4.5	238	0.74
E2	-776	3.8	94	1.09
G1	-750	5.8	146	1.19
E4	-756	7.0	-68	1.25
G3	-750	11.0	160	5.29

passivation of all samples occurred over wide potential range, at least 700 mV, and this may minimize the possibility of the pitting corrosion in this media. It can also be seen that although the passive film forms on the surface of all the tested samples, the property of the passive film shows noticeable differences. Results in Table 4.1, going down from G5 to G3 is in the order of increasing passivation current, ip, determined from the potentiodynamic curves. This shows that the zinc aluminium and zinc nickel alloy coatings have superior corrosion resistance compared to the others and that the conversion coating on zinc and zinc alloy coated steels provides a significant improvement in the corrosion performance in "oxide" solutions compared to "salt" solution. Again, it should be noted that the result from "oxide" solution may not represent the situation in "oxide" timber, as will be shown later.

4.3 Corrosion Performance of Zinc and Zinc Alloy Coated Steel Measured by the Electrochemical Sensor

4.3.1 Corrosion Potential and Polarisation Resistance of Zinc and Zinc Alloy Coated Steels in "Salt" Timber

Eleven types of zinc and zinc alloy coated steel samples were embedded in "salt" timber to make an electrochemical sensor, as described in Chapter 3, Figure 3. A mild steel sample was also embedded for comparison. The specimens were exposed to 100% RH air at room temperature. The corrosion potential and polarisation resistance were measured on at least a weekly basis and the results are shown in Figure 4.8 and Figure 4.9 respectively. Figure 4.8 indicates that the corrosion potential for all samples increases initially with time until they become more or less stable, after a week or so. The corrosion potential of most zinc and zinc alloy coated samples is more negative than that of mild steel, so the coatings will provide some degree of galvanic protection for the substrate from corrosion, depending on the type of coating. It can also be seen that compared to pure zinc, the corrosion potential increases with the addition of alloy element, indicating that the degree of sacrificial protection is reduced. Figure 4.9 shows that the polarisation resistance of most samples approaches a stable value after two weeks. It can be seen that all coated samples have better corrosion resistance than the mild steel. The polarisation resistance of the pure zinc coated sample, which has the poorest corrosion performance among the coatings, is about twice that of mild steel. The addition of alloying elements significantly improves the polarisation resistance, especially 55% Al and 12% Ni. However, it must be stressed that a high proportion of aluminium in a Zn-Al alloy coating may be required to effectively enhance the corrosion resistance since the Zn-5%Al (G6) coated sample showed no apparent advantage. An increase in corrosion resistance was also achieved due to the conversion coating, but the chromate treatment may raise the risk of pitting.

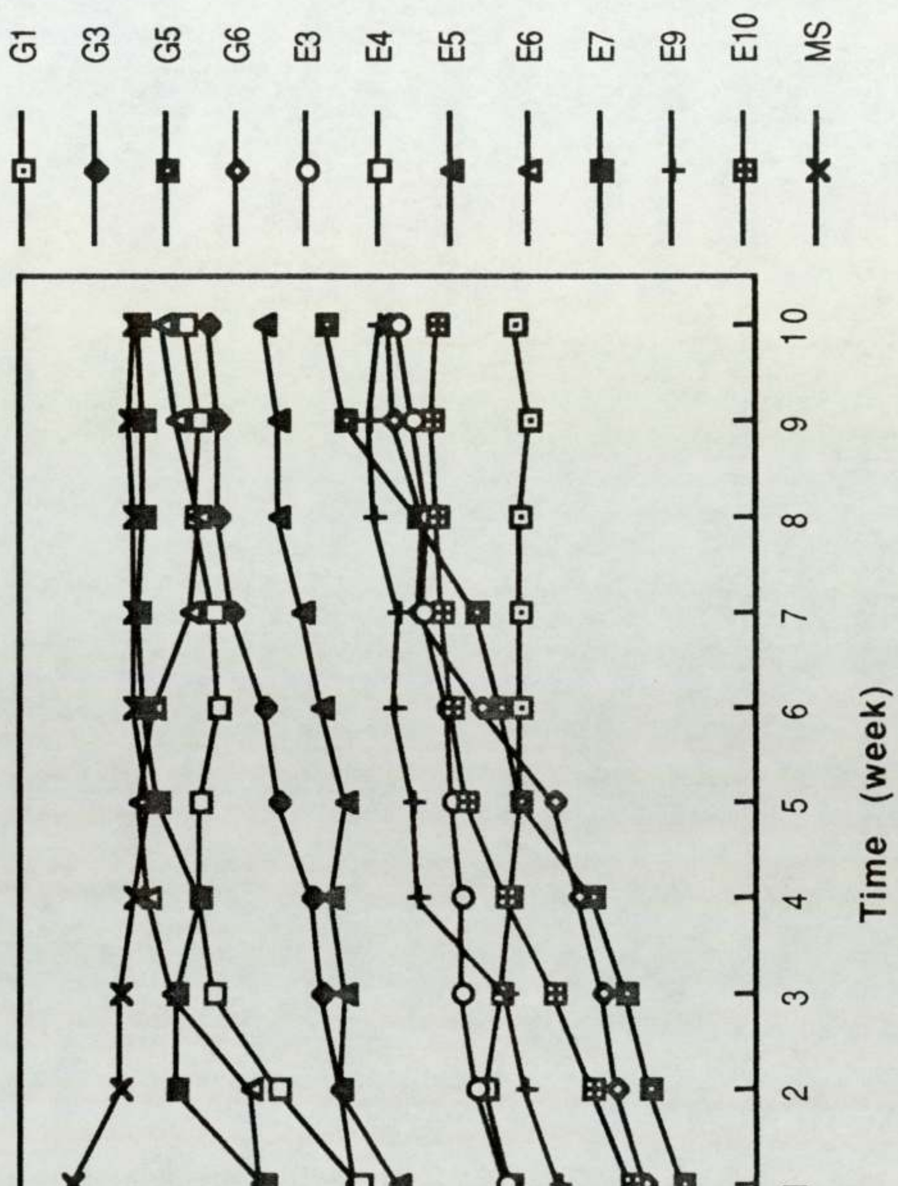


Figure 4.8 The corrosion potential of zinc and zinc alloy coated samples vs time in "salt" wood

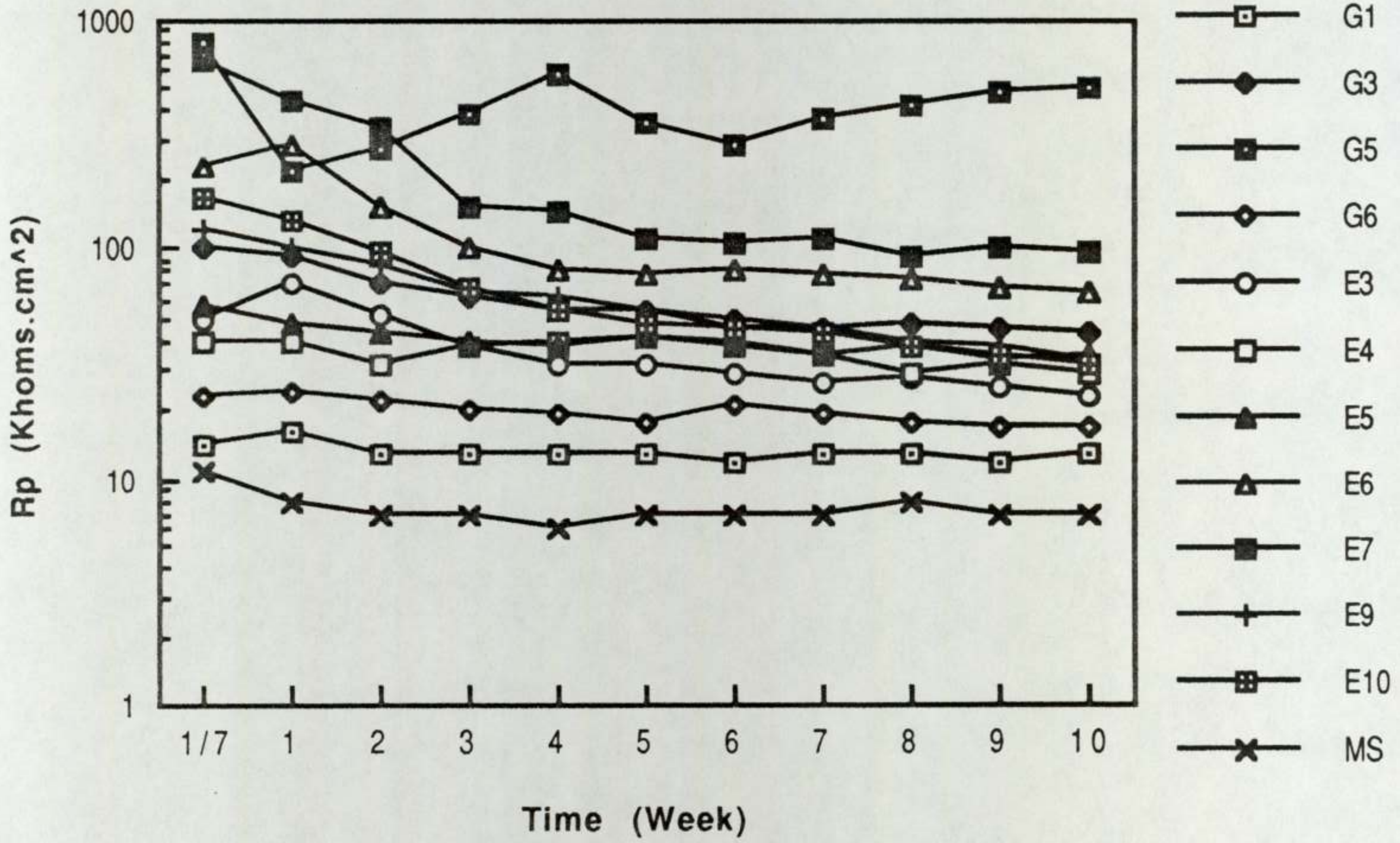


Figure 4.9 The polarisation resistance of zinc and zinc alloy coated samples vs time in "salt" wood

4.3.2 Corrosion Potential and Polarisation Resistance of Zinc and Zinc Alloy Coated Steels in "Oxide" Timber

The corrosion potential and polarisation resistance of this range of zinc and zinc alloy coated steel, as well as mild steel, were also measured in "oxide" wood. The experimental process is the same as that in "salt" wood. The corrosion potential and polarisation resistance of samples vs time are shown in Figure 4.10 and Figure 4.11 respectively. These results suggest that the corrosion potential and polarisation resistance tend to stabilise after a few weeks. Values of polarisation resistance are large at first stage, then fall sharply after several weeks. It is speculated that a very thin passive film is formed on the surface of the samples when in contact with "oxide" wood, but these films are too thin to provide a long period protection for zinc and zinc alloy coated steel. The polarisation resistance approaches a stable value after about three weeks. In "oxide" wood, the conversion coating provides significant improvement for corrosion resistance of zinc and zinc alloy coated steels. The polarisation resistance of samples with conversion coatings is about twice that of those without conversion coatings. The effect of alloy elements is similar to that in "salt" wood, Zn-55% Al (G5) and Zn-12.5 Ni (E6 and E7) coated steel having the best corrosion performance, while other alloy elements also improve the corrosion resistance of zinc coated steel to a certain degree in "oxide" wood.

4.3.3 Tafel Polarisation Curves Measurement Results in CCA Treated Timber

In the above sections 4.1 and 4.3, the polarisation resistance (R_p) has been used to assess the corrosion performance of zinc and zinc alloy coated steels in CCA treated timber. However, the corrosion current must be known for service life prediction. From the polarisation resistance values obtained, it is possible to calculate the corrosion current, I_{corr}, using the Stern and Geary's formula[62], see Formula 4.1 and 4.2.

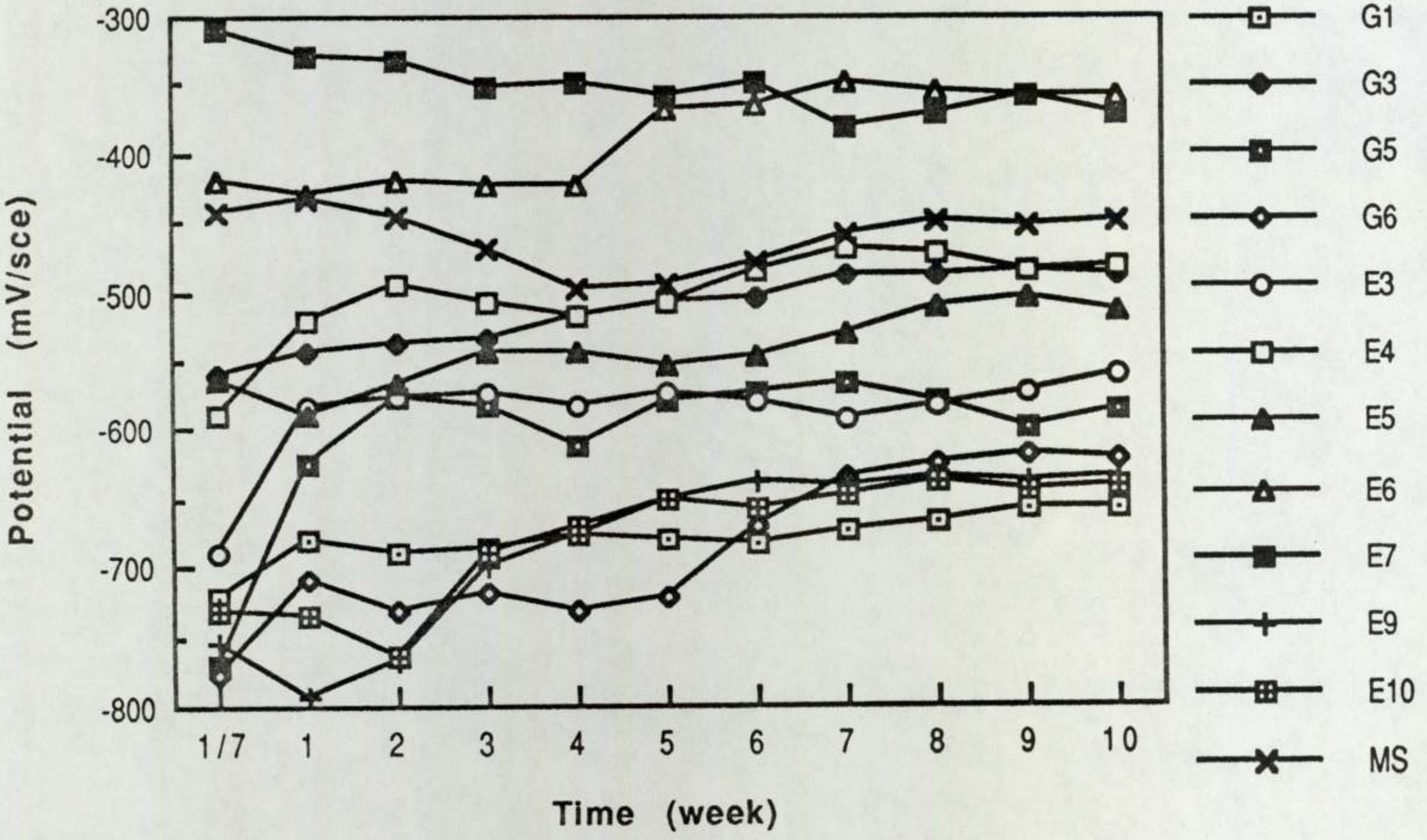


Figure 4.10 The corrosion potential of zinc and zinc alloy coated samples vs time in "oxide" wood

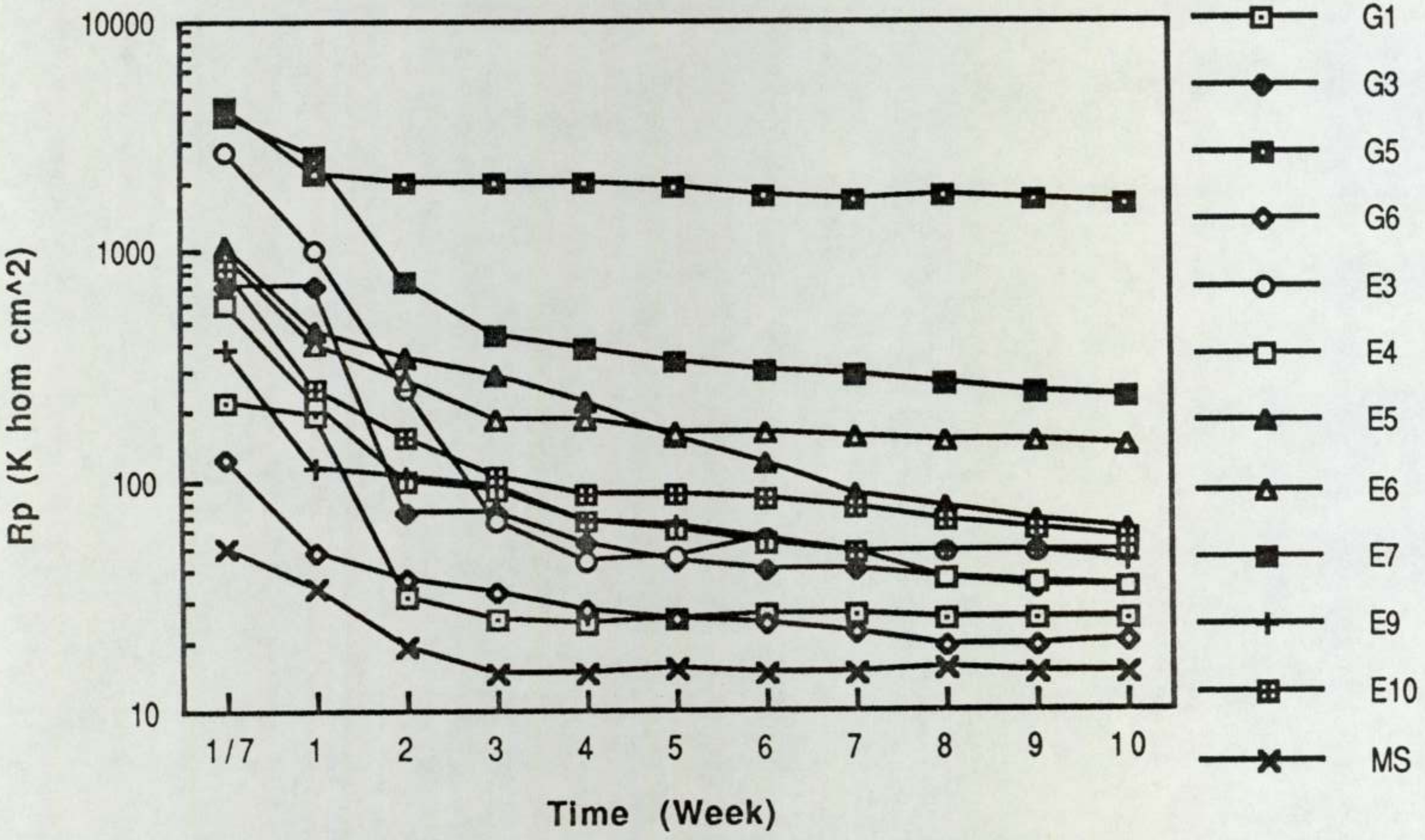


Figure 4.11 The polarisation resistance of zinc and zinc alloy coated samples vs time in "oxide" wood

Tafel polarisation curves have been determined for a number of coated steels after being embedded in water saturated CCA treated timber for ten weeks, as typically shown in Figure 4.12. Values of βa and βc and hence B (mV/decade) calculated from Tafel slopes produced whilst carrying out potentiodynamic polarisation scans are given in Table 4.2.

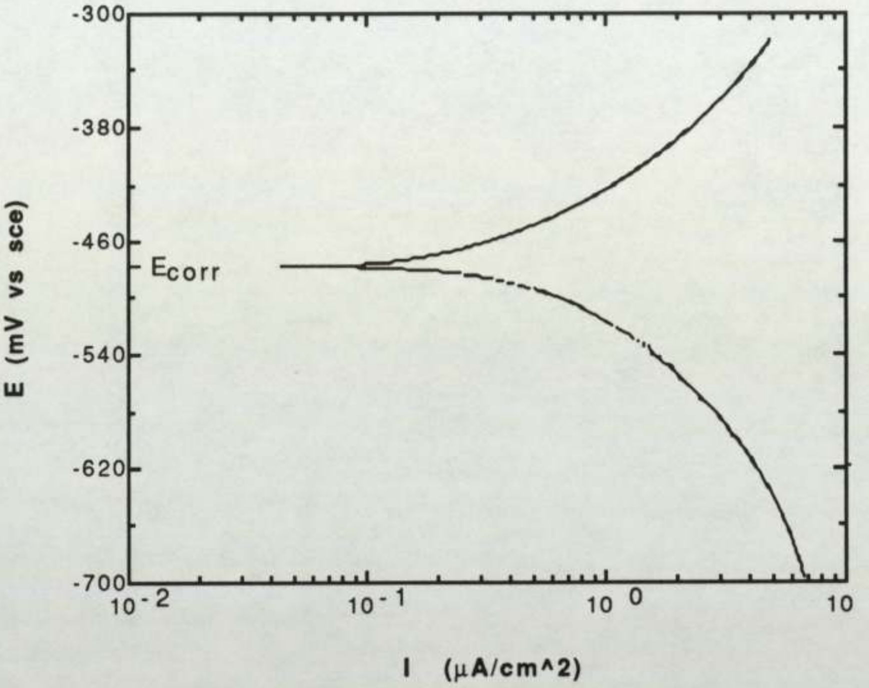


Figure 4.12 The Tafel polarisation curve of sample G3 in "oxide" wood

Table 4.2 βa,βc and B of some galvanised samples in water saturated "salt" and "oxide" wood

Treated timber	Specimen	βa	βc	B
"salt" wood	G1	149	505	50
	G5	403	173	52
	G3	231	375	62
"oxide" wood	G1	172	489	55
	G5	394	235	64
	G3	223	435	64

It can be seen from Table 4.1 that values of βa and βc measured on various coated steels embedded in "salt" and "oxide" wood are rather scattered, but the difference in value of B is not significant. therefore, the value of 58 mV was used for subsequent calculation of I_{corr} in Section 4.5.2.

4.3.4 The Corrosion Potential and Polarisation Resistance of Zinc Coated Steel as a Function of Moisture Content of "Salt" and "Oxide" Wood

Corrosion rates of zinc coated steel in a timber environment are not only related to the inherent corrosion characteristics of the coating materials, but they are also related to electrical conductivity of CCA treated timber which is mainly influenced by the moisture level and the presence of soluble preservatives. Since the concentration of soluble preservatives is constant for timber treated under identical conditions, the corrosion rate will be a function of the moisture content of the timber.

The corrosion potential and polarisation resistance of zinc coated steel were measured as a function of the moisture content of the timber. This work was aimed at determining the critical moisture level at which the sensor works and how the sensor responds to the change of moisture content. The corrosion cell is similar to that described in Chapter 3 (Figure 3.2 and Figure 3.5.), but pieces A and B are much thinner (5 mm). This enabled the cell to more easily reach equilibrium with the surrounding environment. Galvanised zinc coated steel samples (G1) were embedded in "salt" and "oxide" wood. Prior to the measurement, the sensors were exposed to 100% RH air for two weeks during which the cells reach a saturated moisture level. The cells were then placed in a semi-sealed chamber, allowing the moisture content of timber to reduce gradually. The moisture content decreased to 15% in two weeks and then remained constant. The sensors were afterwards re-exposed to saturated air and rapidly reached a saturated moisture level in one week. The corrosion potential, polarisation resistance and the corresponding moisture content were measured at the appropriate interval of time during these processes. The moisture contents of timber were determined by a moisture meter, the values are corrected by an oven drying method (BS 4072[25]).

The corrosion potentials and polarisation resistances as a function of moisture content in "salt" and "oxide" wood are shown in Figure 4.13 - 4.16. It can be seen that the corrosion potential and polarisation resistance of coated steel is strongly dependent on moisture content of timber below about 23%, while it remains approximately constant above that value. These results are in agreement with previous studies[60]. It is also demonstrated that the sensor still operates satisfactorily at 15% moisture content which is similar to the typical "service" moisture level for trussed rafter roofs in U.K.(10-18%)[35]. Furthermore, it can be observed that the sensor is reversible with change of moisture content. There is a delay in the corrosion potential and polarisation resistance response in the reverse cycle, this may be due merely to the way that the moisture content was measured, since the moisture content of the outer timber should be higher than that of the inside timber where the sample electrode was mounted and the higher value of moisture content will be shown on the moisture meter. Above all, it has been demonstrated that the sensor is capable of monitoring corrosion performance of zinc and zinc alloy coated steel in CCA treated timber in "service" condition.

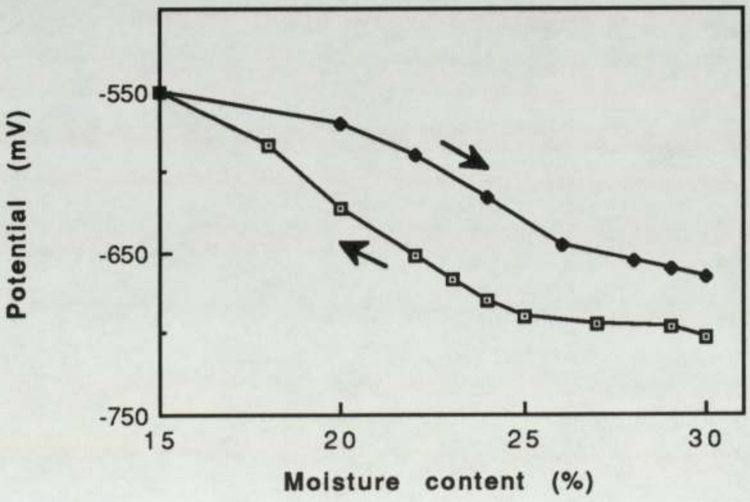


Figure 4.13 The corrosion potential of zinc coated steel vs moisture content of "salt" wood

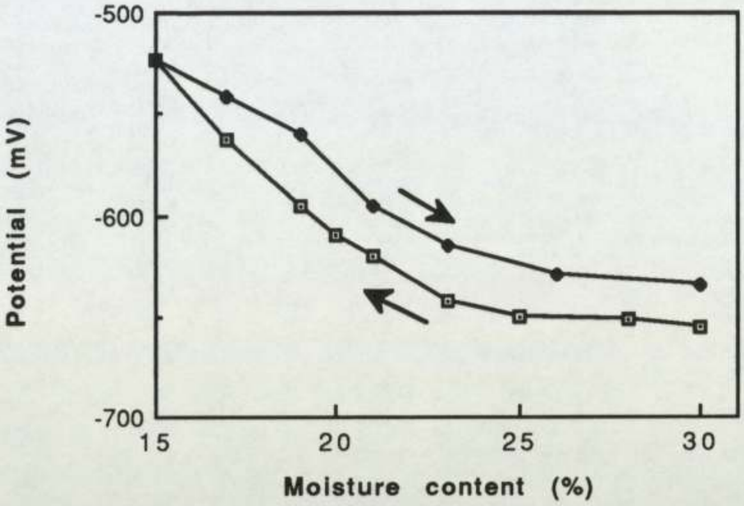


Figure 4.14 The corrosion potential of zinc coated steel vs moisture content of "oxide" wood

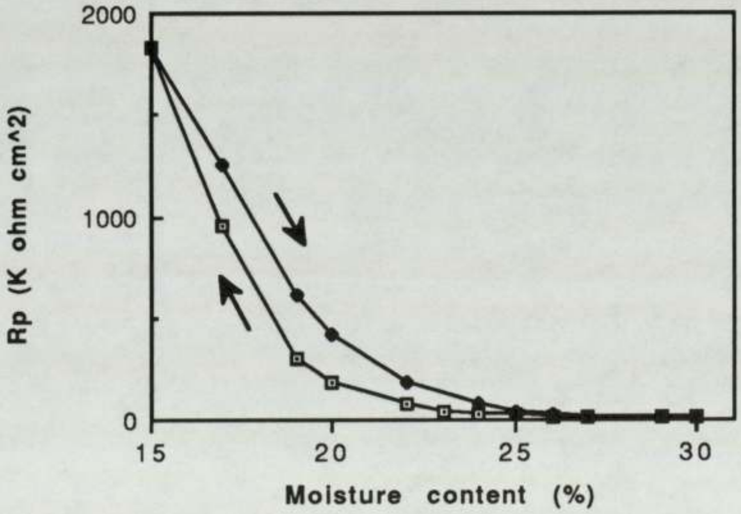


Figure 4.15 The polarisation resistance of zinc coated steel vs moisture content of "salt" wood

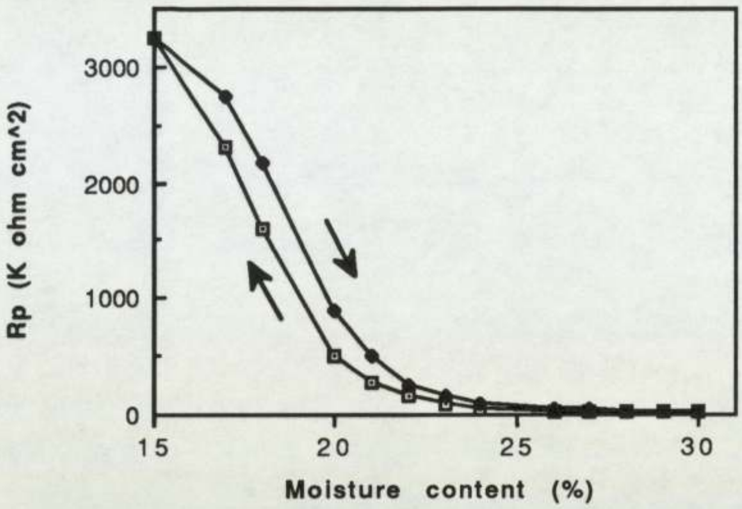


figure 4.16 The polarisation resistance of zinc coated steel vs moisture content of "oxide" wood

4.4 Surface Observation and Analysis

SEM/EDXA have been performed on the as-received specimens and the samples after various corrosion tests in an attempt to characterise the change of surface structure and composition due to the corrosion process. These studies should assist in understanding the corrosion mechanism of zinc and zinc alloy coated steel in timber environments. The results are summarised below.

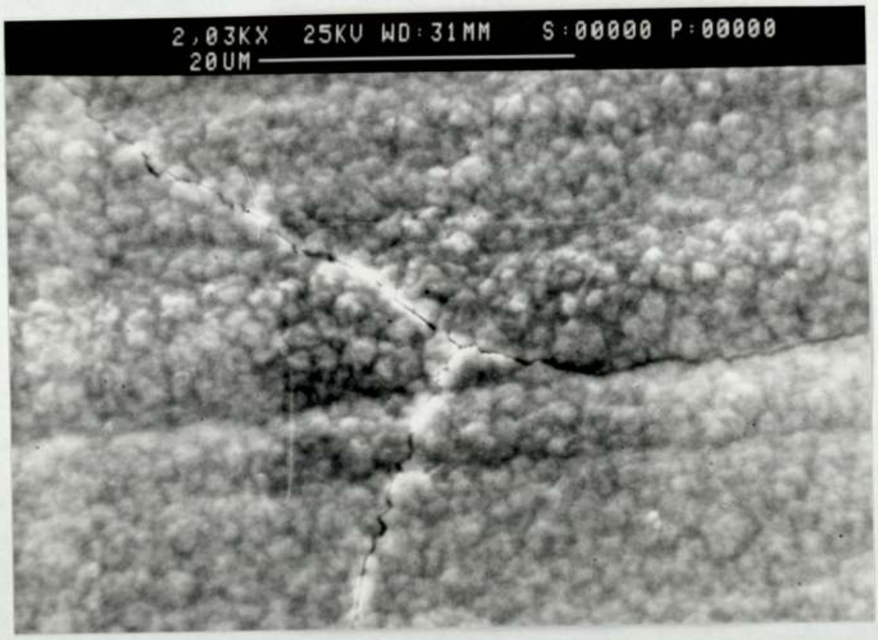
4.4.1 Chromate Conversion Coating

Examination in the SEM of samples with and without chromate conversion coatings did not reveal any significant differences. EDXA confirmed that elemental chromium was present on the surface of all samples with a conversion coating. XPS profile analysis on Zn-Ni specimens with the chromate treatments suggests that approximately 30% Cr exist on the surface, but this decreases rapidly within about a 0.2 μm outer layer. The Cr_2O_3 is the dominant form of the chromate products. XPS profiles on other coatings are being obtained but results are not yet available.

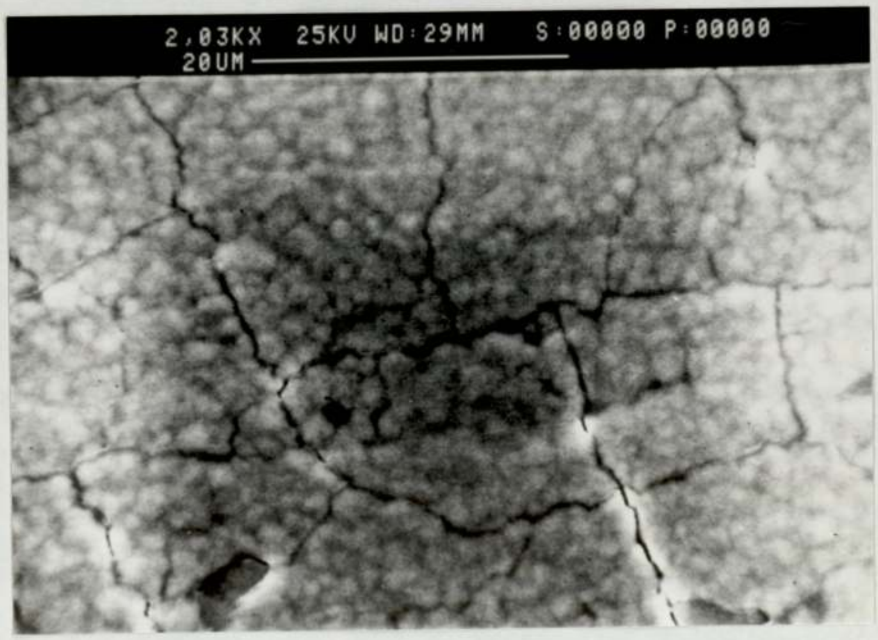
4.4.2 Samples Immersed in CCA Solutions

A Zn-55% Al alloy coated sample immersed in "salt" CCA solution for two weeks was examined in the SEM and analysed using EDXA, no significant change in composition and structure of the sample was found. A Zn-Ni alloy coated sample also showed little change in composition but cracking was apparent on the sample's surface as shown in Figure 4.17 (a) and (b). Copper deposits were detected on all pure zinc coated steel samples after a 24 hour immersion in "salt" CCA solution. The SEM/EDXA results showed that 2-5% copper was present on the surface of samples. Local areas of corrosion were also observed on pure zinc coated steel with conversion coatings, Figure 4.18 (a), resulting in coating exfoliation as shown in Figure 4.18 (b). Similarly areas of exfoliation were also observed on Zn-Co alloy coated steels, as shown in Figure 4.19. The composition analysis revealed that above 90% of iron existed within the pits which confirmed that the coating had been removed completely in a localised area. A large amount of iron was also detected in the cracked areas, suggesting that such coatings do not protect the steel substrate from corrosion. It is considered that there are localised area of stress in the coating which cause cracking on immersion in the test solution. Continued exposure results in exfoliation of the coating.

SEM/EDXA were not carried out on coated samples immersed in "oxide" CCA solution, since, as mentioned earlier, the zinc and zinc alloy coatings were under passivation and the samples remained bright as received after immersion in "oxide" CCA solution for two weeks.

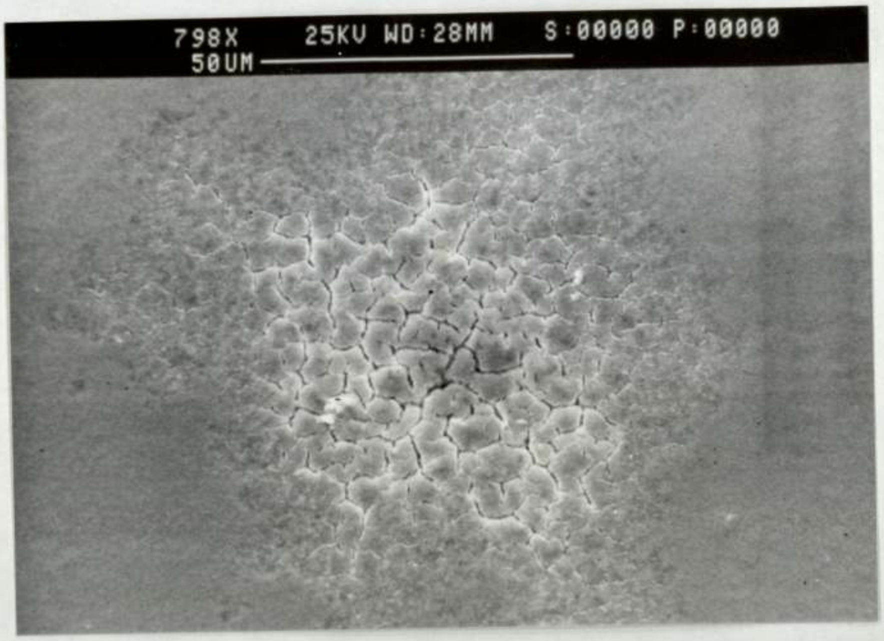


(a) Zn-Ni

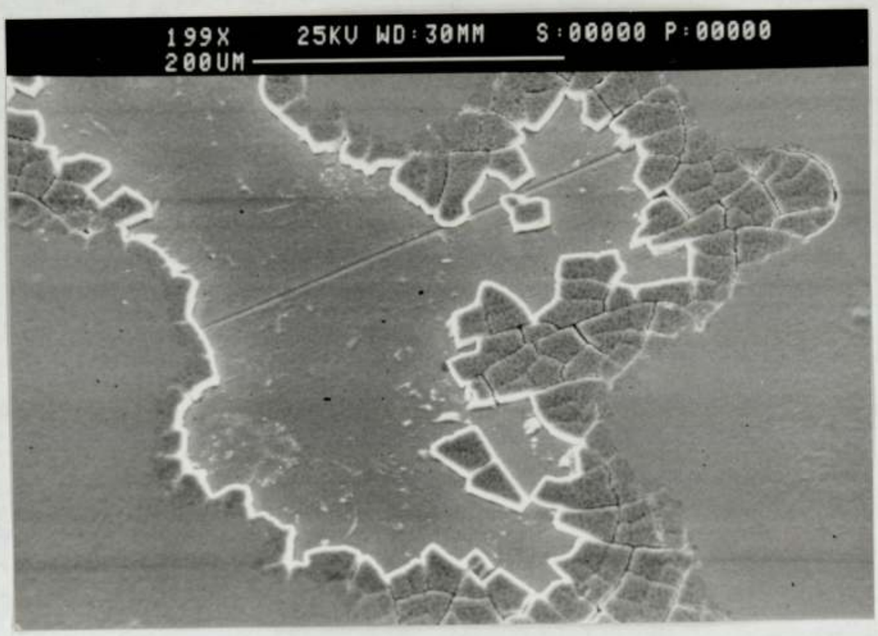


(b) Zn-Ni with chromate treatment

Figure 4.17 Zinc nickel alloy coated samples after two weeks immersion in "salt" solution showing cracking of the coating



(a) Zn



(b) Zn with full passivation

Figure 4.18 Pure zinc coated samples after 24 hours immersion in "salt" solution showing localised areas of (a) cracking and (b) exfoliation

Figure 4.19 Zinc cobalt alloy coated sample after two weeks immersion in "salt" solution showing exfoliated area

4.4.3 Samples Embedded in the CCA Treated Timber

The timber corrosion cells were dismantled after ten weeks corrosion tests. The coated steel samples were examined visually and by SEM/EDXA. The wood samples that were in contact with the coated samples were also analysed by SEM/EDXA and the compositions are given in Tables 4.3 and 4.4. It should be noted that EDXA is unable to detect the light elements such as C, O and H which are the main components of the wood itself and that any element less than 1% was regarded as negligible.

Zn-55% Al coated samples remain bright as received after being embedded in both "salt" and "oxide" treated timber for ten weeks. No evidence of zinc corrosion products could be detected in "oxide" wood sample, while only insignificant amounts of Zn and Al elements existed in the "salt" wood. This agrees with the electrochemical measurement of polarisation resistance; Zn-55%Al coated steel had the highest value of all the samples.

Table 4.3 The composition of "salt" wood sample surface after ten weeks corrosion test

Sample	Element (%)							
	Zn	Cu	Cr	S	Al	Ni	Co	Fe
G1	89.1	3.2	3.0	2.8	/	/	/	/
G3	69.3	5.7	6.3	2.5	/	/	/	11.3
G5	4.9	40.2	40.8	5.0	4.5	/	/	/
E3	65.1	12.1	16.7	2.4	/	/	/	/
E4	46.9	21.3	25.0	2.2	/	/	/	/
E5	40.1	25.3	27.6	2.9	/	/	/	/
E6	15.9	37.6	38.1	3.6	/	1.7	/	/
E7	10.6	38.8	41.3	3.8		1.7		

Table 4.4 The composition of 'oxide' wood sample surface after ten weeks corrosion test

Sample	Element (%)						
	Zn	Cu	Cr	Al	Ni	Co	Fe
G1	75.3	8.4	13.9	/	/	/	/
G3	53.1	12.0	21.9	/	/	/	9.0
G5	/	36.7	60.7	1.2	/	/	/
E3	29.0	21.8	44.2	/	/	/	/
E4	37.0	20.5	38.4	/	/	/	/
E5	20.4	25.9	52.2	/	/	/	/
E6	12.4	35.4	59.8	/	/	/	/
E7	1.1	35.4	59.8	/	/	/	/

Zn-Ni alloy coated steel also showed little change in surface structure and composition and only a small quantity of zinc was found in both "salt" and "oxide" wood samples. The cracking which was observed on samples after immersion in CCA "salt" solution was not evident in the treated timber, Figure 4.20, although the testing period in timber (ten weeks) was much longer than that in the solution (two weeks). On the other hand, localised cracking was observed on Zn, Zn-Fe and Zn-Co coated samples after being embedded in wood, as shown in Figures 4.21 and 4.22. However, corrosion in the treated timber was not as severe as in the "salt" solution. The conversion coating improved the corrosion resistance significantly for all coatings, but cracking and associated pits was found on "full passivation" pure zinc coated steel (E3), as shown in Figure 4.23. The corrosion morphology of these coatings in the "oxide" CCA treated timber is similar to that in the "salt" treated timber, but localised cracking and exfoliation are less evident than that in the latter, as shown in Figure 4.24 and Figure 4.25.

It can been seen from Tables 4.3 and 4.4 that approximately the same proportion of alloy elements exist in the wood samples contacted with Zn-Al (G5) and Zn-Fe (G3) coated steel, suggesting that Al and Fe may not enrich in the coating surface after corrosion. This was confirmed by coated sample surface analysis which showed no change of composition for Zn-Al (G5) and Zn-Fe (G3) coated samples embedded in timber. The Co element has not been detected in the wood samples contacted with Zn-Co coated samples, but neither is there an increase in Co concentration on the Zn-Co coating surface after the corrosion process. Bearing in mind that there is only 1% Co in Zn-Co coating, the enrichment of Co resulting from corrosion may not be significant. No enrichment of Ni element was found on Zn-Ni alloy coated surface, however, considering that only very slight corrosion occurred, dramatic change of the alloy composition would not be expected. No copper deposit was detected on Zn-55%Al (G5) and Zn-Ni (E6 and E7) coated samples, but there was 1-4% Cu on all the other samples. This could be of vital important since the copper deposit may form a galvanic corrosion cell with the undeposited area to result in accelerated corrosion.

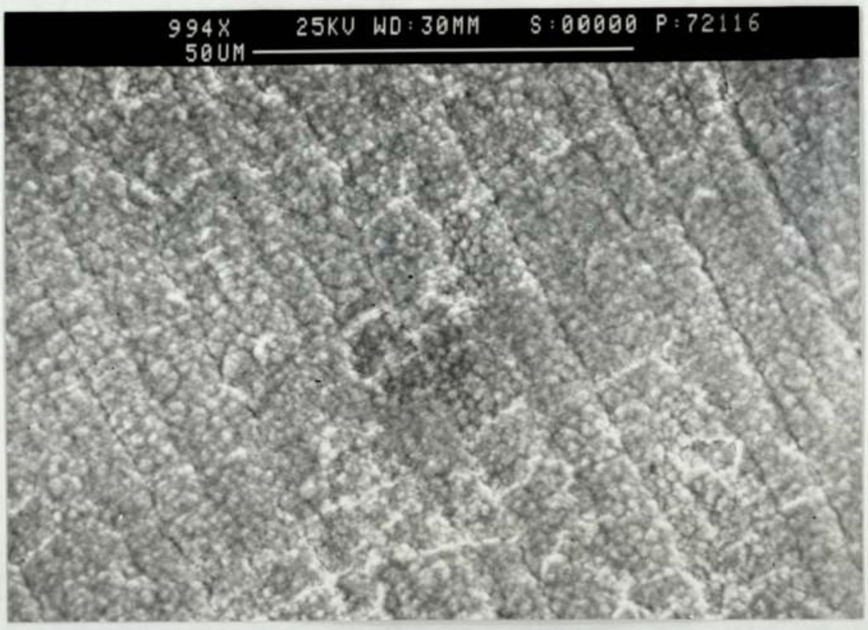


Figure 4.20 Zinc nickel alloy coated sample after being embedded in "salt" timber for ten weeks - no cracking in observed

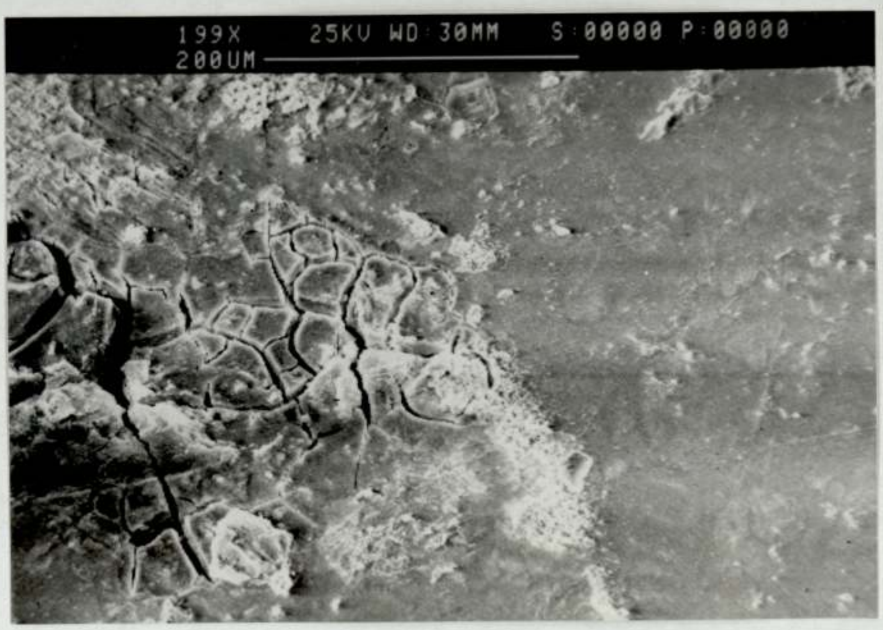


Figure 4.21 Zinc coated sample after being embedded in "salt" wood for ten weeks - localised cracking

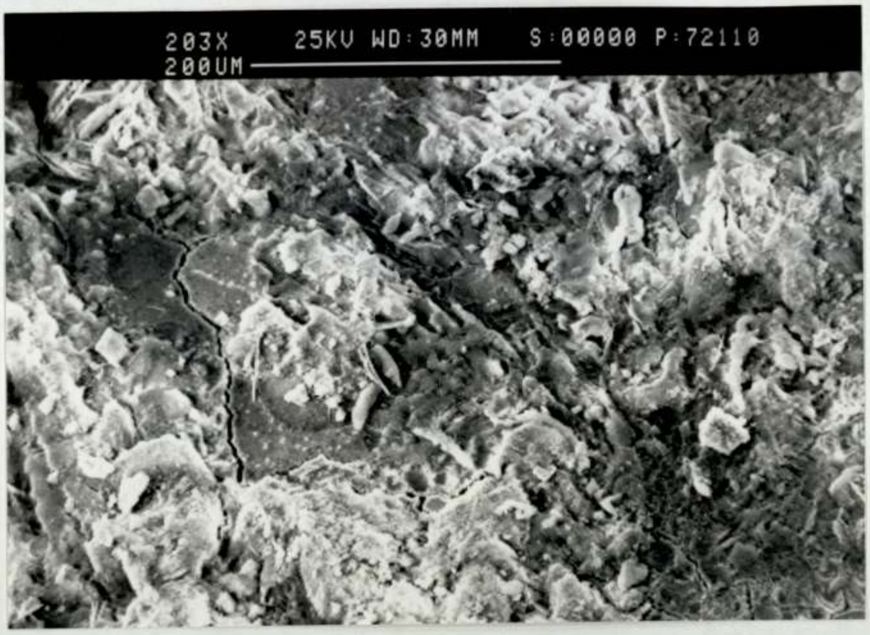


Figure 4.22 Zinc cobalt alloy coated sample after being embedded in "salt" wood for ten weeks

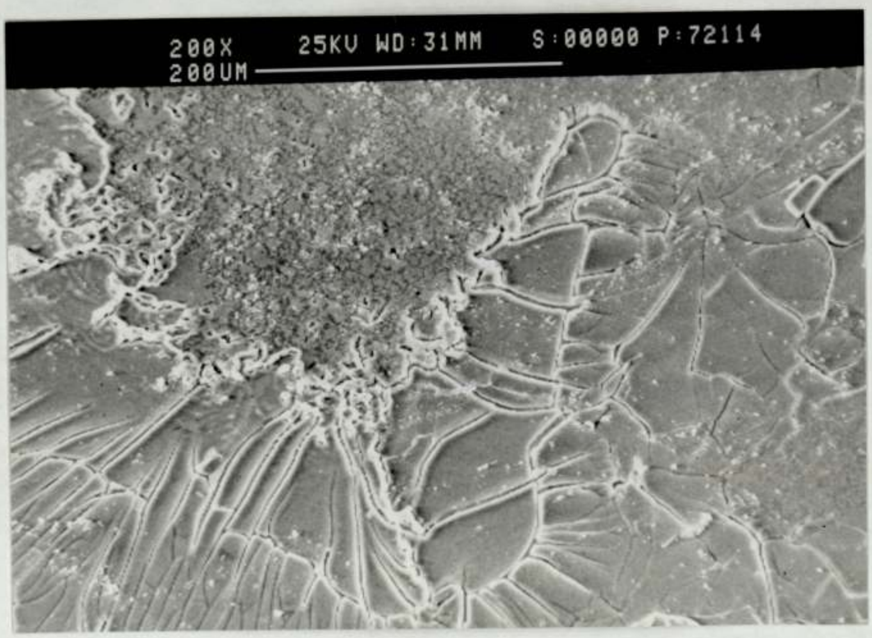


Figure 4.23 Zinc coated steel with "full passivation" sample after being embedded in "salt" wood for ten weeks

Figure 4.24 Zinc cobalt alloy coated sample after being embedded in "oxide" wood for ten weeks

Figure 4.25 zinc coated steel with "full passivation" sample after being embedded in "oxide" wood for ten weeks

4.5 General Discussion

In the present study, Corrosion tests on zinc and zinc alloy coated steel have been carried out in CCA solutions and embedded in CCA treated timber. The coated specimens and the wood in contact with them were subsequently examined by SEM/EDXA. Some general information on the corrosion performance of these materials can be gathered by systematic consideration of these results, as discussed below.

4.5.1 The Corrosion Ranking of Zinc and Zinc Alloy Coated Steel in CCA Solutions and Embedded in CCA Treated Timber

The corrosion ranking of samples can be obtained using polarisation resistance and passivation current results in CCA solutions and CCA treated timber (Section 4.1-4.3), see Table 4.5. It can be seen from Table 4.5, that the results in "salt" solution closely fit those obtained from the sensor embedded in "salt" timber in terms of the rank order of corrosion character of coated steels. However, a smaller value of polarisation resistance was found in "salt" solution than in "salt" timber, and thus corrosion was more rapid in the solution than in the timber. This suggests that "salt" solution is a more aggressive media than "salt" timber, even at saturated moisture content. This is because most of the CCA preservative chemicals are fixed in the timber and the ionic current flowing through the timber is partially retarded by the low conductivity of the timber. On the other hand, the CCA "oxide" solution may not be used to simulate the CCA "oxide" wood. It has been observed that the anodic dissolution behaviour of coated steel in the solution is markedly different from that in the wood. The potentiodynamic polarisation curves of coated samples in the "oxide" solution and the "oxide" timber are shown in Figure 4.26. It is apparent that the coated steel is under anodic passivation in the "oxide" solution, whilst entirely different results were produced in the "oxide" wood which exhibited the typical curve for anodic dissolution of the coated steel and showed no evidence of passivation. Though all coated steels were in a self-passivation state in "oxide" solution, the corrosion ranking of samples is still distinguishable from the passivation current. It is also shown in Table 4.5. The electrochemical results obtained by using the sensor embedded in timber was not confirmed by conventional weight lost measurement. Nevertheless, the composition analysis of the timber surface in contact with coated samples should reflect the degree of corrosion that occurred on the coated sample surface. Also listed in Table 4.5 are the corrosion ranking of zinc and zinc alloy coated steel using zinc concentration of timber surface in contact with coated samples as the indication. The results from electrochemical measurement are consistent with those from SEM/EDXA analysis.

Table 4.5 The corrosion ranking of zinc and zinc alloy coated steel in CCA solution and CCA treated timber

Electrochemical measurement				SEM/EDXA analysis	
"salt" solution	"oxide" solution	"salt" wood	"oxide" wood	"salt" wood	"oxide" wood
G5	G5	G5	G5	G5	G5
G4	E7	E7	E7	E7	E7
E6	E6	E6	E6	E6	E6
E7	E3	G3	G3	E5	E5
E5	G4	E5	E5	E4	E3
E4	E5	E9	E10	E3	E4
G3	G2	E10	E9	G3	G3
G2	E1	E4	E3	G1	G1
G1	E2	E3	E4		
E2	G1	G6	G1		
E1	E4	G1	G6		
E3	G3				

* Every column from top to bottom is in the order of decreasing corrosion resistance

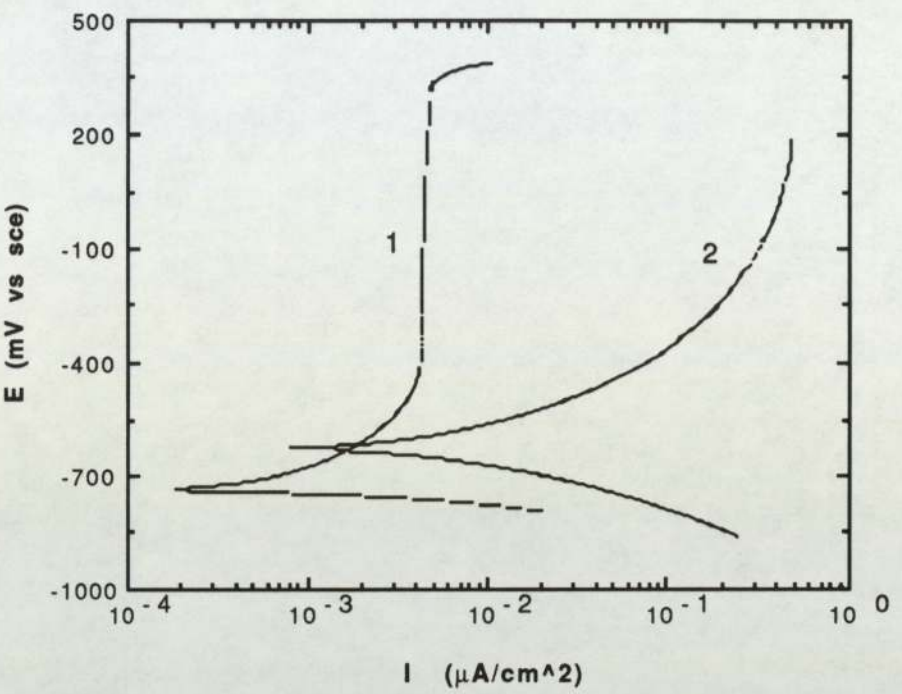


Figure 4.26 Potentiodynamic scan of zinc aluminium alloy coated steel in (1) CCA "oxide" solution, (2) CCA "oxide" wood

4.5.2 Service Life Prediction of Zinc and Zinc Alloy Coated Steel in Contact with CCA Treated Timber

When corrosion current density, I_{corr}, is known, the corrosion rate in term of depth, I_l, can be written according Farady's second law:

$$I_l = \frac{M}{nFd} I_{corr} \tag{4.3}$$

Where I_l = the corrosion rate in term of depth,

M = atomic mass of the metal,

d = density of the metal,

n = oxidation state of the solvated species,

F = Faraday's constant.

If I_l is in units of μm/year and I_{corr} in μA/cm^2, then Equation 4.3 can be written as:

$$I_l = 3.27 \frac{M}{nd} I_{corr} \qquad (4.4)$$

For zinc and zinc alloy coated samples, zinc is assumed as solvated species, M= 65.4, n=2 and d=7.13 (g/cm^3), then,

$$I_l = 15.0\, I_{corr} \qquad (4.5)$$

When corrosion rate, I_l (μm/year), and thickness of coating, l (μm), are known, the service life of coating, T (week) can be calculated from the following equation:

$$T = 52 \frac{l}{I_l} \qquad (4.6)$$

The corrosion current density, I_{corr}, and hence corrosion rate, I_l, and service life,T, of zinc and zinc alloy coated steel in water saturated CCA treated timber have been calculated from the polarisation resistance, R_p, and constant B. The polarisation resistance was taken from that at the end of the tests where Rp reached a stable value and B is assumed as 58 mV as discussed in Section 4.3.3. The results are listed in Table 4.6 together with the coatings thickness and the service life of these coated steels in water saturated CCA treated timber. It can be seen that if the corrosion rate is relatively high then the coating will corroded away in a short period for most of the samples. However, it should be noted that these results were obtained under the accelerated laboratory conditions. In the laboratory, the CCA treated wood was under the water saturated condition which is much higher than that in service. In fact, the moisture content of wood plays an important role in corrosion of zinc and zinc alloy coated steel in timber, as will be discussed below.

Table 4.6 The corrosion current density, corrosion rate, coating thickness and calculated service life of zinc and zinc alloy coated steels in water saturated CCA treated timber

		"salt" wood			"oxide" wood		
Sample	l (µm)	Icorr µA/cm^2	I_l µm/year	T (week)	Icorr µA/cm^2	I_l µm/year	T (week)
G1	30	4.46	66.90	23.3	2.42	36.26	43.0
G3	12	1.35	20.25	31.2	1.76	26.37	23.7
G5	20	0.11	1.65	630.3	0.037	0.55	1890.9
G6	15	3.41	51.15	15.1	2.90	43.45	18.0
E3	10	2.52	37.80	13.8	1.23	18.43	28.3
E4	10	2.00	29.97	17.4	1.76	26.37	19.8
E5	10	1.70	25.51	20.4	0.98	14.68	35.6
E6	10	0.89	13.35	39.0	0.42	6.29	82.6
E7	10	0.59	8.85	58.8	0.25	3.75	138.6
E9	10	1.76	26.40	19.7	1.35	20.23	25.6
E10	10	1.87	28.05	18.5	1.07	16.03	32.4

4.5.3 Corrosion Mechanism of Zinc and Zinc Alloy Coated Steel in CCA Treated Wood

It is probable that when in contact with CCA treated timber, corrosion of zinc may proceed by:

Anodic reaction: $Zn = Zn^{2+} + 2e$

Cathodic reaction: $2H^{+} + 2e = H_2$

or $O_2 + 2H_2O + 4e = 4OH^-$

and/or $Cu^{2+} + 2e = Cu$

The coated sample SEM/EDXA analysis results showed that the corrosion products of zinc and zinc alloy coated samples were likely to be $Zn(OH)_2$, and/or $ZnSO_4$ when the wood was treated with CCA "salt" solution. White solid deposit were observed on the wood and coated samples, especially when pitting corrosion occurred.

The potentiodynamic scanning measurements were conducted on a number of corrosion cells and two typical Tafel plots are shown in Figure 4.27. It can be seen that there is no noticeable difference in polarisation behaviour between results obtained in "salt" and "oxide" CCA treated timber. Figure 4.27 clearly shows that the corrosion process is not subject to the anodic passivation and cathodic diffusion control. The same shape of potentiodynamic curve was also found for the other zinc and zinc alloy coated steels.

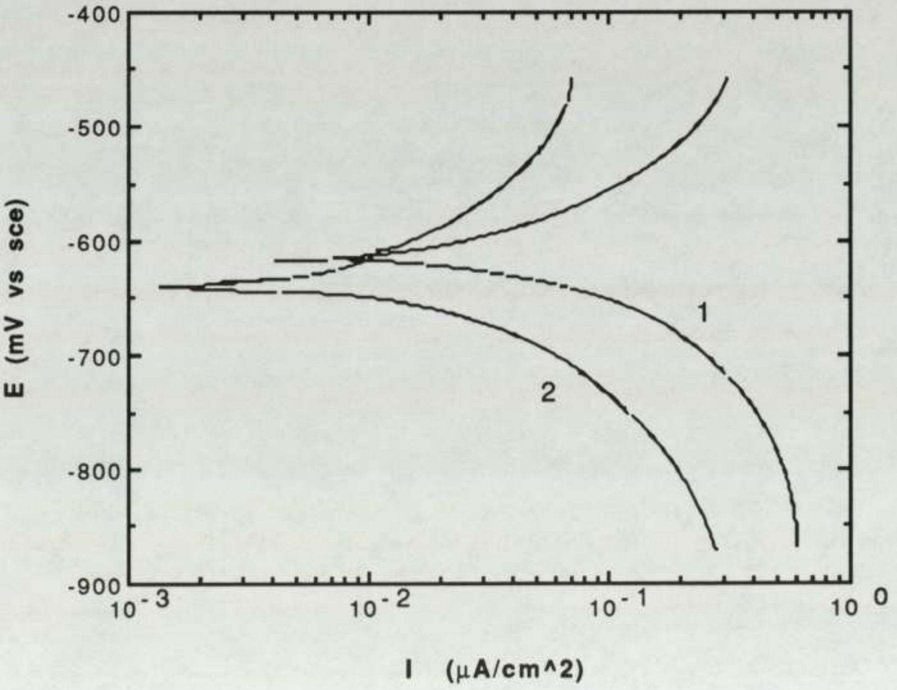


Figure 4.27 The Tafel plots of zinc aluminium coated steel (1) in "salt" wood (2) in "oxide" wood

Therefore, it is probable that corrosion of zinc and zinc alloy coated steel is not completely under cathodic control, at least at high moisture contents. However, the high values of anodic and cathodic slopes observed imply that the transfer of reactants to, or products from, metals is partially hampered by the high resistivity of the timber and/or the corrosion products barrier.

4.5.4 Factors Affecting Corrosion Resistance of Zinc and Zinc Alloy Coated Steel in Timber

The moisture content of timber plays an important role in corrosion of zinc and zinc alloy coated steel when in contact with timber. The 23% moisture content has been found to be critical below which the corrosion rate decreases markedly with decreasing moisture content. For instance, the polarisation resistance rises by orders of approximately two at 15% moisture content compared with water saturated timber. It can be seen readily from Figures 4.14 and 4.15 that the polarisation resistance of zinc coated steel at a typical service moisture content (10-18%) is very high, and in fact, the corrosion rate at that moisture level is negligible. The moisture level mainly affects the conductivity of timber and hence the ionic current flowing between the anodic and cathodic electrode. The corrosion potential moves in a positive direction as the moisture content decreases. A possible explanation is that the corrosion rate is reduced significantly by the high resistivity of timber and it affects the anodic reaction more than the cathodic reaction. At a moisture content above 23%, the corrosion rate remains approximately constant as moisture content changes, probably because the rate is mainly under active control. An apparent implication of this is that the corrosion tests should be carried out for the propose of ranking materials, while the relationship between corrosion rate and moisture content would provide a useful guide on service-life prediction of materials in treated timber.

The CCA formulation also affects corrosion performance of zinc and zinc alloy coated steel. The corrosion resistance in the "oxide" timber is about twice as high as in the "salt" timber, for all coated steel. Since it has the same impact on various samples, the CCA formulation may mainly affect the resistivity of timber. The "salt" CCA contains soluble species (Na^+ and SO_4^{2-}) and the conductivity of timber increases in the presence of these ions.

The beneficial effect on corrosion performance has been found with the addition of all alloy elements, although the degree of corrosion rate reduction depends upon the type and concentration of the alloy element in the coatings. No significant change in the polarisation behaviour has been observed with the addition of alloy elements, but the corrosion potential moves in a positive direction, resulting in a reduction in the electrochemical activity of zinc coated steel. On the other hand, it also reduces the risk of copper deposit which would accelerate corrosion by forming a galvanic cell with the coated steel.

steel in CCA treated timber at a typical service moisture level (10-18%) can be regarded as negligible.

4. The corrosion results in the "salt" solution are similar to those obtained by the electrochemical sensor embedded in the "salt" timber in terms of rank order of corrosion resistance of zinc and zinc alloy coated steels. However, the relatively low corrosion resistance and severe corrosion appearance of samples immersed in the "salt" solution compared with those embedded in "salt" timber, suggests that the "salt" solution is a harsher media than the "salt" wood. Consequently, it can only be considered as an accelerated test. The "oxide" solution may not be used to simulate behaviour in the "oxide" wood. All coated steels are in a self-passivation state and remains bright after immersion in the "oxide" solution, while the corrosion performance of samples with various coatings is still distinguishable from the potentiodynamic scanning curves.

5. Surface observation and analysis have detected no apparent corrosion on Zn-55% Al and Zn-12% Ni coated samples embedded in treated timber. In the case of the other samples localised cracking and exfoliation of coating were observed. This related to areas of stress in the as-received coating. Corrosion products, probably $Zn(OH)_2$ or $ZnSO_4$ were also formed. Copper (~4%) was detected on all but the zinc nickel and zinc aluminium coatings.

6. Estimates of service life have been made and are particularly good for the zinc aluminium coatings. In practice all coatings should exhibit longer lifes since moisture contents would normally be much lower.

7. Corrosion of zinc and zinc alloy coated steels has been suggested under active dissolution control in water saturated treated timber, but the effect on resistivity of timber becomes significant at a low moisture level. The moisture content of timber may affect the anodic process more than the cathodic process.

steel in CCA treated timber at a typical service moisture level (10-18%) can be regarded as negligible.

4. The corrosion results in the "salt" solution are similar to those obtained by the electrochemical sensor embedded in the "salt" timber in terms of rank order of corrosion resistance of zinc and zinc alloy coated steels. However, the relatively low corrosion resistance and severe corrosion appearance of samples immersed in the "salt" solution compared with those embedded in "salt" timber, suggests that the "salt" solution is a harsher media than the "salt" wood. Consequently, it can only be considered as an accelerated test. The "oxide" solution may not be used to simulate behaviour in the "oxide" wood. All coated steels are in a self-passivation state and remains bright after immersion in the "oxide" solution, while the corrosion performance of samples with various coatings is still distinguishable from the potentiodynamic scanning curves.

5. Surface observation and analysis have detected no apparent corrosion on Zn-55% Al and Zn-12% Ni coated samples embedded in treated timber. In the case of the other samples localised cracking and exfoliation of coating were observed. This related to areas of stress in the as-received coating. Corrosion products, probably $Zn(OH)_2$ or $ZnSO_4$ were also formed. Copper (~4%) was detected on all but the zinc nickel and zinc aluminium coatings.

6. Estimates of service life have been made and are particularly good for the zinc aluminium coatings. In practice all coatings should exhibit longer lifes since moisture contents would normally be much lower.

7. Corrosion of zinc and zinc alloy coated steels has been suggested under active dissolution control in water saturated treated timber, but the effect on resistivity of timber becomes significant at a low moisture level. The moisture content of timber may affect the anodic process more than the cathodic process.

Chapter 6

Further work

1. The electrochemical sensor developed in this work could be used to determine the corrosion resistance of selected zinc alloy coated steels in different type of timber treated with commercially formulated preservatives.

   Timber would be in equilibrium with a range of RH to determine their critical moisture content.

2. Fasteners are rarely totally embedded in timber. It would therefore be necessary to set up experiments where specimens are partially embedded in timber and partially exposed to the atmosphere, this forming differential aeration cells.

3. During the present work attempts were made to measure the galvanic current flowing between the working and counter electrodes. Such measurements require less sophisticated instrumentation than in the case in making measurements of polarisation resistance. However, results obtained were very erratic and have not been included in the thesis.

   Since a galvanic sensor would be much easier to use in field studies it is worth trying to understand why the results were so erratic, this modifying sensor design to provide more consistency.

4. Field studies could be carried out in e.g. roof spaces, over long periods of time. This would include studies where insulating materials may result in a different environment around the fastener.

5. Whilst a wide range of zinc alloy conversion coatings are available, others are continually being developed. Since chromates are known to be carcinogenic Health and Safety Regulation may eventually require their substitution. This may also be the case with the timber preservatives themselves. Thus these sensors could be used to evaluate new systems.

REFERENCES

1. D. Jones and D. Brinn, BSC Report, WL/RSC/202/83/D (1983).

2. S. R. Dunbar and W. Showak, Atmospheric Corrosion of Zinc and its Alloys, Atmospheric Corrosion, Ed. W. H. Ailor, Wiley, London, pp.529 (1983).

3. F. C. Porter, A. M. Stoneman and R. G. Thilthorpe, Transaction of the Institute of Metal Finishing, **66**, 28 (1982).

4. J. K. Dennis, N. R. Short, A. Abibsi and S. Zhou, Corrosion Behaviour of Electrodeposited Zinc Alloys, First East-West Convension on Surface Engineering, Bangalore, India, Dec. 16-19, 1992.

5. T. Addaniya, T. Hara, M. Sagiyama, T. Homa and T. Watanabe, Plating and Surface Finishing, **73**, 52 (1985).

6. N. R. Short, A. Abibsi and J. K. Dennis, Transactions of the Institute of Metal Finishing, **67**, 73 (1989).

7. W. M. J. C. Verberne, Transactions of the Institute of Metal Finishing, **64**, 30 (1986).

8. M. Nikolova, I. Kristev, J. Cenov and L. Kristev, Bulletin of Electrochemistry, **3**, 649 (1987).

9. A. Abibsi, N. R. Short and J. K. Dennis, Transactions of the Institute of Metal Finishing, **69**, 45 (1991).

10. A. Abibsi, N. R. Short and J. K. Dennis, Corrosion Resistance Zinc Alloy Coatings, Symposium on Zinc Alloy Electrodeposits, The Institute of Metal Finishing, Birmingham, 19 October (1988).

11. N. R. Short, S. Zhou and J. K. Dennis, Corrosion Behaviour of Passivated Zinc alloy Coated Steel in Hardened Cement Pastes, International Conference on Corrosion and Protection of Steel in Concrete, Shefield, 24-29, July (1994).

12. N. R. Short, J. K. Dennis and S. O. Agbonlahor, Transactions of the Institute of Metal Finishing, **66**, 107 (1988).

13. G. Sergi, N. R. Short and C. L. Page, Corrosion, **41**, 618 (1985).

14. C. L. Page, G. Sergi and N. R. Short, Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete, Proceedings of Third International Conference, Trondheim, Norway, Ed. V. M. Malhotra, American Concrete Institute, pp.887-896, 18-23 June (1989).

15. J. Mackowiak and N. R. Short, International Metal Reviews, **24**, 1 (1979).

16. G. A. Scott, Deterioration and Preservation of Timber in Building, Longmans, London (1968).

17. M. F. Ashby and D. R. H. Jones, Engineering Materials 2, A Introduction to Microstructures, Processing and Design, Pergamon Press, Oxford (1986).

18. W. P. K. Findlay, Timber: Property and Uses, Crosby Lockwood Staples, London (1957).

19. Wood Deterioration and Its Prevention by Preservative Treatment, Volume I, Degradation and Protection of Wood, Ed. D. D. Nicholas, Syracuse University Press, U. S. A. (1973).

20. W. P. K. Findlay, The Preservation of Timber, Adam and Charles Black, London (1962).

21. W. D. Betts, The Properties and Performance of Coal-Tar Creosote as a Wood Preservative, The Chemistry of Wood Preservation, Ed. R. Thompson, The Royal Society of Chemistry, pp.136-169 (1991).

22. BS144, Wood Preservation Using Coal Tar Creosotes, Part 1 (1990).

23. E. A. Hilditch, Organic Solvent Preservatives: Application and Composition, The Chemistry of Wood Preservation, Ed. R. Thompson, The Royal Society of Chemistry, pp.69-87 (1991).

24. BS144, Wood Preservation Using Coal Tar Creosotes, Part 2 (1990).

25. BS4072, Wood Preservation by Means of Copper/Chromiun/Arsenic Compositions (1987).

26. M. Connel, Industrial Wood Preservatives-The History, Development, Use, Advantages, and Future Trends, The Chemistry of Wood Preservation, Ed. R. Thompson, The Royal Society of Chemistry, pp.16-33 (1991).

27. S. E. Dahlgren and W. H. Hartford, Holzforschung, **26**, 62 (1972).

28. S. E. Dahlgren, Holzforschung, **28**, 58 (1974).

29. S. E. Dahlgren, Holzforschung, **29**, 84 (1975).

30. A. Pizzi, J. Polym. Sci., **19**, 3093 (1981).

31. A. Pizzi, J. Polym. Sci., **20**, 707 (1982).

32. A. Pizzi, J. Polym. Sci., **20**, 725 (1982).

33. B. R. Richardson, Wood Preservation, The Construction Press Ltd, England (1978).

34. B. Henshaw, Int. Biodeterior Bull., **15**, 66 (1979).

35. A. P. Mayo, "Trussed Rafter Roofs, Part I An Assessment of Trussed Rafter Manufacture, Site Use and Performance in Service", Building Research Establishment Current Paper, CP 5/83, pp.1-15.

36. BS5268, Structural Use of Timber, Part 3 (1985).

37. BS2989, Continuously Hot-Dip Zinc Coated and Iron-Zinc Alloy Coated Steel Flat Product: Tolerance on Dimension and Shape (1992).

38. BS1449, Stainless Steel and Heat Resisting Steel Plate, Sheet and Strip, Part 2 (1983).

39. D. F. G. Rodwell, "Trussed Rafter Roofs, Part II, The Significance Of Copper-Chromium -Arsenic Treatment on Corrosion of Galvanized Metal Plate Fasteners, Building Research Establishment Current Paper, CP 5/83 pp. 16-23.

40. R. D. Graham, "Wood-Metal Corrosion", Research Bulletin 21, Oregon State University (1976).

41. A. J. Baker, U. S. N. T. I. S., AD Rep., No. 782485/TGA, 8PP Avail. NTIS From: Govt. Rep. Announce (U. S.), **74**, 94 (1974).

42. E. Farber, Industry and Engineering Chemistry, **46**, 1968 (1954).

43. D. F. Packman, Holyforchung, **14**, 178 (1960).

44. P. C. Arni, G. C. Cockrane and J. D. Gray, J. Appl. Chem., **15**, 305 (1965).

45. R. H. Farmer, Corrosion of Metal in Association with wood. Part2: Corrosion of Metal in contact with Wood, Wood, **27**, 442-446 (1962).

46. J. A. Taylor, "Comparisons of Difference in Electrical Conductivity and Corrosivity between CCA-Oxide and CCA-Salt Treated Wood", International Research Group on Wood Preservation, IRG/WP/3178 (1981).

47. A. J. Baker, "Corrosion of Metal in Wood Products", 1st Int. Con. Dur. Bui. Mater. Comp., ASTM 691, 981 (1980).

48. R. S. Smith, E. L. Johnson and A. J. Cserjesi, "Corrosion of Zinc-Coated Nail Used with Preservative-Treated Western Red Cedar Shaks in Service", International Research Group on Wood Preservation, IRP-WP/3197 (1982).

49. "Studies on Corrosion of Metallic Objects in Contact with Preservative Wood in the Open". Swedish Wood Preservation Institute, Nr 144 (1982).

50. E. B. Ormstad, Corrosion of Metals in Contact with Pressure Treated Wood, The Norwegian Institute of Wood Working and Technology, pp. 47 (1973).

51. T. Wallin, "Corrosion of Fasteners in Treated Wood". Scand. Congr. Proc., 6th, 26, 1-7, Swed. Corros. Inst., Stockholn, Swed. (1971).

52. D. W. Simm and H. E. Button, Corros. Prev. Control, **32**, 25 (1985).

53. T. Wallin, "Corrosion of Fasteners in Treated Wood". Scandinavian Lead and Zinc Association, Sweden (1971).

54. R. H. Hill and J. D. A. Fell, "The Corrosion of Lead and its Fixing by Impregnated Timber", Associated Lead Manufactures Ltd, Central Research Laboratories (1981).

55. GKN Laboratory Report (1983).

56. R. A. Laidlaw and R. N. Cox, Int. J. Wood Preserv. **3**, 5 (1983).

57. J. R. Duncan, Met. Corros. Proc., Int. Congr, Met. Corros., 8th, Volume 2, 1773 (1981).

58. R. N. Cox and R. A. Laidlaw, J. Inst. Wood Sci., **10**, 87 (1984).

69. E. J. Jack and S. I. Smedley, Corrosion, **43**, 266 (1987).

60. J. N. Cross, Evaluation of Metal Fastener Performance in CCA Treated Timber, Durability of Building Materials and Conponents, Ed. J. M. Baker etc., E. and F.N. Spon, Cambridge (1990).

61. M. Stern, Corrosion, **14**, 60 (1958).

62. L. M. Callow, J. A. Richardson and J. J. Dawson, Brit. Corros. J. **11**, 123 (1976).

63. L. L. Shreir, Corrosion, Vol.1, Newnes - Butterworths, London (1977).