

STUDY REPORT

SR 241 (2011)

Corrosion of Fasteners in Treated Timber

Z.W. Li, N.J. Marston and M.S. Jones



The work reported here was funded by BRANZ from the Building Research Levy, whose logo is shown above.

© BRANZ 2011 ISSN: 1179-6197

Corrosion of Fasteners in Treated Timber

BRANZ Study Report SR 241

Z.W. Li, N.J. Marston and M.S. Jones

Reference

Li ZW, Marston NJ and Jones MS. 2011. 'Corrosion of Fasteners in Treated Timber'. *BRANZ Study Report 241*. BRANZ Ltd, Judgeford, New Zealand.

Executive Summary

ACQ (alkaline copper quaternary) and CuAz (copper azole) water-borne preservatives are an acceptable alternative to conventional CCA (copper chrome arsenic) for treatment of exterior-grade timbers under NZS 3640. However, their use necessitates achieving a significantly higher retained copper concentration in the timber after treatment than is required for CCA preservative at the equivalent hazard class. Simple electrochemistry suggests timbers containing a higher water-soluble copper concentration are more likely to initiate serious corrosion of susceptible metallic components embedded or in contact with these timbers. Previous laboratory-scale, accelerated tests conducted by BRANZ and other research institutes confirmed the potential for an increased corrosion risk for mild steel and galvanised steel with CuAz and, particularly, ACQ treated timbers.

The long-term durability of metallic fixing components used for ACQ and CuAz treated timbers under real service conditions remains uncertain. Hence this research investigated the corrosion performance of fasteners made from mild steel, galvanised (zinc) steel and austenitic stainless steel inserted into Pinus radiata treated with these preservatives at the H3.2 and H4 hazard classes using a three-year, non-accelerated, field exposure testing scheme at two sites in Wellington, New Zealand. Both surface morphological characterisation and corrosion rate measurement were employed to evaluate the compatibility between metallic fastenings and timbers.

Testing results clearly showed that galvanised and mild steel fasteners embedded into timbers treated with ACQ and CuAz preservatives, particularly at the H4 level, are significantly more degraded through corrosion than corresponding items in CCA treated timbers. The corrosion acceleration of ACQ and CuAz treatment over CCA could be four and nine times for mild steel and zinc-coated steel after one year of exposure at Judgeford, respectively, and be around four times after three years of exposure at Oteranga Bay.

The much higher aggressivity of the ACQ and CuAz treated timbers resulted in more severe corrosion of mild steel and zinc-coated fasteners, leading to heavy iron stain on the surrounding timber cellular structure after only three years. This also made the retrieval of fasteners, particularly screws, difficult. Within longer exposure, the iron and hydroxyl ions released from the corrosion will chemically attack the cellulose components of the timber more seriously and cause significant loss of strength and structural integrity of the joint. "Nail sickness" is a term which has long been used to describe this phenomenon. It would therefore be reasonable to treat the

fastener and the timber as one system so that the durability and safety risks of timber-metal joint induced by metal corrosion can be minimised.

The higher copper retention in ACQ and CuAz treatment is believed to be responsible for this significantly increased corrosive attack. However it is unlikely to be the only mechanism operating. Steel passivation behaviours in CCA and ACQ or CuAz might be different. BRANZ's measurements also indicated that timbers treated with ACQ or CuAz had a higher moisture content than those treated with CCA under identical exposure condition. These two differences may also affect metal deterioration to some extent.

Atmospheric corrosivity of a geological environment affects fastener corrosion. At Oteranga Bay, a (very) severe marine environment (sea spray zone according to NZS 3604) representing a harsher atmosphere than Judgeford (Zone 1), the exposed section of the fastener was attacked more quickly, leading to higher corrosion rates i.e. shorter service life. It is expected that within longer exposures, the influences of different climatic conditions on fastener performance will be demonstrated markedly since the decayed timbers will provide more pathways for ingress of airborne pollutants that can accelerate corrosion on the embedded sections.

Metal corrosion in CCA treated timbers appeared to proceed steadily, while in ACQ and CuAz treated timbers corrosion was decreasing with longer exposure. Service life of metallic components in CCA treated timbers can therefore be predicted based on the corrosion rates measured in this study if the service conditions are similar to the testing conditions. The mechanism behind the time-dependent corrosion behaviour in ACQ and CuAz treatment is not clearly understood at this moment. However, it is quite certain that long-term durability cannot be achieved for mild steel and galvanised steel fasteners when inserted into these timbers as the extremely fast corrosion in the initial stage of exposure will severely damage the integrity of the coating and attack the underlying steel substrate.

Performance of the exposed head and the embedded body of a galvanised (zinc) fastener can be quite different especially when it is embedded into ACQ or CuAz treated timbers exposed to a relatively benign climate such as Judgeford. After three years of exposure, the coating on the head of some nails still appeared to be integral although surface oxidation was observed, while the coating on their shaft had been seriously damaged and the iron-based substrate was then exposed and corroded quickly. This large performance difference makes the identification of any premature failure of fastener and/or timber joint very difficult.

Austenitic stainless steel nails and screws did not show any sign of significant deterioration on their body section when embedded into CCA, CuAz and ACQ treated timbers even after three years of exposure at Oteranga Bay. Their maximum corrosion rate is at least two orders of magnitude lower than that of the mild steel or galvanised steel fasteners under identical testing conditions. Red rust was occasionally found on their heads. This is believed to be a result of the local passivation breakdown and/or iron contamination induced by the driving-in process. Within the present testing timeframe, this localised corrosion was proceeding extremely slowly and had little impact on the performance of fasteners and the integrity of timber structures.

Based on the morphological observations and corrosion rate measurements in this study, it is doubtful that zinc-coated fasteners, including hot dip galvanised nails and mechanically-plated screws, will be able to meet the New Zealand Building Code (NZBC) durability requirement when used in ACQ or CuAz treatment if the timber gets wet. The use of either AISI 304/316 grade of stainless steel, or durable equivalents such as silicon bronze, for structural components and connections would appear to be justified.

This study generated fundamental data reflecting metal degradation in timbers treated with CCA and its alternatives, particularly ACQ and CuAz, through a quasi-realistic approach. It confirmed the suspicion that both ACQ and CuAz treatments confer a greatly enhanced corrosivity upon

timbers relative to CCA treatment. This research begins to establish a complete map showing deterioration of metallic materials in untreated and treated timbers under real service conditions. However the precise mechanism for the increased corrosivity of ACQ and CuAz preservatives is uncertain, the long-term (>15 years) corrosion performance of galvanised and stainless steel fasteners has not been examined, and their durability under wider New Zealand climate conditions (e.g. industrial, geothermal, urban and rural) is still poorly understood.

Keywords: corrosion; field exposure; timber; preservation; CCA; CuAz; ACQ; fastener; mild steel; stainless steel; zinc coating; hot dip galvanising; mechanical plating.

Contents

Page

1.	INTRODUCTION								
	1.1 1.2 1.3	Corrosion of Metal in Timber Testing of Metal Corrosion in Timber – An Overview 1.2.1 AWPA E-12 1.2.2 Embedded Fastener 1.2.3 Non-Accelerated Test 1.2.4 Salt Spray 1.25 Immersion in Preservation Treatment Electrolyte 1.2.6 Polarisation Resistance 1.2.7 Electrochemical Impedance Spectroscopy Objective 1.3.1 Limitation of Accelerated Tests 1.3.2 Objective of Current Research	2 2 3 3 3 4 4 5 5						
2.	EXPI	ERIMENTAL	6						
	2.1 2.2 2.3	Timber – Source and Preservation Treatment Field Exposure Sample Testing	7						
3.	RESULTS								
	3.1 3.2 3.3 3.4 3.5	Initial Copper Content in Timber1Coating Thickness on Hot Dip Galvanised Nails1Corrosion – First Year Exposure13.3.1 Morphological Characterisation13.3.2 Estimation of Corrosion Rate1Corrosion – Second Year Exposure23.4.1 Morphological Characterisation23.4.2 Estimation of Corrosion Rate2Corrosion – Third Year Exposure23.5.1 Judgeford23.5.2 Oteranga Bay3	0 1 1 7 20 23 25 25						
4.	DISCUSSION4								
	4.1 4.2 4.3 4.4 4.5 4.6 4.7	Time-Dependent Corrosion4Location-Dependent Corrosion4Influence of Environmental Corrosivity5Influence of Copper Retention5Performance Difference Between Head and Shank5Treat Fastener and Timber as a System6Comparison Between Different Testing Methodologies6	19 54 56 59 52						
5.	CON	CLUSIONS	;4						
REFE	EREN	CES6	57						

Figures

Page

Figure 1: Photo of the gate-shaped timber structures, designed to incorporate a variety of metallic building fixings......7 Figure 2: Geographic locations of the two field exposure sites (Judgeford and Figure 3: Nails and screws retrieved for characterisation after different years of Figure 4: Average thickness of the zinc coating on the hot dip galvanised nails used in this study11 Figure 5: Surface morphology (before cleaning) of mild steel fasteners embedded into timbers exposed at Judgeford site for one year - (a) untreated, (b) H3 CCA, (c) H4 CCA, (d) H3 CuAz, (e) H4 CuAz, (f) H3 ACQ and (g) H4 ACQ......12 Figure 6: Surface morphology (before cleaning) of zinc coated fasteners embedded into timbers exposed at Judgeford site for one year - (a) untreated, (b) H3 CCA, (c) H4 CCA, (d) H3 CuAz, (e) H4 CuAz, (f) H3 ACQ and (g) H4 ACQ......13 Figure 7: Surface morphology (before cleaning) of stainless steel fasteners embedded into timbers exposed at Judgeford site for one year – (a) H4 CCA, (b) H4 CuAz and (c) Figure 8: Surface morphology of mild steel flashing attached to timber exposed at Judgeford site for one year – (a) untreated, (b) H3 CCA, (c) H4 CuAz and (d) H4 ACQ.15 Figure 9: Surface morphology of hot dip galvanised steel flashing attached to timber exposed at Judgeford site for one year – the timber was treated with H4 ACQ15 Figure 10: Surface morphology of hot dip galvanised steel flashing attached to timber exposed at Judgeford site for one year – (a) H3 CCA, (b) H3 CuAz and (c) H3 ACQ.....16 Figure 11: Surface morphology of hot dip galvanised steel flashing attached to Figure 12: Stained (left) and scratch-corroded (right) areas observed on stainless steel flashings attached to H4 CuAz treated timbers and atmospherically exposed at Judgeford site for one year17 Figure 13: Corrosion rates of mild steel fasteners embedded into timbers exposed at Judgeford site for one year18 Figure 14: Corrosion rates of zinc coated fasteners embedded into timbers exposed at Judgeford site for one year18 Figure 15: Corrosion rate of flashings in contact with timbers exposed at Judgeford site for one year. Note that corrosion rate of galvanised steel flashing in untreated timber is omitted and results are from single specimens so an estimate of uncertainty is impossible. (MS: Mild Steel; HDG: Hot Dip Galvanising)......19 Figure 16: Surface morphology (after cleaning) of mild steel fasteners retrieved from timbers exposed at Judgeford site for two years (these fasteners were inserted into the timber blocks fixed at the lower (side) part of the gate structure and their longitudinal orientation was parallel to the ground) - (a) untreated, (b) H3 CCA, (c) H4 CCA, (d) H3 CuAz, (e) H4 CuAz, (f) H3 ACQ and (g) H4 ACQ......21 Figure 17: Surface morphology of zinc coated fasteners retrieved from timbers exposed at Judgeford site for two years (these fasteners were inserted into the timber blocks fixed at the lower (side) part of the gate structure and their longitudinal

orientation was parallel to the ground) – (a) untreated, (b) H3 CCA, (c) H4 CCA, (d) H3 CuAz, (e) H4 CuAz, (f) H3 ACQ and (g) H4 ACQ22

Figure 21: Surface morphology of mild steel nails retrieved from the top part of the timber gate structure exposed at Judgeford site for three years – (a) untreated, (b) H3 CCA, (c) H4 CCA, (d) H3 CuAz, (e) H4 CuAz, (f) H3 ACQ and (g) H4 ACQ26

Figure 22: Surface morphology of mild steel screws retrieved from the top part of the timber gate structure exposed at Judgeford site for three years – (a) untreated, (b) H3 CCA, (c) H4 CCA, (d) H3 CuAz, (e) H4 CuAz, (f) H3 ACQ and (g) H4 ACQ27

Figure 23: Surface morphology of mild steel nails retrieved from the lower (side) part of the timber gate structure exposed at Judgeford site for three years – (a) untreated, (b) H3 CCA, (c) H4 CCA, (d) H3 CuAz, (e) H4 CuAz, (f) H3 ACQ and (g) H4 ACQ28

Figure 24: Surface morphology of mild steel screws retrieved from the lower (side) part of the timber structure exposed at Judgeford site for three years – (a) untreated, (b) H3 CCA, (c) H4 CCA, (d) H3 CuAz, (e) H4 CuAz, (f) H3 ACQ and (g) H4 ACQ29

Figure 27: Surface morphology of hot dip galvanised nails retrieved from the lower (side) part of the timber gate structure exposed at Judgeford site for three years – (a) untreated, (b) H3 CCA, (c) H4 CCA, (d) H3 CuAz, (e) H4 CuAz, (f) H3 ACQ and (g) H4 ACQ

Figure 30: Corrosion rates of mild steel fasteners embedded into timbers exposed at Judgeford site for three years (these fasteners were retrieved from the top part of the

Figure 34: Mild steel nuts exposed at Judgeford and Oteranga Bay for three years38

Figure 35: Surface morphology of mild steel fasteners retrieved from the top part of the timber gate structure exposed at Oteranga Bay for three years, (a) untreated, (b) H3 CCA, (c) H4 CCA, (d) H3 CuAz, (e) H4 CuAz, (f) H3 ACQ and (g) H4 ACQ40

Figure 36: Surface morphology of hot dip galvanised nails retrieved from the top part of the timber gate structure exposed at Oteranga Bay for three years – (a) untreated, (b) H3 CCA, (c) H4 CCA, (d) H3 CuAz, (e) H4 CuAz, (f) H3 ACQ and (g) H4 ACQ41

Figure 37: Surface morphology of mechanically-plated screws retrieved from the top part of the timber gate structure exposed at Oteranga Bay for three years – (a) untreated, (b) H3 CCA, (c) H4 CCA, (d) H3 CuAz, (e) H4 CuAz, (f) H3 ACQ and (g) H4 ACQ

Tables

Page

Table 1: Preservative corrosion rate (percentage weight loss)
Table 2: Ratio of active constituents in preservative formulations (%w/w) 6
Table 3: Initial total preservative and copper retention in stock timber supplied10
Table 4: Percentage for the corrosion rates of the fasteners inserted into the lower (side) of the gates versus the corrosion rates of the fasteners inserted into the top part of the timber structure 50
Table 5: Corrosion rates of nails measured with different methodologies63
Table 6: Corrosion rate acceleration factors of CuAz and ACQ over CCA65

1. INTRODUCTION

1.1 Corrosion of Metal in Timber

Timber retains its prime importance within the building and construction industry because of its diversity, sustainability, versatility and aesthetic properties [Dinwoodie 2000; Risbrudt 2005]. However it is not durable when exposed to the environment, as it deteriorates due to biological, chemical, mechanical, photochemical or thermal effects [Illston and Domone 2001]. Timber can be protected from the attack of decaying fungi, harmful insects or marine borers by the application of various chemical preservatives [Ibach 1999; Archer and Lebow 2006]. The enhancement of durability will be largely dependent on the type, penetration and retention of the preservative used.

Assembly of timber structures requires the use of various fixing and fastening components, e.g. nails, screws and bolts [Falk and Baker 1993; Soltis 1999]. Most of these are metallic, and their compatibility with timber is therefore critical to the durability and safety of structural joints in timber-framed buildings.

Unfortunately, most timbers are corrosive in nature and will attack susceptible metals embedded into them [Baker 1980; Talbot 1998; Cole and Schofield 2000]. This is a direct result of the hydrolysis of the acetyl radical, a component that comprises approximately 1-6% by weight of dry wood to free acetic acid in the presence of moisture. Formic, propionic, oxalic and butyric acids can be formed in small quantities as well. Timbers therefore have pH values typically ranging from 3.5 to 7.0 and can promote contact corrosion. Besides these organic acids, aromatic phenols may also promote metal corrosion since these compounds are capable of forming chelates with active ferric ions [Krilov and Gref 1986].

Chemicals used for preservation treatments can also present a potential corrosion hazard. It has long been recognised that water-borne preservatives could accelerate corrosion processes for susceptible metals embedded in or in contact with the treated timbers because the metallic ions in the preservative (most commonly copper ions) can act as an added oxidiser [Baker 1988; Zelinka *et al.* 2010]. The metals most susceptible to this galvanic corrosion are steel, zinc, cadmium, magnesium and lead.

Corrosion is responsible for the failure of many timber structures. Weakening is commonly observed in the timber cellular structures that surround the corroding metal. Corrosion of metal together with deterioration of timber causes strength loss of the joint and of the structural integrity of the assembly. "Nail sickness" is a term that has long been used to describe the process by which soft and spongy areas of wood form around corroding fasteners [Baker 1974].

The corrosivity of timbers treated with copper chrome arsenate (CCA) alternatives, e.g. alkaline copper quaternary (ACQ) and copper azole (CuAz), has therefore become a concern due to their considerably higher copper retention after treatment [Kear *et al.* 2005, 2006a, 2009; Zelinka and Rammer 2006, 2009; Rammer *et al.* 2006]. On the other hand, metal corrosion in timbers treated with new preservatives will be further complicated by the variations in their chemical formulations. CCA is composed of a mixture of chromic acid, cupric oxide and arsenic pentoxide [Morrell 2006]. It is supposed that hexavalent chromium, Cr⁶⁺, and/or arsenic species, could provide passivation effects to steel [Murphy 1998]. Probably related to this, metal corrosion in CCA treated timbers has not generally been regarded as a problem because greatly accelerated corrosion of metals was not observed in most situations. In contrast, ACQ and other new preservatives do not contain such inhibitors, and some formulations of ACQ contain chlorides [Freeman *et al.* 2006], which can increase the conductivity of timber, increase corrosion rate, and cause pitting corrosion.

1.2 Testing of Metal Corrosion in Timber – An Overview

Despite a lack of fundamental understanding of metal corrosion mechanisms in timber, there have been several attempts to create qualitative or quantitative testing techniques to evaluate the corrosion performance of metal in timber. Results derived from various sources provide useful information for the development of preservatives, design, construction and maintenance of timber-framed buildings.

1.2.1 AWPA E-12

Accelerated tests following the American Wood-Preservers' Association (AWPA) standard E12-94 *Standard Method of Determining Corrosion of Metal in Contact with Treated Wood* have been widely used by timber preservers and fastener manufacturers for the development of preservatives, timber products and metallic fixing or fastening components. In this standard, a flat metal coupon is sandwiched between two pieces of timber. These timber-metal assemblies are then placed in a conditioning chamber of $49\pm1^{\circ}$ C with RH of $90\pm1\%$. This standard specifies a minimum of 240 hrs of accelerated exposure.

Following this testing procedure, Simpson Strong-Tie investigated how actual fasteners performed in treated timbers [Simpson 2006]. According to this modified procedure, clean and weighed fasteners were driven into the narrow face of a standard 38×89 mm treated timber block 150-230 mm long. This composite specimen was then placed in an environmental chamber at 49°C and 90% RH for 240 hrs. Their results showed qualitatively that ACQ-D, CA-B and SBX (sodium borate) with NaSiO₂ were more than twice as corrosive as CCA-C for the average of G90 and G185 hot dip galvanised steel samples. The sales literature of Chemical Specialties Inc, a provider of an extensive range of advanced wood treatment technologies and services to the global wood treatment industry, also presented corrosion rates (% weight loss) of fixings made of mild steel, zinc-coated steel and stainless steel in CuAz and ACQ treated timbers (Table 1) [CSI-US].

Preservative	Mild Steel	Hot Dip Galvanising	Zn Electroplating			
ACQ-B	0.358	<0.001	<0.001			
ACQ-D	0.326	<0.001	<0.001			
CBA-A	0.340	<0.001	<0.001			
CCA	0.069	<0.001	<0.001			
Untreated	0.023	<0.001	<0.001			

Table 1: Preservative corrosion rate (percentage weight loss)

The corrosion weight loss percentages appear to be insignificant for hot dip galvanised and stainless steel materials, and the corrosion of mild steel articles has clearly been accelerated relative to untreated and CCA treated timbers. In this latter case, the rate of mild steel metal loss has been increased by an approximate factor of five in the ACQ-B, ACQ-D and CBA-A treatments relative to the CCA preservative.

BRANZ also tested the comparative aggressivity of timbers treated with CCA, CuAz and ACQ towards mild steel, hot dip galvanised steel and austenitic stainless steel according to AWPA E12-94 [Kear *et al.* 2006a]. The corrosion rates derived from the mass loss measurements indicated that timbers treated with ACQ and CuAz could be more corrosive than those treated with CCA under identical testing conditions. The

corrosivity of the timber increased reproducibly in the order: Untreated < CCA < CuAz < ACQ. Further, the order of increasing corrosion rate with respect to the preservative retention followed H3.2 < H4 < H5 roughly. Corrosion of hot dip galvanised steel samples, however, did not uniformly increase as a function of the copper retention in CuAz and ACQ treated timbers. It appeared that CuAz (H3.2 and H4) inhibited the corrosion of the zinc coating relative to the untreated timber. Although the highest value of zinc corrosion was still observed with the timbers treated with ACQ, the corrosion rate in this case decreased with increasing copper concentration. Stainless steel, under these accelerated testing conditions, had very favourable corrosion resistance in all treated timbers.

1.2.2 Embedded Fastener

This methodology was developed by BRANZ based on the AWPA E12 procedure [Kear *et al.* 2005]. Its primary objective was to replicate the in-situ fastener positioning prior to subjecting the samples to an aggressive environment to promote corrosive interactions between the nail, the high humidity atmosphere and the timber (with or without preservation chemicals). Timbers were cut to dimensions that suited the size of fasteners. The longest dimension ran in parallel to the wood grain. The samples were exposed to an atmosphere of 49°C and 90% RH for 720 hrs to achieve moisture equilibration. After this, fasteners were manually embedded into these timbers through pre-drilled guiding holes. Samples were then immediately inserted into an environmental chamber pre-conditioned at 49°C and 90% RH for 366 or 385 hrs.

Corrosion rates of mild steel fasteners were measured to be 0.31 ± 0.02 (untreated), 0.31 ± 0.07 (CCA H3.2), 0.35 ± 0.02 (CCA H4), 0.33 ± 0.05 (CCA H5), 0.39 ± 0.03 (CuAz H3.2), 0.29 ± 0.03 (CuAz H4) and 0.58 ± 0.03 mm/y (ACQ H3.2). The corrosion rates of the hot dip galvanised fasteners in the H3.2 treated timbers were 0.11 ± 0.02 (CCA), 0.11 ± 0.02 (CuAz) and 0.22 ± 0.02 mm/y (ACQ), respectively. It appears these data did not show a clear deviation between the types of timber treatment. Moreover, corrosion rates in CCA and CuAz treated timbers were all considerably higher than those measured with the AWPA scheme.

1.2.3 Non-Accelerated Test

Test assemblies were established by BRANZ according to AWPA E12 and exposed at 21°C and 98% RH for 12 months [Kear *et al.* 2007]. The aggressivity of timber towards mild steel and hot dip galvanised coupons basically followed the order of: CCA (H3.2/H4/H5) < CuAz (H3.2/H4) < ACQ (H3.2/H4/H5). At an H5 level, the corrosion rate of mild steel in ACQ was about 10 times greater than that in CCA. Overall, the corrosion rates of mild steel determined using this non-accelerated test were approximately one to two orders of magnitude lower than those derived from the short-term AWPA testing scheme. In addition, the timbers treated with H3.2 and H4 CuAz did not show an inhibition of the reactivity of the zinc coating relative to either the untreated or CCA treated timbers, as noted in the tests using AWPA E12. Again, this long-term test confirmed that stainless steel has a very high corrosion resistance when in contact with timbers treated with CCA, CuAz or ACQ, even at high copper retention levels.

1.2.4 Salt Spray

SENCO (www.senco.com) tested stainless steel, hot dip galvanised and electrogalvanised fasteners in non-arsenate treated timbers according to ASTM-B117 and ASTM-G85. Tests indicated white and red rust at approximately 300 hrs under ASTM-B117 condition on galvanised fasteners. Stainless steel nails did not exhibit any corrosion. Peter and Edwin also tested corrosion performance of nails (copper, iron, painted and galvanised iron) in CCA treated timbers [Peter and Edwin 2008]. One set of panels were exposed in a salt spray chamber maintained at a temperature of 35°C and 95% RH for 480 hrs. The other set of samples were exposed in an estuary for 100 days. The rate of corrosion in the lab condition was found to be significantly higher than that in the field.

1.2.5 Immersion in Preservation Treatment Electrolyte

AWPA Standard E17 Standard Method for Determining Corrosion Rates of Metals in Contact with Treating Solutions is mainly adopted by wood preservers to assess the potential corrosion damage induced by the preservation chemicals to their plant equipment [AWPA 1999]. BRANZ's tests according to this standard showed that the corrosion rates of mild steel samples were consistently lower than that of the hot dip galvanised steel samples [Kear *et al.* 2008a]. A single very high corrosion rate was observed for the galvanised coupon immersed into the dilute CCA solution (1.1% vol.vol.). These findings indicated that an approach using aqueous electrolytes cannot simulate the deterioration of steel, particularly of hot dip galvanised steel when embedded into treated timbers.

A modified approach was therefore developed by using extract solutions from treated timbers [Panasik]. Fasteners were fully merged into a solution from ACQ wood chip leach-out for 30 days. Stainless steel of the 300 and 400 series performed well. Some types of carbon steel with proprietary coatings had very low amounts of corrosion while hot dip galvanised fasteners were covered with corrosion products.

1.2.6 Polarisation Resistance

Linear polarisation resistance (LPR) measures the direct current flowing through the metal-electrolyte interface when the electrode is polarised by a small electrical potential. This current is related to the corrosion current (related to the Tafel slopes) and in turn is directly proportional to corrosion rate [Stern and Geary 1957; Evans and Koehler 1961; Silverman 2000].

Linear polar resistance tests were performed by Kear *et al.* at BRANZ with metals directly immersed into dilute aqueous solutions of preservation chemicals [Kear *et al.* 2008b]. General observations indicated that the corrosion rate of stainless steel was extremely small and again the highest relative rate of corrosion was determined from hot dip galvanised steel in a dilute CCA solution. The relative order of corrosion susceptibility determined could then be described as: Stainless Steel < Mild Steel in CuAz < Galvanised & Mild Steel in ACQ < Galvanised in CuAz < Galvanised in CCA.

Zelinka *et al.* at the Forest Products Laboratory (FPL), USA also found that the measured corrosion rates for mild steel were much lower than expected and the corrosion rate of zinc could not be accurately measured due to plating of copper during testing [Zelinka *et al.* 2007]. Kear *et al.* also found difficulties in their polarisation measurements. The hot dip galvanised samples produced an extremely variable response within a single measurement therefore the near-linear behaviour of the voltametric response was only found in a very narrow range [Kear *et al.* 2008b].

These researchers believed that the poor correlation observed was mainly due to the fact that the solutions of preservatives cannot act similarly to those existing within a treated timber environment. In recognition of this, Zelinka *et al.* ran polarisation tests in water extracts of ACQ treated timber sawdust [Zelinka *et al.* 2008 a and b]. The results obtained with carbon steel, hot dip galvanised and electroplated fasteners appeared to have a relatively good correlation with those derived from exposure under constant conditions (27°C and 100% RH). However, there was a poor correlation between corrosion rates measured in solid timber and the extract for aluminium fasteners.

1.2.7 Electrochemical Impedance Spectroscopy (EIS)

EIS is an electrochemical technique that principally involves applying a small amplitude signal (a voltage usually ranging from 5-50 mV) to the specimen of interest over a wide

frequency range, typically from 0.01 to 100 kHz. Both the magnitude and phase of the current relative to the voltage are measured and a complex impedance is calculated. EIS allows modelling of corrosion reactions with an equivalent circuit model. This mechanistic circuit model can be used to predict how changes in the environment or other parameters will affect corrosion rate [Walter 1986; Scully 1989; Rammelt and Reinhard 1992; Murray 1997].

BRANZ used this technique to study the comparative corrosion performance of mild steel, hot dip galvanised steel and stainless steel when embedded into treated timbers [Kear *et al.* 2006a, 2008c]. It was observed that the CuAz and ACQ treated timbers had considerably lower electrolyte resistance (R_s) values when compared with untreated and CCA treated timbers, thus indicating an increased level of corrosivity when mild steel and hot dip galvanised steel were inserted into these timbers. However, the data on polarisation resistance, R_p , had an extremely poor reproducibility and relative rates of corrosion could not be extracted with any high level of confidence.

1.3 **Objective**

1.3.1 Limitations of Accelerated Tests

From the above sections, it can be seen that many accelerated techniques have been developed and widely used to evaluate the aggressivity of timbers treated with CCA and its alternatives towards typical metallic fasteners. Some methods could produce relatively reliable results showing that timbers treated with ACQ or CuAz may attack mild steel and/or hot dip galvanised steel more quickly than those treated with CCA under identical testing conditions. Meanwhile other techniques (especially electrochemical techniques performed in simple, dilute preservative solutions) had difficulties in differentiating the corrosion performance of different materials inserted into a timber or the comparative corrosivity of timbers treated with different preservation chemicals.

Although tests following the procedures recommended by AWPA E12 are employed by many commercial and research labs, the results obtained must be interpreted carefully. The testing condition is not representative of common exterior corrosion environments and does not reflect specific atmospheric conditions such as marine, industrial and/or urban environments. It is also well accepted that the corrosion rate derived from this accelerated test cannot be extrapolated to all possible scenarios because currently it is impossible to correlate the corrosion of metal in timber exposed to a high temperature and humidity environment to the corrosion rate under real service conditions.

Although electrochemical methods are well established for the study of metal corrosion in aqueous solutions, their application in the measurement of the corrosion rate of a metal in contact with a timber is currently very limited. This is probably related to:

- difficulty in producing a solution that is representative of the micro-environment inside the timber
- non-homogeneous structure, moisture content gradient and non-uniform distribution of preservation chemicals in timber
- extremely high electrical resistance (low conductivity) of timber-based electrochemical cell at low moisture content
- lack of fundamental understanding of processes and mechanisms behind metal corrosion in timber
- > intricate and time-consuming fabrication of corrosion cells.

The results derived from these methods can therefore only be used for comparative purposes if the testing conditions can be well controlled. Misinterpretation of these test results may lead to incorrect material selection and structural design. Significant work

would still be needed to develop these methods and correlate real world performance to the results obtained in lab.

1.3.2 Objective of Current Research

BRANZ's literature survey showed that there is little independently published data dealing with the aggressivity of ACQ and CuAz treated timbers towards typical metallic components for building and construction although they are acceptable in New Zealand standard [see NZS 3640]. More importantly, there is a lack of long-term and reliable exposure data concerning the corrosion performance of typical metallic fixing and/or fastening components in timbers treated with CCA and its alternatives when exposed to the New Zealand environment. This lack of fundamental corrosion data will make it difficult to specify materials that can meet the durability requirement of the NZBC and/or other relevant standards.

To address this information shortage, BRANZ initiated this field exposure test, which evaluates the degradation behaviour of typical metallic fasteners in several water-borne copper-bearing preservative treated Pinus radiata sapwood exposed in two corrosion zones in Wellington, New Zealand. The study was focused on:

- the comparative aggressivity of the timbers treated with CCA and its alternatives, e.g. ACQ and CuAz in typical New Zealand atmospheric conditions
- the influences of macro- and micro-climate on the corrosion performance of metallic fasteners embedded in treated timbers.

New Zealand has a long coastline and a significant portion of its long and narrow territory is marine-influenced. It is therefore very important to understand the potential effects of the deposition of chloride (or other salts) from atmospheric sources on the deterioration and compatibility of metallic fastening materials with timbers treated with ACQ and CuAz, which are believed to be more corrosive than the conventional preservative CCA.

2. EXPERIMENTAL

2.1 Timber – Source and Preservation Treatment

Rough-sawn kiln-dried Pinus radiata sapwood with nominal cross-section dimensions of 100×100 mm and 100×50 mm was custom-treated with three commercially-sourced water-based preservatives, i.e. CCA (oxide), CuAz (CA-B containing tebuconazole) and ACQ (ACQ-B containing didecylthyl ammonium chloride for H3.2 and ACQ-C containing alkylbenzyldimethyl ammonium chloride for H4). The active element ratios of the preservatives used are shown in Table 2.

Preservative	Copper	Chromium	Arsenic	Azole ⁽¹⁾	DDAC ⁽²⁾
CCA	23%	46%	31%		
CuAz	96%			4%	

38 %

Table 2: Ratio of active constituents in preservative formulations (%w/w)

Notes:

(1) Tebuconazole

ACQ

(2) Didecyl dimethyl ammonium chloride

62%

Treatment was undertaken at retention levels appropriate for hazard classes H3.2 and H4 as prescribed by NZS 3640, but to compensate for wood variability the solution strengths indicated were increased by 10%. A 'Bethell' process was also chosen to maximise uniformity of the preservative retention between individual boards within each treated lot. To accomplish this process, a vacuum is drawn on the timber for a predetermined period of time before the treatment chamber is flooded with preservative while maintaining the vacuum. Once the flooding is completed, the pressure in the cylinder is raised and held until the timber refuses to absorb further preservative. Prior to the treatment, the density of each individual timber board was determined based on its weight, moisture content and volume. In addition, each board was weighed after treatment to assess its preservative uptake and active species retention.

Post-treatment, the timbers were stored in a lab with constant environmental conditions, 25°C and 55% RH, for one month. After this storage, these timbers were cut to the required dimensions and the precipitated preservation chemicals were removed from the surfaces. During cutting, the longest dimension of all the timber blocks was selected to run parallel to the wood grain.

2.2 Field Exposure

To evaluate the corrosivity of the various combinations of timber preservative and hazard class, the treated timbers were used to construct gate-shaped structures incorporating mild steel, galvanised steel and stainless steel hardware commonly used for building and construction. A typical structure exposed at BRANZ's Judgeford campus is shown below in Figure 1.



Figure 1: Photo of the gate-shaped timber structures, designed to incorporate a variety of metallic building fixings

In order to evaluate the potential influences of macro-environment on the corrosion performance of fastening components embedded into treated timbers. These structures were exposed on two separate sites that are located in two corrosion zones as defined by the corrosivity map shown in NZS 3604. The first is BRANZ's atmospheric weathering station at Judgeford, located at map coordinates 41.10°S and 174.95°W (Figure 2). This site is in a sheltered semi-rural environment, separated by approximately 5 km from the nearest salt water, a tidal estuary, and further protected from the open sea by gently-rolling hills. It lies within NZS 3604 Zone 1 based on severity of exposure to marine aerosols but is considered a fairly benign example of this classification based upon atmospheric corrosion tests. The other site is on the

beach front of Oteranga Bay located at map coordinates 41.30°S and 174.62°W. It is just several metres away from the breaking surf and is considered as a typical sea spray zone i.e. a (very) severe marine environment.



Figure 2: Geographic locations of the two field exposure sites (Judgeford and Oteranga Bay) in Wellington, New Zealand

Field exposure testing is the simplest and probably the most reliable way to evaluate the corrosion performance of metal in contact with a specified timber exposed to the environment of interest. The metal-timber assembly and the experimental conditions are almost identical to a timber structure in service. Outdoor exposure is therefore the most reliable method to measure the corrosion rate and evaluate the corrosion properties of metal in timber. Field testing has been widely employed for the development of preservatives, timber-based construction materials and timber-metal structures. This technique will provide data that is fundamental to the specification of materials with the required durability.

2.3 Sample Testing

After exposure (one, two and three years), a partial set of the metallic fasteners were collected together with the timber blocks in which they are inserted. Figure 3 details the samples collected for characterisation after different periods of exposure. The fasteners were retrieved by carefully splitting the timbers. The surface morphologies of the fasteners were examined visually and microscopically and recorded digitally. This practice was expected to give a clear indication of the corrosion developed on the metal surface. After this, the samples were cleaned with a wooden knife to remove loosely attached corrosion products on the surfaces, and then immersed into the relevant chemical solution recommended by ASTM G1:

- Mild steel: 0.5L/L HCI + 3.5g/L hexamethylenetetramine (HMT, C6H12O4) at 20-25°C
- ➤ Zinc-coated steel: 100g/L NH₄CI at 70°C
- > Stainless steel: 150g/L diammonium citrate [(NH4)2C6H6O7] at 70°C.

The cleaned samples were then washed with distilled water, dried with warm air and weighed to obtain their mass losses relative to their original weights prior to exposure.

This enabled corrosion rates to be quantified for the various combinations of steel, preservative type and timber hazard class.

For the purpose of average thickness reduction calculation, densities of mild steel, zinc and stainless steel were assumed to be 7.86 g/cm³, 7.14 g/cm³ and 8.0 g/cm³, respectively.

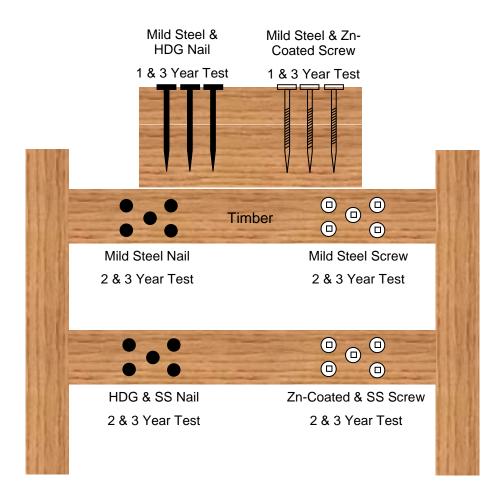


Figure 3: Nails and screws retrieved for characterisation after different years of exposure

As revealed from morphological characterisations (shown in the following sections), the zinc coatings on some fasteners had been completely consumed during this field exposure test. As a result, the corrosion products included both zinc and iron-bearing constituents and the mass loss recorded reflected an indeterminate combination of both the zinc coating and the steel substrate. This complicated the ability to calculate an unambiguous corrosion rate. Analysis in this study simply assumes therefore that the mass loss of all zinc-coated steel components (nails, screws and flashings) was due to the corrosion of zinc alone. The corrosion rates derived from mass loss measurements of those severely corroded screws and nails can therefore only be used as an indication of the corrosivity of timber and degradation of fastener. The mass loss is expressed as a uniform thickness reduction in mm/year and a standard deviation is calculated for the five replicate specimens removed from each variation of timber treatment.

3. **RESULTS**

3.1 Initial Copper Content in Timber

Table 3 details the preservative content achieved in the treated timber stock, compared with the NZS 3640 minimum preservative retention levels. Treatment retention was estimated from the changes in oven-dry density of the timber before and after treatment. These values have then been converted to corresponding estimated copper concentrations using the ratios of active constituents shown in Table 2. The actual values obtained by chemical analysis to characterise the supplied timber prior to commencing leaching experiments are also shown.

Timber Treatment			Retention of Active Agent (%w/w of oven-dry timber)			Copper Concentration (%w/w of oven-dry timber)						
Туре	Copper Content	Hazard Class	NZS 3604	Achieved Retention		Estimated		Chemical Analysis				
CCA	23%	H3.2	0.37	0.48	±	0.05	0.11	±	0.01	0.09	±	0.03
		H4	0.72	0.84	±	0.09	0.19	±	0.02	0.18	±	0.02
CuAz	96%	H3.2	0.22 88	0.24	±	0.04	0.23	±	0.04	0.24	±	0.02
		H4	0.41 6	0.47	±	0.06	0.45	±	0.05	0.39	±	0.05
ACQ	62%	H3.2	0.35	0.39	±	0.06	0.24	±	0.04	0.21	±	0.003
		H4	1.02	1.10	±	0.17	0.68	±	0.10	0.63	±	0.04

Table 3: Initial total preservative and copper retention in stock timber supplied

The mean calculated retention of the H3 CCA treated timbers was significantly above the minimum 0.37% w/w required by NZS 3640, while the calculated averages for the other preservative combinations was observed to be only slightly above that specified in the standard. While the estimated copper retention values from the preservative solution uptake generally agree with the chemical analyses subsequently carried out through Veritec to characterise the timber, it is noted that the statistical dispersion associated with both figures is reasonably high. The coefficient of variation (normalised standard deviation) frequently exceeds 0.1, i.e. there is considerable scatter in the data obtained from analysing different specimens of the same treated timber. Taking the worst case example, the spread of the six individual chemical analyses for the CCA H3.2 hazard class ranged from 0.06 to 0.12 %w/w copper.

This deviation is not entirely unexpected given the inherently non-uniform structure of timber as a natural material. However, the apparent inconsistencies that subsequently arise when dealing with small datasets under such circumstances might make it difficult to discern trends.

3.2 Coating Thickness on Hot Dip Galvanised Nails

The zinc coating thickness of the hot dip galvanised nails used for this study was measured using the procedures recommended by ASTM A90/A90M.

The nails had an average coating weight of $302.3\pm63.3 \text{ g/m}^2$. By assuming the coating is uniform and the density of zinc to be 7.14 g/cm³, the average coating thickness was then calculated to be $42.3\pm8.9 \text{ }\mu\text{m}$. The coating mass measured had a relatively large

variation, ranging from 208 to 444 g/m². A comparison between this measurement and AS/NZS 4680 showed that the coating thickness on these nails could meet the requirements for articles that are centrifuged but not for the requirements for articles that are not centrifuged.

Zinc coatings on screws should be produced by mechanical plating according to NZS 3604 *Timber Framed Buildings* and AS 3566 *Self-drilling Screws for the Building and Construction Industries.* However, the coating thickness on the screws used for this study was not measured since no samples were obtained at the time of coating thickness test.

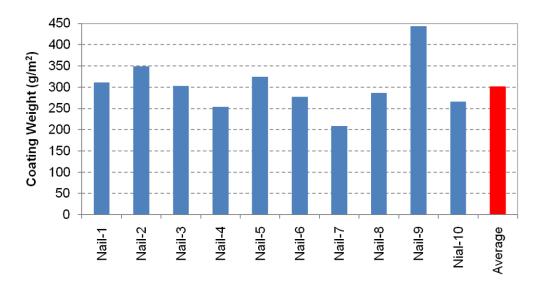


Figure 4: Average thickness of the zinc coating on the hot dip galvanised nails used in this study

3.3 Corrosion – First-Year Exposure

After one year, five nails, five screws and one flashing were retrieved from each timber gate exposed at the Judgeford site (no sample was collected from Oteranga Bay). These fasteners were inserted into the timber block located at the top of the gate-shaped structure and their longitudinal orientation was vertical to the ground.

3.3.1 Morphological Characterisation

3.3.1.1 Fasteners

In general, mild steel nails and screws suffered relatively uniform corrosive attack. However, nails and screws embedded into untreated and CCA treated timbers were much better preserved than those in ACQ and CuAz treated timbers. Even in H3 CuAz and ACQ treated timbers, heavy iron-rich red rust had formed and covered the whole surface areas of the fasteners (Figure 5).

Hot dip galvanised nails demonstrated a better performance than mild steel nails in all timbers (Figure 6). The zinc coating on the head of these nails was still in relatively good condition and no obvious corrosion failure was observed. Instead, corrosion was mainly localised on their shaft and tip areas. This location-related performance difference has probably resulted from the aggressivity difference between the atmosphere and the micro-environment inside the timber, and also from the nail driving-in process. The quantity of corrosion products formed was strongly related to the timber treatment, both with respect to preservative type and Hazard Class.

Corrosion was more extensively developed for nails embedded in the CuAz and ACQ treated timbers, particularly at the H4 treatment level. In these cases, iron-rich red rust could cover most of the shaft area. In comparison, nails in CCA timber were much better preserved.

Patterns of material degradation for the mechanically-plated screws were more complex. The heads of the screws remained basically sound, although a small number showed a partial failure along the margin and at the bottom of the square drive mortise. The spiral sections appeared to be the most susceptible to corrosion of the underlying steel substrate; red iron-rich rust could be easily observed even for those embedded into untreated timbers after one year of field exposure. This suggests stresses associated with the driving-in process have partially damaged the zinc coating, leaving more structural defects. Examination of the corrosion developed on other fasteners strongly supported the additional corrosivity of CuAz and, especially, ACQ preservatives when compared with conventional CCA treatment.

Some screws were broken during the retrieval process. This was mainly due to the heavy rust present in the spiral section which introduces large rotation resistance.

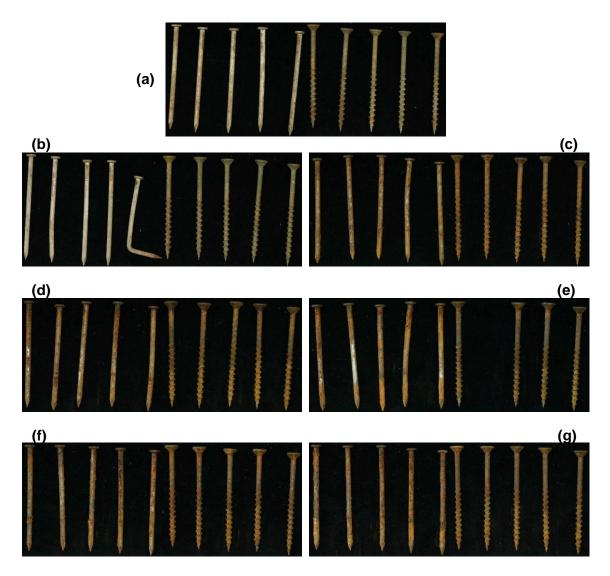


Figure 5: Surface morphology (before cleaning) of mild steel fasteners embedded into timbers exposed at Judgeford site for one year – (a) untreated, (b) H3 CCA, (c) H4 CCA, (d) H3 CuAz, (e) H4 CuAz, (f) H3 ACQ and (g) H4 ACQ

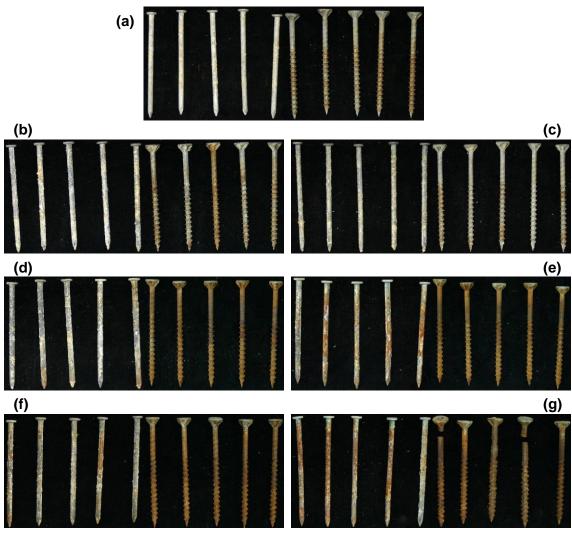


Figure 6: Surface morphology (before cleaning) of zinc-coated fasteners embedded into timbers exposed at Judgeford site for one year – (a) untreated, (b) H3 CCA, (c) H4 CCA, (d) H3 CuAz, (e) H4 CuAz, (f) H3 ACQ and (g) H4 ACQ

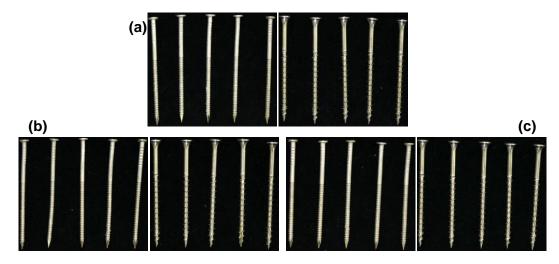


Figure 7: Surface morphology (before cleaning) of stainless steel fasteners embedded into timbers exposed at Judgeford site for one year – (a) H4 CCA, (b) H4 CuAz and (c) H4 ACQ

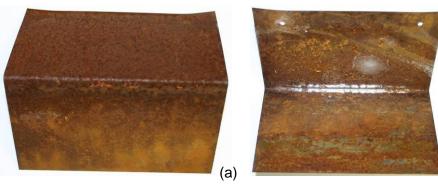
Stainless steel fasteners performed very well in all combinations of preservative type and hazard class. No obvious signs of corrosion were observed on their body sections (Figure 6). Occasionally very limited iron-rich rust (shown as small spots) was observed on the heads. This is likely to be the result of partial damage to the passive film and/or iron contamination from the hammer when the fastener was driven into the timber.

3.3.1.2 Flashings

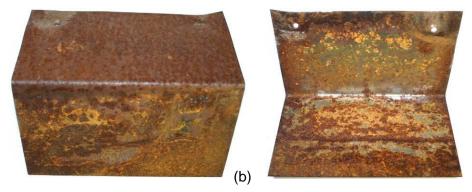
Corrosion behaviour of the angle flashings attached to the exposed timber gate structures was observed to be highly dependent on the combination of both the preservative type and the hazard level of treatment.

The mild steel flashings attached to all combinations of timber preservative and hazard class suffered from relatively uniform corrosion attack on the surfaces directly exposed to the atmosphere. Corrosion on the surfaces in direct contact with the timber was generally observed to be less uniform and was not obviously correlated with preservative or hazard class. Areas that appeared to have been in closest contact with the timber generally showed the most severe corrosion. This spatial dependency indicated that both the timber preservative composition and the environment in the crevice formed between the timber and the steel contributed to the material degradation through chemical and/or electrochemical processes.

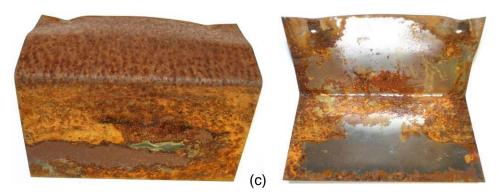
After removal of the corrosion products, unevenly distributed regions characterised by large numbers of small and shallow pits could be observed on the surfaces contacting the timber. The non-uniform distribution of these regions probably reflects variations in contact between the steel and timber in the test structures. The corrosion morphologies of the flashings attached to timbers treated with different preservatives to different hazard levels did not show any significant differences (Figure 8).



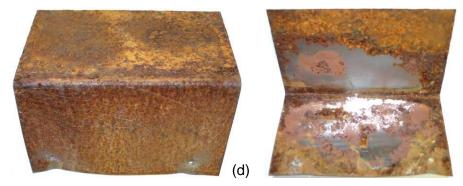
←Front/Back→



 \leftarrow Front/Back \rightarrow



 \leftarrow Front/Back \rightarrow



←Front/Back→

Figure 8: Surface morphology of mild steel flashing attached to timber exposed at Judgeford site for one year – (a) untreated, (b) H3 CCA, (c) H4 CuAz and (d) H4 ACQ

It was quite evident that the hot dip galvanised steel flashings attached to the ACQ or CuAz treated timbers suffered serious attack during atmospheric exposure. Heavy zinc-rich white corrosion products could be seen on the surfaces in contact with the timber. Even more striking was that a significant portion of the surface area that was directly contacting the timber was covered with iron-rich red rust. This implies that the galvanised zinc coating on these areas had been completely consumed by corrosion within one year and then the steel substrate was exposed to corrosive environment.



Figure 9: Surface morphology of hot dip galvanised steel flashing attached to timber exposed at Judgeford site for one year – the timber was treated with H4 ACQ

Consumption of the zinc coating on the galvanised flashings had occurred to a much greater extent with ACQ and CuAz than with CCA in the equivalent hazard class. The galvanised flashings attached to CCA treated timbers developed extensive white zincrich corrosion products, particularly on surfaces in direct contact, and incidences of red rusting were comparatively rare.

It was also evident from Figures 9 and 10 that an increase in the preservative level from H3.2 to H4 significantly accelerated the corrosion process, suggesting some underlying causation related to the retained copper concentration within the timber.



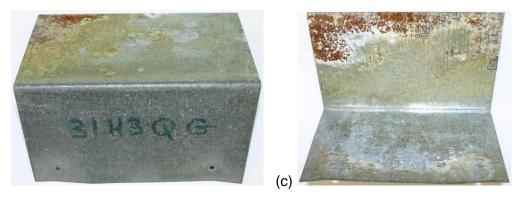


←Front/Back→





←Front/Back→



 $\leftarrow \textit{Front/Back} \rightarrow$

Figure 10: Surface morphology of hot dip galvanised steel flashing attached to timber exposed at Judgeford site for one year – (a) H3 CCA, (b) H3 CuAz and (c) H3 ACQ

When attached to untreated timber specimens, the hot dip galvanised coatings remained completely intact and in reasonably good condition at the end of the 12 months of exposure, as shown in Figure 11. Only limited areas of the surface had darkened, characteristic of zinc oxidation.



Figure 11: Surface morphology of hot dip galvanised steel flashing attached to untreated timber exposed at Judgeford site for one year

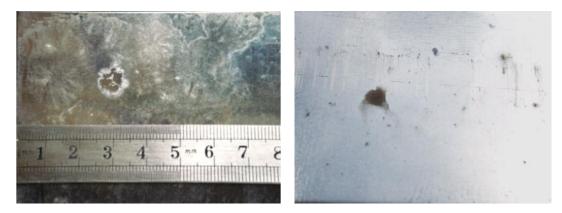


Figure 12: Stained (left) and scratch-corroded (right) areas observed on stainless steel flashings attached to H4 CuAz treated timbers and atmospherically exposed at Judgeford site for one year

All stainless steel flashings performed very well. The most obvious degradation was the development of a diffuse white patina of uncertain origin (Figure 12). Rust did form to a very limited extent in association with scratches caused during construction and installation. The corrosion resistance of stainless steels is largely reliant on the formation and maintenance of thin chromium-rich passive films [Uhlig 1979]. Localised mechanical damage to this passive film introduces weak points and may result in corrosion if this protective film cannot re-form quickly.

3.3.2 Estimation of Corrosion Rate

3.3.2.1 Fasteners

Mass loss measurements were used to numerically quantify metal degradation in various timbers. The results are presented in Figures 13 and 14.

In general, fasteners exhibited a relatively low corrosion rate when embedded into CCA treated timbers, and this is consistent with the surface morphological observations. It is also interesting to note that the mass losses of the fasteners embedded in CCA (H3.2 and H4) treated timbers do not differ greatly from those of the fasteners embedded in untreated timbers. CuAz and ACQ treatments promoted markedly increased corrosion rates. For example, the mild steel nails had a corrosion rate of 6.63×10^{-2} mm/year in H4 ACQ treated timber, while equivalent corrosion rates in H4 CCA and untreated timbers were 1.87×10^{-2} mm/year and 2.66×10^{-2} mm/year, respectively. In addition, an increase of the copper content in the preservation chemicals appeared to increase the aggressivity of the treated timber towards metal. This measurement result also agrees with the morphological characterisation where heavier corrosion products (zinc-rich and/or iron-rich rusts) covered larger surface areas.

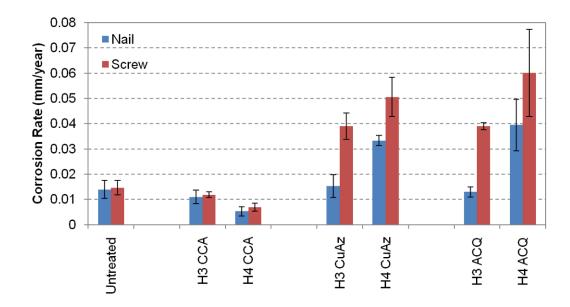


Figure 13: Corrosion rates of mild steel fasteners embedded into timbers exposed at Judgeford site for one year

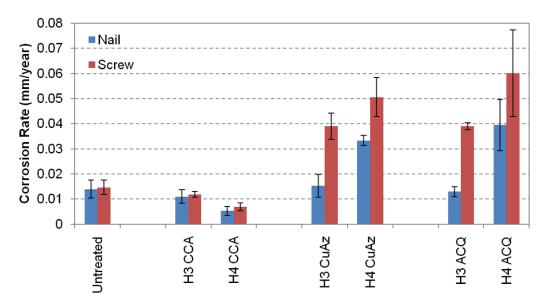


Figure 14: Corrosion rates of zinc-coated fasteners embedded into timbers exposed at Judgeford site for one year

Zinc coatings provided enhanced protection to the steel substrates, reflected in lower mass losses, particularly with hot dip galvanised nails. However as observed from the morphological observations, the coating in the thread area of screws was prone to damage during the driving-in process. Thus, a mechanically applied zinc coating cannot always be anticipated to provide long-term protection from corrosion.

The mass loss of the stainless steel specimens was extremely limited and very close to (or lower than) the value of error associated with the measurement technique. Hence it is impossible to compare the corrosion resistance of the stainless steels embedded into a specified timber or to determine the potential influence of timber preservation treatment on their performance. As a result, their corrosion rates are not reported here. However, this measurement once again indicates that all austenitic stainless steel fasteners had a very favourable level of corrosion resistance when in contact with all types of timbers under the current testing conditions.

3.3.2.2 Flashings

The corrosion rates of the mild steel flashings in contact with different timbers were generally very similar (Figure 15). The only exception was that the flashing attached to the H4 ACQ treated timber showed a much higher mass loss, 2.97×10^{-2} mm/year, which is three to four times higher than the others.

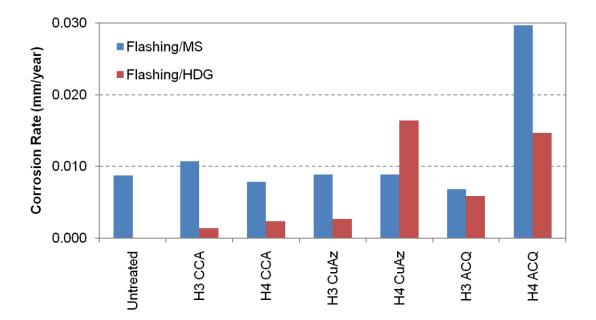


Figure 15: Corrosion rate of flashings in contact with timbers exposed at Judgeford site for one year. Note that corrosion rate of galvanised steel flashing in untreated timber is omitted and results are from single specimens so an estimate of uncertainty is impossible (MS: Mild Steel; HDG: Hot Dip Galvanising)

In the case of the hot dip galvanised steel flashings, it is readily apparent that contact with timbers treated with ACQ or CuAz resulted in a higher corrosion rate than contact with CCA or untreated timbers. Furthermore, an increase of the hazard class from H3.2 to H4 also increased the corrosion rate. This result is consistent with the morphological observations.

As expected, the mass loss of the hot dip galvanised steel flashings was significantly lower than their mild steel flashings counterparts. For example, the galvanised steel flashing in contact with H3 CCA treated timber had a mean corrosion rate of 1.41×10^{-3} mm/year, almost an order of magnitude lower than the equivalent mild steel specimen with a rate of 1.07×10^{-2} mm/year.

When in contact with the H4 ACQ treated timber, the galvanised steel flashing also showed a higher corrosion resistance than the mild steel equivalent, with corrosion rates of 1.47×10^{-2} mm/year and 2.97×10^{-2} mm/year, respectively. The reason for this is simple: not only is zinc a sacrificially protective metal relative to steel, but it also has an atmospheric corrosion rate some 5-10 times lower than low alloyed ferrous materials [Zhang 2000].

However, these results do not yield a straightforward relationship between timber treatment, copper retention level and the induced corrosion rate. The present results only appeared to support that timbers treated with H4 CuAz and H4 ACQ are more corrosive than others. It is believed that the geometric configuration of the steel flashing samples and their physical contacts with timber surfaces made a significant contribution to the results obtained. Under current testing condition, each steel flashing had four distinct surfaces: one surface was directly exposed to the atmosphere, while the other three surfaces were pressed into contact with the mounting timber. However, a uniform contact geometry and pressure between the metal-timber interfaces is unlikely to have been consistently achieved during sample fabrication. Some regions of the surfaces will have been held in tight contact with the timber while gaps may have occurred elsewhere.

This variation in contact area appears to have led to a corresponding variation in corrosion processes. In general, areas that had achieved direct timber contact showed more rapid degradation. This accelerated corrosion is believed to arise from the contribution of a variety of chemical and/or electrochemical processes, such as acids released from timber hydrolysis, non-fixed copper ions deposited on the timber surface and crevice corrosion. The latter would only occur when the geometry of the gap between the timber and the metal was suitable to retain the corrosive medium [Roberge 2008]. Preservative-induced degradation will therefore be restricted to limited areas and result in an under-estimate of the overall corrosion rate, which is normalised to the entire surface area of the flashing. As such, the effect of timber treatment on the corrosion of steel flashing may be under-estimated in the measurements reported in this study.

3.4 Corrosion – Second Year Exposure

After two years, five nails and five screws were retrieved from each timber gate exposed at the Judgeford site. These fasteners were inserted into the timber blocks located on the lower part of the gate structure and their longitudinal orientation was parallel to the ground.

Since these fasteners are different from those tested in Section 3.3 in their orientation and location in the timber gate structure, their corrosion rates and surface morphologies cannot be compared directly. This will be further examined in the Discussion section.

3.4.1 Morphological Characterisation

Again, visual inspections showed that mild steel nails suffered uniform corrosive attack in all timbers. This was indicated by the formation of iron-rich red rust on their surfaces. On some nails inserted into CuAz or ACQ treated timbers, consumption of metal was quite serious, leading to observable thickness reduction in some areas of the shaft. On mild steel screws, serious corrosion was mainly found in the thread area. It was frequently observed that small parts of the spiral burr were lost. On their shank areas, attack was mainly observed as high-density small pits (Figure 16).

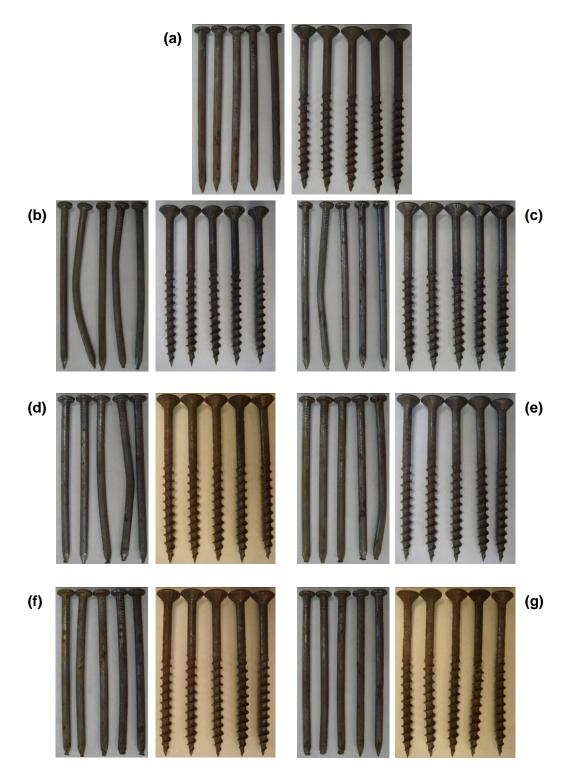


Figure 16: Surface morphology (after cleaning) of mild steel fasteners retrieved from timbers exposed at Judgeford site for two years (these fasteners were inserted into the timber blocks fixed at the lower (side) part of the gate structure and their longitudinal orientation was parallel to the ground) – (a) untreated, (b) H3 CCA, (c) H4 CCA, (d) H3 CuAz, (e) H4 CuAz, (f) H3 ACQ and (g) H4 ACQ

After two years of exposure the formation of red rust on the hot dip galvanised nails in untreated and H3 treated timbers (CCA, CuAz and ACQ) was limited, indicating that

most areas were still protected by the zinc coating. In timbers treated to an H4 level, particularly those treated with CuAz and ACQ, rust formation was quite obvious. Rust could be more easily found on the zinc-coated screws driven into the same timbers. Due to the presence of heavy rust in the thread areas, it was difficult to retrieve screws. Some of them were broken during the extraction process (see Figure 17 f and g). After the removal of corrosion products, it was found that on some screws the threads were severely damaged in some areas and or even partly disappeared (Figure 17).

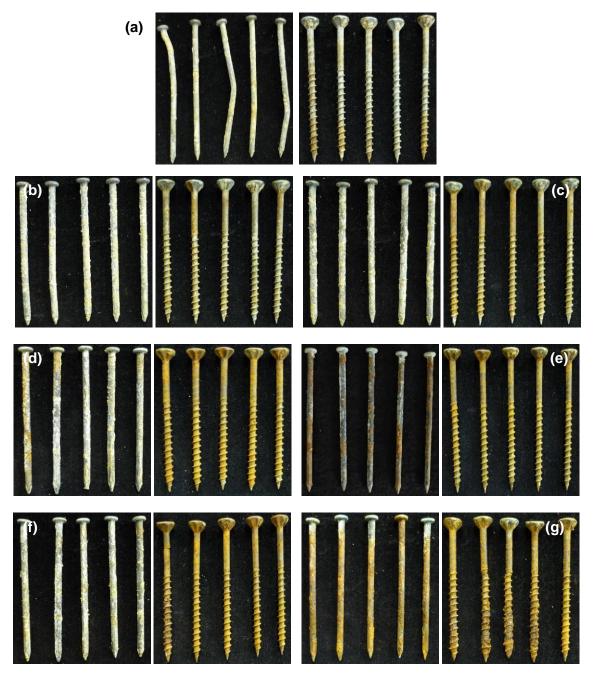


Figure 17: Surface morphology of zinc-coated fasteners retrieved from timbers exposed at Judgeford site for two years (these fasteners were inserted into the timber blocks fixed at the lower (side) part of the gate structure and their longitudinal orientation was parallel to the ground) – (a) untreated, (b) H3 CCA, (c) H4 CCA, (d) H3 CuAz, (e) H4 CuAz, (f) H3 ACQ and (g) H4 ACQ

As expected, all stainless steel nails and screws performed very well in all combinations of preservative type and hazard class. No obvious signs of corrosion failure were found on the shaft/shank of the nails and screws. Very limited rust formation was occasionally found on the top surface of the head (Figure 18).

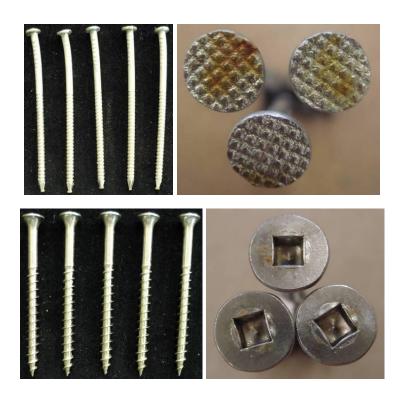


Figure 18: Typical surface morphology of stainless steel fasteners retrieved from H4 ACQ treated timbers exposed at Judgeford site for two years (these fasteners were inserted into the timber blocks fixed at the lower (side) part of the gate structure and their longitudinal orientation was parallel to the ground). Very limited iron-rich rust was occasionally found on the head top surface and the body section is free of damage

3.4.2 Estimation of Corrosion Rate

Measurements showed that the corrosion rates of the mild steel nails and screws inserted into the untreated timbers were higher than those of the nails and screws inserted into H3 and H4 CCA treated timbers. H4 ACQ treated timbers were the most corrosive. Metal corrosion in H3 ACQ, H3 CuAz and H4 CuAz treated timbers was not significantly accelerated in comparison with that in H3 and H4 CCA treated timbers under identical testing conditions (Figure 19). This observation is somewhat different from the results obtained after one year of exposure.

Zinc-coated fasteners in CuAz and ACQ treated timbers were losing their coatings at a higher rate than those in untreated and CCA treated timbers and this trend was particularly obvious for screws. Again, H4 ACQ treated timbers exhibited the highest aggressivity towards metallic fasteners. The mass loss rate of metal in this timber could be two to four times higher than that of metal in CCA and CuAz treated timbers (Figure 20).

The experimental findings from this examination focusing on fasteners with orientation and location different from those in the first-year test further confirmed that CCA alternatives (ACQ and CuAz) present a higher risk of corrosion to metallic fasteners. Based on the corrosion rate data collected, the aggressivity of the timbers towards mild steel and galvanised fasteners generally obeys the following approximate sequence:

> Mild steel: CCA \leq Untreated \leq CuAz < ACQ; and

> Hot dip galvanised steel: Untreated \leq CCA < CuAz < ACQ.

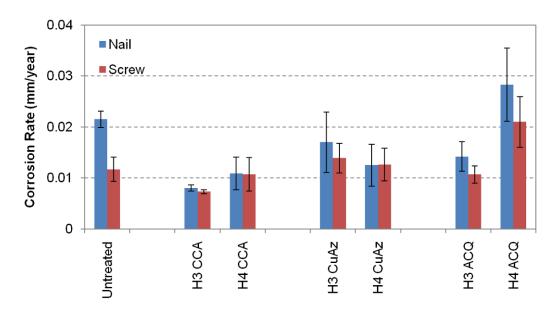


Figure 19: Corrosion rates of mild steel fasteners embedded into timbers exposed at Judgeford site for two years (these fasteners were inserted into the timber blocks fixed at the lower (side) part of the gate structure and their longitudinal orientation was parallel to the ground)

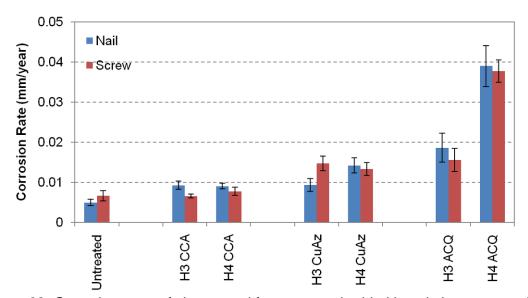


Figure 20: Corrosion rates of zinc-coated fasteners embedded into timbers exposed at Judgeford site for two years (these fasteners were inserted into the timber blocks fixed at the lower (side) part of the gate structure and their longitudinal orientation was parallel to the ground)

The influences of preservation treatment on the performance of stainless steel fasteners could not be evaluated accurately since the mass losses obtained were very

close to the accuracy of the measurement equipment. But this, again, confirmed that stainless steel components had superior resistance to the corrosive attack by these treated timbers.

3.5 Corrosion – Third Year Exposure

After three years, 10 nails and ten screws were retrieved from each timber gate exposed at the Judgeford site. Five of them were inserted into the timber block located at the top of the gate structure and their longitudinal orientation was vertical to the ground, while another five were from the timber block fixed to the bottom part of the gate and their longitudinal orientation was parallel to the ground.

Another set of samples (five nails and five screws) was retrieved from the timber gate structures exposed at Oteranga Bay. These fasteners were inserted into the timber block located at the top of the gate and their longitudinal orientation was vertical to the ground.

3.5.1 Judgeford

3.5.1.1 Morphological observations

It was not surprising to find that after three years of exposure at the Judgeford site, all mild steel nails and screws inserted into the top part of the gate structure were severely corroded. Consequently, an extremely thick scale composed of iron-rich rust was formed on their surfaces (Figures 21 and 22). When these corrosion products were completely removed, serious consumption of the steel substrate could be observed. Since the rust formation was so heavy, it was impossible to differentiate the aggressivity of timbers treated with different preservatives.

Compared with nails, corrosive attack to screws appeared to be more severe. Deterioration of the metal mainly exhibited as partial loss of the spiral burr and the formation of high-density pits of diverse morphologies on the whole body section.

Comparatively, mild steel nails and screws retrieved from the side (bottom part) of the gate structures were in slightly better condition (Figures 23 and 24). On some nails, shiny areas could still be observed on their shafts. The iron-rich rust scale was also thinner. However, observations indicated that untreated timbers attacked mild steel nails and screws more quickly than other timbers, particularly those treated with CCA and CuAz, although ACQ treated timbers still appeared to be the most corrosive.

Although darkening (due to oxidation of the zinc) of the hot dip galvanised coating was quite obvious, signs of red rust were very limited on the hot dip galvanised nails inserted into untreated, H3 and H4 CCA treated timbers that were fixed at the top part of the gate structure. When the corrosion products were completely removed, it could be seen that most of the steel substrate was still covered and protected by the zinc coating (although it is believed that the original zinc coating had been thinned due to corrosion). However, white zinc-rich rust and red iron-rich rust were very obvious on the body section of the nails retrieved from both H3 and H4 CuAz and H4 ACQ treated timbers. After cleaning, uniform corrosion together with the formation of pits (i.e. highly localised corrosive attack) of various sizes could be found on the shafts (Figure 25).

The zinc coating on the head of most hot dip galvanised nails (30 in 35) was still in relatively good condition, showing limited formation of white and/or red rust.

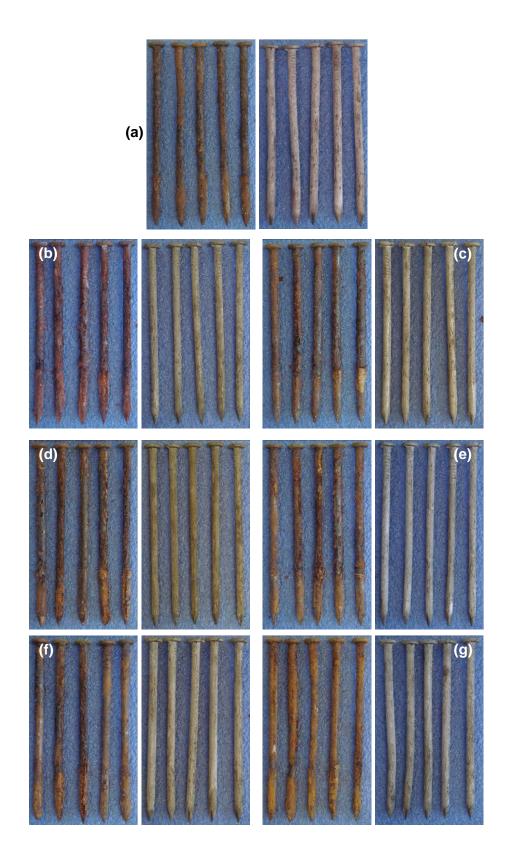


Figure 21: Surface morphology of mild steel nails retrieved from the top part of the timber gate structure exposed at Judgeford site for three years – (a) untreated, (b) H3 CCA, (c) H4 CCA, (d) H3 CuAz, (e) H4 CuAz, (f) H3 ACQ and (g) H4 ACQ

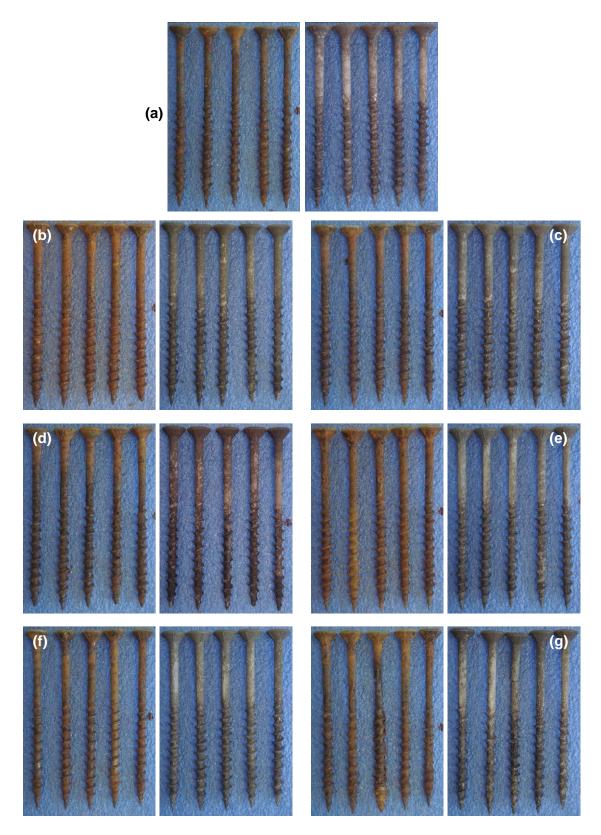


Figure 22: Surface morphology of mild steel screws retrieved from the top part of the timber gate structure exposed at Judgeford site for three years – (a) untreated, (b) H3 CCA, (c) H4 CCA, (d) H3 CuAz, (e) H4 CuAz, (f) H3 ACQ and (g) H4 ACQ

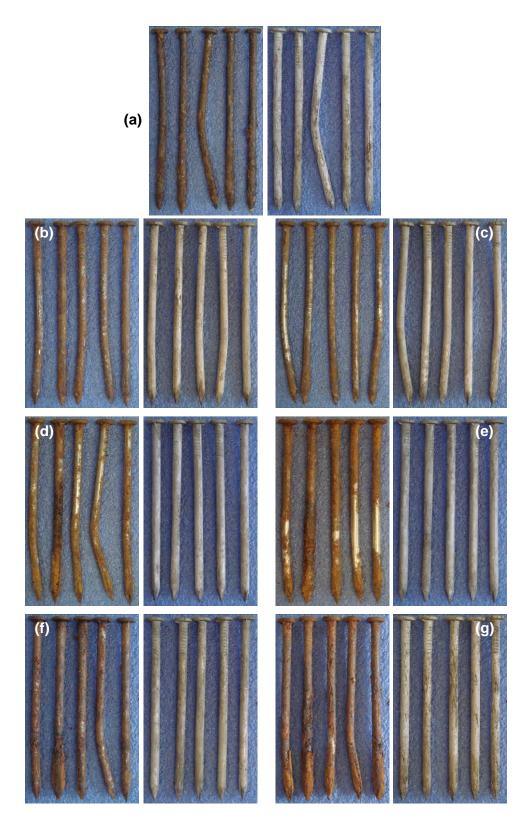


Figure 23: Surface morphology of mild steel nails retrieved from the lower (side) part of the timber gate structure exposed at Judgeford site for three years – (a) untreated, (b) H3 CCA, (c) H4 CCA, (d) H3 CuAz, (e) H4 CuAz, (f) H3 ACQ and (g) H4 ACQ

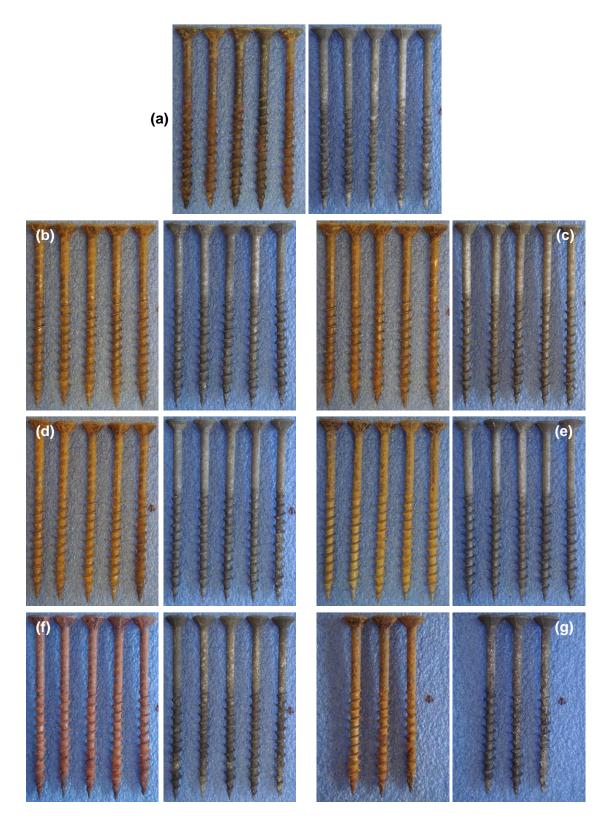


Figure 24: Surface morphology of mild steel screws retrieved from the lower (side) part of the timber structure exposed at Judgeford site for three years – (a) untreated, (b) H3 CCA, (c) H4 CCA, (d) H3 CuAz, (e) H4 CuAz, (f) H3 ACQ and (g) H4 ACQ

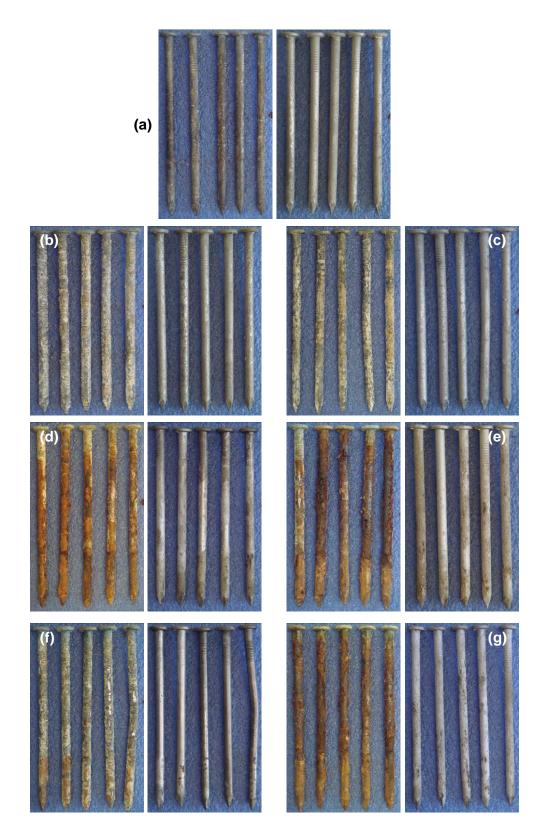


Figure 25: Surface morphology of hot dip galvanised nails retrieved from the top part of the timber gate structure exposed at Judgeford site for three years – (a) untreated, (b) H3 CCA, (c) H4 CCA, (d) H3 CuAz, (e) H4 CuAz, (f) H3 ACQ and (g) H4 ACQ

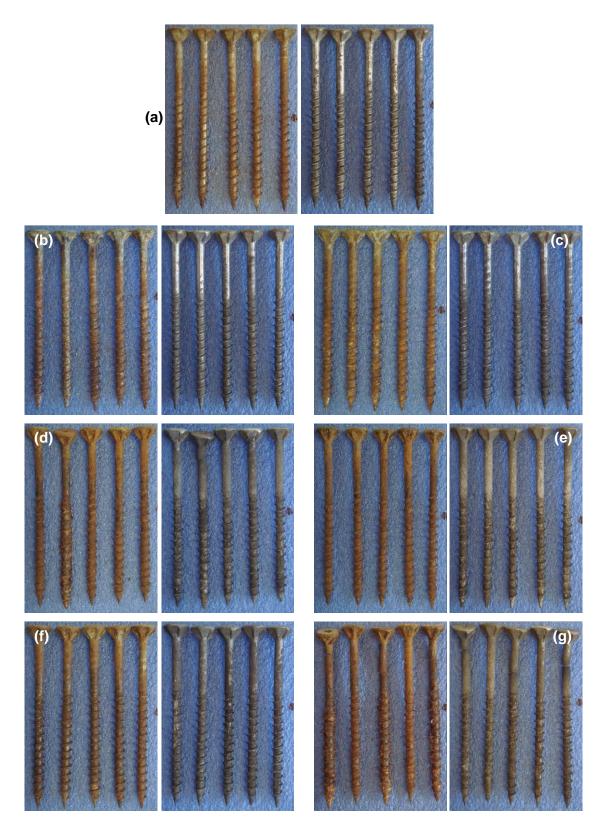


Figure 26: Surface morphology of mechanically-plated screws retrieved from the top part of the timber gate structure exposed at Judgeford site for three years – (a) untreated, (b) H3 CCA, (c) H4 CCA, (d) H3 CuAz, (e) H4 CuAz, (f) H3 ACQ and (g) H4 ACQ

The mechanically zinc-plated screws performed badly. After three years of exposure at the Judgeford site, all zinc-coated screws inserted into the top part of the gate structure showed serious formation of iron-rich rust on almost all their surfaces. Closer observation of the corrosion products remaining on the spiral section also revealed that extensive interactions were taking place between the rust and the surrounding timber structure. The presence of heavy corrosion products in the spiral sections also made retrieval of screws from the timbers, particularly ACQ treated timbers, very difficult. Consequently, some screws were broken (see Figure 26).

After cleaning, the corrosion-induced metal loss from the spiral sections of the screws inserted into CuAz and ACQ treated timbers was marked. The smooth section immediately below the head also suffered from relatively uniform attack, leading to an observable thickness reduction. These screws certainly could not perform their fastening functions properly and safely over any longer exposure.

By contrast, zinc coatings on the head top surfaces of these screws were better preserved. About 19 of 35 screws showed very limited signs of rust development on their heads and occasionally on the body section immediately below the head.

Similar to the mild steel fasteners, the zinc-coated fasteners from the lower (side) part of the timber gate structures were also better preserved than those inserted into the timber blocks installed at the top part of the gate.

Limited iron-rich rust was occasionally found on the nails inserted into untreated, H3 and H4 CCA treated timbers (Figure 27), indicating that the zinc coating was still functioning. This was confirmed by morphological observations of the samples after chemical cleaning. Zinc coatings could still be found on most part of the surface (although it is believed that their thickness had been reduced due to oxidation). Although rust was quite evident on the nails inserted into CuAz and ACQ treated timbers, it was not as heavy as that on those embedded into the top part of the gate structure. Most of them (30 of 35) still had a better preserved head without any red iron-rich rust present.

Limited zinc coating still remained on the body section (particularly on the smooth section between the head and the spiral) of the screws retrieved from untreated, H3 and H4 CCA treated timbers. This condition was better than that of the screws removed from the timbers with the same treatment but located on the top part of the gate structure. However, corrosion on the screws inserted into CuAz and ACQ treated timbers was again quite serious, shown by the formation of heavy iron-rich red rust on their whole body sections. Significant consumption of metal (high density pits and incomplete spiral burrs) could be easily observed on the cleaned samples (Figure 28). All screws inserted into CuAz and ACQ treated timbers had heads that were completely rusted. Only 10 screws in untreated and CCA treated timbers had their heads still protected by the zinc coating.

All stainless steel nails and screws (retrieved from both the top and side parts of the timber structure) performed very well after three years of exposure at the Judgeford site. Material deterioration was only present as extremely limited rust formation on their head top surfaces. Serious damage to their body sections by the corrosive environment inside the timber was not found by either visual or optical characterisations. Since heavy rust was absent from the interface between the fastener and the surrounding timber, it was relatively easy to retrieve these fasteners. This ease of extraction would certainly benefit any maintenance and/or retrofitting activities.

Since the morphology of the stainless steel fasteners located at the side of the gate structure was very similar with that of the stainless steel fasteners located on the top of the gate, digital recording of their surface morphology was not performed and cleaning practice was not applied to obtain their mass losses for corrosion rate calculation.

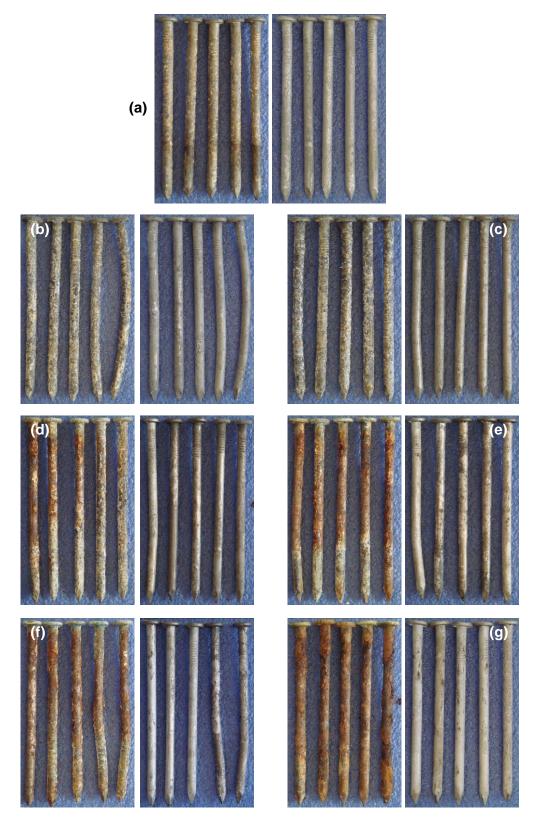


Figure 27: Surface morphology of hot dip galvanised nails retrieved from the lower (side) part of the timber gate structure exposed at Judgeford site for three years – (a) untreated, (b) H3 CCA, (c) H4 CCA, (d) H3 CuAz, (e) H4 CuAz, (f) H3 ACQ and (g) H4 ACQ

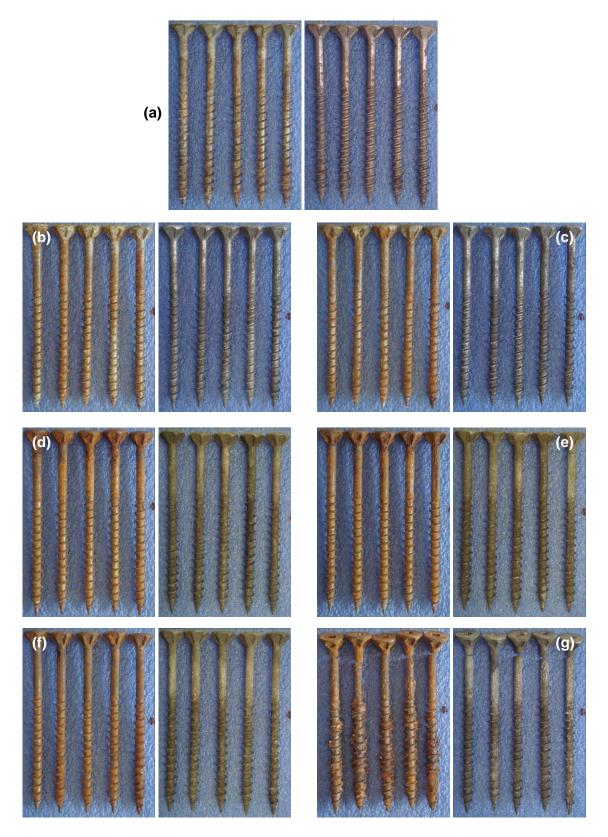


Figure 28: Surface morphology of mechanically-plated screws retrieved from the lower (side) part of the timber gate structure exposed at Judgeford site for three years – (a) untreated, (b) H3 CCA, (c) H4 CCA, (d) H3 CuAz, (e) H4 CuAz, (f) H3 ACQ and (g) H4 ACQ

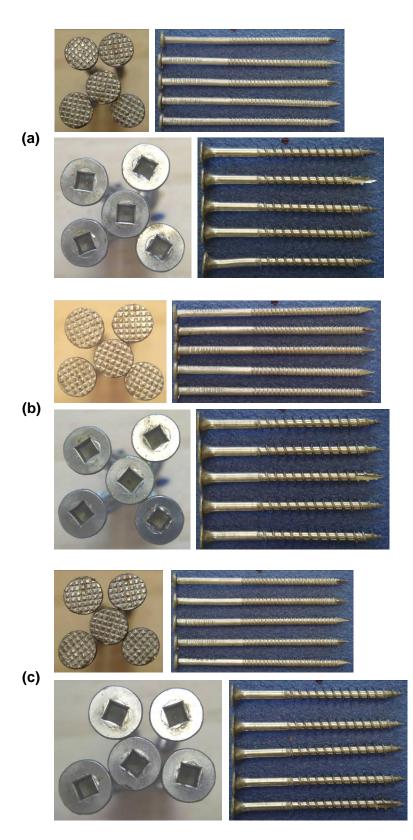


Figure 29: Typical surface morphology of stainless steel fasteners retrieved from the top part of the timber gate structure exposed at Judgeford site for three years – (a) H4 CCA, (b) H4 CuAz and (c) H4 ACQ

3.5.1.2 Estimation of corrosion rates

Average corrosion rates measured for the mild steel fasteners retrieved from the top part of the gate-shaped timber structures after three years of exposure at the Judgeford site showed that the degradation behaviours of these fasteners in timbers of different preservation treatments were somewhat similar (Figure 30).

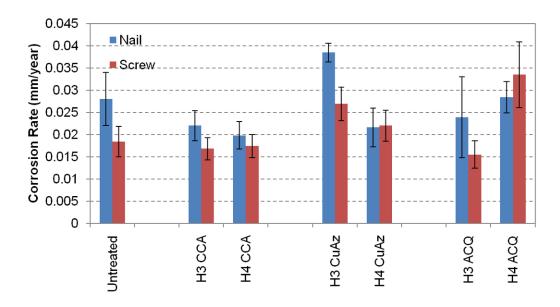


Figure 30: Corrosion rates of mild steel fasteners embedded into timbers exposed at Judgeford site for three years (these fasteners were retrieved from the top part of the gate-shaped timber structure i.e. their longitudinal orientation was vertical to the ground)

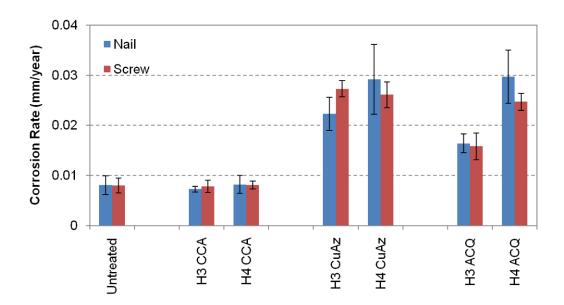
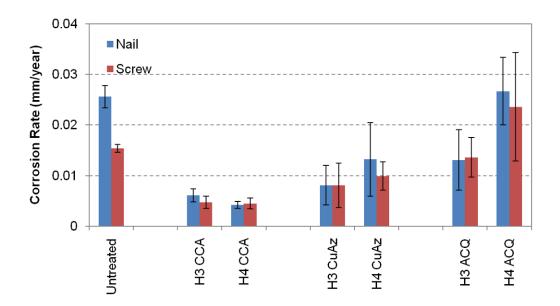


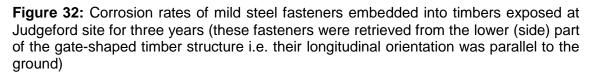
Figure 31: Corrosion rates of zinc-coated fasteners embedded into timbers exposed at Judgeford site for three years (these fasteners were retrieved from the top part of the gate-shaped timber structure i.e. their longitudinal orientation was vertical to the ground)

Although it appeared that ACQ and CuAz treated timbers were more corrosive than untreated and CCA treated timbers, a large difference in their aggressivities was not revealed by the corrosion rate measurements. The corrosivity of the H4 ACQ treated timber was only about 1.9 times higher than that of the H4 CCA treated timbers. This is consistent with the morphological observations. Since mild steel has very low resistance to corrosive attack in treated timbers, once a thick iron-rich rust layer was formed between steel substrate and timber, mass transportation would be somewhat inhibited and further corrosion attack to the steel substrate would be slowed down. This would lead to a smaller phenomenological difference in the timber's corrosivity.

Hot dip galvanised nails and mechanically-plated screws performed slightly better than their mild steel counterparts, particularly in untreated and CCA treated timbers. This might be due to the cathodic protection of the zinc coating (Figure 31). When inserted into either CuAz or ACQ treated timbers, these fasteners still exhibited high corrosion rates, similar to the levels measured with mild steel fasteners. H4 ACQ treatment was found to be 3.6 times as corrosive as H4 CCA treatment. This corrosion acceleration factor is much larger than that observed with mild steel components. This finding from mass loss measurements was fully supported by surface morphological characterisations; most of the zinc coating was consumed and extensive red iron-rich rust was developed. This result again showed that CuAz and ACQ treated timbers exhibited a much higher aggressivity towards zinc-coated components than untreated and CCA treated timbers under identical exposure conditions.

Corrosion rates of the fasteners inserted into the lower (side) part of the gate-shaped timber structures were, in general, lower than those of the fasteners in the top part (Figures 32 and 33). The corrosivity of timbers treated with different preservation chemicals could be clearly distinguished. It is quite obvious that the CCA treated timbers were the least aggressive while the ACQ treated timbers were the most aggressive. For example, H4 ACQ treatment was found to be 6.4 and 3.8 times as corrosive as H4 CCA treatment for mild steel and galvanised steel fasteners, respectively. In addition, an increase of the nominal preservative retention level increased the corrosivity as well.





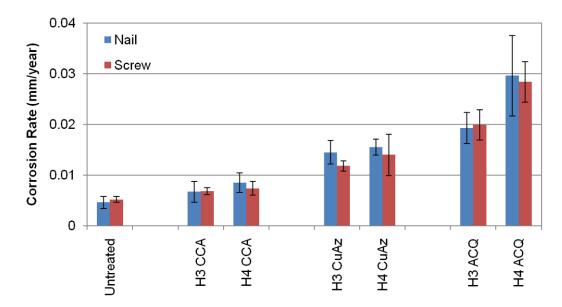


Figure 33: Corrosion rates of zinc-coated fasteners embedded into timbers exposed at Judgeford site for three years (these fasteners were retrieved from the lower (side) part of the gate-shaped timber structure i.e. their longitudinal orientation was parallel to the ground)

One slightly unexpected observation was that the mild steel fasteners exhibited very high corrosion rates when embedded into untreated timber, comparable to those measured within H4 ACQ treated timbers. During sample retrieval, it was observed that these untreated timber blocks showed serious deterioration and had lots of physical cracks. These surface defects could provide more easy pathways for moisture. This may promote hydrolysis of wood cellular components, resulting in a corrosive micro-environment for fast metal corrosion.

3.5.2 Oteranga Bay

Oteranga Bay is severely marine-influenced. The exposure site is located only a few metres away from the breaking surf. The much higher environmental corrosivity of this site can be simply demonstrated by the surface condition of two mild steel nuts exposed at Oteranga Bay and Judgeford for three years (Figure 34).



Figure 34: Mild steel nuts exposed at Judgeford and Oteranga Bay for three years

3.5.2.1 Morphological observations

Mild steel fasteners suffered from severe but relatively uniform attack when inserted into all types of timbers. After chemical cleaning, shaft diameter reduction of nails, partial loss of spiral burr and formation of numerous pits of diverse morphologies on screws could be clearly identified (Figure 35). It also appeared that the corrosive attack to these fasteners was more severe than those exposed at the Judgeford site.

On the surface of the hot dip galvanised nails inserted into untreated and CCA treated timbers, iron-rich red rust was not observed, indicating that the zinc coating was still complete and protecting the steel substrate from the aggressive timber environment (Figure 36). Deterioration of the zinc coating on these nails was mainly shown as darkening, i.e. oxidation of zinc, and formation of white zinc-rich rust (probably a mixture of zinc oxide and hydroxide due to interactions between zinc and moisture). On some samples, partial detachment of zinc coating was found during the retrieval process, indicating degradation of its mechanical properties.

Red iron-rich rust together with heavy white zinc-rich rust appeared on the nails inserted into the H3 CuAz treated timbers. For the nails retrieved from H4 ACQ treated timbers, their whole body section was covered with thick rust, implying the complete consumption of the zinc coating and then direct corrosion attack to the underlying steel substrate of lower resistance.

The heads of most hot dip galvanised nails (23 of 35) were still protected by zinc coating and showed no obvious sign of iron-rich rust formation. However, it was apparent that those nails inserted into CuAz and ACQ treated timbers tended to lose zinc coating from their heads quickly. This was probably related to degradation induced by corrosive chemicals released from these timbers.

In comparison, the situation on the mechanically-plated (zinc) screws was worse, manifesting as red rust formation on most areas even in untreated timbers (Figure 37). In addition, no screw heads retained a good coating and all heads were heavily rusted. This observation implies that the corrosion performance of the zinc coating on the screws was not as good as that of the hot dip galvanised coating on the nails when they were exposed to a harsh environment.

Unsurprisingly, all stainless steel fasteners were performing much better than mild steel and galvanised steel ones. On their body sections, i.e. the parts fully embedded into the timber, no sign of corrosion was observed by either visual or optical characterisations (Figure 37). This further confirmed that stainless steel has superior resistance to corrosion even in timbers exposed to a severe marine environment for a period of three years.

However, more stainless steel fasteners exposed at Oteranga Bay showed slightly serious rust formation on their head top surfaces when compared with the fasteners exposed at the Judgeford site. The situation was slightly worse for the screws that had a rectangular drive mortise in their heads. It is believed that the surface deposition of airborne chloride enhanced corrosion attack to the fastener heads with a locally damaged passive film. Further, mortises like those on the screws tend to collect airborne salt particles more easily than the flat head surface of the nails.

However it must be noted that the extent of this corrosion was still very limited both in affected area and intensity even after three years of exposure. It was not decreasing the corrosion performance of the fastener and/or the mechanical property of the timbermetal joint. It is also believed that this is unlikely to exert any significant negative effects on the joint in the near future.

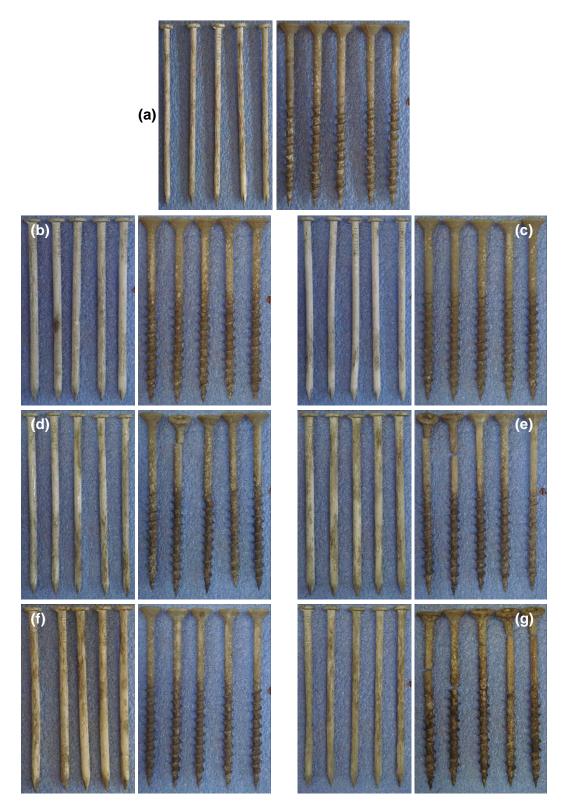


Figure 35: Surface morphology of mild steel fasteners retrieved from the top part of the timber gate structure exposed at Oteranga Bay for three years – (a) untreated, (b) H3 CCA, (c) H4 CCA, (d) H3 CuAz, (e) H4 CuAz, (f) H3 ACQ and (g) H4 ACQ

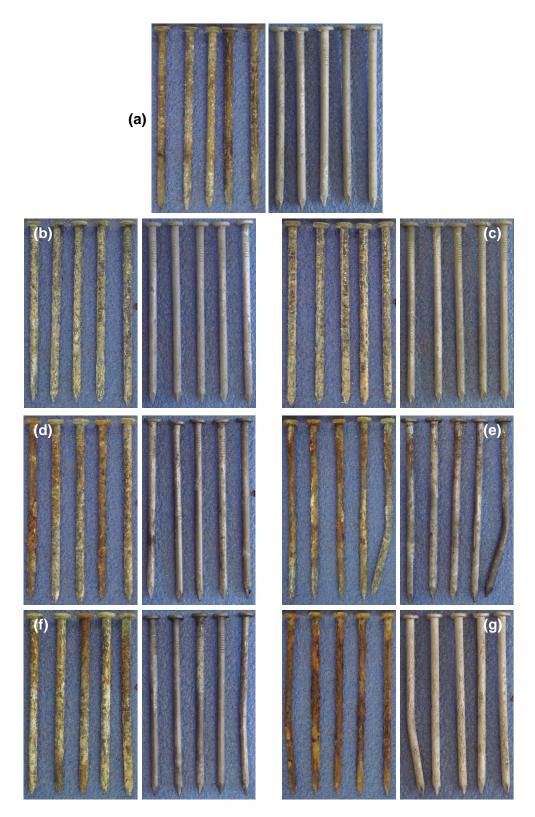


Figure 36: Surface morphology of hot dip galvanised nails retrieved from the top part of the timber gate structure exposed at Oteranga Bay for three years – (a) untreated, (b) H3 CCA, (c) H4 CCA, (d) H3 CuAz, (e) H4 CuAz, (f) H3 ACQ and (g) H4 ACQ

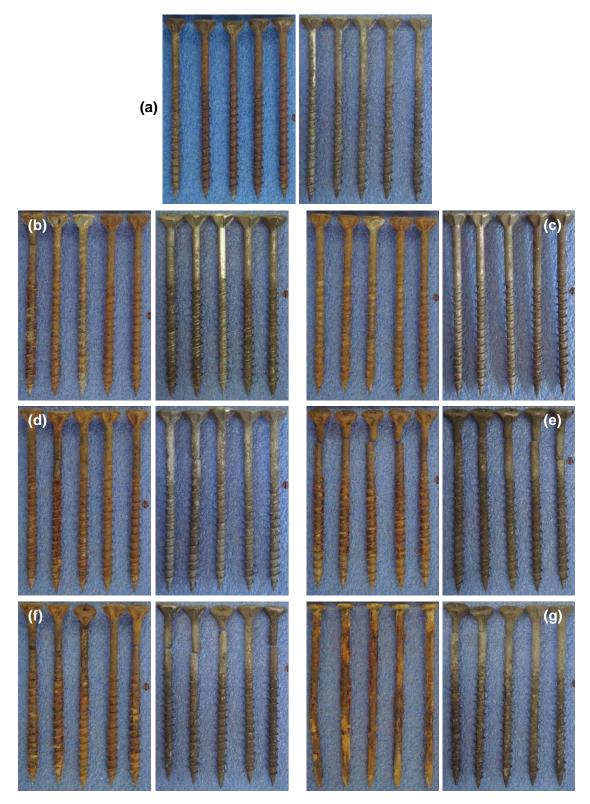


Figure 37: Surface morphology of mechanically-plated screws retrieved from the top part of the timber gate structure exposed at Oteranga Bay for three years – (a) untreated, (b) H3 CCA, (c) H4 CCA, (d) H3 CuAz, (e) H4 CuAz, (f) H3 ACQ and (g) H4 ACQ

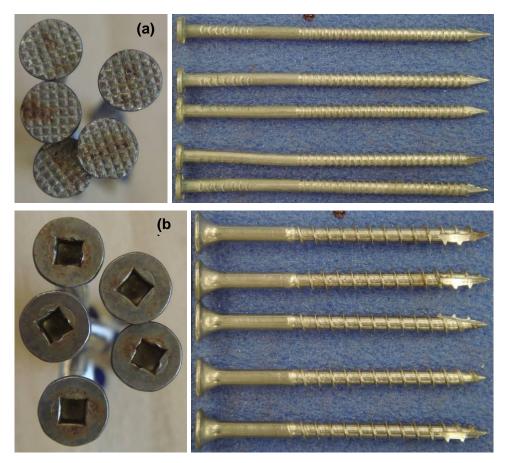


Figure 38: Typical surface morphology of stainless steel fasteners retrieved from the top part of the H4 ACQ treated timber gate structure exposed at Oteranga Bay for three years

3.5.2.2 Estimation of corrosion rates

Corrosion rate measurements showed that the H4 ACQ treated timbers exhibited the highest aggressivity towards mild steel fasteners, while H4 CCA treated timbers had the lowest (Figure 39). The corrosion rate within the H4 ACQ treatment was up to 3.8 times higher than that within the H4 CCA treatment. However, the corrosivities of other timbers, including untreated, H3 CCA, H3 and H4 CuAz, and H3 ACQ treated timbers, were quite similar. The corrosion rates typically ranged from 0.02 to 0.03 mm/year.

The high corrosion rate observed within the untreated timber might be a result of the decay of timber. The decaying timber might absorb more moisture. More importantly, salt particles deposited onto these timber surfaces could penetrate easily and deeply into the timber cellular structure when wetted by rainfall. Higher moisture content over a longer period would accelerate hydrolysis of acetyl radical and probably release more acids for contact corrosion. A high content of chloride ions in the timber micro-environment will attack metal more quickly. These may also increase the timber conductivity, facilitating diffusion processes involved in corrosion. However this hypothesis needs the support of direct experimental evidence.

Certainly, zinc coatings applied on the fasteners were providing protection, supported by the lower corrosion rates measured for all galvanised samples. These measurements also showed a relatively clear trend for the aggressivity of timber towards galvanised fastening products: Untreated \approx H3 & H4 CCA < H3 & H4 CuAz \approx H3 ACQ < H4 ACQ.

The corrosion acceleration imposed by H4 ACQ can be as high as 3.8 times greater than that of H4 CCA.

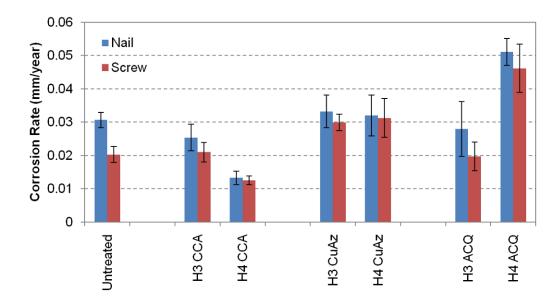


Figure 39: Corrosion rates of mild steel fasteners embedded into timbers exposed at Oteranga Bay for three years (these fasteners were retrieved from the top part of the gate-shaped timber structure i.e. their longitudinal orientation was vertical to the ground)

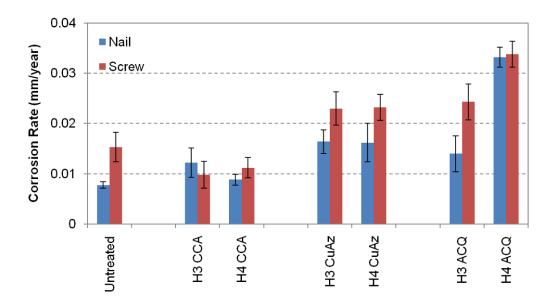


Figure 40: Corrosion rates of zinc-coated fasteners embedded into timbers exposed at Oteranga Bay for three years (these fasteners were retrieved from the top part of the gate-shaped timber structure i.e. their longitudinal orientation was vertical to the ground)

For almost all stainless steel fasteners, the mass loss due to corrosion could not be accurately measured since the value obtained was very close to the accuracy of the measurement equipment. The highest corrosion rate measured (i.e. not averaged by five replicates) for a single fastener was $\sim 5.3 \times 10^{-4}$ mm/year. This is at least two orders of magnitude lower than that of the mild steel and/or galvanised steel fasteners under identical exposure conditions. This, together with morphological observations, confirmed that stainless steel fasteners have extremely high resistance to attack by timbers treated with copper-bearing preservation chemicals.

4. **DISCUSSION**

4.1 Time-Dependent Corrosion

A comparison of the corrosion rates obtained for mild steel and zinc-coated steel fasteners after one-year and three-year exposures at the Judgeford site showed that metal deterioration in untreated and/or CCA treated timbers was progressing steadily, indicating that the corrosivity of these timbers was not changing markedly during this exposure period (Figures 41 and 42). The observation on corrosion of zinc coating in timber is somewhat similar to the finding of atmospheric corrosion test, which showed that the corrosion rate of galvanised zinc coatings is approximately linear with respect to exposure time in most environments [Zhang 2000]. Moreover, H3 and H4 CCA treated timbers had very similar corrosivity, although the preservative retention levels in these two treatments are different. Actually, in some tests H4 CCA exhibited a slightly lower aggressivity towards metallic components than H3 CCA.

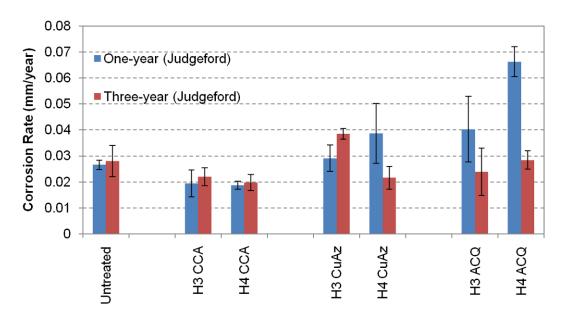
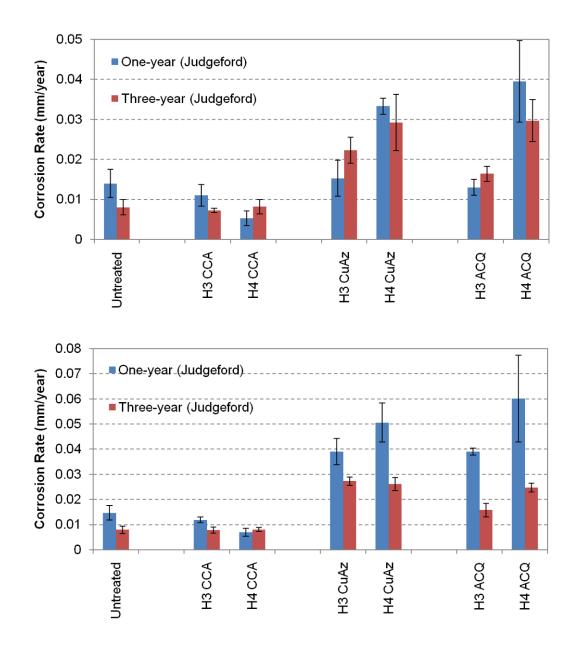


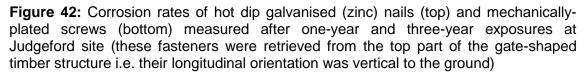
Figure 41: Corrosion rates of mild steel nails measured after one year and three years of exposure at Judgeford site (these fasteners were retrieved from the top part of the gate-shaped timber structure i.e. their longitudinal orientation was vertical to the ground)

However, the corrosivity of timbers treated with H4 CuAz and H3 and H4 ACQ appeared to decrease within extended exposure. The averaged three-year corrosion rates of mild steel nails were 55.8%, 59.3% and 42.8% of the first-year corrosion rates in H4 CuAz, H3 ACQ and H4 ACQ treated timbers, respectively (Figure 41).

For hot dip galvanised nails, the corrosion rates measured after three years of exposure were similar with those after one year of exposure. Although the averaged

three-year corrosion rate was 75.2% of the first-year rate in H4 ACQ treated timber, it could be up to 1.5 times higher than the first-year rate in H3 CuAz treated timber. For mechanically-plated screws, the averaged three-year corrosion rates were normally lower than the first-year rates. For example, in ACQ treated timbers, the third-year rate was about 40% of the first-year measurement (Figure 42). This trend was similar to that observed for the mild steel fasteners.





Measurements with fasteners inserted into the side part of the gate-shaped timber structures generally showed that the averaged two-year and three-year corrosion rates were not quite different in all these timbers. The exceptions were mild steel nails inserted into H4 CCA and H3 CuAz treated timbers and mechanically-plated screws in

H4 ACQ treated timbers (Figure 43). These results also indicated that the corrosion rate of metal in CCA treated timbers was not changing markedly within the timeframe of this field exposure test.

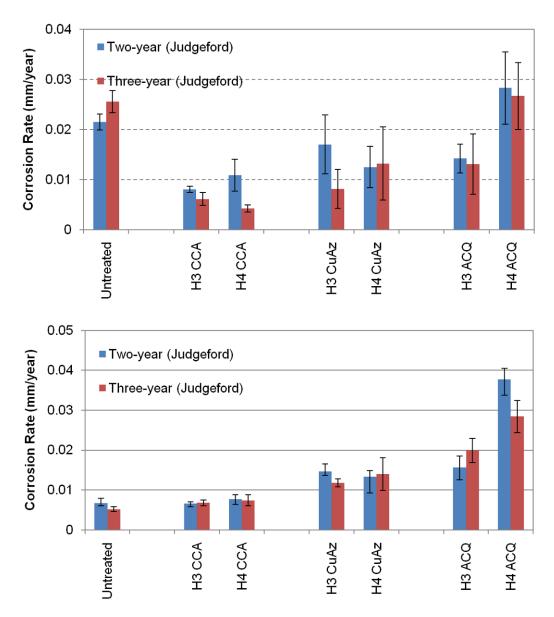


Figure 43: Corrosion rates of mild steel nails (top) and mechanically-plated screws (bottom) measured after two-year and three-year exposures at Judgeford site (these fasteners were retrieved from the lower (side) part of the gate-shaped timber structure i.e. their longitudinal orientation was parallel to the ground)

These observations therefore imply that metal corrosion in timber (especially those timbers treated with CCA alternatives) was changing with exposure time. This, to some extent, will make service life prediction difficult. The mechanisms behind material degradation in timbers, particularly in preservation treated timbers, are not well understood. This lack of fundamental information imposes a barrier to understanding the phenomena currently observed. However it is supposed that the changing behaviour of corrosion rates within short and long exposures could be partly explained from two aspects: changes at the metal-timber interface; and time-dependent timber corrosivity.

Progress of corrosion is controlled primarily by mass transport i.e. continuing supply of active species from the surrounding corrosive media and diffusion of corrosion products away from the corroding metal surface. Ion transport in timber is limited due to its low conductivity and/or dense cellular structure. Once a dense and thick scale of corrosion product has formed at the metal-timber interface, diffusion will be retarded and become the rate-controlling step of the corrosion process. Short supply of active species and the resultant metal surface polarisation will slow down the corrosion process. If fact, a significant corrosion rate decrease was observed with fasteners showing high corrosion rates i.e. mild steel nails/screws and mechanically-plated screws in ACQ treated timbers that were located at the top part of the timber gates. A higher corrosion rate led to a thicker corrosion product scale and thus a higher resistance to diffusion.

On the other hand, the corrosivity of a timber when exposed to the atmosphere will change due to various compositional and structural changes occurring inside it. This will, to some extent, affect the degradation behaviour of metallic components embedded within the timber. In untreated timbers, contact corrosion by acids released from the hydrolysis of wood cellular components is likely to be the governing mechanism. Exposure to ultra-violet (UV) light in solar radiation would degrade lignin, the photo-sensitive component in the middle lamella of the wood structure causing the hemicelluloses to become more vulnerable to hydrolysis [Williams 2005]. Natural weathering also produces cracks and checks that provided easy pathways for the ingress of moisture [Evans *et al.* 2008]. A higher moisture content in the timber would promote corrosion through accelerated hydrolysis and increased conductivity. However, the amount of the photo-sensitive components in timber will decrease with time, gradually slowing down the hydrolysis process and decreasing acid concentration. This in turn will lead to a lower aggressivity towards metals in long-term exposures.

The corrosivity of the treated timbers is mainly related to the dissolution, migration and leaching of preservative components. In the initial stage of natural exposure the nonfixed components, especially those loosely attached to the timber surface, would be washed away, lowering corrosivity. In extended exposures, physical defects would be generated, facilitating moisture ingress. This would change the state of the components of the complexed preservation chemicals and result in their hydrolysis/dissolution, diffusion and re-distribution in the treated timber [van der Sleet *et al.* 1997]. Wetting-drying cycles induced by precipitation and solar heating could drive some dissolved active species from the interior part of the timber to the timber-metal interface. This would supply more materials for the corrosion process. However, some chemical species would be lost when migrating to the exterior surface, lowering the corrosion rate. The much lower corrosion rate for three years of exposure of ACQ treated timbers might then indicate that preservative leaching is a contributing factor.

However, BRANZ's one-year natural leaching tests at the Judgeford site using the same timber stock showed that there was no statistically significant evidence of bulk copper being preferentially depleted from CuAz or ACQ at H3 and H4 classes [Li 2008]. This was supported both by the measured concentrations retained in the weathered timber and also the absence of a significant build-up of copper developing in water used for cyclical leaching experiments. Conflicting results were also found in the open literature when reporting on the leaching resistance of timbers treated with CCA, CuAz or ACQ [Hayes 1994; Lebow 1996; Breslin and Adler-Ivanbrook 1998; Hingston *et al.* 2001; Stook *et al.* 2005].

Further, BRANZ's accelerated tests measuring the corrosion rates of new mild steel and hot dip galvanised steel nails inserted into timbers after natural weathering at the Judgeford site for one year was not able to establish any clear correlation between the extent of corrosion rate decrease and the type of preservative chemicals used. In other words, it was impossible to determine that one preservative would lose its aggressivity at a faster rate than another based on current experimental findings. But it is believed that the results from the short leaching test performed by BRANZ (one year) might not be sufficient to explain the results obtained with longer corrosion tests (three years). More work is necessary to develop a better understanding of the long-term preservative leaching and metal corrosion behaviours in treated timbers.

4.2 Location-Dependent Corrosion

Two sets of fasteners were inserted into two different parts of the gate-shaped timber structures to study the potential effects of location (or micro-climate) on metal corrosion performance. One set of fasteners was embedded into the timber block located on the top part of the gate and their longitudinal orientation was vertical to the ground. The other set was in the timber block located on the lower, side part of the gate and these fasteners were parallel to the ground.

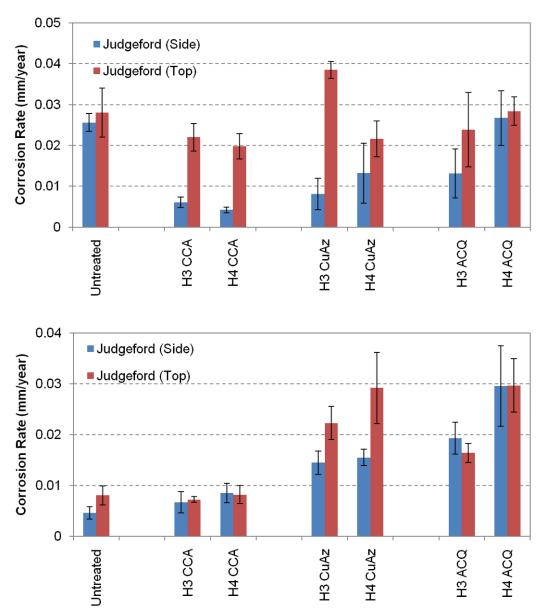


Figure 44: Corrosion rates of mild steel (top) and hot dip galvanised (bottom) nails measured after three years of exposure at Judgeford site

It is supposed that leachants (acids or ions) from the timbers, particularly from the treated timbers, may accelerate degradation of the head of the fasteners (especially zinc-coated parts) inserted into the side part of the timber structure. However, morphological observations of the condition of the fastener's head did not always show this fast deterioration of the zinc coating. This is believed to be a result of inconsistencies in the driving process. It is quite obvious that the top surface of the fastener head was not always on the same level of the timber surface. This would influence the flow-over of leachant from the timber onto these fasteners.

However, current measurements did show that the fasteners inserted into the lower (side) part of the timber gate structure were generally performing better than those inserted into the top part, evidenced by their lower corrosion rates and thinner corrosion product scales (Figure 44). The most obvious difference was found with mild steel fasteners in CCA and CuAz treated timbers. For example, within H3 CuAz treatment, the corrosion rate of the nails on the side was only 21% of the corrosion rate of the nails on the side was only 21% of the corrosion rate of the nails on the top. The opposite was also found, especially with zinc-coated fasteners. Table 4 details the percentage results obtained.

Table 4: Percentage for the corrosion rates of the fasteners inserted into the lower (side) part of the gates versus the corrosion rates of the fasteners inserted into the top part of the timber structure

		Untreated	H3 CCA	H4 CCA	H3 CuAz	H4 CuAz	H3 ACQ	H4 ACQ
Mild Steel	Nail	91.4%	27.7%	21.2%	21.0%	61.1%	54.8%	94.0%
	Screw	83.7%	28.0%	25.9%	30.1%	78.6%	87.7%	70.4%
Zinc- coated	Nail	57.1%	92.3%	103.5%	65.0%	53.1%	117.7%	99.7%
	Screw	65.2%	87.1%	91.6%	43.2%	53.6%	125.9%	115.0%

This performance difference is believed to be partially related to the moisture content difference between these two locations. The top part of the gate structure has two small timber blocks with dimensions of $50 \times 100 \times 300$ and $100 \times 100 \times 300$ mm. The lower, side part has two tightly attached blocks with the dimensions of $50 \times 100 \times 700$ mm.

Embedment of fasteners into the side part was not the same for all types of fasteners. Mild steel fasteners were inserted into the timber block on the south side, while zinccoated and stainless steel fasteners were inserted into the block on the north side.

The major difference between the timber blocks located on the top and side parts is that the cutting sections (vertical to the original wood grain orientation) of the timber blocks on the top part were not sealed and then exposed to the atmosphere directly, while the cutting sections of the timber blocks on the side part were shielded by two larger timber blocks on both ends. During weathering, the top part was more easily wetted by precipitation. Further, with their cutting sections un-sealed and their shorter dimensions, moisture could penetrate quickly and deeply since the longitudinal direction is the most permeable [Rowell 2005], leading to a higher moisture content in these timber blocks. There is no question that a higher moisture content would facilitate a faster corrosive attack on any embedded metallic components.

The moisture content of the timber blocks attached onto the gate-shaped timber structures exposed at the Judgeford site was monitored periodically using an electrical resistance type moisture meter. The measurements were performed intentionally during raining and after a few days of rain to reveal the change in timber moisture content with time. Five measurements were conducted in a configuration of an "X" on each timber surface. However, it must be noted that these measurement results cannot be fully representative to the actual timber moisture content due to the shallow penetration depth of the probes used with the equipment. The thickness of the timber block, 50 or 100 mm, is much larger than the pin length, ~10 mm. If there is a moisture gradient, the meter cannot give a reliable reading of the timber moisture content. Actually, it was observed that during raining the timbers were not uniformly wetted due to their relative orientation to the rain direction. On one surface, severely wet, wet and dry areas could be found. Although calibration can be done with electrical resistance type meter based on equilibrium moisture content measured by oven-dry approach recommended by AS/NZS 1080 [Kear 2006b], it would be extremely difficult to apply this practice to current results. Thus, these results were only presented here to offer a rough comparison, especially for timbers of the same treatment but different physical location.

From Figures 45 and 46, it can be seen that the timber blocks at the top of the gate had a higher moisture content than the blocks at the side. In addition, the south side is generally wetter than the north side. This might be a result of different times of heating by solar irradiation. Actually, the surface temperature of the timber on the south side was measured to be about 2°C lower than that on the north side.

However, these observations cannot explain why zinc-coated fasteners on the north side did not exhibit a lower corrosion rate than those on the top, particularly when inserted into CCA and ACQ treated timbers. This would be expected since the timber moisture content on the north is much lower than that on the top. Obviously corrosion in timbers is governed by many factors and moisture content is just one of them. Moisture can influence acid release and leaching of preservation chemicals, and then the corrosion process. However, the exact influences of moisture content and the contribution of other factors are not completely understood at this moment.

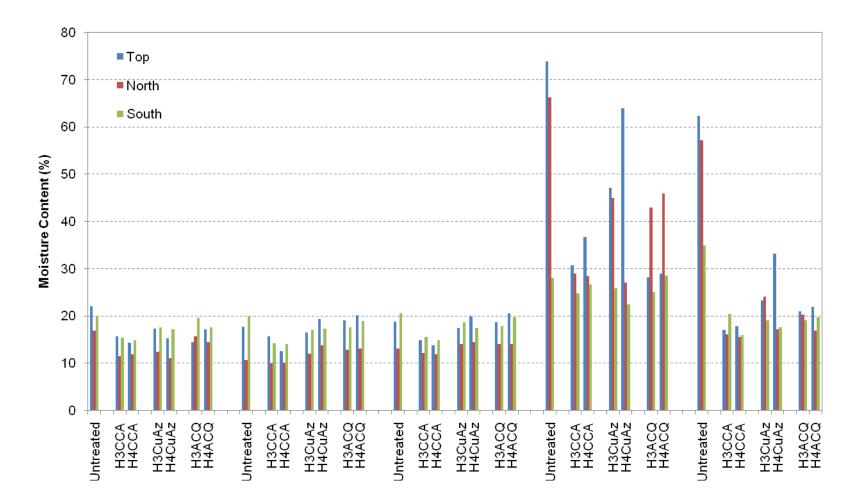


Figure 45: Moisture content of timber blocks exposed at Judgeford site – the date for test is (from left to right): 01/April, 12/April, 13/April, 14/April and 15/April/2010

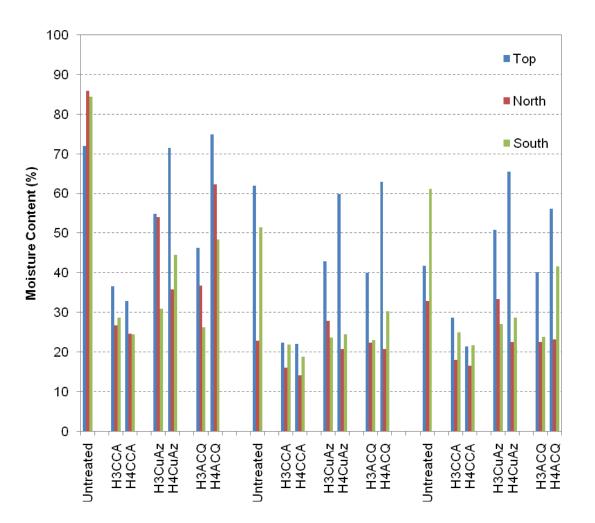


Figure 46: Moisture content of timber blocks exposed at Judgeford site – the date for test is (from left to right): 01/July, 05/July and 14/July/2010

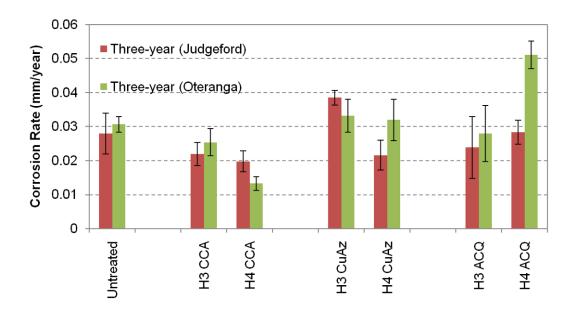
4.3 Influence of Environmental Corrosivity

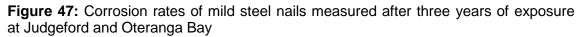
Judging from BRANZ's previous atmospheric corrosivity tests, Oteranga Bay is severely marine-influenced, while BRANZ's Judgeford campus lies in a rural region of average corrosivity [Kane 1995; Haberecht *et al.* 1999]. The environmental corrosivity difference between these two sites has been exemplified already in Figure 34.

A comparison between the corrosion rates and surface morphologies of the fasteners embedded into the timbers exposed at these two sites showed that the macroenvironment was affecting the corrosion process. Mild steel fasteners (including nails and screws) and mechanically-plated screws inserted into the timbers exposed at Oteranga Bay generally had a slightly higher corrosion rate than those inserted into the timbers exposed at Judgeford. However, corrosion rates measured with the hot dip galvanised nails exposed at Oteranga Bay were not always higher than those at Judgeford. Actually, lower corrosion rates were even observed with galvanised nails inserted into H3 and H4 CuAz treated timbers exposed at Oteranga Bay. Those were 56-74% of the rates obtained from the Judgeford site (see Figures 47 through 49).

The atmospheric corrosivity will easily affect the performance of the exposed sections of a fastener. It is believed that if the timber surrounding a fastener is free of physical defects (e.g. cracks), airborne pollutants (e.g. salt particles at Oteranga Bay) will not significantly contribute to corrosion occurring on the deep section of a fastener. After three years of exposure at Oteranga Bay, the formation of large and deep cracks was not observed on the timber surface. As such, only the head top, and probably the section immediately below the head, might still be the section that was affected by the open atmosphere.

Mild steel has very low resistance to corrosion. Its mass loss in a severe marine environment (i.e. Oteranga Bay) could be at least two to four times greater than that in a moderate environment (i.e. Judgeford). Mild steel fasteners would then experience a faster corrosion on their head areas, contributing to a slightly higher corrosion rate when averaged by the whole surface area. This agrees well with the current measurement results.





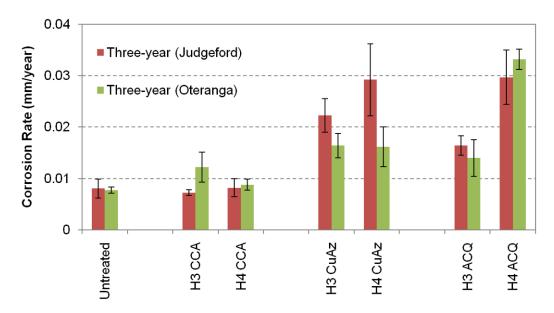


Figure 48: Corrosion rates of hot dip galvanised nails measured after three years of exposure at Judgeford and Oteranga Bay

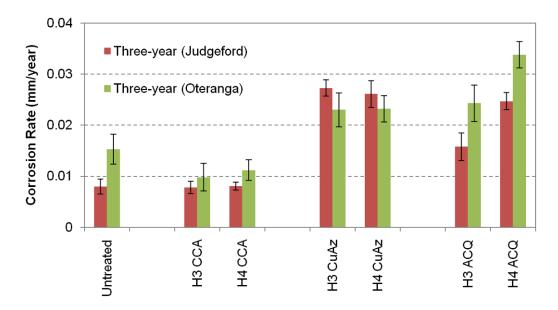


Figure 49: Corrosion rates of mechanically-plated screws measured after three years of exposure at Judgeford and Oteranga Bay

For zinc-coated fasteners, the situation was slightly different. All the screws exposed at Oteranga Bay showed the formation of iron-rich rust on their heads; while some screws (19 of 35) still had relatively good zinc coatings on their heads when exposed at the Judgeford site. The heads of most hot dip galvanised nails (~85%) exposed at Judgeford and Oteranga Bay were also in relatively good condition and showed very limited formation of iron-rich rust after three years.

Zinc coatings on the screws used in this study were produced by mechanical plating and had more physical defects, thus a lower corrosion resistance [Schweitzer 2007]. Without a doubt, deposition of airborne salt particles on their top surfaces was contributing to their accelerated corrosion. In contrast, hot dip galvanised zinc coating has a much better performance. According to the literature, the corrosion rate of a hot dip galvanised coating in a severe marine environment is typically ranging from 4 to >10 μ m/year [Guttman 1968; Sakumoto *et al.* 2004; Zhang 2005]. Given the fact that the hot dip galvanised nails used in this study have an average coating thickness of around 40 μ m, they would be expected to have a durability of 4-10 years when used at Oteranga Bay (without the negative influence of leachant from the treated timber). This is longer than the current testing period of three years. Consequently, corrosion damage to their heads was limited and corrosion-induced mass loss of the head surface was low.

Thus, material deterioration of these hot dip galvanised nails in these timbers was still mainly controlled by the micro-environment inside the timber i.e. the moisture content and the active preservative species. This could partially explain why the hot dip galvanised nails exposed at Oteranaga Bay exhibited a similar corrosion rate to those exposed at Judgeford.

However, it must be emphasised that the differences in the climatic parameters of these two sites, particularly rainfall, mean temperature and wind pattern, will influence timber moisture content, which is a critical factor for timber decay, preservative leaching and metal corrosion in timber. Detailed climatic information would therefore be required for a better understanding of these macro-environment related corrosion performance differences.

4.4 Influence of Copper Retention

While CCA, CuAz and ACQ all contain copper as the principal fungicidal component, the retention levels of copper for each treatment are quite different at the same NZS 3640 hazard class. The results reported in this study indicate that, a specific grade of metallic component may perform quite differently in timber treated with each of the preservatives. This raises the question of whether there are any correlations between the preservative treatment chemistry, timber corrosivity and metal corrosion performance.

Corrosion of metal in treated timbers is a complex process and is not well understood. Several mechanisms have been proposed. One explanation widely cited is the reduction of copper ions by active metallic constituents in steel, such as iron or zinc [Zelinka *et al.* 2010]. According to this hypothesis, a higher corrosion rate would reasonably be expected when a susceptible metal is embedded in a timber with a higher copper content.

Figures 50, 51 and 52 present the correlation between the retained copper content in the freshly treated timber and the experimentally measured corrosion rate of mild steel and hot dip galvanised nails in this study.

In general, the corrosion rate of mild steel and/or galvanised steel fasteners increases with the copper content in the treated timber. For example, nails and screws in CuAz and ACQ treated timbers have a higher mass loss rate than those in CCA treated timbers, where CuAz and ACQ treated timbers do have a higher copper content than CCA treated timbers. This trend is quite obvious for mild steel fasteners in timbers after one year of exposure and hot dip galvanised nails in timbers after three years of exposure. Different behaviours had also been noticed:

- The corrosion rates in H3 and H4 CCA treated timbers are approximately equal (or even lower in H4 CCA treatment) despite the retained copper concentration in H4 being virtually double that in the H3.2 grade.
- The copper content in H4 ACQ treated timber is about 3.3 times as high as the content in H4 CCA treated timber. However the corrosion rate in H4 ACQ treated timber is 3.5 and 7.4 times higher than the rate in H4 CCA treated timber for mild steel and galvanised steel fasteners, respectively.

The copper content in H4 ACQ treated timber is three times as high as the content in H3 ACQ treated timber. However the corrosion rates in H4 ACQ treated timber are only about 1.2-1.8 and 1.8-3.0 times higher than the rates in H3 ACQ treated timber for mild steel and galvanised steel fasteners, respectively.

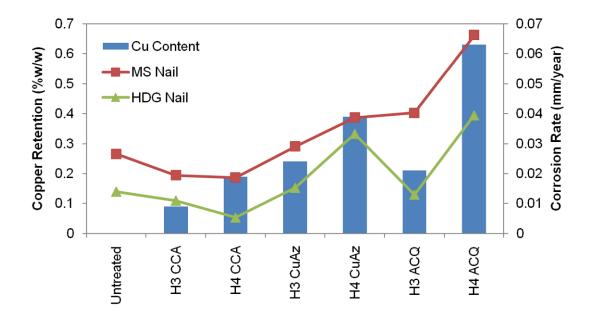


Figure 50: Correlation between copper retention in the freshly treated timbers and corrosion rate of nails embedded in the timbers exposed at Judgeford site for one year

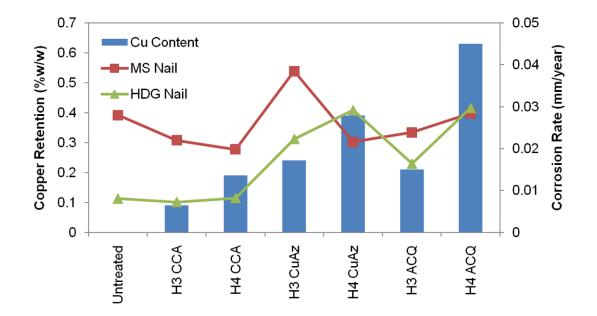


Figure 51: Correlation between copper retention in the freshly treated timbers and corrosion rate of nails embedded in the timbers exposed at Judgeford site for three years

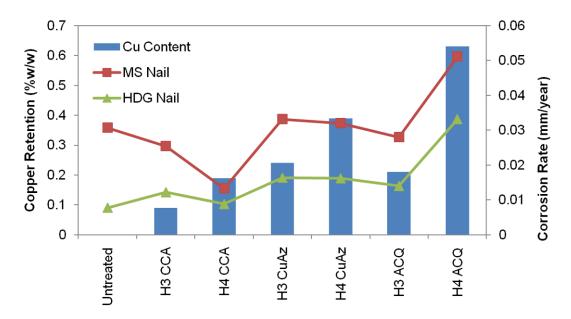


Figure 52: Correlation between copper retention in the freshly treated timbers and corrosion rate of nails embedded in the timbers exposed at Oteranga Bay for three years

These observations indicate that copper retention has a degree of correlation with the corrosion performance of metallic building hardware embedded into treated timbers. However this correlation might only be valid for short testing periods. In extended exposure, the effective copper ions involved in metal corrosion processes would tend to deviate from the original copper retention due to:

- Formation of corrosion products at the metal-timber interface: this will decrease effective copper supply from the surrounding timber.
- State change of preservative during weathering: hydrolysis of preservation chemical in the presence of high moisture content may release more active species. On the other hand, non-fixed components and/or released species will be lost when migrating to the timber surface. This will significantly change the copper content in timber.

This apparent anomaly thus suggests that copper ion reduction is a working mechanism. However, it is unlikely to be the only mechanism actively responsible for the enhanced corrosion rates seen.

It must be realised that the chemistries of these three treatments i.e. CCA, CuAz and ACQ, are quite different in terms of ionic compositions. For example, CCA has hexavalent chromium (Cr⁶⁺) in its composition, which potentially acts as a corrosion inhibitor for steel, and the arsenic may also confer corrosion resistance [Murphy 1998; Zelinka *et al.* 2007]. On the other hand, some formulations of ACQ contain chloride salts that are an obvious risk for increasing the corrosion rate due to the raised conductivity of the timber and the possibility of chloride ion attack. Severe pitting corrosion was found on fasteners embedded into ACQ treated timbers in this study, although chloride could not be detected in the ACQ treated timbers used (probably due to its low content and limitations of the analysis technique).

In addition, measurements shown in Figures 45 and 46 imply that CuAz and ACQ treated timbers tend to have slightly higher moisture content than CCA treatment, although the mechanism behind this is no known (and the results need to be confirmed

using other testing methods). A higher moisture content would facilitate a higher corrosion rate if other conditions are the same.

To allow a better understanding of the complete mechanism of metal corrosion in treated timbers, the micro-environments created by the interactions between moisture, timber cellular components and preservation chemicals should be mapped in as much detail as possible. The following factors might be worthy of further examination:

- fundamental understanding of metal corrosion in untreated timber
- correlations between dimension, preservation treatment, micro-climate and moisture content of a timber
- correlations between weathering time, preservation leaching and metal corrosion kinetics
- > detailed analysis of corrosion products formed on steel and timber surfaces.

4.5 **Performance Difference Between Head and Shank**

In these field exposure tests it was frequently observed that the head of a zinc-coated fastener was still in good condition, while its body section was covered with heavy ironrich rust (i.e. zinc coating on the body had been seriously damaged). This was particularly true for fasteners exposed at the Judgeford site, the more benign climate (see Figures 53 and 54 for two typical examples).

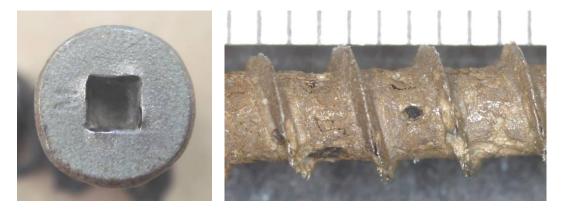


Figure 53: Morphologies of head and thread of a mechanically-plated screw retrieved from H4 ACQ treated timber exposed at Judgeford site for two years. The conditions of the zinc coatings on the head and the body were significantly different



Figure 54: Hot dip galvanised steel nails embedded into H4 ACQ treated timbers exposed at Judgeford site for three years. The formation of iron-rich red rust on the top surface of the head is not as severe as on the shaft

This phenomenon is believed to be a direct result of the difference in aggressivity of the atmosphere and the micro-environment inside the treated timber. The latter, in general, attacks the metal at a greater rate mainly due to acid-involved contact corrosion and galvanic corrosion with the additional influences of oxidisers introduced from the preservation treatment chemicals.

Timbers treated with CuAz and ACQ have a much higher retention of copper ions than those treated with CCA and can attack the metallic components embedded into them at much higher rates if they are frequently wet, leading to significant metal degradation in shorter periods even in mild environments (e.g. Judgeford). This makes the performance difference between the exposed and embedded sections of fasteners even larger. The consequence is that any premature failure of metallic fasteners will be less likely to be identified because they appeared to be in very good condition when inspected from the top. In very harsh environments, this risk might be somewhat lower because the head will fail quickly as well (see Figure 55).

Conversely, the heads of the stainless steel fasteners were always in a worse condition than the body section. This difference is related to the protection mechanism of stainless steel. The driving-in process can, to some extent, damage the chromium-rich passive film originally formed on the top surface. Additionally, iron contaminants can be transferred from the hammer head. These two factors will contribute to fast rust formation. However, this corrosion on limited surface areas was observed to be progressing extremely slowly and did not comprise the performance of fasteners in the timeframe of this field testing.



Figure 55: Cleaned zinc-coated fasteners retrieved from H4 ACQ treated timbers exposed at Oteranga Bay for three years. The zinc coating on the head was consumed and then iron-rich rust was formed. However, it must be noted that corrosion on the body section was still more severe than on the head

4.6 Treat Fastener and Timber as a System

The components of any timber structure need to be held together using fasteners such as nails, screws and bolts. Holding power and corrosion performance are probably the two most important concerns when choosing fasteners. Deterioration of metallic fasteners not only weakens the fastener itself, but the chemical reactions involved in corrosion can also weaken the timber surrounding the fastener. Thus when selecting fasteners for joints, the corrosion performance of the base materials must be considered from at least two aspects:

- > its intrinsic resistance to the corrosive attack imposed by the timber
- the consequence of its deterioration on the properties of the timber and the ongoing performance of the fastener-timber joint.



Figure 56: Iron stains formed by corrosion of mechanically-plated screws in H4 CCA and H4 ACQ treated timbers exposed at Judgeford for three years

It was frequently observed in this study that the much higher aggressivity of the ACQ and/or CuAz treated timbers resulted in more severe corrosion attack to fasteners. This led to heavy iron stain on the surrounding timber after only three years (see Figure 56 for an example). This made the retrieval of fasteners, particularly screws, difficult. More importantly, with longer exposure, the iron and hydroxyl ions released from corrosion will chemically attack the cellulose components of the timber and cause loss of strength and structural integrity of the joint. "Nail sickness" is a term that has long been used to describe this phenomenon [Baker 1974]. It would therefore be reasonable to treat fastener and timber as a system so that the durability and safety risks induced by corrosion can be minimised.

4.7 Comparisons Between Different Testing Methodologies

The AWPA E12 testing procedure and its derivatives have been widely used to determine the comparative corrosivity of timbers treated with different preservation treatments. In general, the higher corrosion risk imposed by CCA alternatives, such as CuAz and ACQ, can be inferred using this accelerated method. However, abnormal phenomena can be observed e.g. the apparent inhibition effect of CuAz compared with CCA [Kear *et al.* 2006a]. On the other hand, this test operated at high temperature (49°C) did generate very high values of corrosion rate. Its results can sometimes be 30 times greater than those found during this field exposure test.

Test	Condition	Material	H3.2			H4			H5		
			CCA	CuAz	ACQ	CCA	CuAz	ACQ	CCA	CuAz	ACQ
AWPA E12 ⁽¹⁾	49°C	Mild Steel	0.074	0.178	0.780	0.062	0.271	0.766	0.121	_	1.493
	90%RH	HDG	0.065	0.038	0.253	0.102	0.031	0.175	0.095	-	0.109
	407 hrs										
Embedded Fastener ⁽¹⁾	49°C	Mild Steel	0.31	0.39	0.58	0.35	0.29	_	0.33	_	_
	90%RH	HDG	0.11	0.11	0.22	~0.10	~0.18	_	~0.125	_	_
	385 hrs										
Non-accelerated ⁽²⁾	21°C	Mild Steel	0.013	0.045	0.070	0.017	0.039	0.087	~0.0095	_	0.095
	98%RH	HDG	~0.0108	0.038	0.026	~0.0104	0.031	0.025	~0.0103	_	0.032
	One year										
Field Exposure	Judgeford	Mild Steel	0.0194	0.0291	0.0403	0.0187	0.0387	0.0663	_	_	_
	One year	HDG	0.011	0.0153	0.013	0.0053	0.033	0.0395	_	_	_
	Judgeford	Mild Steel	0.022	0.0385	0.0239	0.0198	0.0216	0.0284	_	_	_
	Three year	HDG	0.0073	0.0223	0.0164	0.0082	0.0292	0.0297	_	_	_
	Oteranga Bay	Mild Steel	0.0254	0.0332	0.028	0.0133	0.032	0.0511	_	_	_
	Three year	HDG	0.0122	0.0164	0.014	0.0088	0.0162	0.0332	_	-	-

Table 5: Corrosion rates of nails measured with different methodologies

(1) Refer to G Kear, MS Jones and PW Haberecht. 'Corrosion of Mild Steel, HDG Steel and 316 Stainless Steel in CCA, CuAz and ACQ Treated Pinus Radiata', *Proceedings of 16th International Corrosion Congress*, 19-24 September 2005, Beijing, China.

⁽²⁾ Refer to G Kear, HZ Wu and MS Jones. 'Non-Accelerated Weight Loss Studies of Fastener Material Corrosion in Contact with CCA, CuAz and ACQ Treated Timbers', *Proceedings of Corrosion & Prevention 2006*, 19-22 November 2006, The Australasian Corrosion Association (ACA), Tasmania, Australia.

This further confirmed that corrosion rates derived from accelerated tests performed at high temperature and relative humidity cannot be extrapolated to predict the service life of a specific component exposed to real service conditions. It is widely accepted that the high temperature environment may change the materials deterioration mechanism, leading to high corrosion rates and unreliable comparisons.

Comparatively, the non-accelerated test performed in indoor environment of constant temperature (21±2°C) and humidity (98%) produced corrosion rates that are comparable to the field exposure tests reported here. This is particularly true for the CCA treatment. However, its results may still be significantly different from measured values from long-term field exposure tests, especially for ACQ treatment.

These observations imply that a macro-environment of constant temperature and humidity is still not capable of provoking a micro-environment that is similar to the corrosive environment inside a timber exposed to the atmosphere.

When exposed to the atmosphere, timber undergoes various compositional and structural changes that can affect the environment surrounding materials embedded and this affects the material deterioration behaviour. Obviously, precipitation will change the state of preservatives and affect their hydrolysis, migration and presence in timber. Wetting will make some of the treatment leachable i.e. more active components will lose their connection to timber and become free. Solar drying will drive some of the released species to the timber surface through migration. Some of the active components could then be removed from the surface by rain. In addition, weathering-induced cracks and checks provide easy pathways for ingress of moisture to the interior of timber.

Any testing procedure that cannot reproduce these processes will therefore have difficulty in producing reliable results.

5. Conclusions

This study confirms that both ACQ and CuAz treated timbers are capable of greatly accelerating the corrosion rate of mild steel and zinc-coated (hot dip galvanised and mechanically-plated) steel relative to both untreated and CCA treated timbers. At Judgeford, H4 ACQ treatment showed corrosion rate acceleration factors of 3.5 and 7.4-8.6 over H4 CCA towards mild steel and zinc-coated fasteners, respectively. After three years, the acceleration decreased, but corrosion in H4 ACQ was still 1.4-1.9 (mild steel) and 3.1-3.6 (zinc-coated steel) times higher than that in H4 CCA. At Oteranga Bay, the maximum levels of corrosion acceleration were 2.5 and 3.8 within H4 CuAz and ACQ treated timbers, respectively, based on corrosion rates averaged from three-year exposure. This more aggressive behaviour has now been confirmed in both field exposures and the earlier accelerated laboratory studies.

Based on morphological observations and corrosion rate measurements, the aggressivity of timbers approximately follows the order of:

Untreated \approx H3 CCA \approx H4 CCA < H3 CuAz \leq H4 CuAz \approx H3 ACQ < H4 ACQ.

Results demonstrate that metal deterioration in the CCA treated timbers progresses steadily. Based on the corrosion rates measured, hot dip galvanised nails carrying a zinc coating of ~45 μ m may have a predicted service life of eight and five years when used in the CCA treated timbers fully exposed at Judgeford and Oteranga Bay, respectively.

The corrosivity of timbers treated with CuAz and ACQ appeared to decrease with extended exposure, but long-term durability of fasteners in the presence of these treatments cannot be guaranteed. The extremely fast corrosion in the initial stages of

exposure seriously deteriorates metals, particularly the integrity of zinc coatings. As such, the coating on these nails may only be durable for one to three years.

Atmosphere	Exposure	Material	Fastener	Treatment				
	Time			H3 CuAz	H4 CuAz	H3 ACQ	H4 ACQ	
Judgeford	One year	Mild steel	Nail	1.5	2.1	2.1	3.5	
			Screw	2.2	2.0	2.2	3.6	
		Zinc coated	Nail	1.4	6.2	1.2	7.4	
			Screw	3.3	7.3	3.3	8.6	
	Three year	Mild steel	Nail	1.8	1.1	1.1	1.4	
			Screw	1.6	1.3	0.9	1.9	
		Zinc coated	Nail	3.1	3.6	2.3	3.6	
			Screw	3.5	3.2	2.0	3.1	
Oteranga Bay	Three year	Mild steel	Nail	1.3	2.4	1.1	3.8	
			Screw	1.4	2.5	0.9	3.7	
		Zinc coated	Nail	1.3	1.8	1.1	3.8	
			Screw	2.3	2.1	2.5	3.0	

Table 6: Corrosion rate acceleration factors of CuAz and ACQ over CCA

This research indicates that mechanically-plated screws are not durable for use in timbers treated with copper-containing preservatives and exposed to the open atmosphere. The present results showed that after only one year of exposure at Judgeford, iron-rich rust covering 30-50% of surface area had been formed on those screws inserted into CCA treated timbers. Zinc coatings formed by mechanical plating normally have a high porosity and a low bonding strength at the coating-substrate interface. A thick and uniform coating is also difficult to achieve on the spiral section which has sharp edges and irregular surfaces. This makes these areas more vulnerable to corrosion. Furthermore, the driving-in process always, to some extent, damages the coating integrity and introduces more physical defects. As a result, zinc-coated screws are less corrosion resistant than hot dip galvanised nails under identical exposure conditions. In addition, the heavy rust formed on screws of inferior coating quality tends to damage the cellular components of the surrounding timber quickly, leading to premature failure of the joint.

Austenitic stainless steel nails and screws performed very well in all combinations of preservative type and hazard class. No obvious signs of corrosion were found on their body sections after three years of exposure at either Judgeford site or Oteranga Bay. Failure was only shown as the very limited rust formed on the top surfaces of their heads. This was more frequently observed on the fasteners exposed at Oteranga Bay, a severe marine environment. However, a comparison between the conditions of the rust formed after one, two and three years indicated that this corrosion process was progressing extremely slowly and the extent of resultant material deterioration was not affecting the performance of the fasteners or the timber-metal assemblies.

It is clear that the corrosion behaviour of the zinc-coated fasteners reported in this study should be the primary concern of the building and construction industry because:

- hot dip galvanised and/or mechanically-plated steel nails and screws will always be specified over mild steel items for locations that are either periodically or permanently wet
- H3.2 and H4 timbers are used in locations where the moisture content of the timber can be periodically or permanently higher than 18-20%, a critical value for metal corrosion in timber
- metallic fixing components required for use with H3.2 and H4 hazard class timbers treated with different preservatives has not been properly differentiated according to timber corrosivity and material durability in current NZBC Compliance documents.

Given that average corrosion rates of mild steel and zinc-coated items measured were commonly two to three times higher with ACQ or CuAz treatment over CCA if the timber gets wet, it is doubtful that hot dip galvanised nails and mechanically-plated screws will be able to meet the durability requirement of the NZBC and relevant New Zealand standards. The use of either AISI 304/316 grades of stainless steel, or durable equivalents such as silicon bronze, for structural components and connections in ACQ and CuAz treated timbers (H3.2 and above) to meet the 50-year durability requirement would appear to be a sensible interim precaution.

Finally, it should be emphasised that the aggressivity of the new preservatives towards metallic materials under New Zealand conditions is still relatively poorly understood. For example, the influence of the deposition of the chloride from atmospheric sources on long-term (>15 years) corrosion performance of the galvanised and stainless steel fasteners has not been examined. Data on corrosion of metals should be collected from more sites (industrial, geothermal, urban and rural) to establish a complete map concerning the performance of metallic components in timbers treated with CCA alternatives under wider climate conditions across New Zealand. Further work is also required to quantify the influence of micro-climate on metal corrosion in timber.

References

Ajith Peter M and Edwin L. 2008. 'Effect of Chromate Arsenate (CCA) on Corrosion of Metallic Fasteners: Implications in Boat Building'. *Indian Journal of Chemical Technology* 15: 168-173.

Archer K and Lebow S. 2006. 'Wood Preservation'. In *Primary Wood Processing – Principles and Practice* (2nd Edition). Springer, Netherlands.

ASTM International. 2001. ASTM A90/A90M Standard Method for Weight [Mass] of Coating on Iron and Steel Articles with Zinc or Zinc-Alloy Coatings. ASTM, West Conshohocken, PA, USA.

ASTM International. 2003. ASTM B-117 Standard Practice for Operating Salt Spray (Fog) Apparatus. ASTM, West Conshohocken, PA, USA.

ASTM International. 2003. ASTM G1 Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens. ASTM, West Conshohocken, PA, USA.

American Wood Preservers' Association. 1994. AWPA E12 Standard Method of Determining Corrosion of Metal in Contact with Treated Wood. AWPA, Selma, AL, USA.

American Wood Preservers' Association. 1999. AWPA E17 Standard Method for Determining Corrosion Rates of Metals in Contact with Treating Solutions. AWPA, Selma, AL, USA.

Baker AJ. 1974. 'Degradation of Wood by Products of Metal Corrosion'. *Forest Service Research Paper FPL 229.* Department of Agriculture Forest Service, Forest Products Laboratory, Madison, WI, USA.

Baker AJ. 1980. 'Corrosion of Metal in Wood Products'. In *Durability of Building Materials and Components: ASTM STP 691.* Eds PJ Sereda and GG Litvan, ASTM, West Conshohocken, PA, USA, pp.981-993.

Baker AJ. 1988. 'Corrosion of Metals in Preservative-treated Wood'. In *Wood Protection Techniques and the Use of Treated Wood in Construction: Proceedings* 47358. Ed H Margaret. 28-30 October 1987, Memphis, TN, USA. pp.99-101.

Breslin VT and Adler-Ivanbrook L. 1998. 'Release of Copper, Chromium and Arsenic from CCA-C Treated Lumber in Estuaries'. *Estuarine Coastal and Shelf Science* 46: 111-125.

Chemical Specialities Inc, USA. www.treatedwood.com (accessed in October 2010).

Cole HG and Schofield MJ. 2000. 'The Corrosion of Metals by Wood'. In *Corrosion*. Eds LL Shreir, RA Jarman and GT Burstein. Butterworth-Heinemann, Linacre House, Jordan Hill, Oxford OX2 8DP, Great Britain.

Dinwoodie JM. 2000. *Timber – Its Nature and Behaviour* (2nd Edition), E & FN Spon, London, UK.

Evans S and Koehler L. 1961. 'Use of Polarization Methods in the Determination of the Rate of Corrosion of Aluminium Alloys in Anaerobic Media'. *Journal of the Electrochemical Society* 108(6): 509-514.

Evans P, Urban K and Chowdhury M. 2008. 'Surface Checking of Wood is Increased by Photodegradation Caused by Ultraviolet and Visible Light'. *Wood Science and Technology* 42: 251-265.

Falk RH and Baker AJ. 1993. 'Fasteners for Exposed Wood Structures'. *Wood Design Focus* 4(3): 14-17.

Freeman MH, Nicholas DD and Schultz TP. 2006. 'Nonarsenical Wood Protection: Alternatives for Chromated Copper Arsenate, Creosote and Pentachlorophenol'. In *Environmental Impacts of Treated Wood*. Eds TG Townsend and H Solo-Gabriele, Taylor & Francis Group, LLC, Boca Raton, FL 33487-2742, USA.

Guttman H. 1968. 'Effects of Atmospheric Factors on the Corrosion of Rolled Zinc'. In *Metal Corrosion in the Atmosphere*. Eds WH Ailor and SK Coburn, STP 435, ASTM, West Conshohocken, PA, USA, pp.223-239.

Haberecht PW, Kane CD and Meyer SJ. 1999. 'Environmental Corrosivity in New Zealand: Results after 10 Years Exposure'. In *Proceedings of the 14th International Corrosion Congress.* Cape Town, South Africa, 26 September – 1 October 1999.

Hayes C, Curran PMT and Hynes MJ. 1994. 'Preservative Leaching from Softwoods Submerged in Irish Coastal Waters as Measured by Atomic-absorption Spectrophotometry'. *Holzforschung* 48: 463-473.

Hingston JA, Collins CD, Murphy RJ and Lester JN. 2001. 'Leaching of Chromate Copper Arsenate Wood Preservatives: A Review'. *Environmental Pollution* 11: 53-66.

Ibach RE. 1999. 'Wood Preservation'. In *Wood Handbook – Wood as an Engineering Material*. USDA Forest Products Laboratory, Madison, WI, USA.

Illston JM and Domone PLJ. 2001. *Construction Materials – Their Nature and Behaviour* (3rd Edition), Taylor & Francis Group, London, UK.

Kane CD. 1995. 'Atmospheric Corrosion Survey of New Zealand: Six Year Exposure Results'. *IPENZ Transactions* 23(1): 29-39.

Kear G, Jones MS and Haberecht P. 2005. 'Corrosion of Mild Steel, HDG Steel and 316 Stainless Steel in CCA, CuAz and ACQ Treated Pinus Radiata'. In *Proceedings of the 16th International Corrosion Congress*. Beijing, China, 19-24 September 2005.

Kear G, Wu HZ and Jones MS. 2006a. 'The Corrosion of Metallic Fastener Materials in Untreated, CCA-, CuAz- and ACQ-based Timbers'. *BRANZ Study Report 153*. BRANZ Ltd, Judgeford, New Zealand.

Kear G. 2006b. 'The Influence of Timber Treatment Preservative Systems on the Performance of Commercial Resistance-based Moisture Meters'. *BRANZ Study Report 161*. BRANZ Ltd, Judgeford, New Zealand.

Kear G, Wu HZ, Bruce ED, Kane C and Jones MS. 2007. 'Metallic Materials Selection for Timber Treated with Non-CCA-based Copper-rich Preservatives: Implications for Australia'. *Corrosion & Materials* 32(1): 16-21.

Kear G, Wu HZ and Jones MS. 2008a. 'Corrosion of Ferrous- and Zinc-based Materials in CCA, ACQ and CuAz Timber Preservative Aqueous Solutions'. *Materials and Structures* 41: 1405-1417.

Kear G, Wu HZ Jones MS and Walsh FC. 2008b. 'Direct-current Methods for the Estimation of Corrosion Rates in Aqueous Timber Preservatives'. *Australian Journal of Chemistry* 61: 455-465.

Kear G, Wu HZ, Jones MS and Walsh FC. 2008c. 'Impedance Spectroscopy Studies of the Dissolution of Ferrous- and Zinc-based Materials in Aqueous Timber Preservatives'. *Journal of Applied Electrochemistry* 38: 1599-1607.

Kear G, Wu HZ and Jones MS. 2009. 'Weight Loss Studies of Fastener Materials Corrosion in Contact with Timbers Treated with Copper Azole and Alkaline Copper Quaternary Compounds'. *Corrosion Science* 51: 252-262. Lebow S. 1996. 'Leaching of Wood Preservative Components and their Mobility in the Environment'. *General Technical Report FPL-GTR-9* Forest Products Laboratory, Department of Agriculture, Madison, WI, USA.

Li Z. 2008. 'Preservative Leaching and Metal Corrosion in CCA, ACQ and CuAz Treated Timbers'. *BRANZ Test Report to Department of Building and Housing: DC1396.* BRANZ Ltd, Judgeford, New Zealand.

Morrell JJ. 2006. 'Chromated Copper Arsenate as a Wood Preservative'. In *Environmental Impacts of Treated Wood*. Eds TG Townsend and H Solo-Gabriele. Taylor & Francis Group, LLC, Boca Raton, FL 33487-2742, USA.

Murphy R. 1998. 'Chromium in Timber Preservation'. *The Chromium File No. 5*. http://www.icdachromium.com (accessed in October 2010).

Murray JN. 1997. 'Electrochemical Test Methods for Evaluating Organic Coatings on Metals: An Update. Part III: Multiple Test Parameter Measurements'. *Progress in Organic Coatings* 31: 375-391.

Standards Australia. 2002. AS 3566.2 Self-drilling Screws for the Building and Construction Industries. SA, Sydney, Australia.

Standards Australia and Standards New Zealand. 1997. *AS/NZS 1080 Timber – Methods of Test, Method 1: Moisture Content.* SA, Sydney, Australia and SNZ, Wellington, New Zealand.

Standards Australia and Standards New Zealand. 2006. *AS/NZS* 4680 Hot-dip *Galvanised (Zinc) Coatings on Fabricated Ferrous Articles.* SA, Sydney, Australia and SNZ, Wellington, New Zealand.

Standards New Zealand. 1999. *NZS 3604 Timber Framed Buildings*. SNZ, Wellington, New Zealand.

Standards New Zealand. 2003. *NZS 3640 Chemical Preservation of Round and Sawn Timber*. SNZ, Wellington, New Zealand.

Panasik C. ACQ Wood Preservative and Fasteners – Are They Compatible? http://gawain.membrane.com/deck_builders/industry_news/acqarticle.html (accessed in May 2008).

Rammelt U and Reinhard G. 1992. 'Application of Electrochemical Impedance Spectroscopy (EIS) for Characterizing the Corrosion-protective Performance of Organic Coatings on Metals'. *Progress in Organic Coatings* 21(2-3): 205-226.

Rammer DR, Zelinka SL and Line P. 2006. *Fastener Corrosion: Testing, Research, and Design Considerations*. USDA Forest Products Laboratory, Madison, Wisconsin, USA.

Risbrudt CD. 2005. 'Wood and Society'. In *Handbook of Wood Chemistry and Wood Composites*. Ed RM Rowell. Taylor & Francis Group, Boca Raton, Florida, USA.

Roberge P. 2008, *Corrosion Engineering: Principle and Practice*. McGraw-Hill, New York, USA.

Rowell RM. 2005. 'Moisture Properties'. In *Handbook of Wood Chemistry and Wood Composites*. Ed RM Rowell. Taylor & Francis Group, Boca Raton, Florida, USA.

Sakumoto Y, Nomura H, Matsumoto M, Ninomiya A, Miyao T and Sakamoto Y. 2004, 'Durability of Galvanised Light-gauge Steel Shapes'. *Journal of Structural Engineering* 130(1): 70-77.

Schweitzer PA. 2007. *Corrosion of Linings & Coatings* (2nd Edition). Taylor & Francis LLC, Boca Raton, USA.

Scully JR. 1989. 'Electrochemical Impedance of Organic-coated Steel: Correlation of Impedance Parameters with Long-term Coating Deterioration'. *Journal of the Electrochemical Society* 36(4): 979-990.

Silverman DC. 2000. 'Practical Corrosion Prediction Using Electrochemical Techniques. In *Uhlig's Corrosion Handbook* (2nd Edition). Ed R Winston Revie. John Wiley & Sons Inc, New York, USA.

Simpson Strong-Tie. 2006. *Preservative Treated Wood Technical Bulletin T-PTWOOD06*. www.strongtie.com (accessed in December 2007).

Soltis LA. 1999. 'Fastenings. In *Wood Handbook – Wood as an Engineering Material.* Gen. Tech. Rep. FPL-GTR-113. US Department of Agriculture, Forest Products Laboratory, Madison, WI, USA.

Stern M and Geary AL. 1957. 'Electrochemical Polarization'. *Journal of the Electrochemical Society*, 104(1): 56-63.

Stook K, Tolaymat T, Ward M, Dubey B, Townsend T, Solo-Gabriele H and Bitton G. 2005. 'Relative Leaching and Aquatic Toxicity of Pressure-treated Wood Products Using Batch Leaching Tests'. *Environmental Science and Technology* 39: 155-163.

Talbot D and Talbot J. 1998. *Corrosion Science and Technology*. CRC Press LLC, Boca Raton, Florida, USA.

Uhlig HH. 1979. 'Passivity in Metals and Alloys'. Corrosion Science 19: 777-791.

van der Sleet HA, Heasman L and Quevauviller PH. 1997. 'Harmonisation of Leaching/Extraction Tests'. *Studies in Environmental Science* 70: 209-226.

Walter GW. 1986. 'A Review of Impedance Plot Methods Used for Corrosion Performance Analysis of Painted Metals'. *Corrosion Science* 26(9): 681-703.

Williams R. 2005. 'Weathering of Wood'. In *Handbook of Wood Chemistry and Wood Composites*. Ed RM Rowell. Taylor & Francis, Boca Raton, Florida, USA.

Zelinka SL and Rammer DR. 2006. 'Corrosion Avoidance with New Wood Preservatives'. *Wood Design Focus* 16(2): 7-8.

Zelinka SL, Rammer DR, Stone DS and Gilbertston JT. 2007. 'Direct Current Testing to Measure Corrosiveness of Wood Preservatives'. *Corrosion Science* 49: 1673-1685.

Zelinka SL, Rammer DR and Stone DS. 2008a. 'Electrochemical Corrosion Testing of Fasteners in Extracts of Treated Wood'. *Corrosion Science* 50(5): 1251-1257.

Zelinka SL, Rammer DR and Stone DS. 2008b. 'Corrosion of Metals in Contact with Treated Wood: Developing Test Methods'. NACE Corrosion Paper No.08403. In *Proceedings of the NACE International Corrosion 2008 Conference & Expo.* 16 – 20 March 2008, Ernest N. Morial Convention Center, New Orleans, Louisiana, USA.

Zelinka SL and Rammer DR. 2009. 'Corrosion Rates of Fasteners in Treated Wood Exposed to 100% Relative Humidity'. *Journal of Materials in Civil Engineering* 21: 758-763.

Zelinka SL, Sichel RJ and Stone DS. 2010. 'Exposure Testing of Fasteners in Preservative Treated Wood: Gravimetric Corrosion Rates and Corrosion Product Analyses'. *Corrosion Science* 52: 3943-3948.

Zhang XG. 2000. 'Zinc'. In *Uhlig's Corrosion Handbook*. Ed R Winston Revie. John Wiley & Sons Inc, New York, USA.

Zhang XG. 2005. 'Corrosion of Zinc and Zinc Alloys'. In *ASM Handbook, Vol. 13B: Corrosion: Materials*, Eds. S.D. Cramer and B.S. Covino, Jr. ASM International, pp.402-417.