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Corrosion of Mild Steel, HDG Steel, and 316 Stainless Steel in CCA, CuAz and ACQ-Treated Pinus Radiata

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SUMMARY

BRANZ, as an independent testing laboratory to the building industry, has developed an Embedded Fastener Test for the measurement of metallic corrosion rates in treated timbers. In this work, the performance of this embedded fastener methodology has been compared with the American Wood Preservers' Association (AWPA) standard E12-94 test, which uses the corrosion analysis of metallic coupons 'sandwiched' between two timber blocks. The testing focused on the CCA alternatives ACQ and CuAz timber preservative treatments. AWPA E12-94 mild steel corrosion rates in the ACQ-treated timber have been shown to increase by a factor of up to five at the H3.2 hazard level relative to the equivalent CCA-treated timber. 316 stainless steel performed very well for all of the preservative treatments examined. The relative magnitude of corrosion rates measured using the Embedded Fastener Test contrasted significantly with those determined using the AWPA standard methodology. Using commercially available mild steel and hot-dipped galvanised nails, the ACQ-treated timber produced corrosion rates ranging from one and a half to two times that of the equivalent H3.2 CCA-treated samples. It is concluded that the AWPA standard test increases the differentiation of mild steel corrosion rate between timber treatment types, but the relative magnitude of acceleration cannot be directly compared to that experienced by fasteners embedded in the same timbers.

Keywords: timber, corrosion, CCA, ACQ, CuAz, ACQ-B, ACQ-C, CA-B, CCA-C, preservative, weight loss, fasteners, copper, mild steel, hot-dipped galvanised, zinc.

1.   INTRODUCTION

1.1   Recent changes to timber preservation codes of practice

At a global level, chromated copper arsenate (CCA) has provided the core of water-based timber treatments during the last 70 years. The environmental health hazards associated with the presence of arsenic has led to revised formulation standards and codes of use in many developed countries. From December 2003, the preservative-treated timber industry in the USA voluntarily removed use of CCA for residential applications. The United States Environmental Protection Agency (EPA) has now banned the use of CCA-treated wood in residential settings. The June 2004 amendment of the European Union Commission Directive 76/769/EEC also states that arsenic compounds cannot be used for the treatment of preservative-treated timber unless the end use was for industrial installations. Recently, the Australian Pesticides & Veterinary Medicines Authority (APVMA) has also moved to stop the use of CCA timber applications that include human contact. The phasing out process will end in March 2006.

The major commercially available water-based alternatives to CCA are copper azole (CuAz)-based (includes: CA-B and CBA-A formulations) and alkaline copper quaternary (ACQ)-based products

(includes: ACQ-B,-D and ACQ-C). These preservative treatments have considerably higher amounts of copper within the wood than would be expected for CCA-treated equivalents. This is of concern where it is known that at moisture contents greater than 20% wt./wt., the copper in CCA treatments can lead to at least double the corrosion rate of mild steel relative to untreated timber [1-5].

In this work, the corrosive effects of the alternative treatments prior to possible transitions in New Zealand codes of preservative timber application have been quantified. The relative durability of mild steel, hot-dipped galvanised mild steel and 316 stainless steel have been examined in untreated, CCA-treated (H3.2, H4 and H5), CuAz-treated (H3.2 and H4) and ACQ-treated (H3.2, H4 and H5) timber. These hazard classes relate to preservative treatment of timber for the protection from decay and insect attack as specified in NZS 3640:2003 (Amendment 1) [6]. The higher hazard numbers relate to timber applications in more aggressive environments and contain progressively higher concentrations of copper.

1.2   The accelerated corrosion of fasteners in treated timber

General fastener corrosion due to acetic acid attack and differential depolarisation of the metallic substrate due to concentration cells and localised stress corrosion [7-14] can occur in conjunction with oxidation resulting from the spontaneous (galvanic) electrochemical reduction of cupric ions present in preservative-treated wood [1-5]. An important factor to consider is the quantity of copper species fixed within treated timber and the tendency of un-fixed material to be released and participate in the corrosion mechanism [15,16]. The rate of corrosion, in all these cases, is dependent on timber moisture content. Metal loss can become significant at H_2O/timber concentrations greater than 18-20% (weight/weight). In most cases, it is not a weakening of the fastener which is of prime concern, but rather the loss of withdrawal resistance caused by the degradation of the timber by the actions of the corrosion products (nail sickness) [17-22]. There has been a significant amount of research conducted on the degradation of timber and fasteners as a result of CCA-accelerated corrosion rates [23-27]. The continued development of new timber preservative treatments adds another dimension to this degradation issue. Research has indicated that timber treatments based on CCA show a significant increase in the corrosion of mild steel, aluminium alloy and zinc-coated steel fasteners when the relative humidity is high and the timber has high moisture content.

Not surprisingly, however, materials that have more noble electrochemical potentials (in timber) relative to copper, such as stainless steel (AISI 304 and 316), have been found to be unaffected under similar conditions [28]. Low corrosion rates have also been observed for copper and nickel-based components [29] such as silicon bronze, copper, brass, and Monel. In these cases, the potential difference between the cupric ions and the fastener materials is not sufficient to drive a significant current from a galvanic 'immersion deposit' reaction at the timber/fastener.

Independently published data dealing with the copper azole (CuAz: CA-B and CBA-A types) and alkaline copper quaternary (ACQ-B, ACQ-C and ACQ-D types) are rare. Research by SIMPSON Strong-Tie USA [30] shows that testing based on the American Wood Preservers' Association standard E12-94 [31] ACQ-D induced zinc corrosion rates twice those observed during the same test for CCA-C treated timber. No significant corrosion was observed in either case when either 304 or 316 stainless was incorporated. The sales literature of other commercially available products recommends the use of fixings made of stainless steel, and hot-dipped galvanised mild steel in CuAz- and ACQ-based timber [32].

The corrosion rates (% weight loss) from this research using the AWPA E12-94 test method are shown in Table I. The corrosion weight loss percentages appear to insignificant for hot-dipped galvanised and stainless steel materials, and the corrosion of mild steel articles has clearly been accelerated relative to untreated and CCA-treated timber. 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.

Table I: Preservative corrosion rates (percentage weight loss) [32]

Treatment type	Mild steel	Hot-dipped galvanised steel	Zinc electroplated steel
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

2.   EXPERIMENTAL PROCEDURE

2.1   Overview of testing methodologies

For the determination of corrosion rates in CCA, CuAz and ACQ preservative treatments, both the industry standard American Wood Preservers' Association (AWPA) E12-94 [31] accelerated corrosion test and the BRANZ developed Embedded Fastener Test have been applied.

- The AWPA E12-94 standard describes a metallic coupon (flat plate) as the geometry of interest, and a timber block 'sandwich' assembly, which is exposed at 49±1ºC and 90±1% relative humidity over a period of approximately two weeks. This methodology is an industry standard internationally recognised by both fastener producers [30] and the timber treatment industry [32]. The standard was originally produced with the aim of determining the relative corrosivity of timber treatments, rather than the corrosion resistance of fastener materials and the localised effects of metallic substrate geometry.

- The BRANZ developed test also involves the exposure of embedded fasteners at 49±1ºC and 90±1% relative humidity over a period of approximately two weeks. This methodology allows a direct analysis of the influence of the generic nail and screw geometry (either manual or pneumatic insertion). Geometrical factors and the influence of differential exposure surfaces are included and considered when using this test programme.

Both tests are accelerated and absolute values of durability cannot be directly inferred. All exposures are performed in triplicate and initiated using pre-equilibrated timber specimens of known moisture content. Post-exposure analysis is both qualitative (visual) and quantitative (weight loss determinations leading to thickness loss rates). The main difference between the AWPA and the embedded fastener tests is that existing commercially available nails are examined rather than flat coupons, which would almost certainly have a different physical and chemical metallurgy to the fastener product of interest. Moreover, geometrical effects such as differential aeration, internal stress and coating variability are more accurately represented.

2.2   Environmental chamber test conditions

The accelerated conditions of temperature and relative humidity were achieved using an environmental chamber. The climatic system was monitored and maintained on a daily basis and independently calibrated using a Sensirion SHT15/75 combined humidity and temperature sensor-based system (temperature: –40 to +123.8ºC; humidity: 0 to 100). Values of absolute accuracy of this sensor are ±2% at 75% RH, ±2% 90% RH, ±4% 100% RH. For a temperature range of 5 to 40ºC the accuracy value is ±0.4ºC. All timber samples were mounted on polymer-based, meshed shelving to ensure uniform vapour transfer and to prevent the pooling of liquids.

2.3 Metallic materials

2.3.1 AWPA E12-94 coupons

Cold rolled mild steel, hot-dipped galvanised (centrifugal) mild steel and 316 stainless steel surfaces were examined using the AWPA E12-94 test regime. Metallic coupons of approximately 1.5 x 25 x 50 mm were cut to shape prior to delivery. No holes were drilled into the coupons during the zinc-coating process.

2.3.2 Nail fasteners

One generic type of mild steel and two generic types of hot-dipped galvanised (HDG) nails were incorporated in the embedded fastener testing. Neither of the galvanised nails supported organic or conversion coatings. The hot-dipped galvanised nails have been distinguished as TYPE A and TYPE B. The approximate dimensions of each nail type are presented in Table II.

Table II. Description of nail types

Identification	Length / mm	Approx. area / mm^2	Visual condition pre-exposure
Mild steel	50	460	Dull grey finish with very low level localised red rust
HDG TYPE A	50	460	Relatively dark and dull zinc-coating
HDG TYPE B	90	900	Relatively bright zinc-coating

2.3.3 Surface preparation prior to exposure

All metals were abraded prior to use with 180 (110N; A wt.) and 150 (130N; C wt.) garnet paper and de-greased with an acetone/ethanol mixture and air dried. Each metal weight loss sample was then weighed in grams to four decimal places. Contact with the equilibrated timber specimens was made immediately after the cleaning sequence.

2.3.4 Surface preparation post-exposure

The following chemical cleaning procedures were selected from ASTM G1 – 90 [33]) to remove corrosion products from all of the metallic weight loss specimens:

- bright steel   200 g dm^{-3} di-ammonium citrate ($[NH_4]_2HC_6H_5O_7$) 20 min at 75-90ºC
- HDG mild steel   100 g dm^{-3} ammonium chloride (NH_4Cl) 2-5 min at 70ºC
- 316 stainless steel 150 g dm^{-3} di-ammonium citrate ($[NH_3]_2HC_6H_5O_7$) 10-60 min at 70ºC

Freshly polished materials (supporting only thin thermal oxides) were used as a control measure in each case as a corrective method.

2.4 Timber treatment and supply

2.4.1 Timber treatment

All of the supplied timber was cut to approximate 45 x 45 mm (±2 mm) cross-sectional lengths prior to custom preservative treatment as directed by BRANZ. CCA oxide-treated (CCA-C), CuAz-treated (CA-B) *Pinus Radiata* and a batch of untreated timber were taken from the same holding source. The active azole in the CuAz case was tebuncanzole (molecular weight of 307.8 g mol^{-1}). The H3.2 and H5 ACQ-treated *Pinus radiata* contained the active ingredient DDAC (didecylthyl ammonium chloride) and the H4 grade contained BAC (alkylbenzyldimethyl ammonium chloride). The molecular weight values of these active ingredients (values supplied by the timber treatment plants) are 362.1 g mol^{-1} and 340±99 g mol^{-1}

respectively (the latter contains a broad range of materials). The ACQ formulations can be described as ACQ-B (H3.2 and H5) and ACQ-C (H4). When used, the LOSP (light organic solvent preservative) H3.1 timber was commercially sourced. In all cases, the wood was cut and finished to 45 x 45 x 3000 mm lengths prior to the preservative pressure treatment at each specific plant. At least three complete lengths of timber were supplied for each treatment level. The timber was stored for at least one month at 25ºC and 55% RH prior to use. After this minimum period, the material was cut to the required exposure sample size and finished (power sander using aluminium oxide 80 grit sandpaper) to remove any precipitated preservation chemicals at original surfaces.

2.4.2   Timber sampling and quantitative analysis

All samples for corrosion and elemental/molecular analysis were taken 150 mm away from major defects such as surface knots. The chemical analysis samples (45 x 45 x 100 mm) were cut from the centre of each of the selected lengths of timber. Estimated values of preservative components were determined by Scion (formerly Forest Research Institute Ltd, Rotorua, New Zealand) from samples selected and supplied by BRANZ. Compositional testing was performed according to the American Wood Preservers' Association standards: AWPA A11-93 [34], AWPA A7-93 [35], AWPA A28-01 [36], AWPA A18-99 [37] and AWPA A21-00 [38].

In order to maximise the representative sampling of the population of timber lengths supplied to BRANZ, three distinct lengths of treated timber were selected for each batch of preservative type. This also applied to the untreated timber. Each length of timber was then BRANZ coded as Ax, Bx or Cx, where 'x' is the BRANZ laboratory number given to each preservative type and level. Thus, specifically measured levels of preservative components can be assigned to each result obtained from any timber specimen used in the corrosion analysis procedures. (With the AWPA E12-94 testing, only timber taken from an identical BRANZ timber code was used to complete the two-part sandwich exposure cell.) In this manner, the corrosion rate of each metallic sample could be associated with a specific length of supplied timber and also directly compared to the behaviour of the other metallic species for identical conditions. Similarly, any corrosion rate measured with any one experimental method using a specific length of timber could be directly compared with confidence to the results of the alternative methodologies which have used timber from that original length of timber.

2.4.3 Timber moisture equilibration

Moisture conditioning of the pre-cut timber samples to constant weight was performed according to ASTM D 4933 – 99 [39] under constant environmental conditions of 49±1ºC and 90±1% relative humidity. The standard weight loss method of moisture content, as described by AS/NZS 1080.1:1997 [40], was used in all cases to assess timber water retention.

2.5   Exposure cells

2.5.1 AWPA E12-94 standard corrosion test cell

Full details of the experimental procedure and test cell can be found in E12-94 [31]. In compliance with this standard, the metal coupon samples (described earlier) of each material were compressed between two moisture equilibrated blocks (approximately 19 x 38 x 75 mm) of untreated and treated timber. Compressive contact was applied using nylon fastenings at each end of the blocks. In this work, exposure was applied over a 407 h period.

2.5.2 BRANZ Embedded Fastener Test cell

A novel test method, known as the BRANZ Embedded Fastener Test (BEFT), has been developed to identify the differential performance of fasteners as a function of preservative timber treatments. The objective was to replicate the in-situ fastener positioning prior to subjecting the samples to an aggressive environment (49±1ºC and 90±1% relative humidity), and to promote corrosive interactions between the

nail specimens, the high humidity atmosphere and the treated timber. The timber samples were cut to the dimensions 20 x 45 x 60 mm (or length 100 mm nail TYPE B), where the longest dimension ran in parallel to the grain of the wood structure. The samples were allowed to achieve complete moisture equilibration. The fasteners were manually embedded into pre-drilled holes using a hammer. The guiding holes were generally 60% of the diameter of the nail samples of interest. In every case, the freshly embedded fasteners were immediately inserted into the controlled environmental chamber which was preconditioned at 49±1°C and 90±1% humidity. The 385 h period of exposure applied for this testing approximates one of the conditions suggested by AWPA E12-94 [31]. On completion of the exposure test, the exposed surfaces of the test pieces were photographed. The nails were carefully removed from the surrounding timber. A visual analysis was then performed in conjunction with further photography. Finally, the fasteners were subjected to corrosion product removal and weight loss analysis.

3. RESULTS AND DISCUSSION

3.1 Timber preservative analysis

Table III gives the minimum molar (mol kg^{-1} oven dry timber) preservative treatment hazard levels of the timber specimens as calculated from weight percentage data defined in NZS 3640:2003 [6] (see Table IV). The results of the timber analysis as performed by Sion are presented in Tables V and Figure I. Table V provides a comparison between the directly measured timber analysis data and the preservative limits as specified in NZS 3640. Unlike the concentrations expressed as total weight of preservative to dry weight of timber (as used in NZS 3640), molar concentrations give an absolute value of the amount of copper present in each of the treated timbers. In this work, the relative weight contributions of all the preservative ingredients have been extracted from the overall minimum weight percentage values presented in NZS 3640 using the molar mass values of each component (presented in Section 2.4.1). It was assumed that the relative concentration of each component in aqueous solution is identical to that retained in the treated timber as specified in Table IV. Assuming that, for a given set of experimental conditions, only the magnitude of cupric ion concentration on a copper reduction accelerated corrosion mechanism is significant, we can predict that at each prescribed hazard level the corrosivity should increase in the order CCA → CuAz → ACQ. At the H3.2 level, the ratio of molar concentrations of copper will be 1.00 : 2.13 : 3.33 respectively. At the H4 level, the equivalent relationship is 1.00 : 2.03 : 5.00. The true scale of corrosivity, however, will be dependent on the availability of un-fixed copper and its rate of transfer within the timber.

Table III.   Minimum moles per kilogram concentrations of copper in preservative-treated timber as calculated from weight percentage data presented in NZS 3640:2003 (Amendment 1) [6]

	Moles of copper per kg of basic density timber / mol kg^{-1}		
Hazard level	**CCA**	**CuAz***	**ACQ**
H3.2	0.015	0.032	0.050
H4	0.029	0.059	0.145
H5	0.038	–	0.192

* Note that the practical research presented here was initiated prior to the introduction by Amendment 1, NZS 3640 of the CuAz H5 hazard level.

Table IV. Relative proportions of preservative timber treatment components in aqueous solution [6]

	Component (% wt./wt.)				
	Cu	**Cr**	**As**	**DDAC**	**Azole**
CCA	23-25	38-45	30-37	–	–
ACQ	57-66	–	–	33-44	–
CuAz	95.8-96.4	–	–	–	3.6-4.2

Table V. Elemental/molecular concentrations (mol kg^{-1}) of the preservative-treated timber components and minimum specified (NZS 3640:2003 [6]) values of preservative retention (Note that molar concentrations calculated at BRANZ from Scion percentage wt./wt. results and all weight values are given for basic density timber.)

Description	BRANZ I.D.	Concentration / mol kg^{-1}					Actual total mass retention / % wt./wt.	Total mass min. required retention / % wt./wt. [6]	Min. required penetration / mm [6]	Actual % sapwood / % penetration
		Cu	Cr	As	DDAC/BAC*	Tebucan-azole				
Sample Set 1										
CCA-treated timber										
H3.2	A1	0.02360	0.04615	0.01735	-	-	0.52	0.37	25	100/100
H4	A2	0.04092	0.09038	0.04138	-	-	1.04	0.72	25	90/100
H5	A3	0.06609	0.13654	0.07074	-	-	1.66	0.95	30	90/100
CuAz-treated timber										
H3.2	A4	0.06137	-	-	-	1.23 x 10^{-3}	0.428	0.2288	25	90/90
H4	A5	0.11173	-	-	-	0.94 x 10^{-3}	0.739	0.416	25	100/100
ACQ-treated timber										
H3.2	A6	0.06452	-	-	9.67 x 10^{-3}	-	0.76	0.35	25	100/100
H4	A7	0.07868	-	-	7.35 x 10^{-3}	-	0.75	1.02	25	100/100
H5	A8	0.19828	-	-	36.45 x 10^{-3}	-	2.58	1.35	30	100/100
Sample Set 2										
CCA-treated timber										
H3.2	B1	0.02203	0.03654	0.01201	-	-	0.42	0.37	25	100/100
H4	B2	0.02518	0.05769	0.02670	-	-	0.66	0.72	25	60/80
H5	B3	0.05508	0.11154	0.05739	-	-	1.36	0.95	30	100/100
CuAz-treated timber										
H3.2	B4	0.06137	-	-	-	0.49 x 10^{-3}	0.405	0.2288	25	100/100
H4	B5	0.07081	-	-	-	0.97 x 10^{-3}	0.48	0.416	25	35/40
ACQ-treated timber										
H3.2	B6	0.06452	-	-	9.39 x 10^{-3}	-	0.75	0.35	25	100/100
H4	B7	0.07868	-	-	7.06 x 10^{-3}	-	0.74	1.02	25	100/100
H5	B8	0.20458	-	-	40.87 x 10^{-3}	-	2.78	1.35	30	100/100
Sample Set 2										
CCA-treated timber										
H3.2	C1	0.02360	0.04231	0.01602	-	-	0.49	0.37	25	100/100
H4	C2	0.02518	0.05769	0.02670	-	-	0.66	0.72	25	90/100
H5	C3	0.06609	0.13654	0.07208	-	-	1.67	0.95	30	100/100
CuAz-treated timber										
H3.2	C4	0.06924	-	-	-	6.11 x 10^{-3}	0.628	0.2288	25	95/100
H4	C5	0.04092	-	-	-	34.47 x 10^{-3}	1.321	0.416	25	5/5
ACQ-treated timber										
H3.2	C6	0.05823	-	-	9.39 x 10^{-3}	-	0.71	0.35	25	100/100
H4	C7	0.08340	-	-	8.24 x 10^{-3}	-	0.81	1.02	25	100/100
H5	C8	0.18412	-	-	36.73 x 10^{-3}	-	2.5	1.35	30	100/100

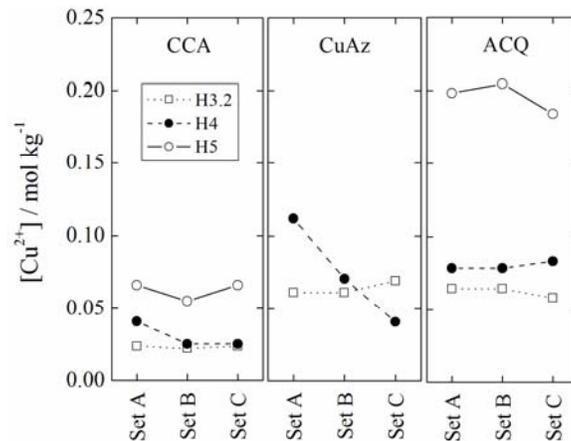* H3.2 and H4 ACQ-treated timber = DDAC; H5 ACQ-treated timber = BAC

Figure I. Directly measured copper concentrations in the CCA, CuAz and ACQ-treated timber samples used in this work (data adapted from weight percentage data)

CCA H4 (B2 & C2) and ACQ H4 (A7, B7 & C7) timber specimens had lower total mass percentage preservative retentions than the minimum limits for specified in NZS 3640. All of the CuAz specimens were in excess of the minimum requirements in this case. In terms of molar percentage copper content, CCA H4 (B2 & C2), ACQ H4 (A7 & B7 & C7), ACQ H5 (C8) and CuAz H4 (C5) had lower retentions than the limits calculated from NZS 3640.

In terms of sapwood penetration, CCA H4 (A2 & C2) and CCA H5 (A3) had values less than 100%. Samples CCA H4 (B2), CuAz H3.2 (A4) and CuAz (B5 & C5) had less than 100% sapwood and the total value penetration in each of these cases was also lower than 100%. This non-conformity was particularly severe for CuAz H4 samples B5 and C5 where % penetration / % sapwood was 35/40 and 5/5 respectively and accounts for the sharp drop-off in CuAz H4 copper concentration from Set A to Set C observed in Figure I. In the corrosion analysis to follow, each corrosion rate measured in this work was traced to the preservative retention associated with a specific sample of treated timber and, as in the case of Section 3.4, normalised accordingly.
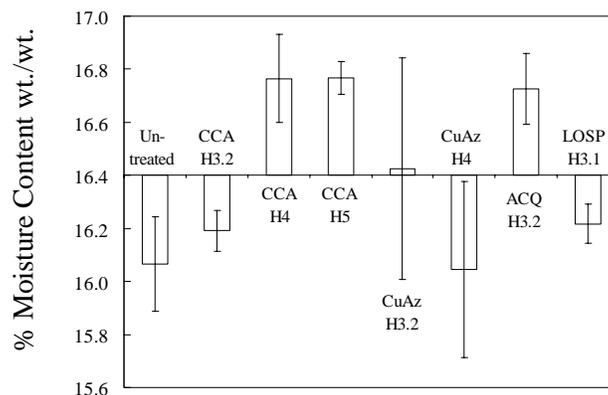

Figure II. Mean moisture contents of timber blocks (19 x 38 x 75 mm) fully equilibrated (dry to wet) at 49±1ºC and 90±1% relative humidity (Overall mean moisture content (as presented in the figure) is 16.4+/- 0.3% wt./wt.)

3.2 Moisture content analysis

The results of timber moisture content for a selected range of timbers as experienced during testing at 49±1ºC and 90±1% relative humidity are presented in Figure II. These samples (excluding the LOSP specimens) were taken from the same laboratory stock as used for all the other procedures in the work. The overall mean value of moisture contents was 16.4%, where the precision was relatively high with a range of ±0.3% wt./wt. There does not appear, in this case, to be any significant trend in moisture content as a function of preservative type and hazard level.

3.3 AWPA test results

Thickness loss results measured using the standard AWPA E12-94 test are presented in Figure III using both linear and logarithmic scales. The large differentiation in the overall mean mild steel corrosion rates can be easily observed using the linear scale, where corrosion rates range from 0.048±0.013 mm y^{-1} (untreated) to 1.493±0.082 mm y^{-1} (ACQ H5). Mean thickness loss rates of the H3.2 level treatments were 0.074±0028 mm y^{-1} (CCA), 0.178±0.067 mm y^{-1} (CuAz) and 0.780±0.082 mm y^{-1} (ACQ).

At the H4 level, equivalent thickness loss rates were 0.062±0.020, 0.271±0.186 and 0.766±0.127 mm y^{-1}. Although it must be considered at this stage that the CuAz H4 level treatment was deficient in copper content, the magnitude of this discrepancy does not account for the three-fold decrease in corrosion rate relative to the ACQ H4 treatment (this value was a factor of 12 times larger relative to the H4 CCA treatment). Indeed, all of the ACQ H4 timber specimens (A7, B7 & C7) had lower total mass percentage preservative retentions than the minimum limits for specified in NZS 3640. This later point can be observed in the low mean value of ACQ H4 corrosion rate for mild steel (Figure III), which deviates from the expected sequence for the order of increasing corrosion rate H3.2 < H4 < H5.
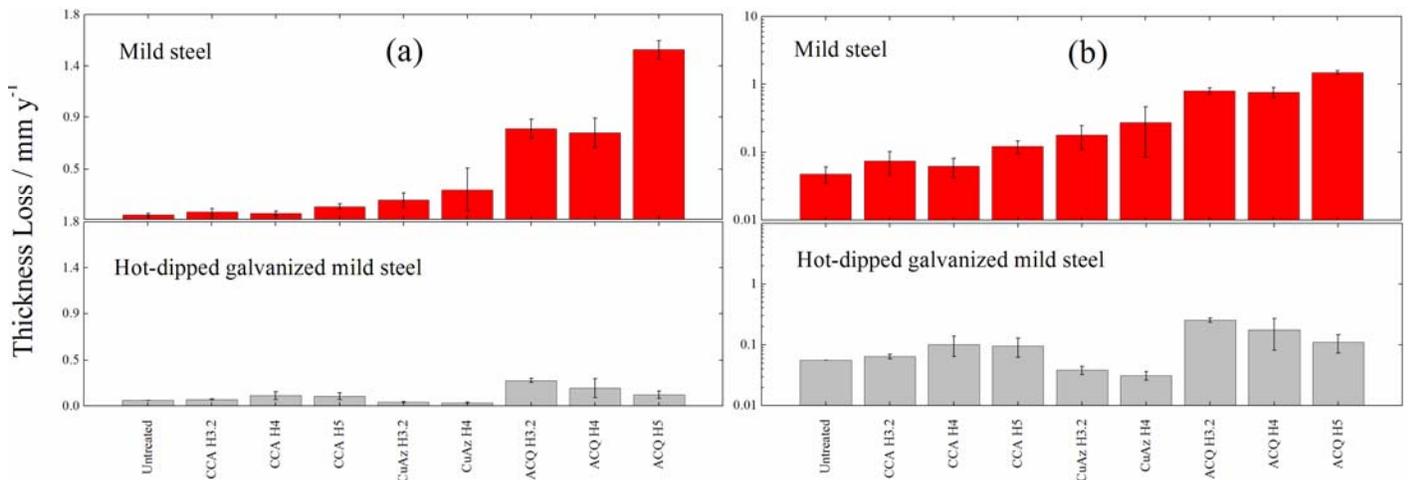

Figure III. (a) Linear and (b) logarithmic mean thickness losses of the mild steel and hot-dipped galvanised steel coupons post-exposure under conditions specified in AWPA E12-94

At the H5 level, the CCA and ACQ mild steel coupon corrosion rates were 0.121±0.025 mm y^{-1} and 1.493±0.081 mm y^{-1}, respectively. This represents an increase in the corrosion rate by a factor of 12 relative to CCA H5 when ACQ is applied. At a qualitative level, the extent of the mild steel corrosion induced by exposure to the H3.2, H4 and H5 ACQ-treated timber can be observed visually in Figure IV. The quantity of visible iron corrosion product increased in the order Untreated < CCA < CuAz < ACQ. In

all cases pitting of the ACQ exposed surfaces was severe in comparison to the alternative treatments and most damage occurred at the edges of the coupons.

In contrast to the behaviour of the mild steel coupons, the corrosion rates of the hot-dipped galvanised mild steel coupons did not uniformly increase to such a level with an increasing CuAz and ACQ timber copper concentration. In fact, using the AWPA standard test, the CuAz treatments (H3.2 0.038 ± 0.006 mm y^{-1} and H4 0.031 ± 0.005 mm y^{-1}) appeared to inhibit the corrosion rate of the galvanised layer relative to untreated timber (0.056 ± 0.001 mm y^{-1}). The highest values of zinc corrosion, however, were measured in the ACQ-treated timbers (H3.2 0.253 ± 0.020 mm y^{-1}, H4 0.175 ± 0.094 mm y^{-1} and H5 0.109 ± 0.037 mm y^{-1}).

It should be also noted that the magnitude of corrosion rate decreased with increasing concentration of ACQ preservative treatment. The equivalent CCA-treated timber corrosion rates did not decease with hazard level number, where intermediate values of H3.2 0.065 ± 0.006 mm y^{-1}, H4 0.102 ± 0.037 mm y^{-1} and H5 0.095 ± 0.033 mm y^{-1} were measured. Relative to the CCA treatments, therefore, the equivalent ACQ timbers increased the corrosion rates by mean factors of 3.8 (H3.2), 1.7 (H4) and 1.5 (H5).

The results of the 316 stainless steel weight loss tests (Figure V) indicate that any mass loss due to corrosion in the treated timbers was less than the precision of the measurement technique. Thus, 316 stainless steel is predicted to have favourable corrosion resistance in copper-based timber preservative treatments.
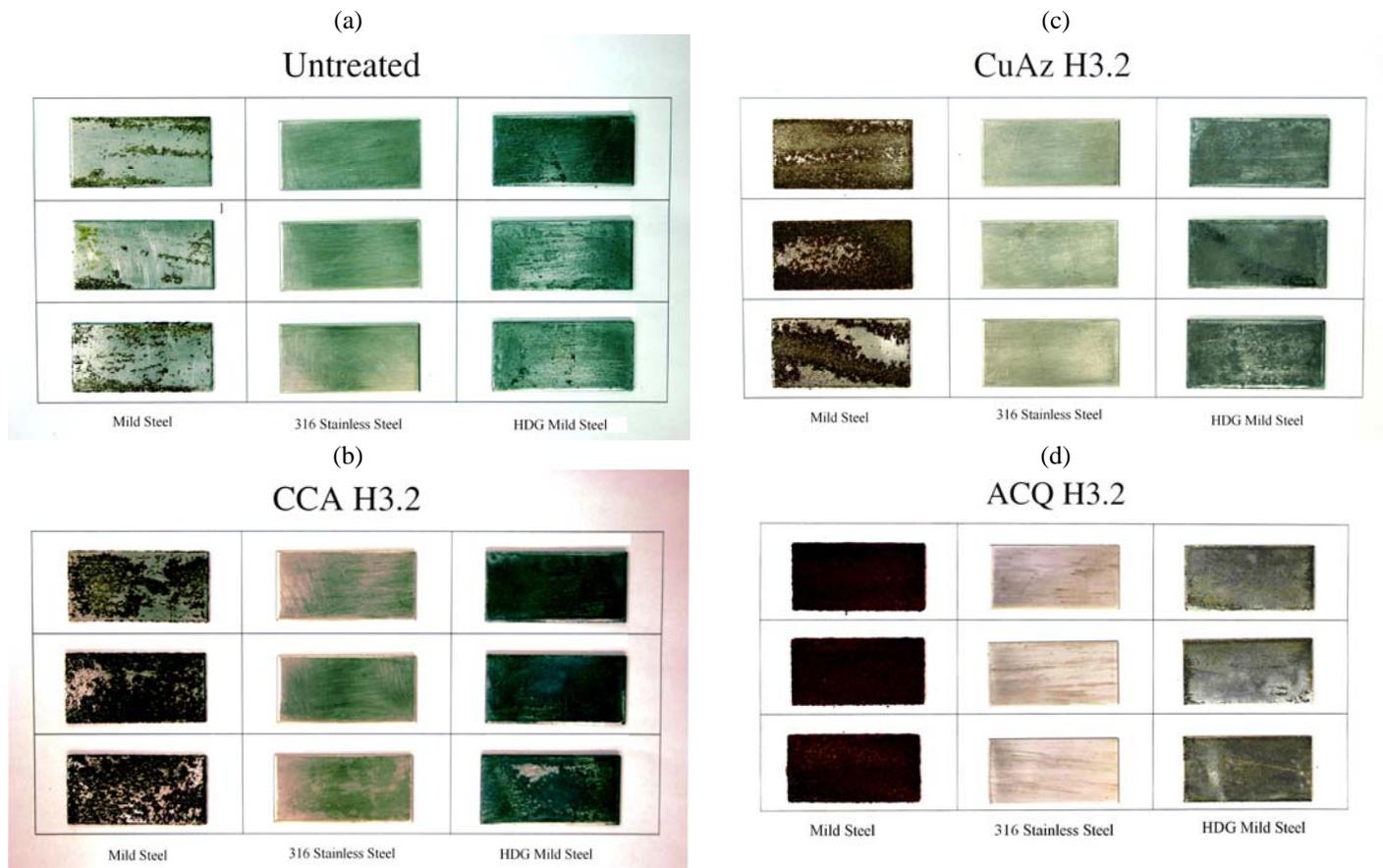

Figure IV. (a) Untreated, (b) CCA, (c) CuAz and (d) ACQ H3.2 hazard level coupons post-exposure under conditions specified by AWPA E12-94
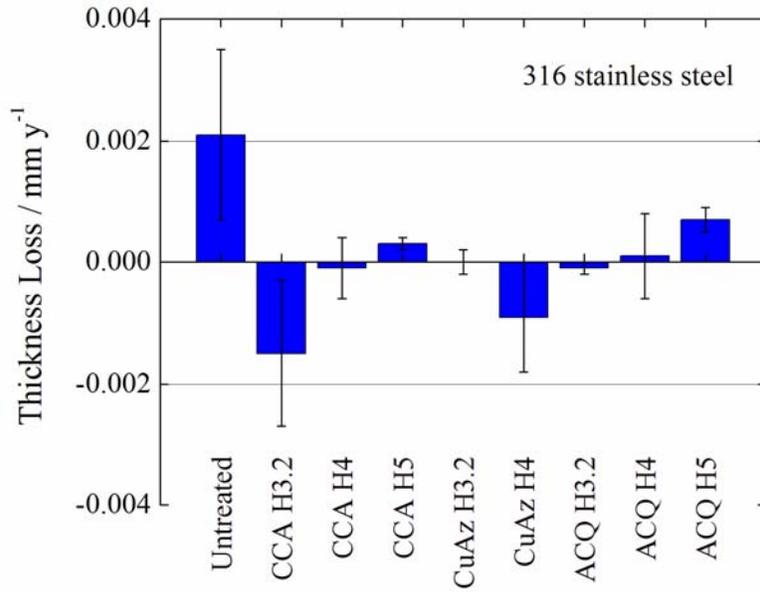
Figure V. 316 stainless steel coupon thickness loss (relative to the overall mean) post-exposure under conditions specified in AWPA E12-94
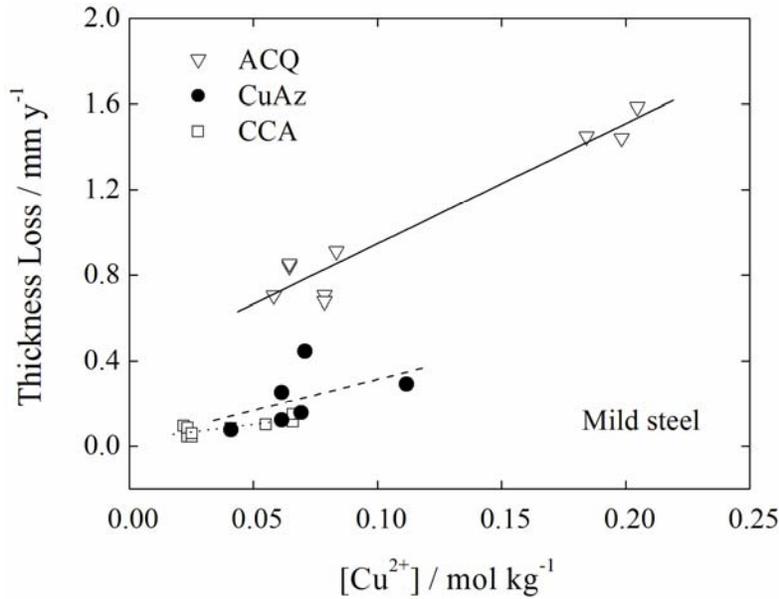

Figure VI. Mild steel coupon corrosion rates in the CCA, CuAz and ACQ-treated timbers as a function of independently measured copper ion concentration

Individual corrosion rates of the AWPA E12-94 coupons are presented as a function of experimentally derived copper concentrations (mol kg^{-1}) in Figures VII for the mild steel. Considering these results, the lowest values of corrosion rate were calculated for the CCA and CuAz treatments. The H3.2 and the H4 ACQ treatments contained an approximately equivalent amount of copper to the CCA H5 and CuAz H3.2, H4 and H5 timbers. The values of ACQ corrosion rates at these levels of copper concentration, however,

were some three to five times greater than these CCA and CuAz hazard conditions. Assuming a reaction controlling step at the mixed (corrosion) potential, which is controlled by the rate transfer (diffusion) of cupric ions within the timber, i.e. where the cathodic cupric ion reduction reaction is limiting, it must be considered that the copper within the ACQ-treated wood may not be 'fixed' to the same extent as in the CCA and CuAz samples. In diffusion controlled processes, a higher mass transfer coefficient (produced as a result of a greater availability of cupric ions) will lead to increased reaction rates [41].

3.4 BRANZ Embedded Fastener Test results

Note that the embedded fastener data do not currently include results measured in H4 and H5 ACQ timbers. The results of the embedded fastener testing produced a series of corrosion rates of similar relative order, but the amount of deviation between timber treatments was of a much lower magnitude. The metallic thickness loss rates for the mild steel and hot-dipped galvanised (TYPE A and TYPE B) fasteners are presented in Figure VII. The mean mild steel corrosion rates range from 0.30 ±0.03 mm y^{-1} (LOSP) and 0.31±0.02 (untreated), 0.31±0.07 (CCA H3.2) to 0.39±0.03 mm y^{-1} (CuAz H3.2), 0.29±0.03 mm y^{-1} (CuAz H4) and 0.58±0.03 mm y^{-1} (ACQ H3.2). The mean CCA H4 and H5 values were 0.35±0.02 mm y^{-1} and 033±0.05 mm y^{-1}, respectively. The CCA and CuAz values are all somewhat higher than the equivalent AWPA E12-94 test results. For example, taking the H3.2 hazard level, the embedded fastener results were approximate factors of 4 (CCA) and 2 (CuAz) higher than the AWPA 'sandwich' test results. Conversely, the mean AWPA ACQ H3.2 test corrosion rate was slightly higher than the embedded fastener result by 34%.

As expected, the corrosion rates of the hot-dipped galvanised fasteners were lower than the mild steel alternative. The decrease in corrosion rate observed using the galvanised fasteners at the lower hazard level of H3.2 was essentially very similar to that determined using the galvanised AWPA coupons. Using the AWPA test, the zinc-coated sample H3.2 timber corrosion rates were 13% (CCA), 78% (CuAz) and 68% (ACQ) lower than the mild steel coupons. The range of equivalent values for commercial fasteners was TYPE A 69% (CCA), 71% (CuAz) and 50% (ACQ); TYPE B 64% (CCA), 78% (CuAz) and 62% (ACQ).

Overall, the ACQ H3.2 treatment produced the largest thickness losses of both the mild steel and the two types of hot-dipped galvanised fasteners. In all cases, the ACQ H3.2 values (0.58±0.03 mm y^{-1} [mild steel], 0.29±0.01 mm y^{-1} [TYPE A] and 0.22±0.02 mm y^{-1} [TYPE B]) were approximately 1.5 to 3 times that measured for the CCA H3.2 timber (0.31±0.02 mm y^{-1} [mild steel], 0.095±0.02 mm y^{-1} [TYPE A] and 0.11±0.02 mm y^{-1} [TYPE B]) and CuAz H3.2 (0.39±0.03 mm y^{-1} [mild steel], 0.09±0.01 mm y^{-1} [TYPE A] and 0.11±0.02 mm y^{-1} [TYPE B]) timber treatments.
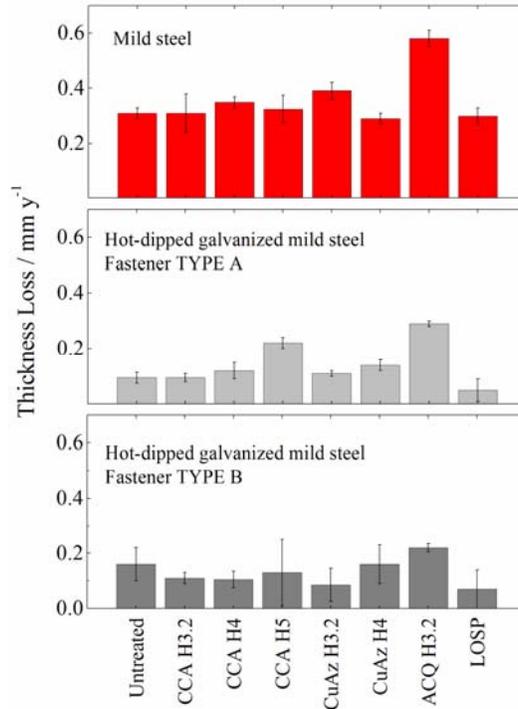
Figure VII. Mean thickness losses of mild steel and TYPE A and TYPE B hot-dipped galvanised steel embedded fasteners

Although, it is not possible to directly deduce the influence of the cupric ion on mild steel corrosion using the BRANZ Embedded Fastener Test, the exposure of the nail head in this manner is probably more representative of field applications. During embedded exposure, a number of different corrosion mechanisms can dominate at the corrosion potential (see Section 1.2). The relative contribution to the overall corrosion current of each mechanism will depend on the particular part of the fastener which is under study.

4. CONCLUSIONS

- Under the conditions applied in this work, AWPA E12-94 mild steel corrosion rates in the ACQ-treated timber have been shown to increase by a factor of up to five at the H3.2 hazard level relative to the equivalent CCA wood-based electrolyte. This difference increased to a factor of 12 at H5 hazard levels.

- Using the BRANZ developed Embedded Fastener Test; a factor of two-fold increase in corrosivity was measured for mild steel corrosion at the ACQ H3.2 hazard level relative to the equivalent CCA-C wood-based electrolytes.

- In the majority of cases, the hot-dipped galvanised mild steel corrosion rates were generally some 50 to 80% lower than those measured for the mild steel materials.

- The severity of mild steel corrosion has been shown to increase in the order: Untreated < CCA < CuAz < ACQ.

- Hot-dipped galvanised steel corrosivity generally increases according to: CuAz $\cong$ CCA < ACQ.

- The 316 stainless steel performed without significant corrosion losses in all of the preservative treatments examined.

- The results of the BRANZ Embedded Fastener Test have produced a series of corrosion rates of a similar relative order to those produced using the AWPA E12-94 methodology. The amount of deviation between timber treatments measured using the Embedded Fastener Test on mild steel, however, was of a much lower magnitude than those measured when directed by the AWPA E12-94 test regime.

5. ACKNOWLEDGEMENT

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