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CORROSION OF METAL FASTENERS EMBEDDED IN TIMBER

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CORROSION OF METAL FASTENERS EMBEDDED IN TIMBER

ABSTRACT

The practical problems caused by corrosion of metal fasteners in timber are discussed. The main material covered is timber treated with copper-chromium-arsenate (CCA) preservatives. Some of the experimental background is outlined for advice on using timber with moisture contents below 20% unless special fastener materials are used. The dangers of timber degradation through reaction with the corrosion products of iron are also discussed. It is postulated that the free Cu:Cr ratio in the treated timber has a significant effect on corrosivity.

KEYWORDS

Arsenic; Chromium; Copper; Corrosion; Corrosion protection; Decaying; Deteriorating; Durability; Electrolysis; Failure; Fixing devices; Iron; Metals; Moisture; Preservatives; Timber; Treated Timber; Water; Wet.

INTRODUCTION

The corrosion of metals embedded in timber is important because it can limit the usefulness of timber as a structural material. Corrosion of the metal, leading to weakening of it, is not the only problem. Interaction of the corrosion products with the timber, leading to discoloration or, in some conditions, to degradation of the timber is an equally important consideration.

The study of metal-timber interactions has a long history. An early important study was made of such interactions in boats (1). A comprehensive bibliography of publications to 1976 has been published (2), and there have been more recent reviews of some of the corrosion-related issues (3,4) and some general advisory papers (5,6).

Treated timber is used very extensively in New Zealand as a building material. Any wet timber can be an inherently corrosive medium for steel fasteners. The addition of copper, chromium and arsenic salts as preservative treatment (referred to as CCA treatments) can heighten the corrosion. Building Research Association of New Zealand (BRANZ) has therefore, for several years, been promoting a programme of research to provide better background information on this sort of corrosion, the problems it causes, and some means by which the problems can be avoided. This paper summarises the results of this programme, and places them in context with studies reported by other laboratories. It concentrates on CCA treatments because these are the most widely used preservation methods

for timber that may become wet in service in New Zealand (i.e. moderate to severe decay hazard).

THE BACKGROUND TO THE PROBLEM

Timber can be a naturally corrosive medium. Many timbers contain significant levels of organic acids (especially acetic acid). However, problems of fastener corrosion arise only when the timber is damp, because dry timber has high electrical resistivity. The corrosion mechanisms involved are generally understood to entail attack by these organic acids and by creation of differential aeration cells which may be established irrespective of timber acidity. The "critical" timber moisture content for such cells to be established (i.e. for the timber resistivity to be lowered sufficiently) is generally held to be 20%. This moisture content can be established by equilibration of the timber in an atmosphere of 82% relative humidity and 15°C (7). A higher moisture content would be expected to heighten corrosion problems.

In the differential aeration cell, the head of the fastener has a much greater access to oxygen than the embedded part of the fastener. The head therefore becomes the cathode, at which oxygen reduction (to yield hydroxide) occurs, while the embedded part is the anode, and corrodes. Because the timber is still of moderate resistivity, the worst corrosion occurs just below the head.

If timber remains wet for long periods in service, it may rot. Pinus radiata, the most plentiful exotic timber resource in New Zealand, requires a preservative treatment if it is to be used in damp situations. The most effective treatments for protection of softwoods to be used in ground contact are based on copper, chromium, and arsenic salts. The formulation is balanced to give the best compromise between long-term stability of the preservative in the timber (termed "fixation") and efficacy of rot prevention.

This introduces the possibility of galvanic corrosion by interaction of the copper ions from the preservative with fasteners in the timber. Some formulations also contain counter-ions (sodium - or potassium - and sulphate) which raise the conductivity of the treated timber. This introduces the paradox - the timber resource is made useful for wet conditions (which enhance corrosiveness of the timber) by a treatment which improves the timber durability but further enhances the possible corrosion problems.

A useful first step in avoiding corrosion problems is avoiding the use of the timber until fixation (which may take only a week in summer but a few months in winter) has had a chance to occur. However, it will not totally prevent corrosion. A misconception exists that once such treated timber has been dried, the preservative salts are completely fixed and cannot cause corrosion problems. This is false. The deposition of the preservative involves chemical equilibrium (8), (9). Various theories have been proposed to explain the fixation process. However, it is generally accepted that small amounts of preservative remain mobile in the wood and so could contribute to corrosion. This has been shown in studies of leachability of the preservative salts (10) (11). (This is also often demonstrated by the deposition of basic copper salts on the timber surface around exposed fastener heads, where hydroxide generated at the cathode of

the corrosion cell (the fastener head) reacts with free copper ions). Thus, even if such treated timber has been stored indoors for several years, when the timber is re-wetted the traces of salts are free to migrate within the timber and become involved in corrosion reactions. Fixation has been claimed to be faster, the higher the temperature is (12). However, simply air drying at moderate temperatures may not be effective. It seems that moisture must also be present (11).

There exists a need to understand more precisely the phenomena that are occurring. This understanding is not helped by the multiplicity of tests that have been reported on corrosivity measurements. Some have suggested that CCA treatment does not markedly heighten the timber corrosivity (e.g. (13)) but most say it does. Most say that salt-formulation CCA treatments are more corrosive than oxide formulations (e.g. (14)) but one study found both higher and lower corrosivity, depending on exposure conditions (15). As Bailey and Schofield (4) have indicated, the high timber resistivity has meant that most electrochemical investigations have been carried out on timber saturated with water. There is discontinuity in the curve of water uptake of timber between 25 and 30% moisture content, as the fibre saturation point is exceeded. Saturation of the timber may allow modelling of the corrosion processes in saturated timber, but it is uncertain whether the same processes occur at the moisture contents below fibre saturation that are found for most timber framing in buildings (e.g. (16), (17)). Research projects were developed to examine, under reproducible conditions, the rates of corrosion and the effects of variations in ratio of copper and chromium, and these are discussed in the following sections.

ELECTROCHEMISTRY OF THE CORROSION REACTIONS

Bailey and Schofield (4) suggested that the high resistivity of timber made AC impedance techniques highly appropriate for study of these corrosion reactions. (In these techniques, the timber resistivity can be accounted for in the analysis of the results). At the time that their paper was published, BRANZ was funding a contract to investigate the application of such techniques to corrosion of zinc and iron in CCA-treated timber, and these results have now been collated (18). A preliminary paper on the electrochemical technique used has already been published (19).

The experiments were not totally successful. The greatest problem was the variability from piece to piece of the timber. From the point of view of this paper, the practical results concern the mechanism of the corrosion, the effect of moisture content, the effect of preservative salt concentration in the timber, and the relative rates of corrosion of iron and zinc.

Cells were constructed using a working electrode plate of zinc or iron clamped tightly between sawn-open halves of blocks of *Pinus radiata* (Figure 1). This cell assembly was equilibrated at different relative humidities to give timber moisture contents of approximately 13-14%, 22%, 26% and 28%, and some cells were also saturated with water. *Pinus radiata* blocks which were untreated or treated to C7 or C2 Specification (20) were used.

Some experiments were done after equilibration of the cell in a pure nitrogen atmosphere. This appeared to reduce the corrosion current by

approximately 50%. It appears that hydrogen ions and copper ions can adequately carry the cathodic current in the absence of oxygen.

Other evidence also pointed to corrosion processes being under diffusion control. The nitrogen-atmosphere experiments suggest that the cathodic reactions will be diffusion controlled if fastener heads are protected from oxygen. Other experiments, where the cell was equilibrated in air, found that the rate of corrosion was faster when the electrode was at right angles to the timber grain than when the electrode was parallel to the grain. This implies that diffusion of anodic products away from the electrode might also be an important process. Diffusion of ions through timber is faster along the grain than across it.

Evidence of the complexity of the corrosion process came from long-term monitoring of the cells. The polarisation resistance of the working electrode was measured at intervals of 300 days or more. For cells with a moisture content of 23% or less, these measurements implied the corrosion rate was slowly decreasing. This seemed to be related to the build-up of corrosion products found at the timber-metal surface when the cell was disassembled. In the very wet electrolyte systems, the polarisation resistance measurements suggested that corrosion was accelerating. This could not be correlated with electrode appearance. These electrodes were also extensively covered with corrosion product layer when examined.

The "polarisation resistance" measurement of the corrosion rate was checked by weighing the electrodes before and after the cell was monitored. The corrosion rates for iron and zinc were comparable, yielding further evidence that a diffusion-controlled rather than activation-controlled process was being assessed.

The effect of preservative concentration was difficult to assess, since nominally similar batches gave rather different answers. (This helped to produce the hypothesis that the ratio of elements from the treatment process is an important parameter in determining corrosiveness, as discussed in the next section). There was some evidence that for a single batch of timber, the higher the preservative concentration the greater the corrosivity. However, the resistivity of the untreated timber seemed as important a factor, if not a more important one.

The previous proposals of a threshold moisture content of around 20% for the corrosion were confirmed by this study. In both treated and untreated timber, there appeared to be a difference of about a factor of 10 between mass loss of zinc at 14% timber moisture content from that at 23% moisture content. This trend also held for iron in untreated timber, but for iron in CCA-treated timber the scatter was too great to derive a relationship.

The results found in this study compare fairly well with those reported by Simm and Button (22). These studies also involved electrochemistry using treated timber as electrolyte, but had to use heavily wetted blocks because they were using DC electrochemical techniques. They, too, found problems with timber variability. Thus, predicted corrosion rates for mild steel in 7.9 kg.m⁻³ CCA treated timber ranged from 45 to 170 um/yr while for zinc in this system, values from 76 to 124 um/yr were predicted. This suggests, as did the AC impedance study, little real difference in mild steel and zinc corrosion rates in treated timber. Table 1 is reproduced from Reference 22, and shows the order in which these authors ranked

corrosion susceptibility as a result of their electrochemical measurements.

Three entries in particular should be discussed. Firstly, while the aluminium alloy gave quite favourable electrochemical values, traces of deposited copper were subsequently found on the surface. This has quite serious implications for longer term corrosion of the aluminium. Secondly, chromating the zinc did not affect its susceptibility to corrosion in treated timber very much. Moving from sapwood to heartwood had much more effect. (Possibly this was due to lower preservative levels in the heartwood, a hypothesis which is not investigated by Simm and Button. No copper was found on the zinc electrode removed from heartwood after the test, whereas it was present on all the other electrodes except stainless steel which had been in CCA-treated timber).

The third point of interest was that the stainless steel electrodes gave very low predicted corrosion values. Most other investigations (e.g. (3), (15)) have also found favourable behaviour of austenitic stainless steels in this application. It would seem that austenitic stainless steel is a suitable material for this use, provided there is reasonable assurance that the conditions for stress cracking will not be present (i.e. warm, chloride-containing conditions).

THE EFFECT OF DIFFERENT RATIOS OF CHEMICALS IN CCA PRESERVATIVE FORMULATIONS

It was noted earlier that contradictory reports have been published on the corrosivity of CCA-treated timber. Finding a way to reconcile these reports is hindered by two factors:

- (a) Many of the papers which discuss this topic have been presented to meetings and not subsequently published, so that only a few workers know of them, and
- (b) Many papers do not supply information on the actual concentrations of chemicals in the timber.

Chromates are known to be good corrosion inhibitors (21). It is known that some chromate can be free in CCA-treated timber and so could be inhibiting corrosion. It is also known that the amounts of free copper and chromate in the timber are considerably affected by the ratio of copper to chromate (10). Table 2 lists the Cu: Cr ratios in treated timber used in studies referred to in this paper. It highlights the paucity of information from which to work in assessing the likely comparability of studies. There seems scope for a study (similar to that reported by Smith and Williams (10) on leachability of components as a function of element ratio) on the corrosivity of timber as a function of element ratio.

Details have been published previously (23) of an electrochemical evaluation of electrode behaviour in an agar gel, as a very rapid method of screening for possible severe corrosion problems of fasteners in treated timber. It has two advantages, compared with timber: that the concentrations of chemicals added to the gel can be controlled very closely, and the distribution through the gel is even (as opposed to the anisotropic properties that timber possesses, and the variability in distribution of preservative chemicals through timber (24)). There are

uncertainties in the method due to voltage drops due to the resistivity of the gel between electrodes, and an unknown degree of fixation of the chemicals to the gel.

This screening technique has been developed further (25) to examine the effect of using a slightly different medium (with a starch used as the immobilising agent) and to examine the effects of interactions of chemicals. The concentrations of Cu(II), Cr(VI) and As(V) used were chosen arbitrarily. They should be realistic because they represent a few per cent of the required preservative retention levels (20). Similarly, 0.044M Na₂SO₄ was added to the gel to represent the "carrier" salts from the treatment. (This added salt is desirable to provide increased conductivity in the cell. The assessment method works without it, but less well.)

The effect of a change (both the single trace addition and that as part of a Cu-Cr-As system) in the Cr(VI) concentration was assessed as part of the experimental programme. Some of the results are summarised in Table 3. Changing the chromate concentration from zero to 0.25mM had no statistically significant effect. However, on increasing the Cr(VI) concentration to 2.5mM, (and so reducing the Cu/Cr ratio from about 12:1 to about 1:1) statistically significant corrosion inhibition occurred on galvanised steel, brass and aluminium.

Chromate is generally regarded as inhibiting the anodic reaction in corrosion cells by forming a less reactive film over the surface. There is some danger that too small a concentration will enhance corrosion, rather than inhibit it, by creating variable surface chemistry. There is evidence from Table 3 that this corrosion enhancement could be happening at the "low" concentration on aluminium, and the "high" concentration on mild steel.

Table 3 indicates that it could be worthwhile pursuing further the much slower processes involved in corrosivity testing using actual timber. The biggest experimental difficulty could be in obtaining adequate amounts of timber which have the various ratios of chemicals in them.

BREAKDOWN OF THE TIMBER MATRIX

Once iron ions are liberated into the timber matrix, they can react with the chemicals constituting the timber. Previous studies (26) (27) showed that there appeared to be a loss of tensile strength of the timber, indicating degradation of the cellulose component.

These studies had not resolved the mechanism of the interaction. Subsequently, mechanisms have been proposed for radical routes (28,29). BRANZ therefore sponsored a study of this mechanism and of the effects of various chemicals on the rate of degradation (30).

1,5-Anhydrocellobiitol, a molecule which incorporates one acetal linkage which closely resembles the glycoside linkage of cellulose, was used as a model compound, and its rate of degradation (by oxidation of the glycoside linkage) in the presence of various additives to the solution was studied. In an aqueous solution containing 0.001M iron ions, with oxygen bubbled through, 40% of the compound had been degraded after days at room temperature. By heating the solution to 80° C, this proportion was

increased to 70% after 28 days. The reaction rate was negligible if the solution was not oxygenated or the iron was omitted.

Other metal ions were then added. Copper (II) salts had little effect on the degradation reactions. Chromate ions also had little effect when alone, but markedly inhibited degradation in presence of iron ions. Arsenate had no effect, neither causing degradation when present on its own, nor altering the degradation rate when present with iron ions. This same behaviour was observed for chromium (III), zinc (II) and aluminium (III) ions.

The experiment was repeated, at 20° C with hydrogen peroxide additions rather than oxygen bubbling through the solution. This was done on the basis that hydrogen peroxide is involved as an intermediate in the air oxidation of cellulose, and with the expectation of accelerating the degradation process. This acceleration was found to occur. Though the temperature was 60° C lower, degradation in the presence of iron ions was almost complete within 5 days. The only added ion which produced different behaviour from an aerated solution was chromate. It no longer inhibited the degradation when on its own in solution, but actually enhanced it, and provided minimal inhibition when present with iron ions. (The formation of peroxy chromium complexes was suggested as the reason for this, but it was not proved conclusively.) Although it is not recorded in the published paper (30), chromium (III) ions had no effects in this solution different from those in the oxygenated solution).

From the point of view of this paper, the important result to emerge from this study was that zinc, aluminium, copper and chromium (III) ions, irrespective of the medium, did not produce significant degradation of the anhydrocellobiitol. This suggests it may be acceptable to have these ions free in the timber, but unacceptable to have iron ions - or to put it another way, it may be acceptable to have zinc-coated steel products corrode slightly (to lose some of the zinc coating) provided the steel substrate is not exposed. Aluminium or copper fasteners, even if they corrode slightly should not cause timber degradation, and so the chief question to be faced with these is the suitability of the fastener for its structural purpose.

AVOIDING PROBLEMS

Whitney (31) gave a comprehensive list of means by which corrosion problems on bolts in timber poles used for pole house construction could be avoided. This is a specific application where a little corrosion does not cause extensive weakening of the embedded metal because of the large cross-section of the bolts but could create considerable problems if the timber began to break down. Keeping iron ions away from the timber is therefore the major requirement.

Hot-dipped galvanising is the absolute minimum requirement for protection. (Zinc electroplating produces a much thinner zinc film, and so will expose the underlying steel to the timber much more quickly.) Sometimes even this hot-dipped zinc coating may be lost too quickly, and additional protection is needed (for example, in situations which are very wet, such as close to the ground). The methods for this discussed by Whitney (31) ranged from coating with grease to application of a heat-shrink plastic sleeve.

However, all these methods are recognised to have some danger of operator error. Using powder-coated galvanised steel bolts (32) is one way to avoid some of the possibility of error.

Because such powder coating is applied in a factory situation, there is a chance that it will be done under optimum conditions. The coating covers the bolt head, and so it is easy to inspect that appropriately coated bolts have been used. The question of the danger of the powder coating softening through long-term exposure to pine oils has been raised. Though no cases of this have been reported, it is not possible to rule out. However, it is regarded as a negligible problem in that the coating will still inhibit diffusion processes to and from the zinc surface, and so render protection. Using powder-coated hot-dipped galvanised steel bolts also is cheaper than using stainless steel (or silicon bronze) bolts in such situations. Using these more resistant metals is the solution proposed by the Greater London Council (GLC) (33) where heavily treated timber is to be fixed for long-term outdoor service.

When there is danger of the fastener losing its ability to function (such as can happen with nails or thin-plate fasteners), then using a corrosion-resistant metal is a much more appropriate response. Four different applications of nails or staples in timber should be considered.

The first case is that of a very acidic timber being used, untreated. Aluminium or copper or stainless steel are appropriate fastener materials in this case (6).

The second case is that of treated timber which is to be fastened and will remain wet for long periods in service. If copper is present in the preservative, the environment can be very corrosive for aluminium or hot-dipped galvanising. A study of 53 hot-dipped galvanised nails from an 8-year old timber fence at BRANZ Judgeford research station showed that over 60% of the nails had lost so much zinc that the steel was beginning to corrode. The residual zinc weights on the nails are shown in Figure 2. Zinc electroplated mild steel bolts which had held gate hardware were also studied. These bolts had lost virtually all their zinc and the result was severe corrosion of the underlying steel. Copper is a satisfactory fastening material in this application, though surface staining around the heads of exposed fasteners can cause some aesthetic problems. The most favoured material for nails or staples in this application is austenitic stainless steel.

Plastic-coated mild steel nails have been produced, and suggested as suitable for such uses. However, if any rupturing of the plastic coating occurs the steel underneath can corrode. While the plastic layer may keep the corrosion products away from the timber, the nail may lose sufficient strength to be rendered ineffective. Such nails should be avoided unless the plastic coating is in turn applied over a hot-dipped galvanising layer.

The third case is that of timber which is occasionally wetted in service, but is generally at or below 20% moisture content. Under these conditions, hot-dipped galvanised nails should be adequately durable, and where these have been punched and stopped, they have proved satisfactory for painted external weatherboards.

If timber remains dry in service, mild steel is a satisfactory material for fasteners.

Indeed, an important factor in avoiding problems is keeping any timber as dry as possible in service, and particularly avoiding collection of water at joints which are secured by metal fasteners. Often, the simple precaution of running one additional weatherboard around the base of cladding can protect a whole row of nailed or bolted joints in framing.

Nail plates pose a special problem. They have a much greater cathode-to-anode area ratio than are of thin-gauge material and so could lose a significant portion of their strength if corrosion occurred. Thus, any corrosion problems could be very serious. European Agreement requirements (34) for the effective use of galvanised steel nail plates (or toothed plate connectors) are that the timber around the nail plate will never have a moisture content greater than 22%, and that the moisture content will not exceed 18% for any significant period. These values correspond to equilibration of *Pinus radiata* to atmospheres at 15°C with 87% and 80% relative humidity respectively (7). During the building process, it is probably not practicable to require that timber framing on the site does not get wet, as complying with the Agreement recommendations (34) would require. Traditional practice in New Zealand has been to allow nail-plated trusses to be fully exposed to the weather while the building claddings are applied. This does not yet seem to have resulted in serious nail plate degradation problems such as have been reported from other countries (e.g. (35)), but it would obviously be sensible to minimise the exposure of such timber components to the weather.

CONCLUSIONS

There can be problems of materials degrading when metals interact with timber (particularly treated timber) in which they are embedded. However, an understanding is developing of the processes involved and how to minimise degradation problems. Some tips for avoiding problems are:

- (a) The moisture content of the timber in service should be as low as possible.
- (b) Recognise that if moist conditions exist, heavier preservative treatments will be required for timber, and that these treatments may introduce more severe corrosion problems and necessitate the use of special fastener materials.
- (c) Do not use recently treated timber (treated within, approximately, the previous two weeks) because the salts which are free in the timber could cause severe corrosion problems in metals coming into contact with the timber. Allowing fixation to proceed will lessen these problems, though never totally prevent them.

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investigations of cellulose degradation reactions and of measurements of corrosion rates in timber using AC impedance techniques.

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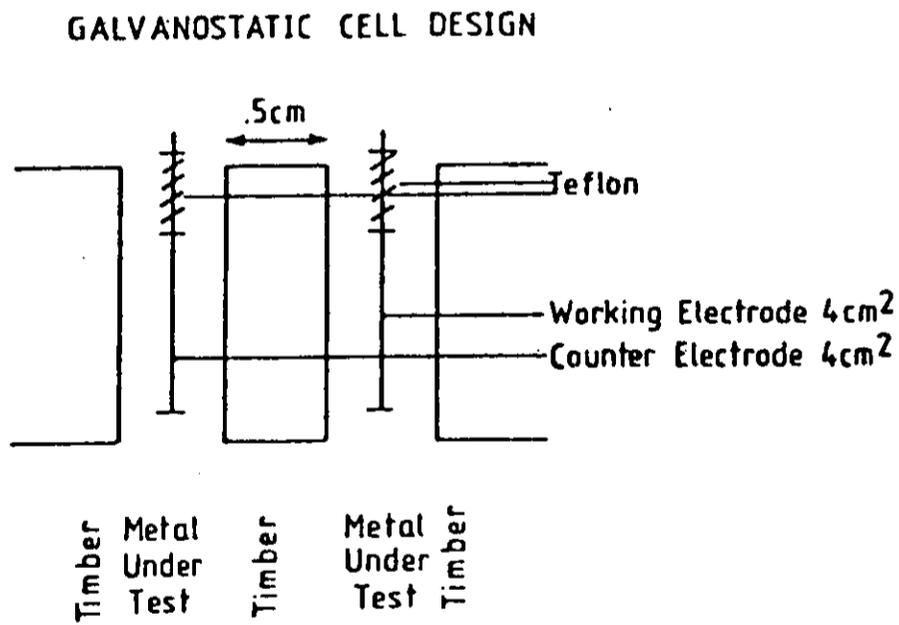
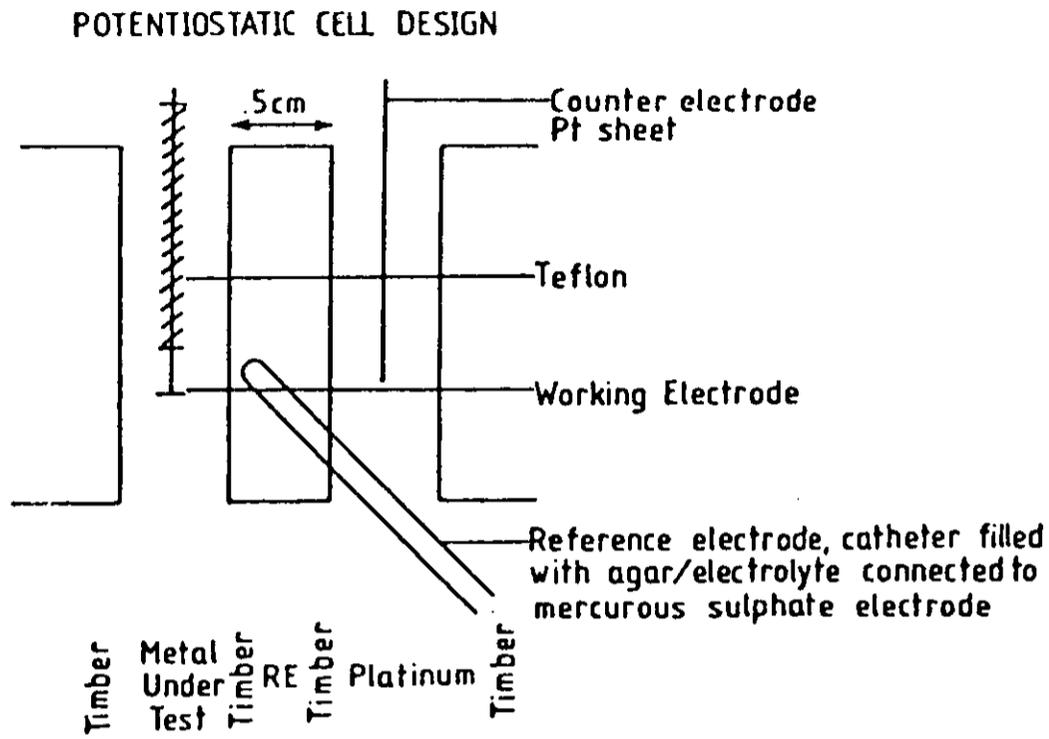


Figure 1 : Cell designs used in study of, metal electrochemistry using a treated timber electrolyte. (from contract report submitted by Smedley).

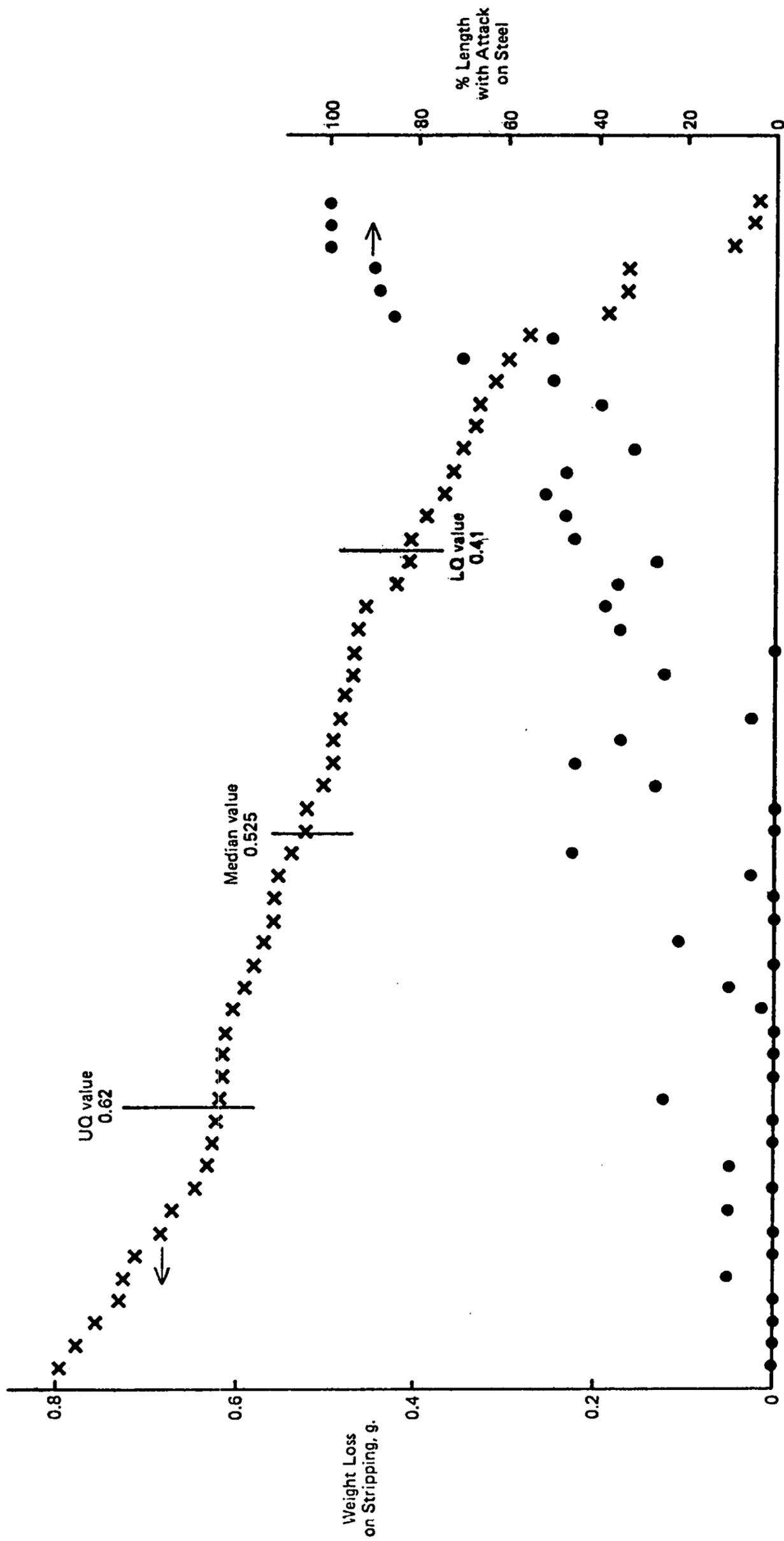


Figure 2 : Residual zinc weights and assessment of attack on steel for hot dipped galvanised steel nails taken from CCA-treated timber fence after eight years.

TABLE 1. ORDER OF CORROSION ACTIVITY (from (22))

<u>Metal/Wood Combination</u>	<u>Relative Corrosion</u>
Zinc/C C A treated Steel/C C A treated Passivated Zinc/C C A treated Steel/Untreated Aluminium alloy/C C A treated Zinc/Untreated Zinc/C C A. treated heartwood Aluminium alloy/untreated Stainless steel/C C A treated Stainless steel/Untreated	Highest corrosion  Lowest corrosion

TABLE 2. TOTAL COPPER TO TOTAL CHROMIUM RATIOS IN TREATED TIMBER
IN REPORTS OF INVESTIGATIONS OF CCA-TREATED TIMBER
INTERACTIONS WITH METALS

Reference	Timber species	Cu/Cr ratio in CCA salt formulation	oxide formulation
3	Southern yellow pine	not used	insufficient data
8	<u>Pinus sylvestris</u> , <u>Picea abies</u>	not used	insufficient data
9	Various	insufficient data	not used
10	lime, scots pine	various ratios	not used
11	Various	insufficient data	not used
13	not given	insufficient data	not used
14	<u>Pinus sylvestris</u>	0.51	0.34
15	<u>Pinus sylvestris</u>	Approx 0.4	Approx 0.5
18	<u>Pinus radiata</u>	1.0	not used
24	Various	not used	insufficient data

TABLE 3. EFFECTS OF Cr(VI) CONCENTRATIONS ON POLARISATION
RESISTANCE VALUES (OHMS) MEASURED FOR METALS IN STARCH GELS

	Cr only			Cu x Cr x As		
	No Cr	Low	High	No Cr	Low	High
Mild Steel	450	450	275	250	300	180
Galvanised Steel	280	340	1350*	110	95	350*
Brass	6000	8500	14500	515	630	12000*
Aluminium	7400	6500	25000	630	340	20000*

- Notes:
1. "Low" implies $2.5 \times 10^{-4}M$; "High" implies $2.5 \times 10^{-3}M$ $K_2Cr_2O_7$
 2. The chemical components other than Cr (VI) in the CCA addition are $0.044 M Na_2SO_4$ (present in all gels), $3 \times 10^{-3} M CuSO_4$, and $2.7 \times 10^{-3} M As_2O_5$.
 3. * implies significant difference of this "high" value from that for the corresponding "low" entry. There were no significant differences between "No Cr" and "low" entries.
 4. The higher the numerical value, the greater the resistance to corrosion.

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Corrosion of metal fasten
ers embedded in timber.Co

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