Corrosion of Embedded Ferrous Metals in Woods

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Abstract

Wood is a widely used renewable material. The corrosion has been observed for ferrous metals embedded in the wood. The wood is a corrosive material by its nature. The corrosivity of wood is highly depending on its speciation and its natural constituents e.g. moisture, acetic acid, ester, as well as added chemicals such as salt, fungicide, pesticide, fire-retardant etc. Corrosion scientists also believe that wood provides a corrosive environment through permeable structure acting as an electrolyte sponge. Recent research is not only focusing on understanding the corrosion mechanisms but also on test methods to evaluate its corrosion behavior. Efforts are made on numeric simulation to quantitatively determine the corrosion performance of the metal embedded in woods. Various building codes and technical bulletin have provided the directive and guidance to mitigate such risks.

Introduction

Timber is the most widely utilised natural materials in human history. It is a renewable material and readily available. Ferrous metal fasteners and fixtures are often used in the timber structure. They are generally reliable and maintenance free. However, the pre-mature corrosion failures are identified in the history [1]. Field experience and test even suggested higher corrosion risk for outdoor applications [2]. If not attending carefully, it will lead to serious consequence.

The corrosion in wood usually refers to three related but distinguished topics:

1) corrosion on metals embedded in woods, such as fasteners and nails in buildings;
2) corrosion of metal in wooden environment, such as display cabinet etc [3];
3) degradation of wood itself due to its interaction with metal and metal corrosion products [4, 5].

In this summary, the focus is on the first the scenario, while the ferrous metal fixtures embedded in a timber environments. This is common in household, in which nails, fasteners, flashes are used in timber frame, fence and furniture etc. in some case, the corrosion of these embedded metal fixture cause the failure of the structures. The understanding and mitigation of embedded ferrous metal in wood is of importance for building industry and property owners (Figure 1).

Figure 1 Corrosion of ferrous metal fixture embedded in timber structure [6]

There has been lots of research in this topic since 1950s. It attracted further attention recently due to the phasing out of some types of wood treatment chemicals [6], e.g. Copper-Chrome-Arsenic(CCA).

Corrosion mechanism in wood environment

Wood as a corrosive environment

Natural corrodents

Wood is a natural polymer with principal constituents of cellulose (Figure 2), hemicellulose and lignin.

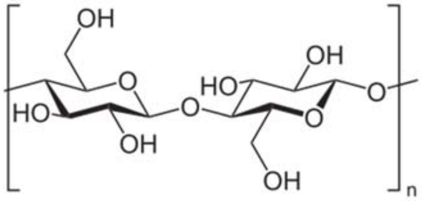


Figure 2 Chemical structure of cellulose

Cellulose is sugar molecules joined in long chains. Portion of hydroxyl radicals is combined with acetic acid radicals forming of ester. The chemistry of wood is analysed through wood extract chemistry, which is a mixture of organic acids (mainly acetic and formic acid), tannins (or more broadly, polyphenols) and phenols with two or three adjacent hydroxyl groups (e.g., catechol and pyrogallol) [7].

Due to variety and complexity of wood, the corrosivity of wood is quite complicated. It is highly depending on the speciation and growing environment. NPL's guide [8] suggested some key elements in this regard:

1) Initial acid content
2) Total amount of acetyl available for hydrolysis
3) Hydrolysis reaction kinetics, i.e., the readily available acetyl for hydrolysis

Acetic acid

Acetic acid is one of most important naturally occurring corrodents in wood [8]. Acetic acid is a byproduct from wood hydrolysis reaction.

For ferrous metal embedded, the corrosivity of wood can be measured by acetic acid as an indicator. However, the hydrolysis is a slow reaction and only occurs while the moisture content exceeds the threshold. The release of acetic acid can last for life span of the wood structure. Therefore, it is essential that two factors are considered:

1) pH of the wood, which is an indicator the corrosivity of wood from acetic acid at time of testing;
2) The acetic acid capacity, which is an indicator of the total amount of ester groups can be hydrolysed to produce the acetic acid

The relative acidities of wood were studied by mixing of 5 parts of distilled water with 1 part of wood sawdust [8]. It was reported that corrosivity of woods is significantly different. pH of some aggressive timbers (e.g. oak, sweet chestnut and western red cedar) can be as low as 3.4. Others show moderate corrosivity with pH ranging from 5.0 to 8.8 (e.g., elm, parana pine). The experiment also confirmed that release of acetic acid could last for long time as long as damp condition persisted. This is largely aligning with the corrosion observed, e.g screws in eucalypts suffered severer corrosion than those embedded in acacia wood since the eucalypts extract showing lower pH [9].

Moisture content

The amount of moisture is the most important single factor for the corrosion. Wood is a hydrophilic polymer and can hold over 200% of its dry weight as water. It can exist in wood as free water (liquid water or water vapor in cell lumina and cavities) or as bound [7]. The threshold moisture content is required for sustaining the corrosion. It was reported that dry timber has little effect on metal corrosion. However, when the moisture content of the treated wood approaching to about 20 percent, the electrical conductivity increases to where corrosion can occur [10]. Below this threshold, embedded metals normally show no significant corrosion. Corrosion rate increases with moisture content and maximized at near or above fiber saturate point, which normally occurs at approximately 30% moisture.

The moisture in wood creates a corrosive environment for ferrous metal embedded. There are multiple implications for the progress of the corrosion [7]:

1) by prompting acetic acid through hydrolysis reaction of cellulose;
2) by uptaking oxygen to produce electrochemical concentration cells;
3) by breaking down the passivating layer with dissolved solid, e.g. chlorides

It was reported that birch developed aggressive acidity by storing under damp conditions at 48^{o}C. value of pH dropped from initial 4.60 to 3.32 within 126 days storage [8]. The moisture of timber has more complicate influence other than producing acetic acid. For example, it also helps releasing of tannins, which is a mild corrosion inhibitor for embedded ferrous metals. Zelinka and Stone suggested that tannins decreased the corrosion rate at a given pH., whereas, lowering the pH increased the corrosion rate at a given level of tannins. They developed an isocorrosion map for the water extracts to reflect the general corrosion trending for the different wood species [7].

Processing chemicals as corrodents

a) Salt from drying process

Sodium chloride, sodium nitrate or urea are the most common salts used in wood salt seasoning dry process. It was reported that up to 4% of slat can be introduced into wood by this process. Salt absorbed by the wood lowers the vapour pressure of water. Meanwhile, it prompts the corrosion of embeded metals such as screws, brackets and other metallic compounds. As an example, salt seasoned the maple, which is often used as an intricate action parts in piano, is often found to sustain this kind of corrosion.

b) Fire retardant

The most commonly used chemicals for fire-retardant are mono- and di-ammonium phosphate, ammonium sulphate, boric acid and borax. Ammonium sulphate is acidic and considered as corrosive (report for boric acid/borax study).

there is controversy for the boron compounds [11]. Some suggested it is not corrosive. However, Baker et al believed that it is corrosive in humid environment [10]. Since some of fire retardant are hygroscopic, it can be corrosive to metal embedded even with low relative humidity environment [10]. Other formulations do include corrosion inhibitors such as sodium dichromate and ammonium thiocyanate.

c) Wood preservatives

There are various types of wood preservatives in use as fungicide and termiticides showing different corrosive nature:

1) non-corrosive wood preservatives
   Creosote or coal tar oil and zinc naphthenates have minimum corrosion impact on ferrous metals. Baker et al reported that corrosion of metals in oil type preservatives is usually not a problem except in railroad ties. The discrepancy in corrosion performance is more from the construction method rather than wood species and chemical in use. In wharf and shoreline bulkhead construction, the timber structure is pre-drilled with the holes before it is treated with creosote or coal tar oil with pressure impregnation process. Therefore, the core holes are filled with oil type inhibitor. Even assembled ferrous metal fasteners ((normally hot dip galvanized steel) are exposed to salt water, the corrosion is insignificant. Whereas in rail ties application, the holes and the rail spikes are performed after treatment. It shows severer corrosion even rainfall water appears less aggressive than in wharf application [10]
2) Corrosive wood preservative
   Copper-Chrome-Arsenic (CCA) was the most widely used and studied corrosive wood preservative until recent years [2]. Although the chromate showing some corrosion inhibitive effect, sodium sulphate and copper compounds are quite aggressive for embedded metal. It is normally believed that fixed chemical compounds having less corrosive effect. However, these compounds can be leached in fresh treated timber and after exposure to wet service conditions [12]. It is recommended to avoid use timber immediately after its treatment.
   Alkaline Copper Quaternary (ACQ) has been introduced as a CCA replacement due to environmental and health concern while CCA been gradually phased out in United states, European Union and Australia. Alkaline copper quaternary (ACQ) is a mixture of copper oxide (67%) and a quaternary ammonium compound (DDAC-didecyldimethylammonium chloride or carbonate 33%) [7]. When it was first commercially available, the quaternary ammonium compound was made with a chloride formulation but was almost exclusively replaced with a carbonate formulation [7]. Recent research demonstrated that ACQ treated timber showing aggressive corrosive nature, potentially due to it is high copper content formula [13].

Major Corrosion mechanisms

The corrosion of embedded metal in wood is rarely induced by a single mechanism. Crevices corrosion and galvanic corrosion, are the two most common corrosion mechanisms.

Crevices corrosion mechanism

Cervices corrosion mechanism is considered as a major mechanism for isolated metal fastener in damp wood. It was noted that the exposed end of a steel fastener quickly shows evidence of hydroxyl ion (OH^-) formation. This indicates that the exposed head of a nail, or of some other metal fastener, becomes the cathode and the shank becomes the anode of a galvanic corrosion cell. This is a result of electrochemical differential concentration cell [10] (Figure 3).

Figure 3 Crevices corrosion in metal bolt embedded in wood

The chemical reaction at the cathode (exposed end) can be written

$O_2 + 2H_2O + 4\,e \rightarrow 4OH^-$

The reaction at the anode for a steel nail (buried end) can be written as follows:

$Fe \rightarrow Fe^{2+} + 2\,e$

Ferrous ions (Fe(II)) liberated at the anode are oxidized readily to form ferric ions (Fe (III)) and can react to form either black iron tannate dyes or oxide. Damp wood can be considered as an electrolyte or slightly acidic solution. Soluble chlorides present in the bulk solution can migrate to a steel nail and result in accelerated corrosion of the nail. As the reactions at the anode and the cathode proceed, chloride ions (Cl^-) and hydroxyl ions (OH^-) migrate from the bulk solution into the crevice between the nail and the wood. Ferrous and ferric ions formed at the anode in the crevice react with hydroxyl ions in both the crevice and bulk solution to form insoluble iron hydroxides depending on the availability of oxygen. The formation of insoluble iron hydroxide in the crevice leaves the solution more acidic because of the relative decrease in concentration of hydroxyl ions compared to that of the hydrogen ions (H^+). The solution within the crevice thus becomes acid due to high concentration of (H^+). This can be demonstrated from most of metal loss is in part submerged in damped wood (Figure 3).

This corrosive environment is the reason of protective corrosion product film different to that formed in atmospheric corrosion [14]. It is a common mis-conception of referring the embedded corrosion in wood as atmospheric corrosion [15]. Whereas, two may end up with quite different corrosion behaviors for ferrous metal. In atmospheric environment, galvanic zinc forms hydrozincite and smithsonite, which provides better protection for the underlying steel than geothitie (α -FeOOH), commonly known as red rust from bared steel. This is the exact reason galvanic zinc coated steel renders better corrosion protection than bared steel under atmosphere. However, in damped wood environment with localized acidic crevices, different corrosion products formed. There was no smithsonite on the zinc fasteners observed. Instead, namuwite {Zn2(SO4)(OH)6 4H2O}, simonkolleite {Zn5(OH)8Cl2 (H2O)}, and in some cases hydrozincite are the corrosion product. The lack of a protecting passive layer explains why galvanized fasteners corrode more rapidly than steel fasteners in some solid wood [7].

Galvanic corrosion mechanism

Galvanic corrosion mechanism is also termed as dissimilar metals mechanism, in which two different metals in contact stay in a corrosive environment forming a galvanic cell. This results in an accelerated corrosion of the less corrosion resistant metal and very little attack of the more noble metal. As discussed before, waterborne preservatives such as CCA, CuAz and ACQ containing copper salts can deposit small quantities of metallic copper causing dissimilar metal corrosion.

The importance of cupric ions on the corrosion mechanism in preservative treated wood is partially agreed with high content of copper in newer ACQ recipes than that in CCA, although there is no clear evidence of function of cupric ions in fastener's corrosion product [7]. It was reported that severity of mild steel corrosion increases in the order of untreated, CCA CuAZ and ACQ. Hot-dipped galvanized steel corrosivity generally increases according to order of CuAz/CCA, ACQ [16].

Stress corrosion cracking

Caustic stress corrosion cracking is rare but not none reported in wood corrosion. Caustic stress corrosion cracking of tempered carbon steel nails (quenched and tempered AISI 1035 carbon steel) has been observed when used in Douglasfir (Pseudotsuga menziesii (Mirb.) Franco) and western larch (Larix-occidentalisNutt.) exposed to a warm humid environment over log heating chambers in veneer mills. Although chloride stress corrosion cracking of austenitic stainless steel is widely known by corrosion engineers, , there is no report of chloride stress corrosion in wood application for 316 and 304 [10].

Test methodology

There is lack of universal and widely accepted test methodology for severity of the embedded metal corrosion in wood. This is partially due to the nature of timber and variety of their service conditions. The pH values of woods are of direct relevance to corrosion by contact. For example, experience has shown that four most acidic woods, such as oak, sweet chestnut, western red cedar and Douglas fir, showed more corrosive nature towards metals embedded under damp conditions. However, that is not the full story. Acid content varies with the section of timber pieces, from heartwood to sapwood (heartwood being usually somewhat more acid). For deeply embedded fasteners, some physical properties, such as permeability of wood towards water, oxygen and carbon dioxide, also plays a part. Iron fasteners in impermeable woods, such as the white oaks, can last a long time even in immersed conditions, probably due to lack of oxygen and of carbon dioxide to decompose the initial acetate corrosion product. Tannins in wood act as corrosion inhibitors, or as an oxygen scavengers to inhibit the crevices corrosion [8]. Timber process method, for example, kiln drying, will have the unexpected effect on wood's corrosive nature by driving more acetic acid out at least in the initial stage [17]. These all aggravated the complexity in designing a universal corrosion testing method. Zelinka and Rammer summarized 22 different testing methods that had been previously used to evaluate their effectiveness [18]. These testing practices can be grouped into the following category:

1) Exposure test
   in which temperature and relative humidity is close to realistic environment, e.g. ASTM International standard G198 "Standard test method for determining the relative corrosion performance of driven fasteners in contact with treated wood [19]". The goal of this type of test method is to evaluate fasteners the relative corrosion resistance similar to the service environment. It specified temperature of 32° C and a cyclic fog relative humidity conditions as testing conditions. There is the argument whether wood is more likely to remain damp condition for extend period of time after rainfall. This may lead to underestimate of corrosive environment in this "cyclic fog" test.
2) Accelerated test
   is using higher temperature and humidity condition to accelerate the corrosion. The purpose of this type of testing is to evaluate the corrosivity of the wood environments rather than provide the corrosion rates in service, e.g. AWPA standard E12, "Standard method of determining corrosion of metal in contact with treated wood" [12]. The test method places metal coupons between two blocks of treated wood and exposes the "sandwich" in a high-temperature (50° C) high-humidity (90% RH) environment for 120 days with specified torque imposed from nylon bolts. Normally, average weight loss rather than corrosion rate is reported as the results of the test [7]
3) Electrochemical test
   is a test to polarize the metal and evaluate its corrosion rate. The inherent drawback of this type of the test is only wood extract rather than wood itself can be used in the test. Therefore, the results are more for comparative purpose than the actual corrosion rate study. Zelink et al utilised polarization resistance measurements in the wood extract to determine to corrosion rate of metal fasteners. They found it having excellent correlation to corrosion rates of fasteners embedded in wood conditioned at 100% RH for 1 year. This is understandable, since wood with 100%RH has similar chemistry to wood liquid extract. However, it is still difficult to determine the actual corrosion rate for ferrous metal fastener under embedded condition by electrochemical test. They concluded that these measurements could not be used to predict corrosion rate of metals embedded in treated wood.
   Kear et al. [16]used impedance spectroscopy, large perturbation potentiodynamic polarization, and polarization resistance measurements to characterize the corrosion performance of mild steel, stainless steel, and galvanized steel in dilute solutions of wood preservatives and found reasonable correlation between this test with the AWPA E17 test.

4) Corrosion rate by digital image evaluation
   In many testing methods, corrosion was reported as a percentage weight loss instead of a true corrosion rate because the surface

area of threaded fasteners could not be calculated readily. Rammer and Zelinka developed a method to calculate the surface area of threaded fasteners from digital images which allows for calculate the surface penetration rate rather than general weight loss. Zelinka et al claimed it a true corrosion rate [7].

Corrosion life prediction

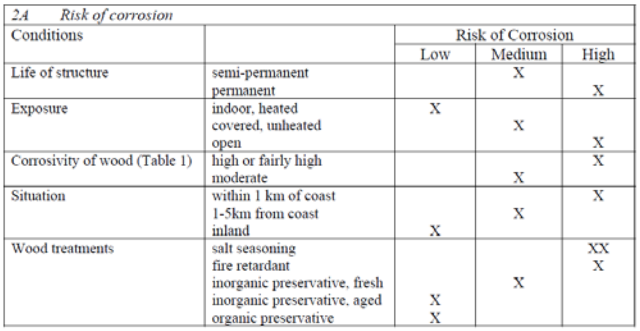
Field exposure method

There were some extensive field exposure trials to investigate the effect of wood on metal fasteners. For example, Research Institutes of Sweden performed long term (up to 9 years) [1]outdoor exposure test to determine the corrosion rate of metal nails and screws in furfurylated and heat-treated wood. This provides a clear guidance for the reliability of embedded metal fastener, particularly under specified exposure environment [17].

Qualitative method

NPL provides a qualitative risk assessment to understand the service condition and further mitigating the corrosion of embedded metal fasteners [8] in which length of storage, exposure conditions, treatments, geo locations and corrosivity of wood are taken into consideration for the risk (Table 1).

Table 1 Qualitative corrosion risk for wood structure (extracted from [8])



2A Risk of corrosion

Conditions		Risk of Corrosion		
		Low	Medium	High
Life of structure	semi-permanent		X	
	permanent			X
Exposure	indoor, heated	X		
	covered, unheated		X	
	open			X
Corrosivity of wood (Table 1)	high or fairly high			X
	moderate		X	
Situation	within 1 km of coast			X
	1-5km from coast		X	
	inland	X		
Wood treatments	salt seasoning			XX
	fire retardant			X
	inorganic preservative, fresh		X	
	inorganic preservative, aged	X		
	organic preservative	X		

Quantitative method

It is more beneficial for industry having predicted corrosion rate to estimate the design life and life cycle maintenance cost. Since the corrosion test has difficulties to provide such information, efforts were made to use numeric model to fill the gap. Australia CSIRO has engaged by Forest and Wood Products Australia (FWPA) to developed a systematic approach in assessing the corrosion rate of embedded metal in wood [20].

The research initiative has built a physical mode to study the service life of timber structures in Australia. A prediction models to estimate the corrosion of fastener embedded in the wood was developed under this project. The physic model of embedded metal corrosion is illustrated in Figure 4

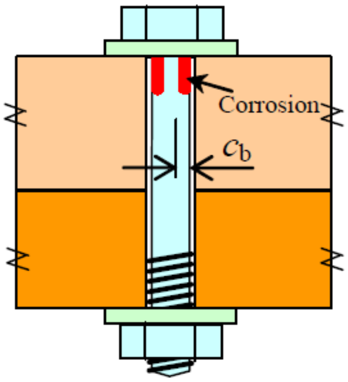


Figure 4 Physical model of embedded metal corrosion in wood (extracted from [20])

The corrosion model considered the following factors:

1) timber acidity
2) timber moisture content
3) wood treatment (CCA treated or untreated)
4) burial depth of the metal fasteners
5) climate and hazardous zone

The model is calibrated by 120 days exposure experiment and verified with 2 years exposure testing for both untreated wood and water bourn preservative treated chemicals

For untreated wood, it can be expressed as:

$$c_o = \frac{1}{2}\left[f_{120}(BTM_{max}) + 0.3 f_{120}(BTM_{mean})\right]$$

For CCA treated wood, it can be expressed as

For Zinc $c_o = 1.3 f_{120}(BTM_{mean})$
For steel $c_o = 2.1 f_{120}(BTM_{mean})$

In which BTM mean and BTM max is the mean and maximum seasonal moisture contents of timber in building, f120 is the corrosion depth at 120 days. The corrosion depth of embedded fasteners in t year is computed by

$$c = c_o\, t^n$$

Zelinka et al intended to integrate the corrosion model with heat and moisture transporting model to establish a prediction model for the embedded metal. The numeric mode is calibrated with one-year field exposure data. It was identified that the rainfall is the most sensitive factor for the embedded corrosion [21].

Mitigation

The corrosion mitigation is only effective by follow the best engineering practice [7] [8]. There are basically two aspects to be managed: one from timber as a corrosive environment, the other from corrosion resistance of ferrous metal fasteners.

Moisture management for timber

Moisture management is the most practical way to minimize the corrosion. The corrosion won't be sustained without sufficient moisture content in timber. There are some specific requirements for managing the moisture:

a. End grain moisture insulation
   It was observed that the moisture uptake from properly treated end grain is the great risk for embedded metal corrosion, e.g. offcut without proper sealing from end. It was reported moisture can travel up to 10 times faster through the end grain.
b. Moisture ingression management
   The proper design to shield the structure off the ingression of moisture is also critical to minimize the corrosion.

Corrosion resistance of ferrous metal

The Standard AS 3566 [22, 23] requires minimum corrosion resistance levels under accelerated testing to the following levels:

1) 1000 hours salt spray testing
2) 15 cycles Kesternich (acid rain) testing
3) 2000 hours QUV testing (for organic coatings)
4) 1000 hours humidity testing.

1) Proper use of coatings

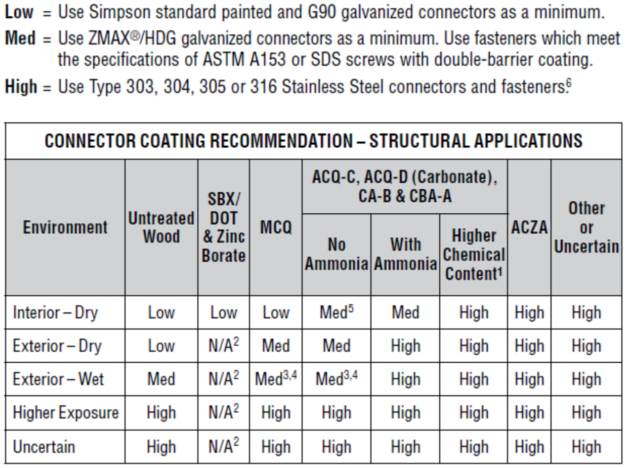
The coatings are common mitigation for metal corrosion. The limitation of coating in particulate application has to be evaluated carefully. There is also report that Steel nails coated with zinc, cadmium, and tin-cadmium do not appear suitable when long damp service is required [24] . The most common coating in use is zinc plating, hot dip galvanizing or polymer coating with varnish or other paint coating for specific purposes. Hot dip galvanizing is the most commonly used economical method of improving the durability of nails in timber, as it applies a very heavy coating to the fastener compared to zinc plating. In addition, the alloying of the zinc to the steel in the hot dip galvanizing process provides an extremely hard and durable coating providing better mechanical protection for coating. The thickness of the hot dip galvanized coating is generally in excess of 40 microns and is typically 6-8 times the thickness of zinc plating used on fasteners [25]. Electroplated fastener and metal products are typically not accepted by the building codes for use in exterior application, regardless of the type of wood in use [26, 27].

The integrity of coating is critical to achieve the desired corrosion protection goal. Coatings failure often happens during the installation. The fixtures with a nonmetallic coating had much worse corrosion performance after its integrity been compromised. This kind of risk can be minimised by implement of practice of pilot hole drilling.

2)Materials selection

Some vendors provided their own technical guidance on the selection of fastener materials [15, 28, 29]. According to technical bulletin of Simpson [30], standard painted and G90 galavnised is a minimum requirement for preservative treated timber, while Type 304/316 stainless steel is highly recommended in high corrosive environment outline in the Table 2.

Table 2 Fastener materials selection recommendation example (extracted from [30])



Low = Use Simpson standard painted and G90 galvanized connectors as a minimum.
Med = Use ZMAX®/HDG galvanized connectors as a minimum. Use fasteners which meet the specifications of ASTM A153 or SDS screws with double-barrier coating.
High = Use Type 303, 304, 305 or 316 Stainless Steel connectors and fasteners.[6]

CONNECTOR COATING RECOMMENDATION – STRUCTURAL APPLICATIONS

Environment	Untreated Wood	SBX/ DOT & Zinc Borate	MCQ	ACQ-C, ACQ-D (Carbonate), CA-B & CBA-A			ACZA	Other or Uncertain
				No Ammonia	With Ammonia	Higher Chemical Content[1]		
Interior – Dry	Low	Low	Low	Med[5]	Med	High	High	High
Exterior – Dry	Low	N/A[2]	Med	Med	High	High	High	High
Exterior – Wet	Med	N/A[2]	Med[3,4]	Med[3,4]	High	High	High	High
Higher Exposure	High	N/A[2]	High	High	High	High	High	High
Uncertain	High	N/A[2]	High	High	High	High	High	High

Field experience indicating stainless steel types 304 and 316, copper, and silicon bronze appear to be suitable material for fasteners when long damp service is required in ACA-, CCA I-, and CCA II-treated wood. [24].

316 stainless steel shows no significant corrosion losses in all of the preservative treatment in market including borax, ACQ, CCA, CuAz etc. [16]

It was interesting to noted that stainless steel, even having satisfied corrosion performance, has a tendency to pop-out [1]. It appears the profile design with proper friction and grab of nail is critical for stainless steel nails.

Summary

Corrosion of embedded ferrous metal in wood is a topic has been explored for many decades. However, it is still of the great interest due to widely used of wood as a renewable materials and complexity caused by the variety of the woods and their processing. Most recently, with the phasing out of traditional preservative CCA, the new preservative chemical brought in the further uncertainties in corrosion of embedded metal fasteners. More research efforts have been progressed to develop the numeric model to predict its life span for improved reliability and lower maintenance cost.

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