DEGRADATION OF WOOD BY PRODUCTS OF METAL CORROSION

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ABSTRACT

A description is given of the source of metal corrosion products that cause wood deterioration around corroding metal in wet wood, such as in rail ties, wooden vessels, and exposed wooden construction. Corrosion of isolated steel fasteners in wood and the formation of acid conditions around the corroding steel is explained in terms of "crevice corrosion." The source of acid and alkaline conditions around corroding metals undergoing galvanic corrosion and the source of alkaline conditions around catholically protected metal are also explained. Several prevention methods are included.

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A weakening is commonly observed in the wood that surrounds corroding metal, such as nails, spikes, screws, bolts, and plates in house siding, rail ties, boat docks, highway trailer beds, and wooden vessels. Wet wood not only causes metals to corrode because wood is slightly acid, but when a metal fastener is embedded in wet wood, certain conditions are created that can accelerate the corrosion of the metal. The corrosion products often can result in slow deterioration of the wood surrounding the metal. Corrosion of the fastener with deterioration of the wood causes loss of strength to the joint and to the structural integrity of the assembly.

Weakened wood is frequently noted around nails in old, weathered house and barn siding that is wetted by rain and snow. The wood that surrounds the nail is usually stained black. Nails pull from the siding with little resistance and frequently come out with some wood attached to the shank. After corrosion has progressed, the shank of the nail under the surface of the wood will corrode away and appear as shown in figure 1. Railroad spikes become loose because of weakened wood around the shank of the spikes. Rail tie plates also corrode and weaken the wood under the plate to the extent that the tie plate crushes the wood. Wooden vessels are said to have "nail sickness" because of weakened wood around metal fasteners and fittings.

The causes and cures of wood weakened around corroding metal have been the subject of several research publications. Marian and Wissing (6-8)-[2] have reported on the chemical analysis and the physical properties of wood in contact with corroding iron. Farber (1) and Savard and Caumartin (10) have shown the iron content of rail ties is high under tie plates and near rail spikes; they indicate the loss of strength is due to the corroding iron. Pinion (9) has reported the corrosion of fasteners in wooden vessels is due to oxygen concentration gradients between the exposed end of a fastener and the end embedded in wet wood.

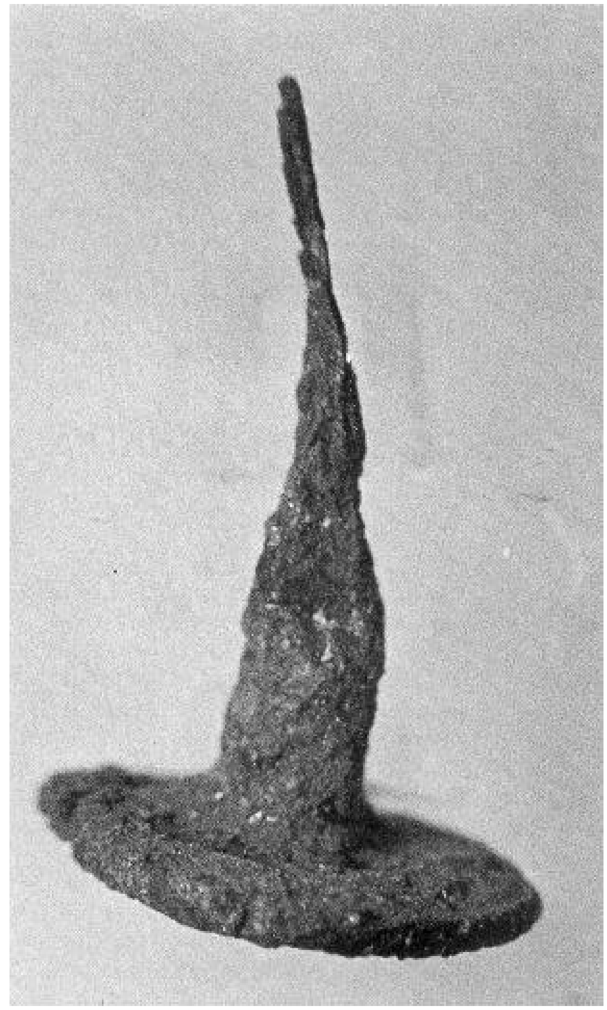

Figure I.—Nail removed from barn siding shows crevice corrosion. (Note that shank has corroded away, whereas head and upper part of shank remain.) *(M141 788-8)*

1 Maintained at Madison, Wis., in cooperation with the University of Wisconsin.

2 numbers in parentheses refer to literature cited at end of this report.

He points out that oxygen concentration gradients can result when wood species with different water permeabilities are fastened together in wet conditions.

This report describes the theory of metal corrosion that relates to the source of the corrosion products that can cause deterioration in the wet wood that surrounds corroding metal fasteners. Some prevention methods are included. Included also are explanations for the cause of wood deterioration around metal fasteners on wooden minesweepers (5).

CORROSION OF A SINGLE METAL FASTENER IN MOIST WOOD

Theory of electrolytic corrosion can be used to explain why a metal corrodes in wet wood and the corrosion products that are formed. For a single or an isolated metal fastener in wet wood, corrosion can be explained in terms of crevice corrosion. This type of corrosion occurs in crevices such as along riveted and welded joints of tanks and pipes. The following explanation of corrosion of a steel nail in wet wood is similar to that of crevice corrosion of a riveted section of-steel in aerated seawater by Fontana and Greene (3) and a report on the degradation of wood by metals by Pinion (9). Figure 2 shows the conditions that are possible after corrosion has progressed.

Pinion noted that the exposed end of a steel fastener in wet wood quickly shows evidence of hydroxyl ion (OH^-) formation. This indicates that the exposed head of a nail or of some other fastener forms the cathode and that the shank must form the anode of a galvanic corrosion cell. The chemical reaction at the cathode can be written as:

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

The reaction at the anode for an iron nail can be written as:

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

Ferrous ions (Fe^{++}) liberated at the anode are not stable and further react to form ferric ions (Fe^{+++}) and react to form either black iron tannate dyes or rust. Iron ions are active catalysts, and they promote chemical reactions that cause strength loss to cellulose and to wood (6).

Soluble chlorides that are present can form acidic conditions around a steel nail in wet wood, and result in accelerated corrosion of the nail and weakening of the wood. As the reactions at the anode and the cathode proceed, chloride ions ($C1^-$) and hydroxyl ions (OH^-) migrate from the bulk solution into the crevice between the nail and the wood (fig. 2). Iron ions formed at the anode in the crevice react with the hydroxyl ions (OH^-) from the water in the crevice and with those that have migrated to form insoluble iron hydroxides. The formation of insoluble iron hydroxide in the crevice leaves the solution 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^+ and accumulation of chloride ions ($C1^-$). These conditions accelerate the corrosion of iron and the formation of more acid. Fontana and Greene (3) report that the fluid within the crevices exposed to neutral dilute sodium chloride solution has been observed to contain 3 to 10 times as much chloride as the bulk solution and to possess a pH of 2 to 3. The acid conditions developed along the shank cause the cellulose of the wood to hydrolyze and weaken the wood.

The hydroxyl ions formed at the external cathode usually will not affect the wood if the exposure is to free water that will wash them away before any appreciable concentration of hydroxide can be formed.

Copper and copper alloys undergo a different form of crevice corrosion than do ferrous or aluminum-based metals when immersed in flowing water (2). With copper and copper alloys, copper enters solution at both the exposed surface and the surface within the crevice. At the exposed surface the copper ions are washed away by the water. This results in higher concentrations of copper ions in the crevice relative to the concentrations at the exposed end, and it establishes a differential metal-ion corrosion cell. The higher concentration of copper ions in the crevice causes the copper metal in the crevice to become cathodic; then the exposed copper metal is anodic. The predominant cathodic reaction is the reduction of oxygen to form hydroxyl ions (alkaline conditions) that in time will cause deterioration to the adjacent wood. This could explain the weakened wood around isolated silicon bronze bolts in minesweepers (5).

Crevice corrosion usually requires an incubation period to develop, but once started it proceeds at an ever-increasing rate.

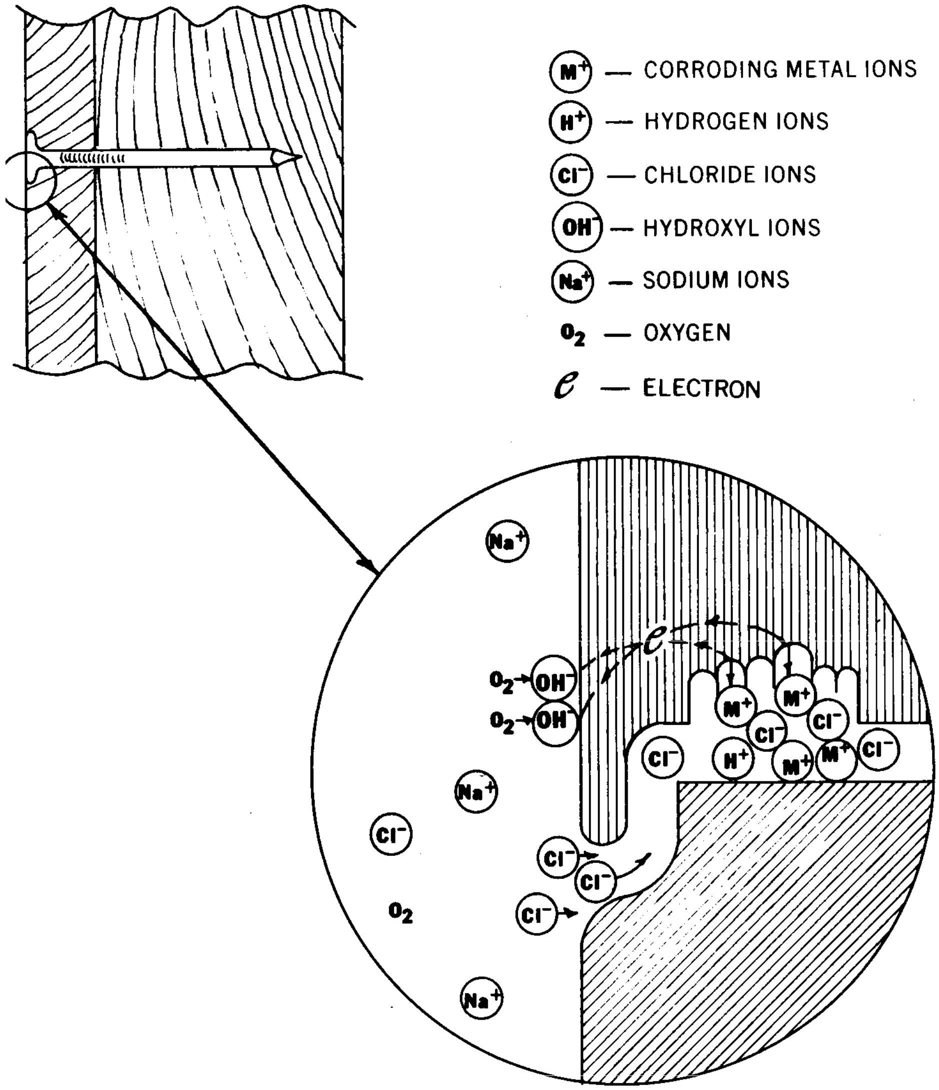

Figure 2.—Schematic of conditions possible after crevice corrosion has progressed.

CORROSION OF DISSIMILAR METALS IN MOIST WOOD

Dissimilar metals in contact in a corrosive or a conductive solution form a galvanic cell that results in more corrosion of the less corrosion-resistant metal and less corrosion of the more resistant metal. The galvanic series of metals and metal alloys can predict the possible galvanic relationships. Thus with dissimilar corroding metals in electrical contact, the most noble metal forms the cathode and the least noble forms the anode. Corrosion or loss of metal occurs at the anode. It is possible that acid could accumulate adjacent to the anode if it is embedded in wood as has been explained. Also, if the anode is iron, active ferrous ions can cause degradation of wood. At the cathode, the chemical reaction depends on the conditions. In neutral conditions, the reaction is:

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

In acid conditions, the reaction is:

$$O_2 + 4H^+ + 4e \rightarrow 2H_2O$$

Since wet wood is acid with a pH range from 4 to 6, the second equation probably best describes the initial cathode reaction. This reaction consumes H^+ ions, and after H^+ ions are depleted, the reaction can be described by the first equation. This explains the common evidence of alkaline conditions around a cathode in wood. After a number of years, the accumulation of alkali will weaken the wood. The oxidation of cellulose is accelerated by alkali in the presence of atmospheric oxygen (4).

CATHODICALLY PROTECTED METAL IN WOOD

The formation of alkaline conditions at the cathode and the resulting wood degradation describe what occurs in wooden vessels around metal that is being catholically protected against corrosion. It is common to protect metal on ships from corroding by cathodic protection, by attaching zinc or magnesium anodes to the vessel and connecting these either directly or by a conducting wire to the metal to be protected. The anode is a sacrificial metal, and it corrodes preferentially to the other metal. For a wooden vessel, the metal to be protected is purposely made a cathode to protect it from corrosion. It is often overlooked, however, that the alkaline reaction product at the cathode, in time, can result in strength loss to the adjacent wood. The end result is that, although the metal does not corrode, the wood surrounding the fastener may fail. The vessel can literally "stew in its own juices" until the wood disintegrates near the protected metal. It probably requires more than 10 years to produce conditions that can cause much loss in strength to the wood, but severe strength loss has been noted in wooden vessels 20 years old. Figure 3 shows some planking removed from a 20-year-old vessel. The wet hull planking was fastened to internal silicon bronze structural straps that were catholically protected. Carbonate salts with pH of 11 were found in the wood in contact with the bronze. The alkaline salts deteriorated the wood.

PREVENTIVE MEASURES

To reduce wood deteriorating around metals in wet wood, metals resistant to corrosion in wet wood and in the surrounding conditions should be specified, and the metals should be used in a manner so that crevice corrosion does not occur. To prevent crevice corrosion, individual fasteners in wood expos-

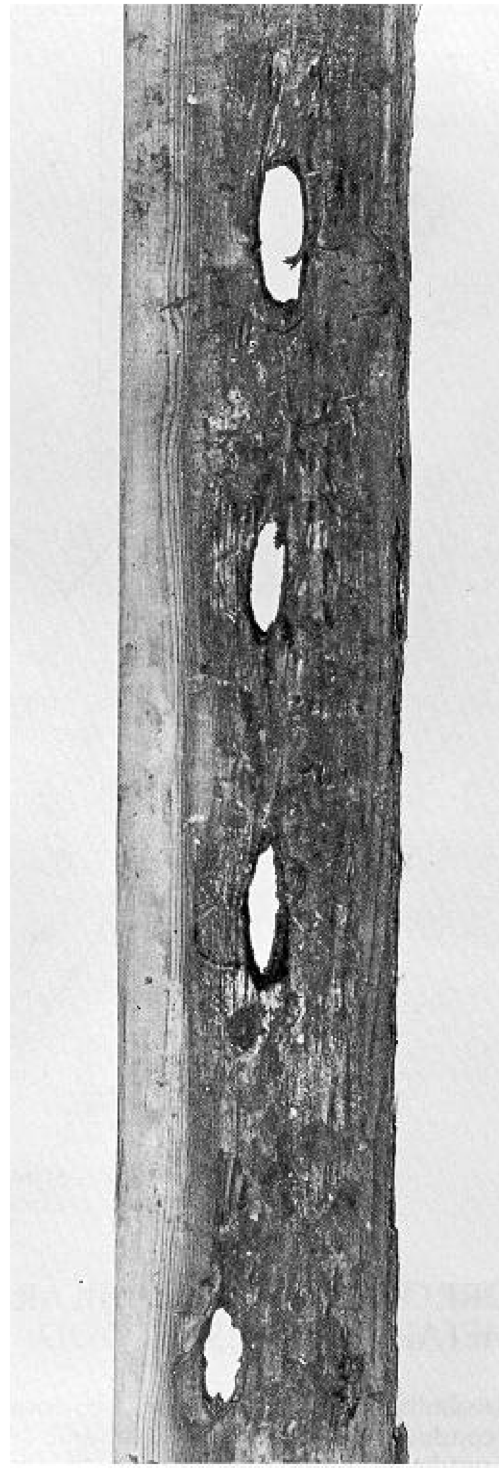

Figure 3.—Hull plank from 20-year-old wooden ship shows wood degradation around silicon bronze lag bolts. The lag bolts held a silicon bronze brace to the plank; brace and bolts were connected to ship's cathodic protection system.

ed to water should be countersunk and covered with plugs of the same species of wood. To prevent dissimilar metal corrosion, two different metals should not be used for fasteners. For instance, washers should be of the same material as the bolt. When dissimilar metals are used in wet wood, they should be insulated from each other with an electrically nonconductive material. Cathodic protection of metal on wooden vessels should not be attempted for metal embedded or surrounded by wet wood unless the metal is coated with an impermeable plastic film, such as epoxy resin. For catholically protected metal exposed to water that will wash away the cathode reaction products, no plastic coating is necessary. The number and the placement of the sacrificial anodes should be carefully considered so that the metal is not "overprotected," which could result in excessive amounts of alkaline cathode reaction products.

SUMMARY

Describing chemical reactions around isolated metal fasteners in terms of crevice corrosion can explain the reasons why wood degrades around individual metal fasteners in wood. With some metals, the wood degrades because acid accumulates in the crevice. Migration of chloride ions into the crevice accelerates the corrosion rate that in turn accelerates the production of acid. This acid condition will develop rather quickly in seawater, but it should be remembered that most natural waters also contain soluble chlorides. Thus, this explanation can also explain how a rail spike corrodes and causes damage to wood. In addition to the acid accumulation along the metal embedded in the wood, with iron there is an additional reaction between iron ions and wood that causes wood degradation. With copper and copper alloys, crevice corrosion causes alkaline corrosion products to form in the crevice. This explains the common occurrence of alkaline conditions around isolated copper alloy fasteners in wooden vessels.

Galvanic corrosion of dissimilar metals connected in wood can result in the following conditions. At the anode, metal ions will go into solution. If the anode is iron, the iron ion will react with wood and result in wood deterioration. If the metal is embedded in wood and soluble chloride salts are present in the surrounding solution, acid conditions can develop around the metal. These acid conditions will cause wood deterioration. At the cathode, alkaline conditions can form that will also cause wood deterioration if the metal is embedded in the wood. If the metal is not embedded in the wood and the reaction products cannot accumulate, there is no reason to suspect any wood deterioration.

Cathodic protection on wood vessels should be done with care so that the products of the cathode reaction do not accumulate and cause wood deterioration.

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