THE FIXATION CHEMISTRY OF AMMONIACAL COPPER WOOD PRESERVATIVES

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Summary

This paper reviews recent research on the fixation chemistry of ammoniacal copper compounds. Based upon a nitrogen analysis of two year old ammoniacal copper arsenate (ACA) treated spruce poles, it was found that the nitrogen content remained elevated above background. The fixation of ammoniacal copper carbonate in wood was found to be a function of the ammonia concentration in the treating solution. Resistance of the copper to leaching, improved at higher ammonia concentrations. Conversely, the application of heat to the treated wood enhanced the copper leaching. The pH of the leachate from boring removed from ammoniacal copper treated wood was monitored and compared to the amount of copper present in the leachate. It was confirmed that the pH could be used to monitor the fixation process. The results confirmed that fixation of ammoniacal copper could take more than two weeks to reach completion. Taxifolin, an extractive found in Douglas-fir heartwood, reacted with ammoniacal copper sulphate solutions to form a black insoluble precipitate - which would render treated wood, dark in colour. Reactions of ammoniacal copper solutions with vanillin, a lignin model compound, produced a stable copper-ammonia-vanillin complex, lending support to the importance of such reactions during the fixation of ammoniacal copper preservatives in wood. It was concluded that there are several reactions which cause copper to be retained in wood, some of which are based upon the formation of di(ammine)copper(II) compounds.

1. Introduction

The fixation of preservatives to the wood substrate is extremely important, since it impacts greatly both on the performance and the environmental impact of the treated product. For the most widely used copper based preservative in North America, chromated-copper-arsenate (CCA), it is known that the components are rendered insoluble through a series of chemical reactions involving the reduction of chromium (4-6, 11, 14-16, 23 and 26). This has lead to research on techniques for accelerating the fixation of CCA so that the conversion of chromium is completed before the wood leaves the treating cylinder area.

Although identified as an excellent wood preservative over 50 years ago (8), very little is known of the fixation of ammoniacal copper arsenate (ACA) or other ammoniacal copper formulations [such as ammoniacal copper citrate, ammoniacal copper zinc arsenate (ACZA) or ammoniacal copper quaternary chloride (ACQ) in wood]. With the increased treated wood in service, it is important to better understand the fixation of ammoniacal copper based preservatives, both in terms of understanding the fixation mechanism and also in developing analytical methods for determining when fixation is complete.

Hartford (9) suggested that during the fixation of ACA, the ammonia in the solvent was lost leading to precipitation of insoluble copper arsenite in the wood. This was later understood to be incorrect since during the production of ACA the arsenic underwent oxidation from the trivalent state to the pentavalent form. The reaction would then appear to be:

$$3Cu(NH_3)_4^{2+} + 2AsO_4^{3-} \leftrightarrow Cu_3[AsO_4]_2 + 12NH_3\uparrow$$

This explanation was challenged when it was observed that ACA-treated spruce poles retained enhanced nitrogen levels more than two years after treatment (18). Clearly, a reaction between the ammonia and either the copper in the preservative, or the wood substrate, had resulted in complex formation, which lead to some of the nitrogen being bound in the wood. Analysis of four zones: at the surface (0 to 5 mm), at the limit of the copper penetration, the heartwood just beyond the limit of the copper penetration, and the centre of the cross section showed that the nitrogen level was greatly enhanced in the ACA treated wood (Figure 1). In addition, there was evidence that the ammonia had penetrated beyond the penetration by the copper into the spruce poles, since a slight enhancement of the nitrogen in zone 3 was observed (Figure 1).

The amount of nitrogen seemed to be related to the level of treatment (Figure 2) with higher nitrogen concentrations being related to higher ACA retentions. The intercept of the regression was 0.07 % which was close to the background level found in the field samples. It had been postulated that one of the reasons for the excellent penetration of ammoniacal copper preservatives was the wall swelling characteristics of the ammonia. Subsequent examination of this same pole material after almost ten years of field exposure confirmed that the nitrogen remained enhanced (20). Clearly, the fixation of ammoniacal copper preservatives in wood was not as simple as first thought and fixation reactions involving the ammonia were possible.

2. Monitoring fixation in wood treated with ammoniacal copper preservatives

2.1 Fixation of ACA in small blocks.

One of the early investigations carried out by the NSERC/Industrial Chair in Wood preservation at UBC, examined the relationship between the pH of the leachate from ACA-treated wood and the loss of copper and arsenic. Small ponderosa pine (*Pinus ponderosa* Laws.) sapwood blocks (19 mm x 19 mm x 19 mm) were treated with 1% ACA in a vacuum desiccator for 30 minutes after which they were placed on the bench to dry. At selected time intervals, blocks were placed in a beaker of distilled water and leached ultrasonically for one hour. They were then oven dried prior to being ground to 20 mesh sawdust and analysed for copper and arsenic using x-ray spectrometry. The pH of the leachate was measured. It was concluded from the pH measurements that the blocks took over 3 days to lose all reactive ammonia, at which time the pH of the leachate returned to that of the leachate from untreated control blocks (Figure 3). While the loss of copper related very well to the change in pH of the leachate, the arsenic depletion was rapid at first and then became more or less constant at about 12 %. This suggested that at least 12 % of the arsenic was not complexed by the copper in the wood. Such unbound arsenic would be lost from the treated wood during service. An examination of ACA-treated western white spruce poles, ten years after treatment and field exposure, revealed that loss of arsenic had occurred, particularly at the lower retentions (Figure 4). The ratio of copper to arsenic (expressed as oxides) which in freshly treated wood was 1:1, became approximately 1.5:1. The loss of copper mirrored the change in the leachate pH, reaching a non-detect level after about 50 hours. However, this fixation time was influenced by the limits of the x-ray spectrometer (50 ppm) to determine the copper in the solution.

2.2 Fixation of ammoniacal copper citrate in softwood lumber

This strategy of monitoring the copper leached from the treated wood was therefore adopted during a subsequent examination of ammoniacal copper citrate fixation in softwood lumber. Jack pine (*P. banksiana* Lamb.), lodgepole pine (*P. contorta* Dougl.) and white spruce (*Picea glauca* Voss.) incised boards (5 x 15 cm) were commercially treated with approximately 2 % ammoniacal copper citrate solution. The boards were selected for heartwood content. Immediately following treatment three cores 10 mm in length were removed from the heartwood face of each board. The sampling positions were distributed along the full length of the board. Each core was transferred directly from the core-borer into a sample bottle containing 50 ml of distilled water. The bottle was capped to prevent loss of ammonia. It was returned to the laboratory where it was placed in an ultrasonic bath for one hour to remove any mobile copper. The core was then removed and oven dried. The leachate was analysed for the pH and also for the copper content using atomic absorption spectrometry. The boards were stored horizontally, with each board placed on supports with free air movement on all four faces. They were stored under cover under ambient conditions (*ca.* 22 °C). The boards were sampled up to 60 days after treatment.

The copper leached from the cores over the 60 day sampling is shown in Figure 5. It can be seen that almost 30 days were required for the copper in the leachate to reach a constant level of approximately 1 ppm. This data corresponds to the pH information (Figure 6) in which approximately 30 days were required for the pH of the leachate to return to that of the distilled water controls. This would suggest that under optimum conditions for each board, the time to fixation was one month. When boards are close piled, a longer time for complete ammonia loss may be required.

The fixation time was influenced by the preservative retention. The copper content in the jack pine was *ca.* 12 kg/m^3. Similar studies on the lodgepole pine boards showed that only 14 days were required to fix the ammoniacal copper citrate when the retention of copper was only 6.8 kg/m^3.

3. Influence of ammonia concentration and post treatment heat on the fixation of ammoniacal copper preservatives.

3.1 Leaching with distilled water

The loss of copper from ammoniacal copper - treated wood is an important aspect with respect to the environmental acceptability of a preservative system. Leaching studies have found that the copper in ammoniacal copper systems is generally well bound to the wood and is not notably leachable. However, many aspects of the treatment can influence the amount of copper lost from the treated wood and the object of the work summarised here is to examine the influence of the ammonia and external heat on the copper depletion from treated wood. Since all of the samples were small wood blocks, the leaching of the copper will be maximised so that losses from wood in service would be slower.

In order to identify the effect of ammonia concentration on the fixation of ammoniacal copper chemicals, ponderosa pine sapwood blocks (19 x 19 x 19 mm) were impregnated with copper carbonate dissolved in ammonium hydroxide. The solutions contained 1 % copper (expressed as CuO) dissolved in ammonium hydroxide containing 2 to 16 % ammonia. Following treatment the blocks were immediately wrapped in polyethylene and allowed to fix for one week under ambient conditions (20 °C), before being either oven dried or air dried on metal racks at 20 °C for a further week. Each group of blocks were leached in distilled water for one week. The results clearly showed that increasing the ammonia content in the treating solution improved the degree of copper fixation (Figure 7). However, the ammonia levels required to achieve any significant improvement were too high to be of use in commercial practice.

It is now well established the rate of CCA fixation in timber can be greatly enhanced , by increasing the temperature while maintaining a high humidity (1, 3 and 7). This also causes a rapid disappearance of the chromium(V) intermediate formed in the wood (22). A similar action may be considered for timber treated with ammoniacal copper preservatives. The results of this study would showed that the application of heat caused an increased degree of copper leaching, presumably due to a more rapid loss of ammonia (Figure 7). Thus different approaches to accelerate the fixation of ammoniacal copper preservatives will have to be designed.

3.2 Leaching with buffered solution

Studies on the depletion of preservatives from treated wood have shown that under acidic conditions, particularly conditions in which a chelating agent such as citric acid is employed, a severe loss of copper is observed (2, 24). It was reported that 7.5 mg/m^3 of copper could be removed from CCA-treated wood during a laboratory leaching regime in a simulated acid rain. Cooper confirmed the extremely high loss of copper from 10 x 40 mm blocks soaked in sodium hydroxide/citric acid compared to similar blocks soaked in acidified (sulphuric acid/nitric acid). Only 2 to 6 % of the copper was removed after 13 days using the acidified solution at a pH of 5.5, compared 50 to 80% depletion in the sodium citrate solution.

Small blocks (19 x 19 x 19 mm) were treated with ammoniacal copper carbonate solution and sealed in plastic bags to allow the preservative to fix. After one week the blocks were removed from the bag. They were allowed to dry in the laboratory at ambient temperature for a further two weeks. The blocks were sorted and some retained for analysis while others were selected for leaching in either distilled water or a sodium citrate buffer solution. The results are shown in Table 1. Almost 4% of the copper was removed by the water leach compared to 70% by the buffered solution. Interestingly, the further reduction in the ammonia content by the citrate buffer compared to that caused by the water was small (6.5 %). This suggested, that the only a small part of the ammonia present in the wood, was bound to the copper.

4. Reaction of ammoniacal copper preservatives with extractives

It is well known that ACA often reacts with Douglas-fir heartwood to produce a very dark (almost black) coloured wood. This is not the case with other softwoods. Neither is the reaction found with other copper preservatives. If ammoniacal copper preservatives are to achieve their full commercial potential in end-uses where appearance is important, the cause of this reaction must be understood and overcome. An investigation of the extractives found in Douglas-fir heartwood was therefore initiated (21).

Blocks of Douglas-fir heartwood were chipped, ground to sawdust, and extracted with either acetone or diethyl ether for 24 hours. The two solutions were filtered, concentrated under vacuum at 20 °C and the residues dried under vacuum at 30-40 °C to constant weight. The acetone-extracted wood sawdust was re-extracted for 24 hours with distilled water at 40 °C. The extract was filtered and concentrated at 60 °C under reduced pressure to produce a third residue. Solutions containing 2 % (w/w) of each of the three residues in methanol were reacted with a 1.5 % (w/w) solution of copper sulphate in ammonium hydroxide. Only the acetone extract formed a dark coloured precipitate.

Subsequent experiments focused on identifying a component in the extractives that reacted with ammoniacal copper solutions to produce the black colour. Based upon melting point, FTIR spectra, mass spectrometry, and NMR spectrometry it was shown that taxifolin in Douglas-fir heartwood could react with ammoniacal copper solutions to produce a black precipitate. The reactivity of taxifolin was then examined against various copper solutions - copper sulphate, ammoniacal copper sulphate, copper sulphate made alkaline by excess sodium hydroxide and CCA. Ammonium hydroxide was also tested. Only the combination of ammonium hydroxide and copper sulphate produced the black precipitate.

A more detailed analysis of the black precipitate was made using FTIR and it confirmed that the taxifolin had reacted with copper via some of the hydroxyl groups. In flavanones, copper can be attached to either the 3-hydroxy and 4-keto, or 5-hydroxy and 4-keto groups, forming a 6-membered or 5-membered ring. In taxifolin the reactivity of the proton on the 5-hydroxyl group conjugated with benzene ring *A*, is greater than that on the 3-hydroxyl group, so that copper chelation to the *A* ring is anticipated. This reactivity of the 5-hydroxyl group has been confirmed by Porter and Markham (17) who demonstrated that metal ions were preferentially chelated at this position in dihydroflavonols. Following initial complex formation involving the 5-hydroxyl and the ketone groups, reaction with the 3-hydroxyl group is then eliminated. However, further co-ordination is possible through the 3' and 4' hydroxyl groups of taxifolin. The 3-hydroxyl and 7-hydroxyl groups are either not involved in bonding, or participate in intermolecular bonding, with the formation of a polymeric structure.

An analysis of the black precipitate was performed. The results suggested that the composition of the complex was:

$$\mathbf{[Taxifolin]_2.Cu_3(NH_3)_4.2H_2O}$$

Calc. C: 38.96; H: 3.35; N: 6.26; Cu:21.12
Found C: 38.29; H: 3.48; N:6.74; Cu: 21.04

This corresponds to two taxifolin moieties bridging a central copper atom with a further copper atom being bonded via the 3' and 4' oxygen atoms on ring B of taxifolin. It is also suggested that two ammonia ligands are also bonded to this copper atom.

5. Reactivity of ammoniacal copper sulphate and Vanillin, a lignin model compound

In order to better understand the nature of the copper complex formed in wood, reactions of ammoniacal copper solution with model compounds were investigated. In this study vanillin was used to imitate the abundant guaiacyl units of lignin in wood, to investigate the possible reaction between lignin and ammoniacal copper (25). Guaiacyl units constitute 80-90 % of the aromatics in lignin

Vanillin was dissolved in 5 % ammonium hydroxide solution and an ammoniacal copper solution added drop-wise with stirring. Evaporation of the ammonia from this solution under reduced pressure at 40 °C, produced a green crystalline precipitate. A single crystal of the copper-vanillin complex was obtained through careful recrystalization in an ammonium hydroxide solution. The FTIR, mass spectrum and ESR spectra were recorded. The elemental analysis of the green vanillin-copper-ammonia complex $C_{16}H_{20}N_2O_6Cu$ was:

Found: C, 47.87 %; H, 4.92 %; N, 6.81 %; Cu, 16.0 %;
Calcd: C, 48.01 %; H, 5.01 %; N, 7.01 %; Cu, 15.9 %.

The structure of the complex is comprised of a central copper (II) ion bonded to two vanillin and two ammonia molecules. The perspective view of the complex with numbering system is presented in Figure 8. In the complex, both the methoxy and phenolic oxygen atoms of each guaiacyl unit co-ordinate to the copper, together with nitrogen from two ammonia molecules to form a six co-ordinated molecule. The copper atom displays a distorted octahedral co-ordination. The Cu-O (phenolic oxygen atoms and the Cu-N (ammonia nitrogen) form a square plane around the central copper. The very distorted octahedral configuration is completed by the Cu-O (methoxy oxygen atoms) which are co-ordinated at an angle about 75° to the plane. The structure clearly shows that the ammonia had not reacted with the vanillin.

The FTIR spectra of the polycrystalline green solid and pure vanillin were compared. In the spectrum of the complex, new peaks appeared in the region of 3200-3400 cm^{-1} due to N-H vibration. The spectrum of the copper complex also contains a new peak at 448 cm^{-1} assigned to Cu-N bonding.

Ammoniacal copper solution readily formed a water insoluble complex with vanillin, providing support for the hypothesis that, during fixation, ammoniacal copper preservatives react with the guaiacyl units on lignin to form stable copper-nitrogen complexes. The formation of such complexes supports the finding of enhanced nitrogen content in ammoniacal copper treated wood observed by Ruddick (18). It may also help explain the changes which occur in the physical properties of the ammoniacal copper treated wood. The water insoluble copper complexes formed in the treated wood will be expected to be highly leach resistant (11, 19), and may also induce water repellent properties in the wood (12). The formation of cross-linked copper-lignin complexes in ammoniacal copper treated wood may also be responsible for the enhanced protection against photodegradation (10), reported to occur in ammoniacal copper treated wood during above ground weathering exposure tests (13).

6. Conclusions

During the fixation of ammoniacal copper preservatives in wood, several reactions may be proposed to take place. These include:

reaction of ammonia from the solvent with the wood substrate;
the formation of di(ammine)copper(II) complexes with the heartwood extractives;
the formation of di(ammine)copper(II) lignin complexes;
the precipitation of copper compounds in the wood; and
possible copper complexes with cellulose or lignin.

The relative imprecate of these reactions is the subject of ongoing research.

7. References

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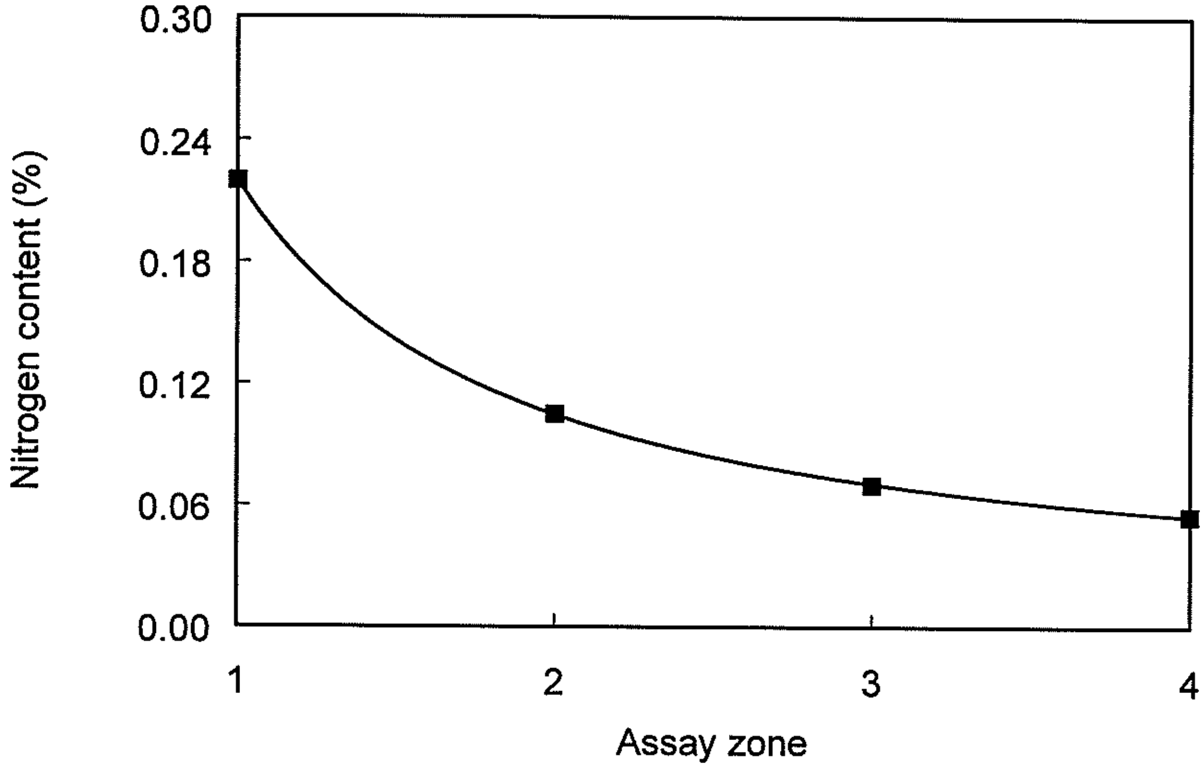

Figure 1. Nitrogen content of two year old spruce pole sections at four assay zones. Zone 1 - at the surface (0 to 5 mm); Zone 2 - at the limit of the copper penetration; Zone 3 - the heartwood just beyond the limit of the copper penetration; and Zone 4 - the centre of the cross section.

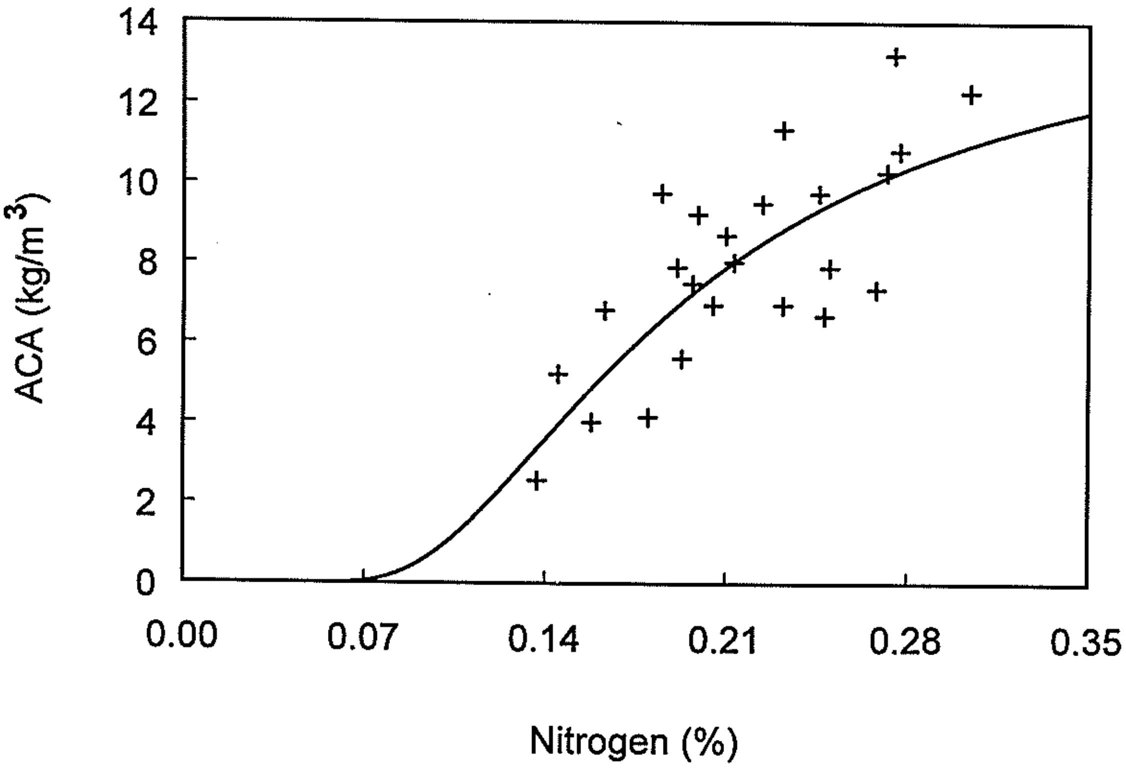

Figure 2. Nitrogen content in ACA-treated poles as a function of the retention.

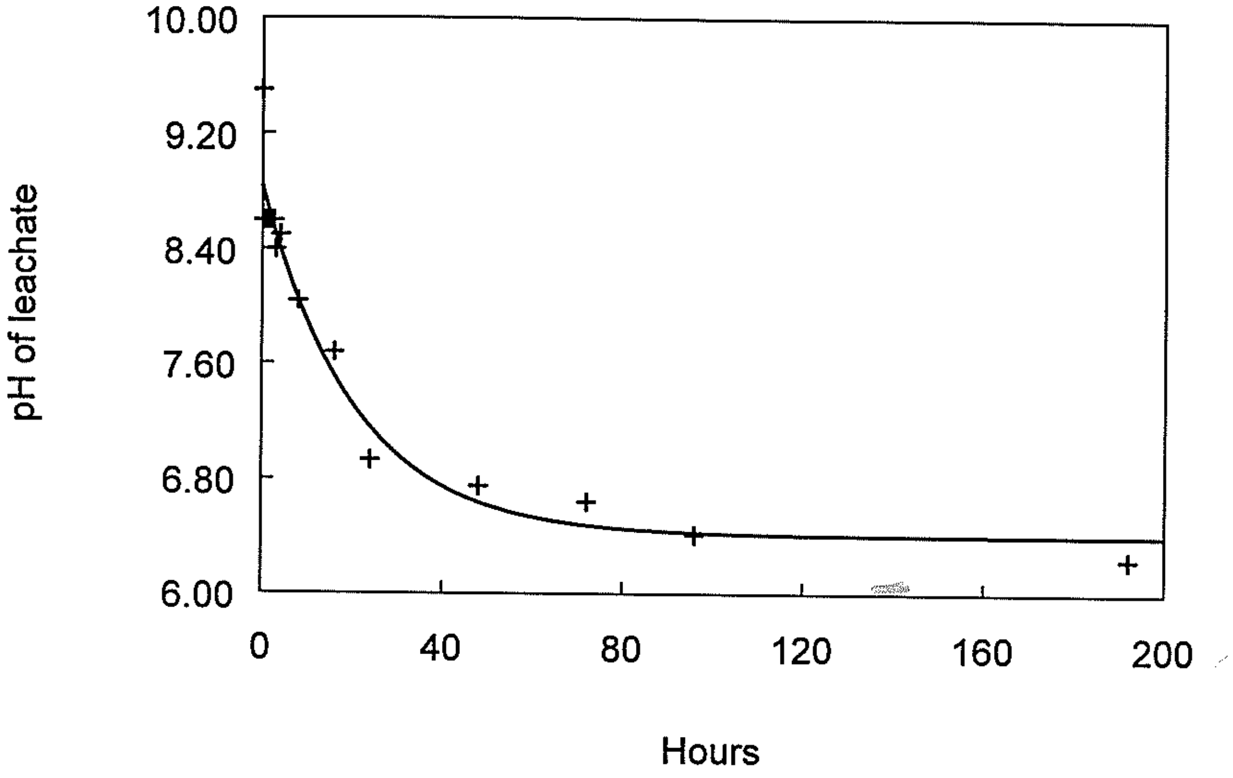

Figure 3. Reduction in the leachate pH from the ACA-treated blocks, as a function of fixation time.

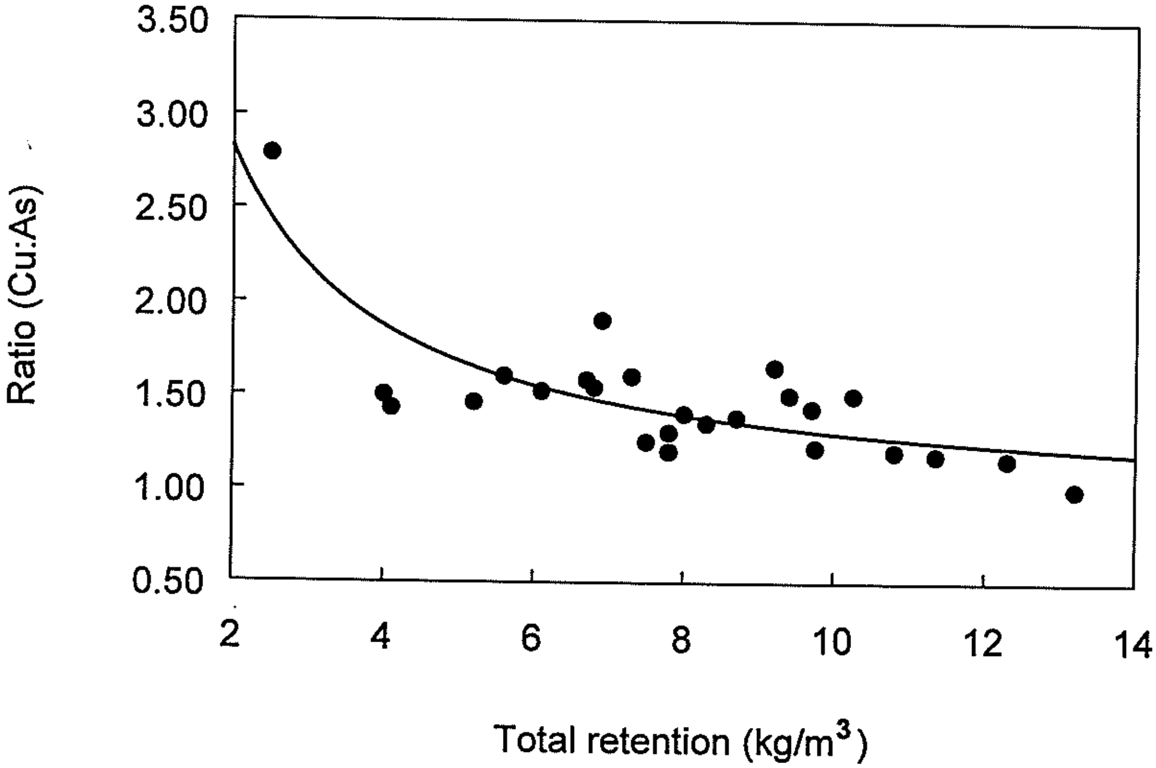

Figure 4. Ratio of CuO to As_2O_5 as a function of ACA retention in treated poles after ten years field exposure.

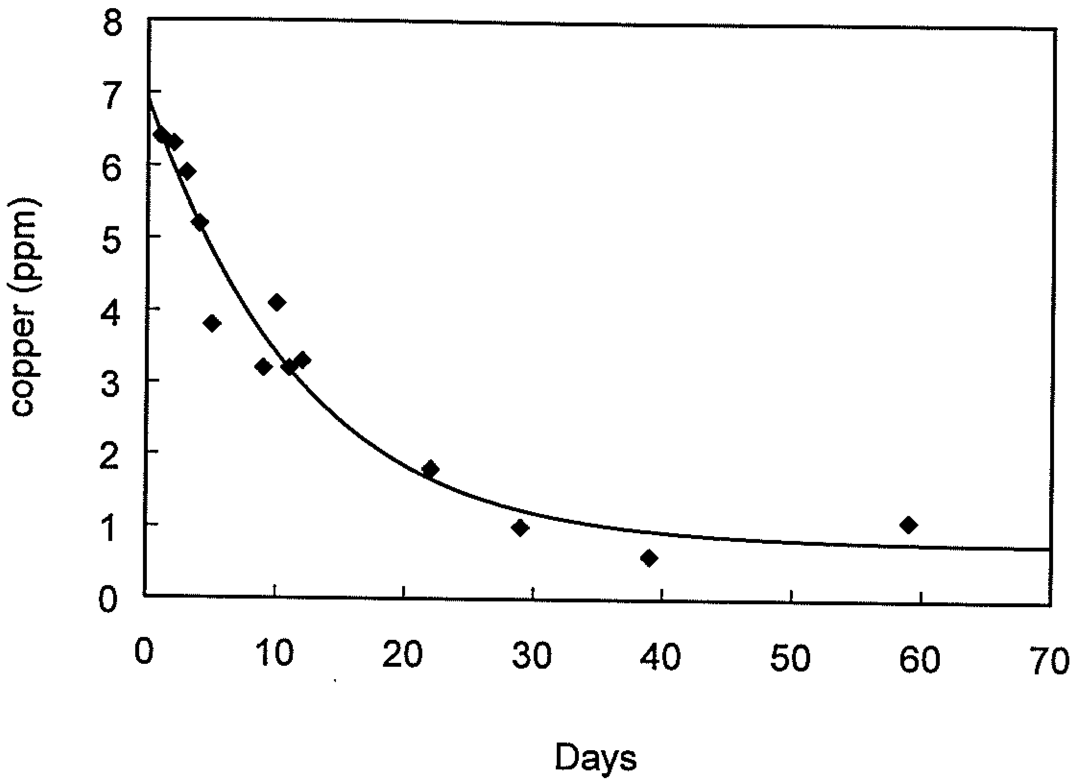

Figure 5. Copper content in leachate from cores, removed from ammonical copper citrate treated wood.

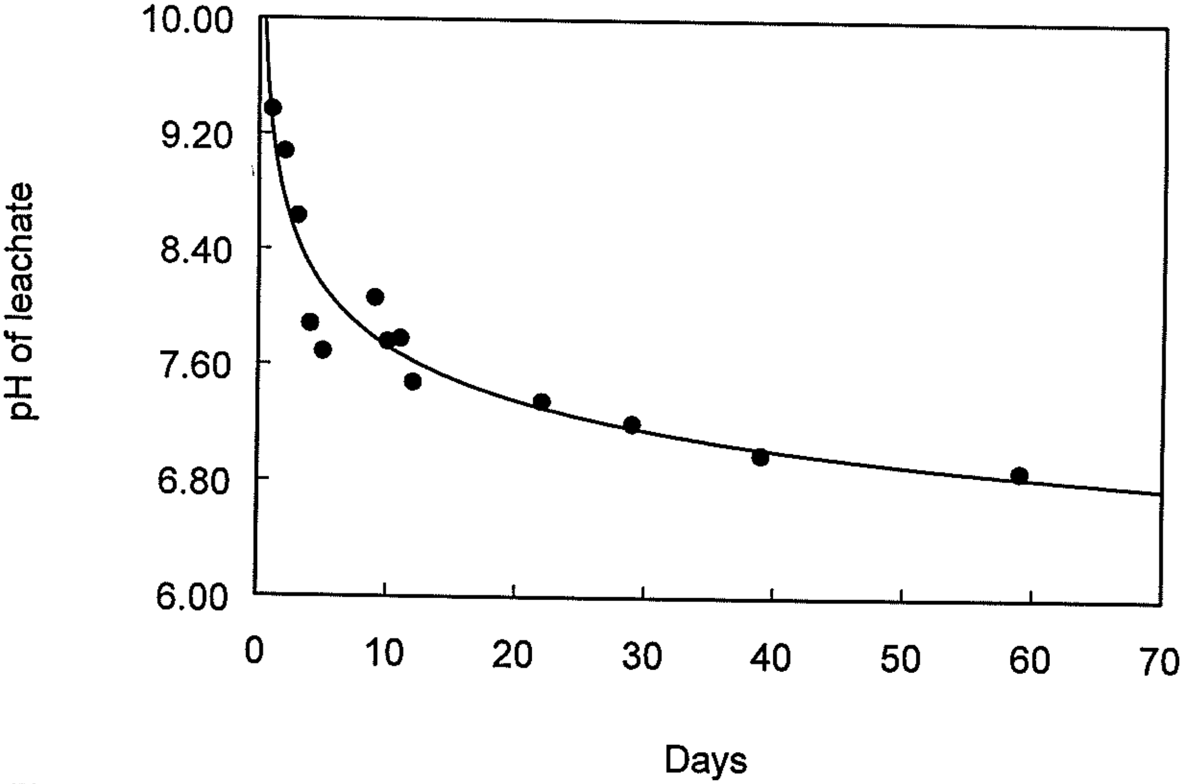

Figure 6. The pH of the leachate from cores removed from ammonical copper citrate treated wood.

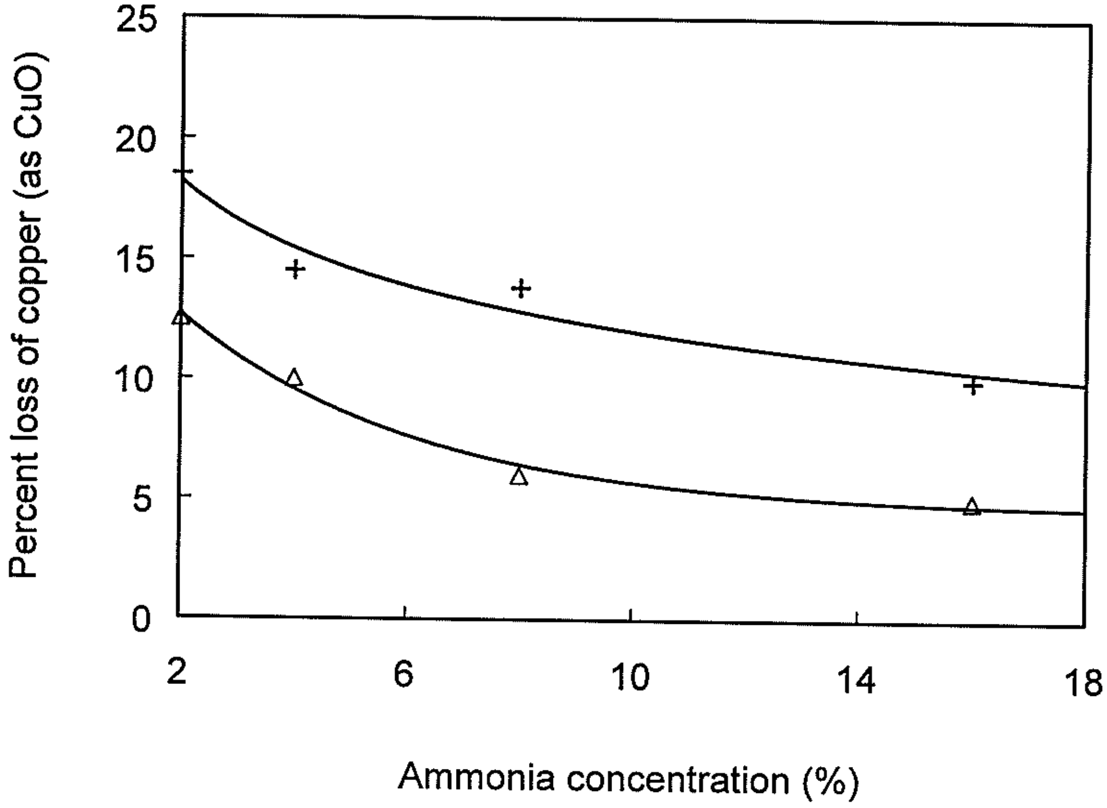

Figure 7. The influence of (i) ammonia concentration and (ii) heating ammoniacal copper-treated wood following treatment, on the permanence of the copper. (upper curve - oven dried; lower curve - air dried wood)

Table 1. Leaching of copper from ammoniacal copper carbonate-treated wood

	Before Leaching Percent (w/w)	After Leaching distilled water Percent (w/w)	 citrate buffer Percent (w/w)
Copper	1.49	1.43	0.38
Nitrogen	0.76	0.34	0.29
Mole ratio			
N:Cu	2.3	1.1	3.4

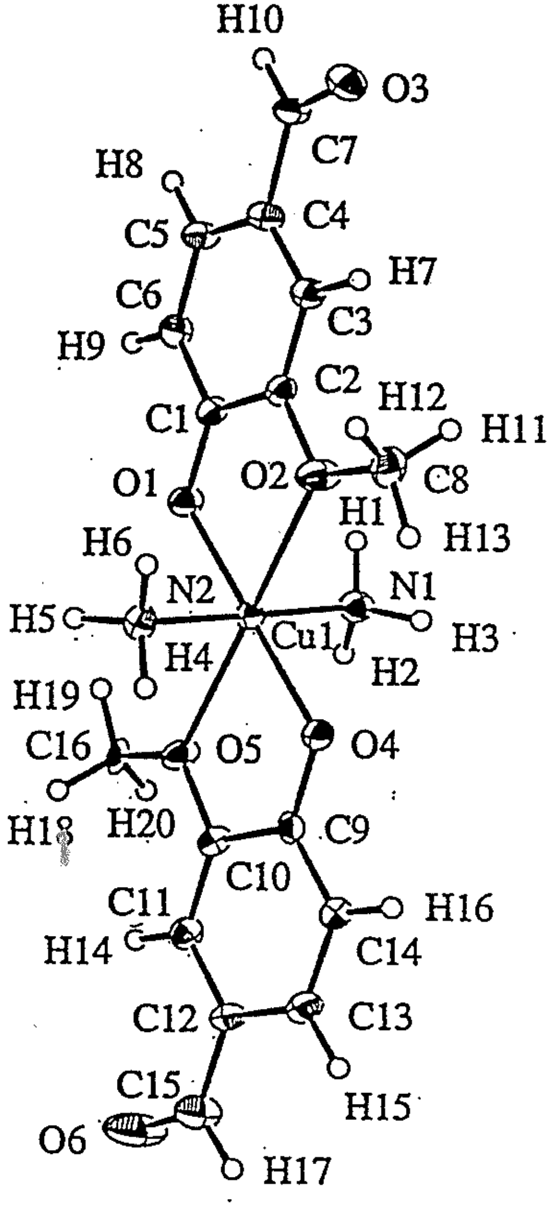

Figure 8. Perspective view of Cu(II)-bis(vanillinato)bis(ammonia) with the atomic numbering; 33% probability thermal ellipsods are shown for the non-hydrogen atoms.