INVESTIGATION OF THE DISTRIBUTION OF COPPER ETHANOLAMINE COMPLEXES IN ALKALINE COPPER QUAT (ACQ) WOOD PRESERVATIVE

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Abstract

MINTEQA2, an equilibrium speciation model for aqueous systems was used to study the alkaline copper quat (ACQ) solution composition. The model results show that ionic strength of the solution (related to concentration of charged species in solution) has little effect on the distribution of complexes. At solution pH < 7, uncomplexed Cu^{2+} , and +2 charged ML_1 and ML_2 type complexes are the major species in the solution. Under these conditions, the uncomplexed Cu^{2+} can react with anionic species (e.g., bicarbonates, carbonates) and precipitate out of solution. At a solution pH between 7 and 10, the + 1 charged ML₂ complex is the major species; its concentration decreases at a solution pH>10, and the distribution of copper as neutral CuL₂ type complexes increases. At a solution pH < 7 an increase in concentration and an increase in proportional amount of ethanolamine ligand to copper in ACQ solution results in increased coordination of copper with ethanolamine ligand and decreased free copper ions in the solution, reducing the ability of copper to fix by precipitation. At a solution pH > 7, these changes reduce copper distributed as + 1 charged ML₂ type complex and increase +2 charged CuL₃ and CuL₄ type complexes. The + 1 charged copper ethanolamine complex, which is hypothesized to be the most desirable complex species to maximize fixation reaction in wood after ACQ treatment, is maximized at a solution pH between 8.5-9 and Cu to EtAmOH ratio of 1: 3, which is slightly below the minimum ratio allowed in AWPA and CSA preservative standards. This study suggests the possibility of reducing the copper to ethanolamine molar ratio to 1:3 and narrowing the pH range of ACQ to 7.5 to 9 instead of 8 to 11 recommended in AWPA standards to improve fixation.

1. Introduction

Alkaline copper quat (ACQ), a copper amine based wood preservative, introduced as potential replacement for chromated copper arsenate (CCA) for residential applications has been shown to be an effective wood preservative to enable wood to resist fungal attack. Even though copper is not as toxic or carcinogenic as arsenic and chromium in CCA, high copper leaching from copper amine based preservative treated wood may result in future restriction of the system. It is very important that the copper content in the treated wood is chemically bound or fixed to the wood to

ensure the efficacy of treated wood in service as well as to minimize the environmental impact of treated wood. Although ACQ is highly commercialized in North America, especially for residential applications, chemistry of copper amine in solution as well as its fixation chemistry after treatment with wood is not well elucidated in the literature.

ACQ wood preservative has copper (Cu) as well as a quaternary ammonium compound (didecyl dimethyl ammonium chloride or carbonate (DDAC) in ACQ-type D) as active ingredients. According to American Wood Protection Association standards, ACQ-D can be prepared by dissolving copper salt such as copper carbonate (CuCO₃) in monoethanolamine (EtAmOH) solvent; the weight of monoethanolamine has to be 2.75 ± 0.25 times the weight of copper oxide (which corresponds to a copper to monoethanolamine molar ratio of 3.2 to 4) along with the cobiocide DDAC at copper oxide to DDAC ratio of 2:1 resulting at solution pH between 8-11 depending on buffers and other additives in the formulation . Commercial ACQ has Cu to EtAmOH molar ratio close to 4 and solution pH around 9. Criteria for setting Cu to EtAmOH molar ratio and pH of the resulting solutions are not explained well in the literature, which further hinders the ongoing efforts to understand the mechanism of ACQ fixation in the wood as well the efforts to minimize the leaching from ACQ treated wood during outdoor exposure.

In ACQ solution, pH-independent DDAC will be dissociated and stay positively charged. Copper in ACQ solution can complex with monoethanolamine, a neutral ligand (L) and present in the form of copper ethanolamine complexes (Table 1) with varying metal ligand stochiometries. These complexes can be divalent cationic (double positive charged), monovalent cationic (single positive charged) or neutral (1, 3, 5, 6, 7, 13, 20, 22, 23).

Even though the mechanism of fixation of ACQ components in wood after treatment is not clear in the literature, there is general agreement that copper undergoes a cation exchange complexation reaction with carboxylic groups in the hemicelluloses and phenolic hydroxyls in the lignin of wood (2, 9, 10, 16, 21, 26), and extent of fixation of copper varies with wood species, post treatment temperature and relative humidity, copper retention and formulation parameters such as copper sources, type of amine, amine to copper molar ratio and pH of copper amine solution (8, 12, 24, 25). Quaternary ammonium salts also undergo electrostatic interaction and cation exchange with dissociated (anionic) carboxylic groups and phenolic hydroxyls in the wood (4, 11).

For complexation and fixation reactions copper ethanolamine complexes with wood functional groups, the neutral species is unlikely to react or fix by ion exchange and the divalent species may be less efficient in its fixation compared to monovalent species because of higher stability in solution hence lower reactivity with wood, it can react with two cation exchange sites in wood, hence limiting the wood's capacity to fix more copper and stearic hindrance are expected when neighboring sites are already taken. It is postulated that maintaining a higher proportion of monovalent cationic species in the solution may be the most desirable for high levels of copper fixation because of its lower stability in solution, hence expected higher reactivity with wood consuming only one site in the wood for each copper atom. However, this has not yet been demonstrated in the literature.

Concentrations of different copper ethanolamine complexes in ACQ solution and the charge associated with complexes depend on solution parameters such as ionic strength, Cu to EtAmOH molar ratio and pH, which can affect the fixation of copper in wood. Investigating the distribution of different complexes in such solutions at various solution parameters using conventional chemical means would involve many hours of laboratory time. However in recent years software such as MINTEQA2 has become available that assists in the modeling composition of complex systems at various solution parameters.

MINTEQA2 an equilibrium speciation model developed by Allisson Geoscience Consultants Inc. is a software package that enables the distribution of equilibrium concentrations of different ionic entities in aqueous solutions to be examined. It can be used to calculate the mass distribution between dissolved, adsorbed and multiple solid phases under various conditions. MINTEQA2 has an extensive thermodynamic database that is adequate for solving a broad range of problems without the need for user-supplied equilibrium constants. The database of the model can be easily edited if the database is found to be incomplete or inadequate for a particular problem. The model requires input data regarding the concentration of component species and other invariant measurement of the system such as ionic strength, temperature, pH etc depending on the case specific need. MINTEQA2 uses the input data to compute the equilibrium concentrations of different entities in the system posed in the program.

This study describes the use of MINTEQA2 Version 1.5 to model the composition of ACQ solutions at different concentrations at various solution parameters such as ionic strength, Cu to EtAmOH molar ratio and pH. The objective is to investigate the distribution of copper ethanolamine complex species in ACQ solution in order to optimize solution parameters to keep copper complexes thought to be more desirable at a higher proportion in the solution to maximize fixation. This particular study is expected to provide valuable information regarding the possibilities of further optimization of copper amine based preservative formulations. It is also expected to provide insight into the fixation mechanism of these copper amine based preservatives in wood.

2. Methodology

MINTEQA2 version 1.5 software, (Allisson Geoscience Consultants Inc. 2003) an equilibrium speciation model for aqueous systems, was used to study equilibrium distribution of possible copper ethanolamine complex species as a function of ACQ solution parameters such as ionic strength, Cu to EtAmOH molar ratio and pH at different ACQ concentration.

The thermodynamic database MINTEQA2 was edited to add monoethanolamine as a component species and major copper ethanolamine complexes from the literature summarized in Table 1 as reaction species. The required thermodynamic data, stability constant (LogK) of the complexes at a given temperature were collected from the National Institute of Standards and Technology database as well as stability constant references (14, 15, 18, 19). Linear fit in excel was used to extrapolate to Log K values at zero ionic strength for the copper ethanolamine complexes which had published Log K values for different ionic strengths at 25°C. In the case of neutral CuL₂ type

complex, Log K value at 30°C from the literature was used to extrapolate to a Log K value at zero ionic strength because of the limited data available at 25°C, assuming minimal variation in Log K value with 5°C change in temperature. The Log K value of the +1 charged CuL₂ type complex at zero ionic strength was extrapolated from a single value reported by Tauler et al. (1986) (23) using MINTEQA2 because of the limited published data for this complex. Log K value at zero ionic strength of the +1 charged CuL₂ type complex was adjusted in the editing process and fixed at a particular value so that MINTEQA2 calculated the same Log K value as reported by Tauler et al. (1986) (23) at 1M ionic strength. Log K values of copper ethanolamine complexes extrapolated for zero ionic strength at 25°C, summarized in Table 1, were used to edit the thermodynamic database in MINEQA2.

In this study, apart from the above mentioned copper ethanolamine complexes listed in Table 1, protonation of monoethanolamine ligand ($[H(EtAmOH)]^{+1}$) as well as any possible formation of hydroxide, carbonate or bicarbonate was also considered. ACQ parameters such as concentration of copper, concentration of the monoethanolamine ligand, amount of carbonate and ionic strength of the solution, summarized in Table 2 were calculated assuming ACQ solution has a CuO to DDAC ratio of 2:1, copper carbonate (CuCO₃) is the source of copper and DDAC in the solution is an equal weight mix of carbonate and bicarbonate forms.

In order to run the program, ACQ system parameter such as ionic strength, concentrations of copper, monoethanolamine and carbonate (Table 2), temperature and pH were used as input parameters. In the 'general parameters' window of the program, the ionic strength of a particular ACQ concentration and a default temperature of 25⁰C were entered. This particular temperature was used because most of the stability constant values were available for that particular temperature. In the 'total concentration' window, copper, monoethanolamine and carbonate were selected as component species and the corresponding concentrations of the components at different ACQ concentration (Table 2) were entered as mol/l. In the 'equilibrium constraints' window, the pH of the ACQ system was entered. 'Sensitivity analysis' of the program was used to study the distribution of different ionic entities in ACQ solution for different sensitivity parameters such as ionic strength, pH and monoethanolamine concentration.

3. Results and Discussion

Effect of ionic strength on distribution of copper ethanolamine complexes in ACQ solution having a CuO to DDAC ratio of 2:1 and Cu to ethanolamine ratio of 1:4 at a solution pH of 8.7 is summarized in Figure 1. Results show that ionic strength has no or minimal effect on the distribution of copper ethanolamine complexes in ACQ solution.

Appendix 1 and Figure 2 summarize the effects of solution pH on protonation of ethanolamine and distribution of different copper ethanolamine complexes in different ACQ solution concentrations at different Cu to ethanolamine ratios. Both Appendix 1 and Figure 2 are for 1.0% ACQ, having different Cu to ethanolamine ratios, but Appendix 1 is scaled for higher concentration on the Y axis to include protonation of amine and development of deprotonated amine as a function of solution pH. Results show that some ethanolamine stays protonated

(charged) at even high pH and that uncharged amine only appears in significant amounts at above neutral pH. At lower pH, most of the available ethanolamine in the solution is protonated (Appendix 1). Protonated ethanolamine ([H(EtAmOH)]⁺¹, shown as [HL]⁺¹ (the red line G in the figures), ligand will not coordinate with copper so there is no copper complex formation at lower acidic pH range. Thus, at low solution pH, most of the available copper in the solution is free or uncoordinated copper (Cu⁺²) (Figure 2 solid blue line I). At low pH < 6, most of the carbonate in the solution exists as $H_2CO_3(aq)$ (Figure 3 broken chocolate line L), hence complete precipitation of the copper in the form of $CuCO_3$ in the solution is expected below a solution pH of 3.5. Increasing solution pH results in a proportional decrease of protonated ethanolamine ligand (Appendix 1 solid red line G), and a corresponding increase of neutral ethanolamine ligand (EtAmOH, shown as $[L]^0$ in the figure) (Appendix 1 solid pink line H), which can coordinate with copper to form copper ethanolamine complexes. Increase in solution pH > 8.5 results in significant excess amounts of neutral ligand in the solution even after coordination of the ligand with copper, and the proportion of the excess neutral ethanolamine ligand increases rapidly as solution pH increases (Appendix 1). For example for 1% ACQ solution having Cu to EtAmOH ratio of 1: 4, increase in solution pH from 8.5 to 10 and 11 resulted in increase of the excess neutral ligand in the solution from 3% to 32% to 46% respectively (Appendix 1b). An increase in the ratio of monoethanolamine to copper in the solution results in an increase in the excess amount of neutral ligand. For example in case of 1% ACQ at a solution pH of 10 increase in proportional amount of monoethanolamine to copper from Cu to EtAmOH ratio of 1:3 to 1:4 and 1:10 resulted in an increase of excess neutral ligand in the solution from 22% to 32% and 53% respectively (Appendix 1). A further increase in solution pH to > 11 result in deprotonation of the majority of the protonated amine (>99%). Similar trends in change in concentration of protonated ethanolamine and neutral ethanolamine ligand with increase in solution pH and monoethanolamine to copper ratio was observed for 0.5% ACQ and 1.5% ACQ.

Significant coordination of copper with ethanolamine ligand is possible only above a solution pH of 3.5 (Figure 2). Neutral ligand formed in the solution can coordinate with copper at various copper to ethanolamine stochiometries to form CuL₁ (+2 charged), CuL₂ type (+2 charged), CuL₂ type (+1 charged), CuL₂ type (neutral), CuL₃ type (+2 charged), CuL₄ type (+2 charged) depending on pH and Cu to EtAmOH ratio in the solution. At a solution pH > 3.5 ethanolamine start coordinating with copper to form +2 charged CuL₁ type complex and at solution pH from 3.5 to 6 it is the major species in the solution, reaching its maximum concentration at pH 5.5 to 6 (Figures 2 solid lemon green line A). At this pH, copper is mainly distributed as CuL₁ complex and CuCO₃(aq) (Figure 2 broken orange line M). At solution pH < 6, the concentration of non copper carbonates HCO₃⁻² decreases with decreasing pH while non copper carbonate H₂CO₃(aq) increases correspondingly (Figure 2 broken green line K and broken chocolate line L respectively); the concentration of CO₃⁻² was close to zero at these conditions. Presence of free copper and carbonates at pH < 6 indicates the precipitation of copper in form of copper carbonates.

Copper starts to coordinate with two ethanolamine ligand molecules to form +2 charged CuL_2 type complex at solution pH > 5 and reaches the maximum concentration at solution pH between 6.5 to 7 (Figures 2 solid light blue line B). Copper ethanolamine complexes, +2 charged CuL_1

and CuL_2 type along with $CuCO_3(aq)$ are the major species in ACQ at solution pH between 6 to 7. Minor amounts of additional divalent complexes with higher ligand content CuL_3 and CuL_4 type (Figure 2 solid dark green line C and solid black line D respectively) start appearing in the solution at pH between 6 to 7 and 7.5 to 8 respectively, and reach maximum concentrations at pH 8.5 to 9 and 9.5 to10 respectively. These complexes are more predominant in ACQ solutions at higher concentrations and higher ethanolamine ligand to copper ratios (Figure 2c & Appendix 3c). At pH 7, uncomplexed copper ion in ACQ with Cu to EtAmOH ratio of 1:4 is only 0 - 2.5% of the total copper. At pH > 7 there are no free copper ions in the solution, indicating that precipitation of copper in ACQ solution is not expected at solution pH > 7.

Copper ethanolamine complex, +1 charged CuL_2 type, starts to appear in the solution at a pH close to 6, as a result of the deprotonation of the hydroxyl group of the ethanolamine ligand, or alternatively as a result of the deprotonation of bonded water molecule of the complex in aqueous solution as shown in Table 1. It is the predominant species between pH 7 and 10 and reaches it's maximum concentration of 80 to 86% of available copper in solution at pH 8.5 to 9 and declines significantly at solution pH>10 (Figure 2 solid purple line E). The copper ethanolamine complex, neutral CuL_2 type, starts to appear in the solution at pH 8 to 8.5; the concentration of copper distributed as the neutral complex increases with pH and, represents most of the copper (>99%) in solution at pH between 12 to 12.5 (Figure 2 solid yellow line F).

Solution pH is the major parameter affecting the distribution of copper ethanolamine in the solution; however ACQ concentration and Cu to EtAmOH ratio in the solution also affect the distribution of complexes. At solution pH <7, increase in concentration and increase in proportional amount of ethanolamine ligand to copper in ACQ solution result in decrease of free copper in the solution, indicating a higher degree of coordination of copper with ethanolamine ligand. For ACQ with Cu EtAmOH ratio of 1:4, increasing the concentration of ACQ at pH =6 resulted in a decrease of free copper in the solution from 0.5% to 1%, and 1.5% resulted in a decrease of free copper in the solution from the 29%, 17% and 12% respectively. For the same conditions, +2 charged CuL₁ type complex increased from 24% to 30% to 32% respectively and the copper distributed as +2 charged CuL₂ type complex increased from 7% to 14% to 20% respectively (Figure 2b, Appendix 2b & 3b). A similar pattern was observed for ACQ with Cu to EtAmOH ratio of 1:3 and 1:10. For 1% ACQ solution, an increase in Cu to EtAmOH ratio from 1:3 to 1:4 and 1:10 resulted in a decrease of free copper in the solution from 20% to 17% and 7% respectively at solution pH = 6. For these conditions, copper distributed as +2 charged CuL₁ type complex increased from 27% to 30% and 34% respectively and the percentage of copper distributed as +2 charged CuL₂ type complex increased from 10% to 14% and 40% respectively (Figure 2). Concentration of non copper carbonates such as CO_3^{-2} , HCO_3^{-2} and $H_2CO_3(aq)$ in the solution are not influenced by concentration of ACQ solution and Cu to EtAmOH ratio (Figure 2, Appendix 2-3). At a solution pH<7, the amount of copper precipitation is expected to decrease with increase in ACQ concentration and the proportional amount of ethanolamine to copper, as free copper decreases with increasing concentration and proportional amount of ethanolamine to copper.

At solution pH >7, an increase in ACQ concentration and increase in proportional amount of ethanolamine ligand to copper in ACQ solution resulted in a decrease in the amount of +1

charged CuL₂ type complex, which is expected to favor fixation reactions. These conditions also resulted in an increase in the +2 charged CuL₃ and CuL₄ type complexes. For ACQ solution with Cu to EtAmOH ratio of 1:4, an increase in concentration of ACQ from 0.5% to 1% and 1.5% resulted in a decrease in the +1 charged CuL₂ type complexes from 86% to 81% to 78% respectively at a solution pH of 9. At pH 9 the +2 charged CuL₃ type complex increased from 2% to 7% and 10% respectively. At the same time, the increase in the +2 charged CuL₄ type complex was from 0% to 1% and 2% (Figure 2b, Appendix 2b & 3b). For 1% ACQ solution, the increase in ratio of ethanolamine ligand to copper in the solution from 1: 3 to 1: 4 and 1: 10 resulted in the decrease of the +1 charged CuL₂ type complexes from 82% to 81% and 61% respectively at pH = 9. For the same pH he +2 charged CuL₃ type complex increased from 4% to 7% to 22% respectively with the change in copper to ethanolamine ratio same time copper distributed as the +2 charged CuL₄ type complex increased from 0% to 1% and 10% respectively (Figure 2).

Solution parameters pH and Cu to EtAmOH ratio are the main factors to be considered in optimizing ACQ formulations at a particular concentration for better performance. +1 charged CuL₂ type complex, which is hypothesized to be the most desirable species in ACQ solution to favour fixation after treatment with wood, reaches the maximum concentration at a solution pH of 8.5 to 9. If proposed future testing confirms this hypothesis, this study suggests there is a benefit to narrowing the recommended ACQ solution pH range of 8-11 for ACQ wood preservatives in AWPA standards (e.g., to 8 to 9). The higher percentage of copper distributed as less or non-reactive neutral CuL₂ type at a solution pH > 10 support this recommendation. Increasing the proportional amount of ethanolamine ligand to copper in the formulation reduces the +1 charged CuL₂ type complex in the solution. Figure 3 summarizes the effect of increasing the ethanolamine to copper ratio on the distribution of different complexes at an equilibrium solution pH of 8.7, the pH at which the +1 charged CuL₂ type complex is maximized. The +1charged CuL₂ type complex reaches a maximum at a Cu to EtAmOH ratio of 1:3, although it is only slightly lower at the AWPA recommended ratio of 1:4. This suggests that a Cu to EtAmOH ratio of 1:3 is the optimum to maximize the distribution of copper as this particular complex. These results suggest the possibility of reducing the Cu to EtAmOH ratio of ACO from 1: 4 to 1: 3. Reduction in the proportional amount of EtAmOH in the formulation is not expected to result in any precipitation in solution, as any expected formation of copper hydroxide re-dissolves at basic pH when EtAmOH to Cu ratio is more than 2 (Tauller et al., 1986) and there is very little free copper ion available to precipitate carbonates.

Commercial ACQ solutions have pH close to 9 and Cu to EtAmOH ratio close to 1:4. Reduction in solution pH is observed during fixation of ACQ in wood after treatment, before the pH is dropped close to 6 and fixation is maximized. We propose that pH-controlled fixation reaction of copper in ACQ treated wood may be explained as follows: Immediately after the treatment of wood with ACQ solution, + 1 charged CuL₂ type complex, which is the major copper ethanolamine complex at a pH of 8.5 to 9, initiates ion exchange reaction with wood components such as carboxylic and phenolic groups, resulting in pH reduction of the solution. This drop in pH of the solution in the wood after the initial reaction results in a reduction of +1 charged CuL₂ type complex and an increase +2 charged CuL₂ type complex as the major reaction species in ACQ solution in the wood. Further reaction of the complex species with wood reduces the pH to

below 7 to initiate de-amination of copper ethanolamine complexes leaving free copper in the solution. Carbonates in the solution are expected to react with free copper in the solution to form copper carbonate (less soluble) precipitates in the wood. Below pH 7, +2 charged CuL₁ and CuL₂ type complex become the dominant species to aid further possible ion exchange reactions. The amount of copper fixed in the wood is mainly as a result of ion exchange type reactions happening at a solution pH > 7 and precipitation as well as ion exchange reaction at a solution pH < 7. As pH controlled fixation reactions are limited by the wood's capacity to neutralize the higher solution pH (close to 9 for commercial ACQ) to a pH close to 6 it may be possible to accelerate the pH drop and facilitate fixation by further lowering the commercial ACQ pH of 9. Solution pH > 7 is necessary to avoid precipitation of copper in the solution. Hence this study recommends investigating whether a pH of 7.5 -9 instead of 8-11 recommended by AWPA standards is feasible. A Cu to EtAmOH ratio of 1: 3 is recommended to maximize fixation reactions instead of 1: 4 for the following reasons: 1) +1 charged CuL_2 type complex, which is expected to favor ion exchange reactions immediately after treatment, is maximum at 1:3 ratio at a pH 8.5 to 9.2) A decrease in free copper in the solution occurs with an increase in ethanolamine to copper ratio at pH < 7, so more free copper will be available with a ratio of 1:3 to enhance copper carbonate precipitation reaction during fixation reaction below pH 7.3) Higher ligand ratio increase the chances of neutral ML_2 , +2 charged ML_3 and ML_4 type complex in the solution. Neutral complex cannot fix or react with wood. ML₃ and ML₄ type complexes may leach easily from treated wood as the water solubility of these complexes are enhanced because of more hydroxyl group from the ligand compared to other complex with less number of ligand (17).

4. Conclusions

1. MINTEQA2, an equilibrium speciation model for aqueous systems, is a helpful tool to study the alkaline copper quat (ACQ) solution composition at different concentrations and for various solution parameters such as ionic strength, Cu to EtAmOH molar ratio, additives and pH.

2. Solution pH is the key parameter determining the distribution of copper ethanolamine complexes in the solution. For the ACQ formulation considered here, at acidic solution pH, most of the ethanolamine is protonated and will not coordinate with copper. Deprotonation of protonated ethanolamine ligand begins at a solution pH > 3.5 and it begins to coordinate with copper.

3. At a solution pH between 3.5 and 7, +2 charged CuL_1 and CuL_2 type are the major species in the solution.

4. Increase in pH above 7 results in no free copper ion in the solution and precipitation of copper in ACQ solution is not expected above a solution pH of 7.

5. At solution pH between 7 and 10, +1 charged CuL_2 type complex is the major species in ACQ solution. At a solution pH>10, distribution of copper as +1 charged CuL_2 type complex

decreases and the distribution of the neutral CuL_2 type complex increases and becomes the dominant species in the solution.

6. At pH <7, an increase in concentration and an increase in proportional amount of ethanolamine ligand to copper in ACQ solution result in a decrease of free copper in the solution indicating higher degree of coordination of copper with ethanolamine ligand. The same change at a solution pH >7 result in decrease of the +1 charged CuL₂ type complex and an increase in the +2 charged CuL₃ and CuL₄ type complexes.

7. +1 charged CuL_2 type complex, hypothesized to be the most desirable complex species to maximize fixation reaction in wood after ACQ treatment, is maximized at a solution pH of 8.5 - 9 and Cu to EtAmOH ratio of 1:3. This study suggests the possibility of reducing the copper to ethanolamine molar ratio 1:3 and narrowing the pH range of ACQ to 7.5 to 9 to improve fixation.

5. Literature

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Complex	Legends in	Description	Equilibria	Log K
	figures			

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Table 1. Extrapolated Log K value of copper ethanolamine complexes for zero ionic strength at 25^{0} C.

[H(EtAmOH)] ⁺¹	[HL] ⁺¹	Protonation of amine	$H^+ + (EtAmOH) \square$ $[H(EtAmOH)]^{+1}$	9.51
[Cu(EtAmOH) ₂] ⁺²	$[CuL]^{+2}$	CuL ₁ type, +2 charged	$Cu^{+2} + (EtAmOH) \square \\ [Cu(EtAmOH)]^{+2}$	4.47
$[Cu(EtAmOH)_2]^{+2}$	$\left[\text{CuL}_2\right]^{+2}$	CuL ₂ type, +2 charged	$Cu^{+2} + 2(EtAmOH) \square$ $[Cu(EtAmOH)_2]^{+2}$	8.32
[Cu(EtAmOH)(EtAmO)] ⁺¹ Or [Cu(EtAmOH) ₂ (OH)] ⁺¹	[CuL ₂] ⁺¹	CuL ₂ type, +1 charged	$Cu^{+2} + 2(EtAmOH) + OH^{-} \square$ $[Cu(EtAmOH)(EtAmO-)]^{+1} + H_2O$ Or $Cu^{+2} + 2(EtAmOH) + H_2O \square$ $[Cu(EtAmOH)_2(OH)]^{+1} + H^{+}$	1.43
$[Cu(EtAmO-)_2]^0$ Or $[Cu(EtAmOH)_2(OH)_2]^0$	[CuL ₂] ⁰	CuL ₂ type, neutral	$\begin{array}{c} Cu^{+2} + 2(EtAmOH) + 2OH^{-} \\ [Cu(EtAmO-)_{2}]^{0} + 2H_{2}O \\ \\ Or \\ Cu^{+2} + 2(EtAmOH) + 2H_{2}O \\ [Cu(EtAmOH)_{2}(OH)_{2}]^{0} + 2H^{+} \end{array}$	-8.4
[Cu(EtAmOH) ₃] ⁺²	$\left[\text{CuL}_3\right]^{+2}$	CuL ₃ type, +2 charged	$Cu^{+2} + 3(EtAmOH) \square$ $[Cu(EtAmOH)_3]^{+2}$	10.5
[Cu(EtAmOH) ₄] ⁺²	$\left[\mathrm{CuL}_{4}\right]^{+2}$	CuL ₄ type, +2 charged	$Cu^{+2} + 4(EtAmOH) \square$ $[Cu(EtAmOH)_4]^{+2}$	11.1

Table 2. Alkaline copper quat (ACQ) solution parameters

ACQ (%)	CuCO ₃	DDAC	CO ₃ in	Monoethanolamine (EtAmOM)	
CuO:DDAC	(M)	(M)	ACQ	in ACQ (M)	Ionic

= 2:1			(M)	Cu: (EtAmOH)			strength
				1:4	1:3	1:10	(M)
0.5	0.042	0.004	0.045	0.164	0.126	0.420	0.173
1	0.084	0.009	0.090	0.328	0.252	0.840	0.347
1.5	0.126	0.013	0.136	0.491	0.378	1.260	0.520



Figure 1. Effect of ionic strength on the distribution of copper ethanolamine complexes in 1% alkaline copper quat (ACQ) solution having CuO to DDAC ratio of 2:1 and Cu to EtAmOH ratio of 1: 4. *Note:* In the figure legend A is $[CuL_{2}]^{+2}$, B is $[CuL_{2}]^{+2}$, C is $[CuL_{3}]^{+2}$, D is $[CuL_{4}]^{+2}$, E is $[CuL_{2}]^{+1}$, F is $[CuL_{2}]^{0}$, G is $[HL]^{+1}$, H is [L], I is Cu^{+2} , J is CO_{3}^{-2} , K is HCO_{3}^{-1} , L is $H_{2}CO_{3}(aq)$ and M is $CuCO_{3}(aq)$.



Figure 2. Effect of pH on the distribution of copper ethanolamine complexes in 1% alkaline copper quat (ACQ) solution having CuO to DDAC ratio of 2:1 a) Cu to EtAmOH ratio is 1:3, b) Cu to EtAmOH ratio is 1:4, c) Cu to EtAmOH ratio is 1:10. *Note:* In the figure legend A is $[CuL_{2}]^{+2}$, B is $[CuL_{2}]^{+2}$, C is $[CuL_{3}]^{+2}$, D is $[CuL_{4}]^{+2}$, E is $[CuL_{2}]^{+1}$, F is $[CuL_{2}]^{0}$, G is $[HL_{2}]^{+1}$, H is [L], I is Cu^{+2} , J is CO_{3}^{-2} , K is HCO_{3}^{-1} , L is $H_{2}CO_{3}(aq)$ and M is $CuCO_{3}(aq)$.



Figure 3. Effect of Cu to EtAmOH ratio on the distribution of copper ethanolamine complexes in alkaline copper quat (ACQ) at an equilibrium solution pH of 8.7. *Note:* In the figure legend A is $[CuL_{2}]^{+2}$, B is $[CuL_{2}]^{+2}$, C is $[CuL_{3}]^{+2}$, D is $[CuL_{4}]^{+2}$, E is $[CuL_{2}]^{+1}$, F is $[CuL_{2}]^{0}$, G is $[HL]^{+1}$, H is [L], I is Cu^{+2} , J is CO_{3}^{-2} , K is HCO_{3}^{-1} , L is $H_{2}CO_{3}(aq)$ and M is $CuCO_{3}(aq)$.



Appendix 1. Effect of pH on protonation of ethanolamine and distribution of copper ethanolamine complexes in 1% alkaline copper quat (ACQ) solution having CuO to DDAC ratio of 2:1 a) Cu to EtAmOH ratio is 1:3, b) Cu to EtAmOH ratio is 1:4, c) Cu to EtAmOH ratio of 1:10. *Note:* In the figure legend A is $[CuL_{2}]^{+2}$, B is $[CuL_{2}]^{+2}$, C is $[CuL_{3}]^{+2}$, D is $[CuL_{4}]^{+2}$, E is $[CuL_{2}]^{+1}$, F is $[CuL_{2}]^{0}$, G is $[HL]^{+1}$, H is [L], I is Cu^{+2} , J is CO_{3}^{-2} , K is HCO_{3}^{-1} , L is $H_{2}CO_{3}(aq)$ and M is $CuCO_{3}(aq)$.

APPENDIX



Appendix 2. Effect of pH on the distribution of copper ethanolamine complexes in 0.5% alkaline copper quat (ACQ) solution having CuO to DDAC ratio of 2:1 a) Cu to EtAmOH ratio is 1:3, b) Cu to EtAmOH ratio is 1:4, c) Cu to EtAmOH ratio is 1:10. *Note:* In the figure legend A is $[CuL]^{+2}$, B is $[CuL_2]^{+2}$, C is $[CuL_3]^{+2}$, D is $[CuL_4]^{+2}$, E is $[CuL_2]^{+1}$, F is $[CuL_2]^0$, G is $[HL]^{+1}$, H is [L], I is Cu^{+2} , J is CO_3^{-2} , K is HCO_3^{-1} , L is $H_2CO_3(aq)$ and M is $CuCO_3(aq)$.



Appendix 3. Effect of pH on the distribution of copper ethanolamine complexes in 1.5% alkaline copper quat (ACQ) solution having CuO to DDAC ratio of 2:1 a) Cu to EtAmOH ratio is 1:3, b) Cu to EtAmOH ratio is 1:4, c) Cu to EtAmOH ratio is 1:10. *Note:* In the figure legend A is $[CuL]^{+2}$, B is $[CuL_2]^{+2}$, C is $[CuL_3]^{+2}$, D is $[CuL_4]^{+2}$, E is $[CuL_2]^{+1}$, F is $[CuL_2]^0$, G is $[HL]^{+1}$, H is [L], I is Cu^{+2} , J is CO_3^{-2} , K is HCO_3^{-1} , L is $H_2CO_3(aq)$ and M is $CuCO_3(aq)$.