



Emission Minimization of Ammoniacal/Amine Copper Preservatives

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What emissions must be considered

- **Copper**
- **Solvent (ammonia or amine)**
- **Co – biocides or complexing agents**

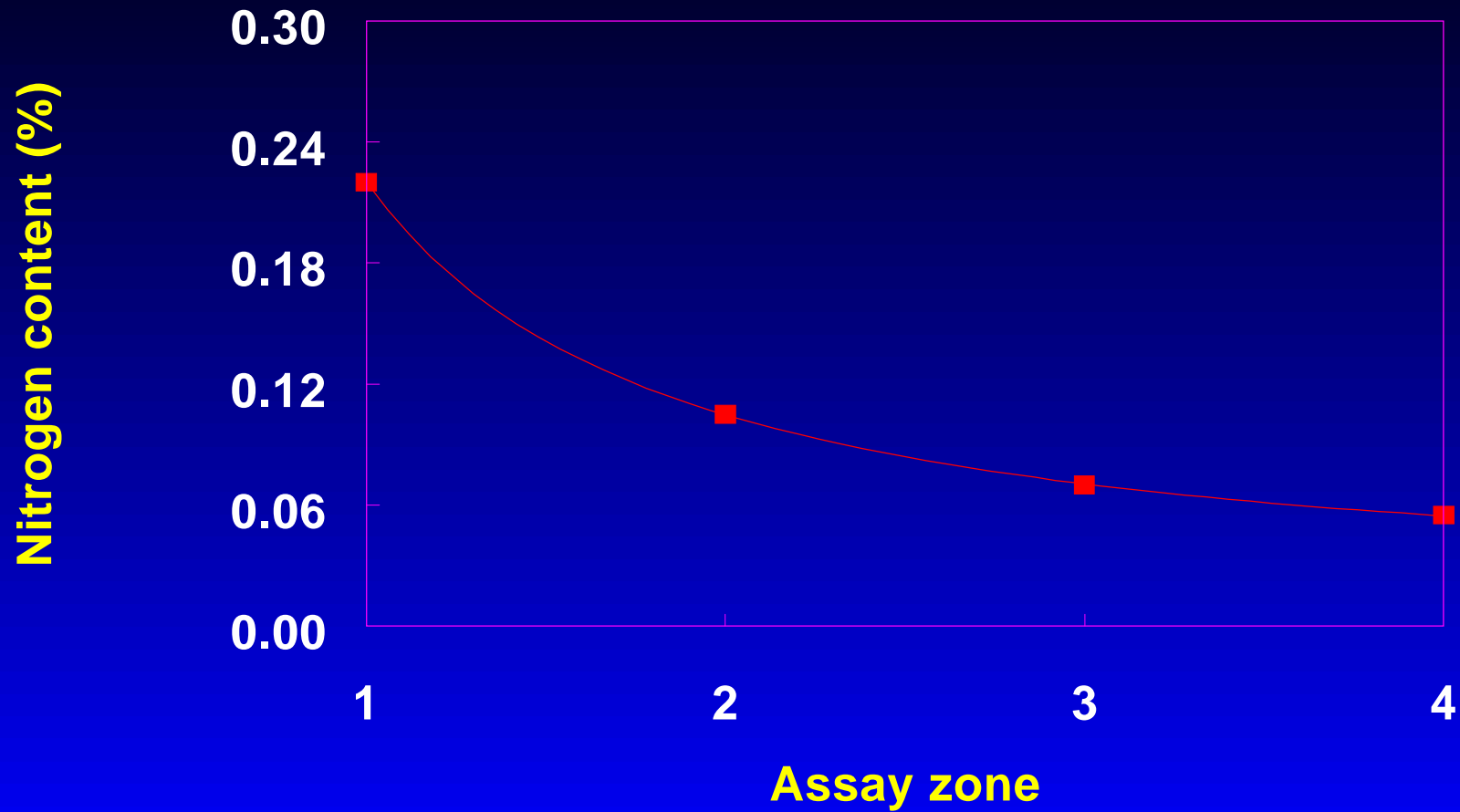


Fixation of ammoniacal copper arsenate



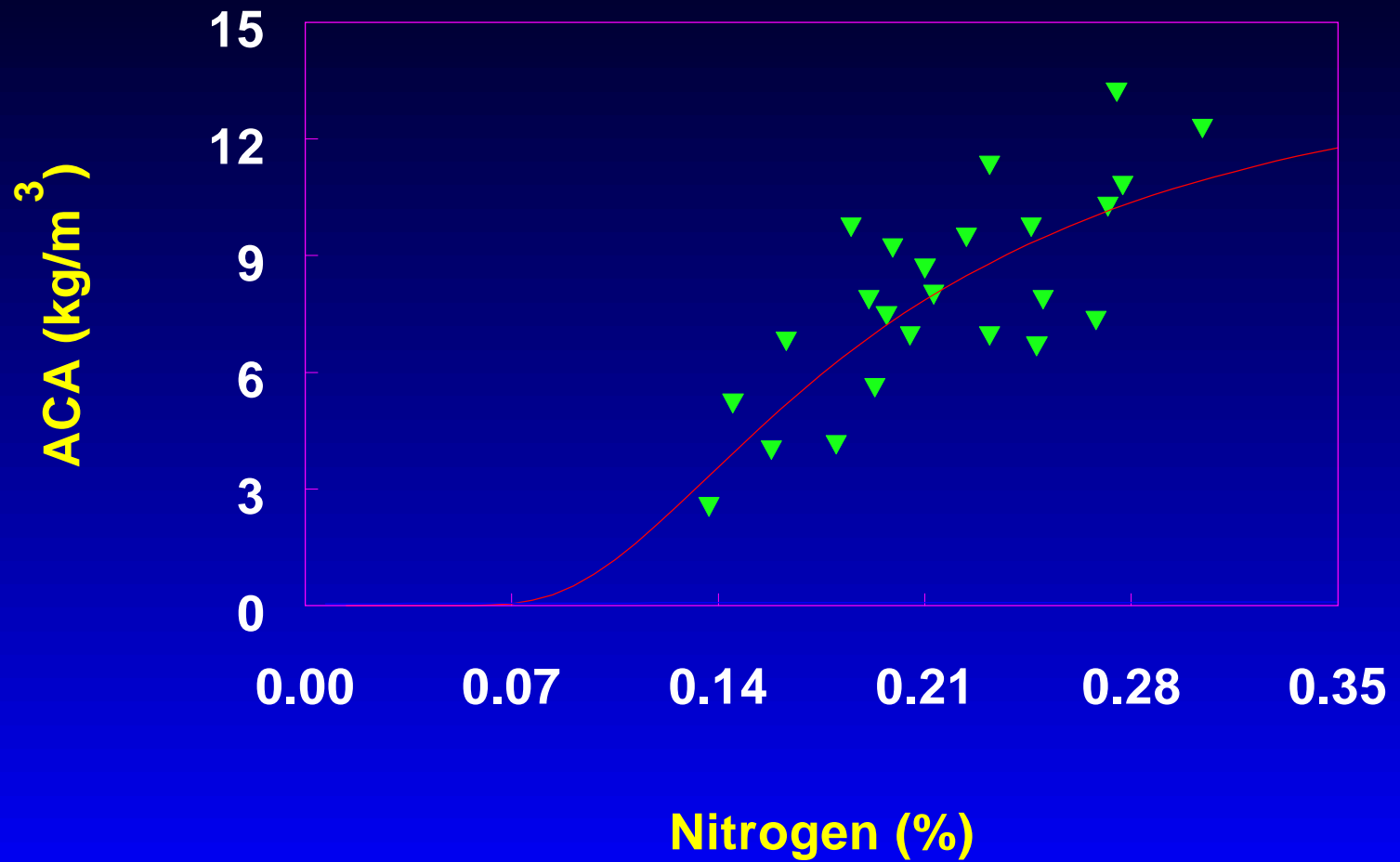


Nitrogen content in ACA treated wood





Graph of ACA versus nitrogen content





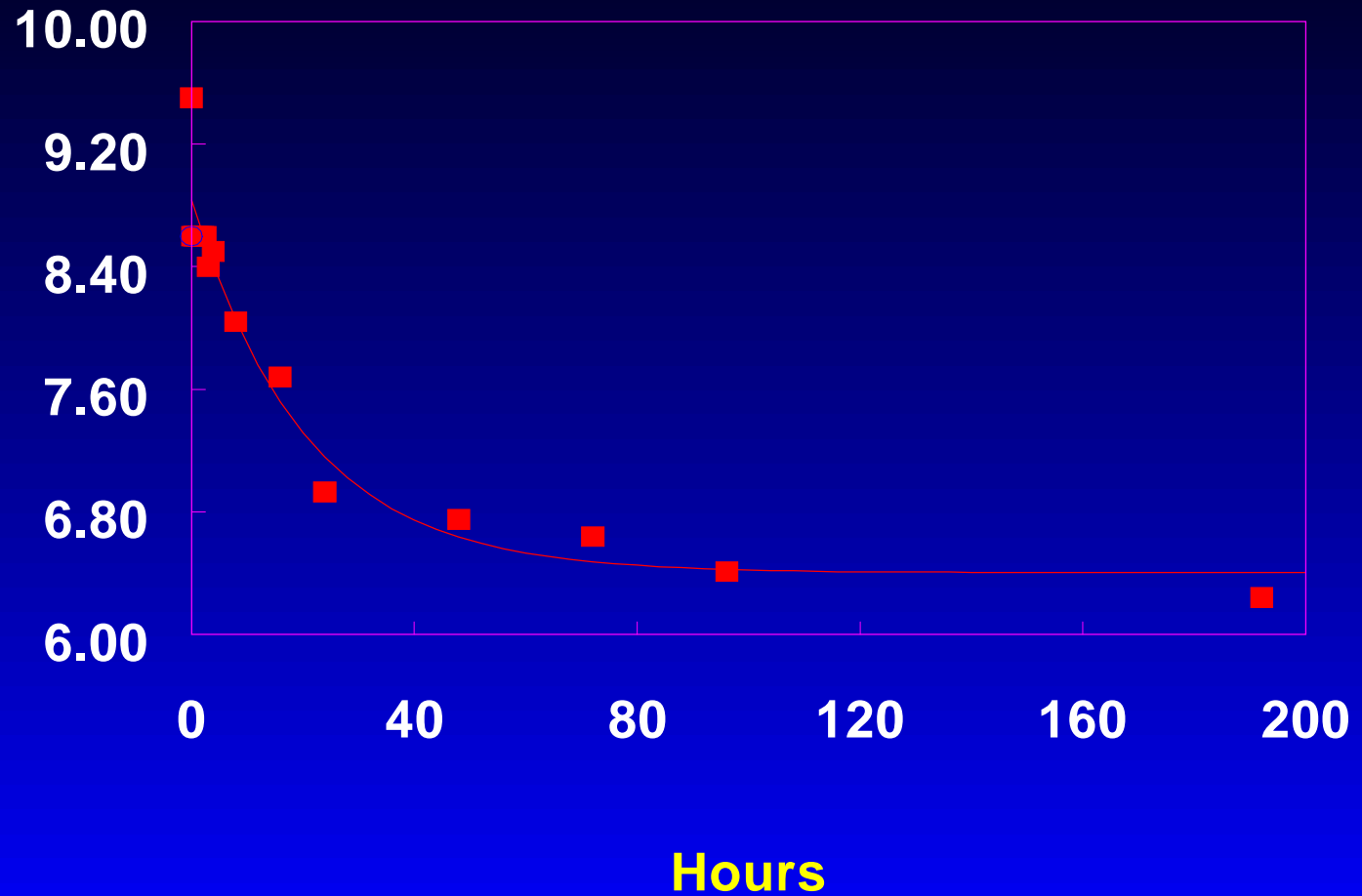
Fixation of ammoniacal copper systems





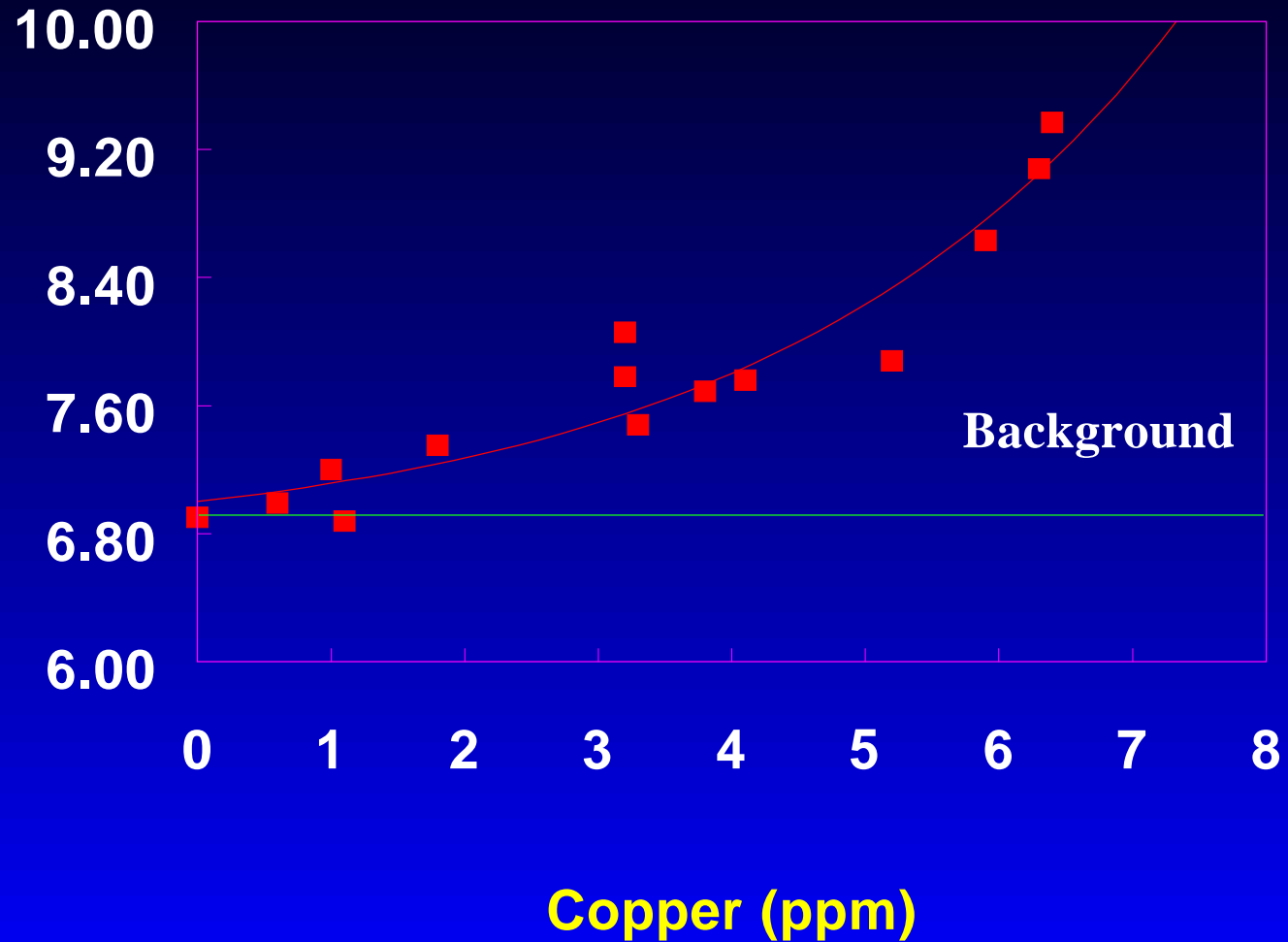
Change in pH with fixation time ACA

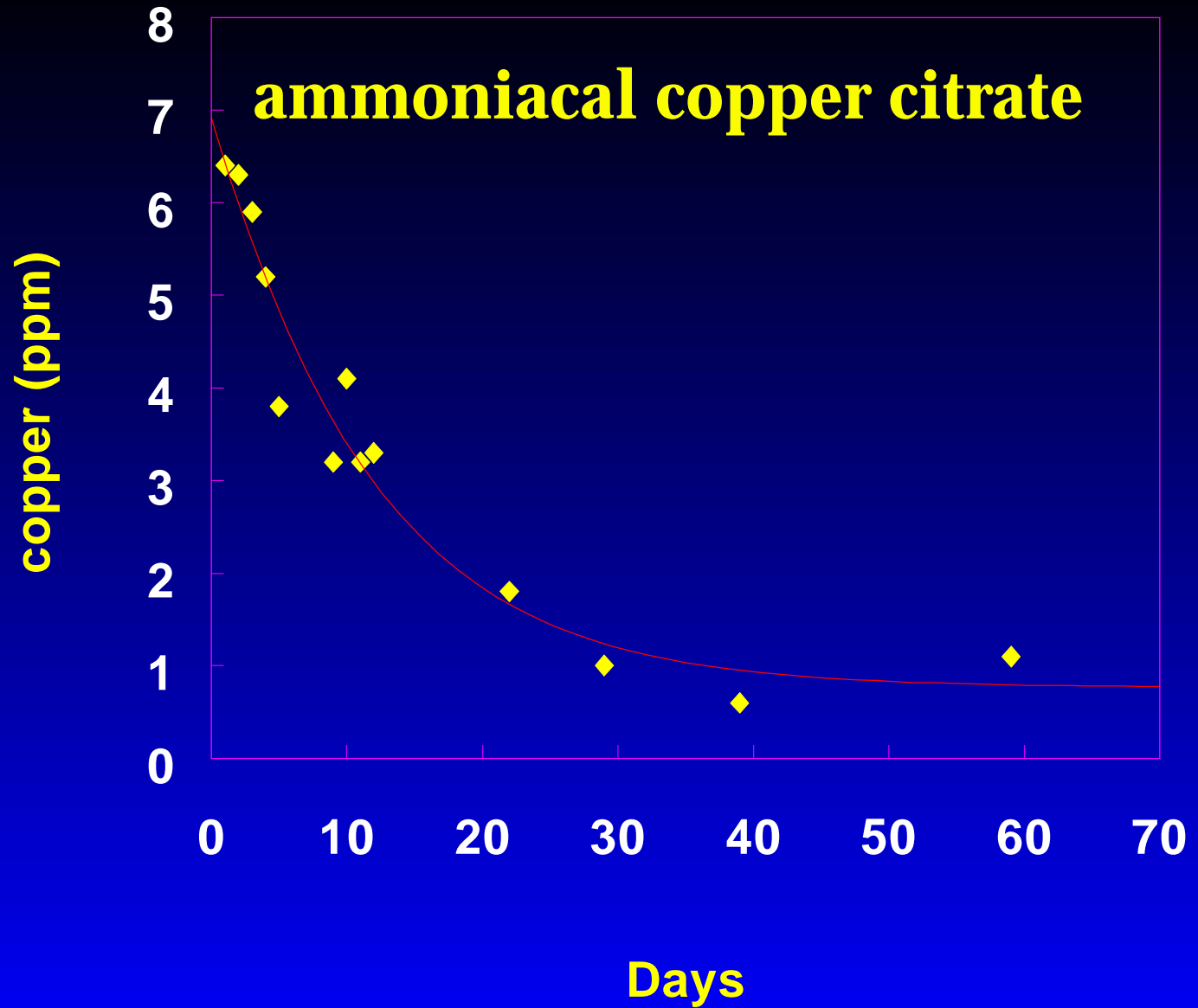
pH of leachate





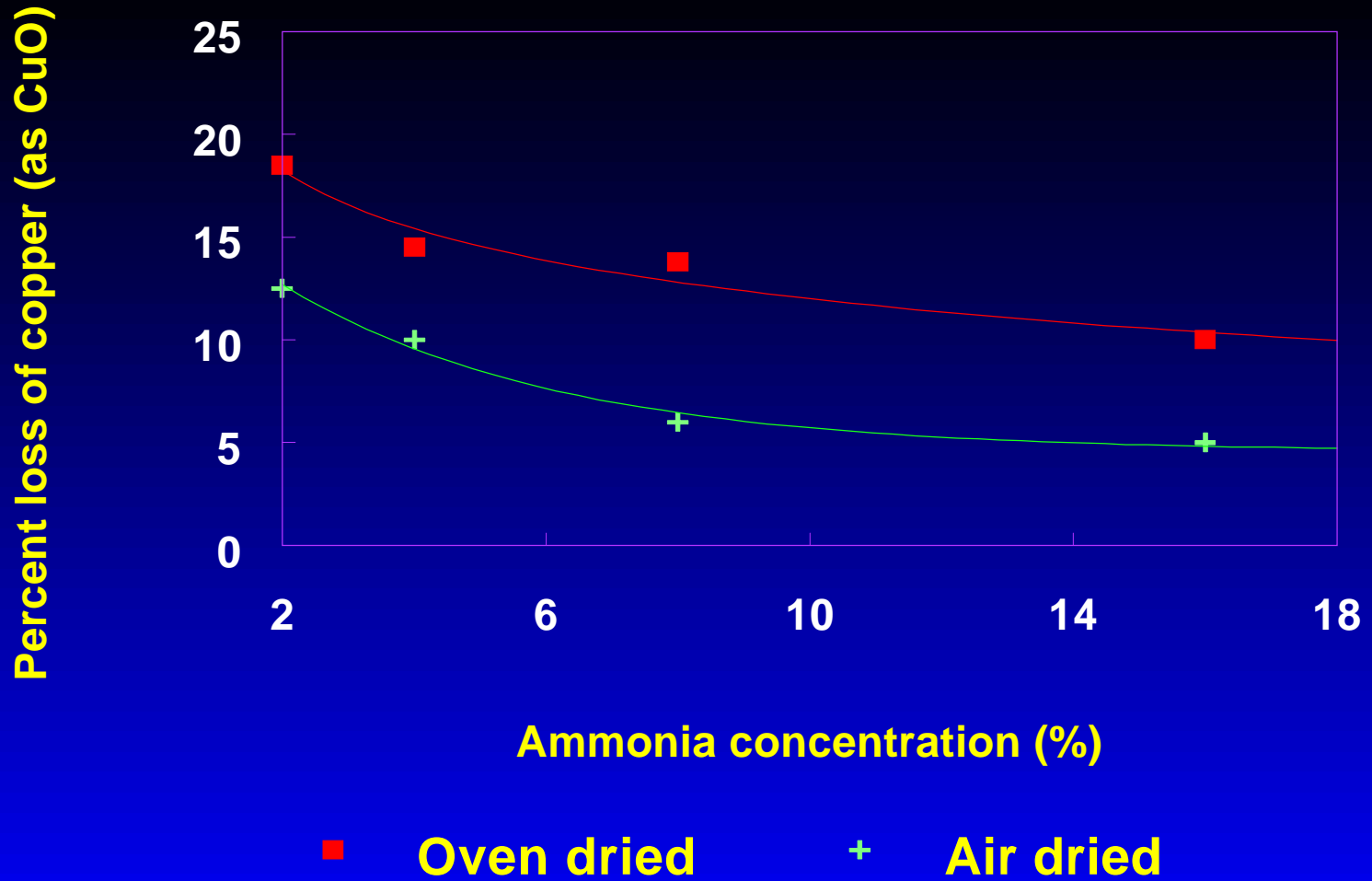
Graph of pH versus copper leached Ammoniacal copper citrate





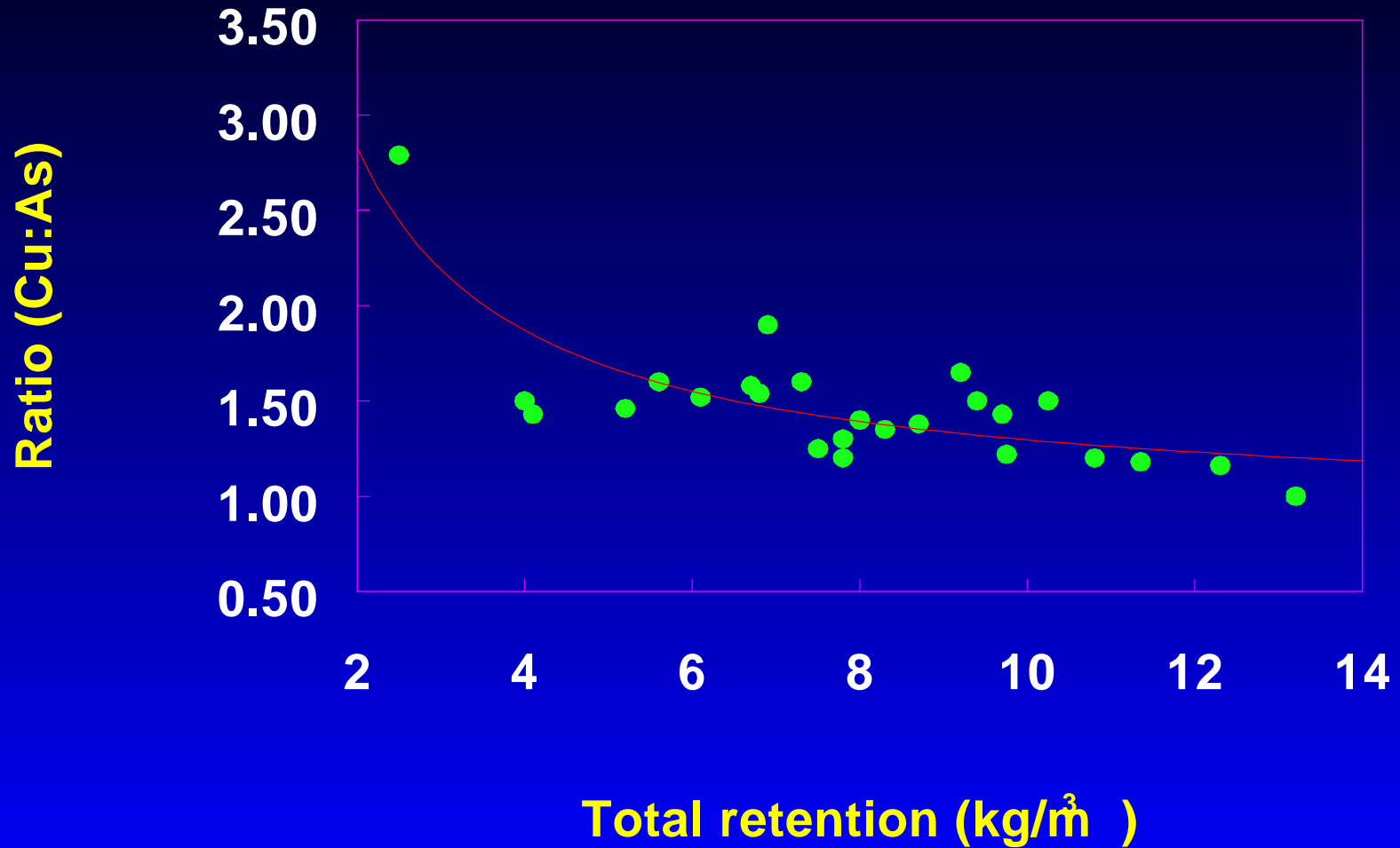


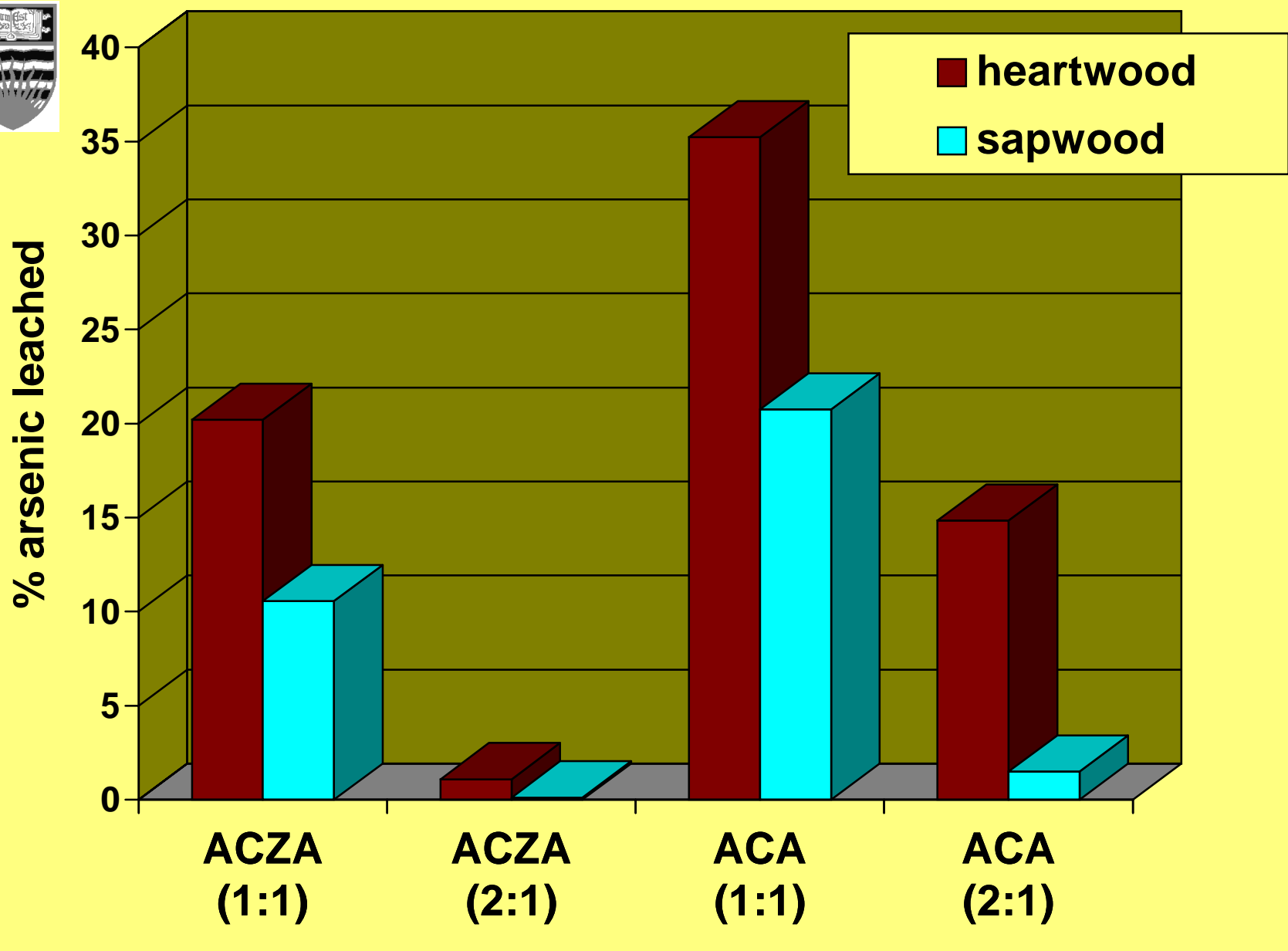
Copper loss as a function of ammonia and temperature





Ratio of copper to arsenic in ACA - treated wood

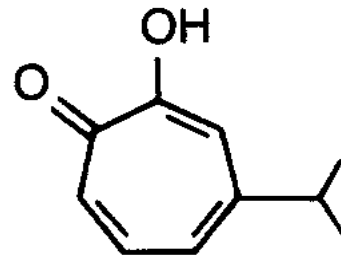




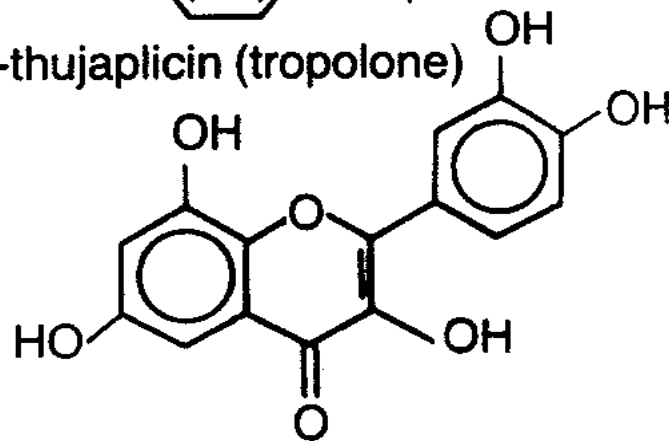
Lebow and Morrell, 1995



Extractive reactions



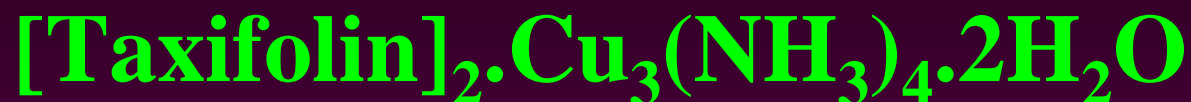
β -thujaplicin (tropolone)



Quercetin (flavonoid)



Ammonical copper complexes with taxifolin



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**



Solvent properties

Solvent	B.pt (°C)	pK _b	
NH_3	-33.3	4.75	
$\text{HO}(\text{CH}_2)_2\text{NH}_2$	171	4.17	MH
$\text{NH}_2(\text{CH}_2)_2\text{NH}_2$	117	~4.3	en



Fixation of amine copper systems



- pH decreases
- No loss of solvent by evaporation
- Loss of solvent from treated wood?



Fixation of monoethanolamine copper systems



pH 5-7

7-10

>10

Solution pH is >10

Treated wood pH is <7



Fixation of amine copper systems

Possible reactions

At pH 7 to 10

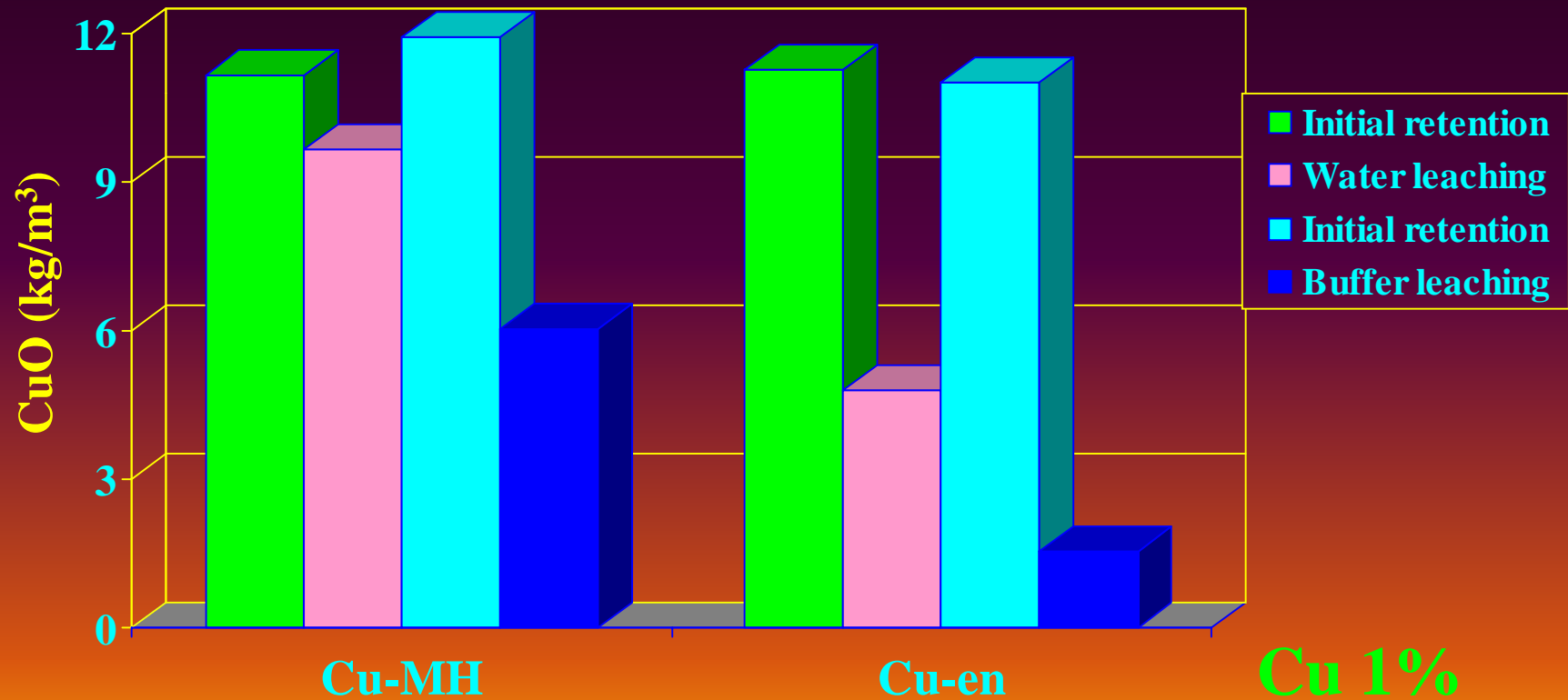


At pH <7





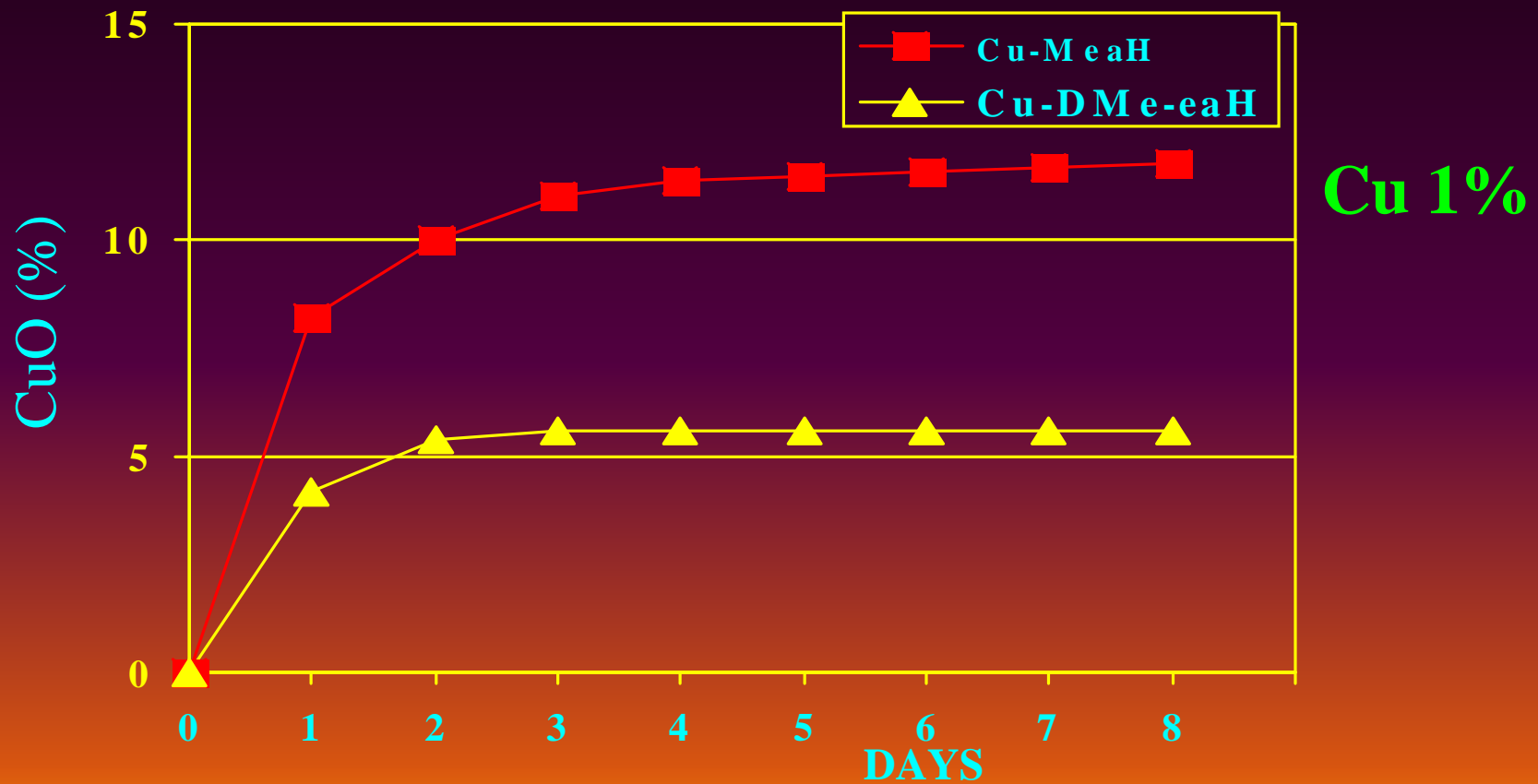
Copper content in copper amine treated wood before and after leaching



Cu 1%



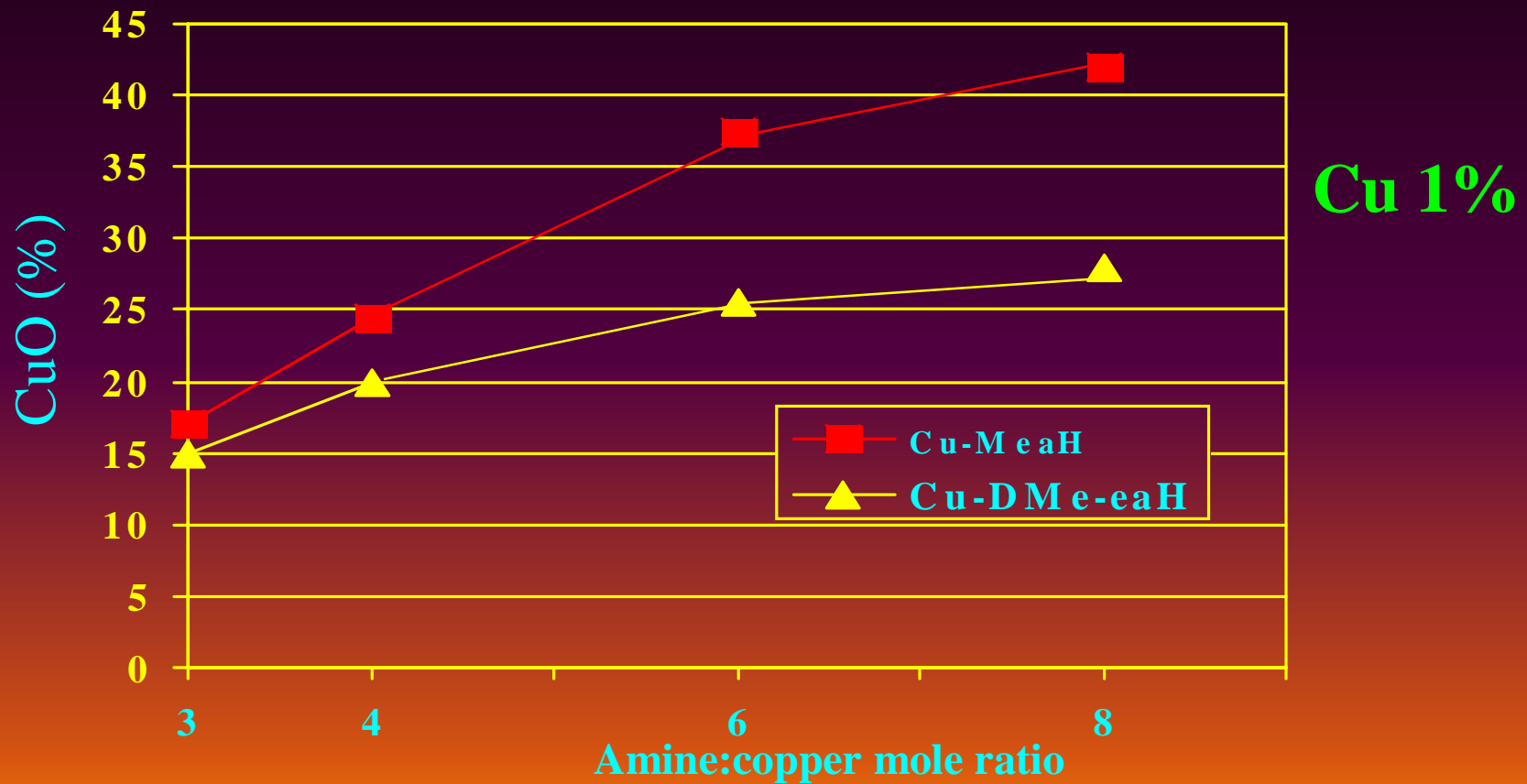
Influence of amine on percent copper leached from treated wood



Zhang & Kamdem, 1999



Influence of amine on percent copper leached from treated wood



Zhang & Kamdem, 1999

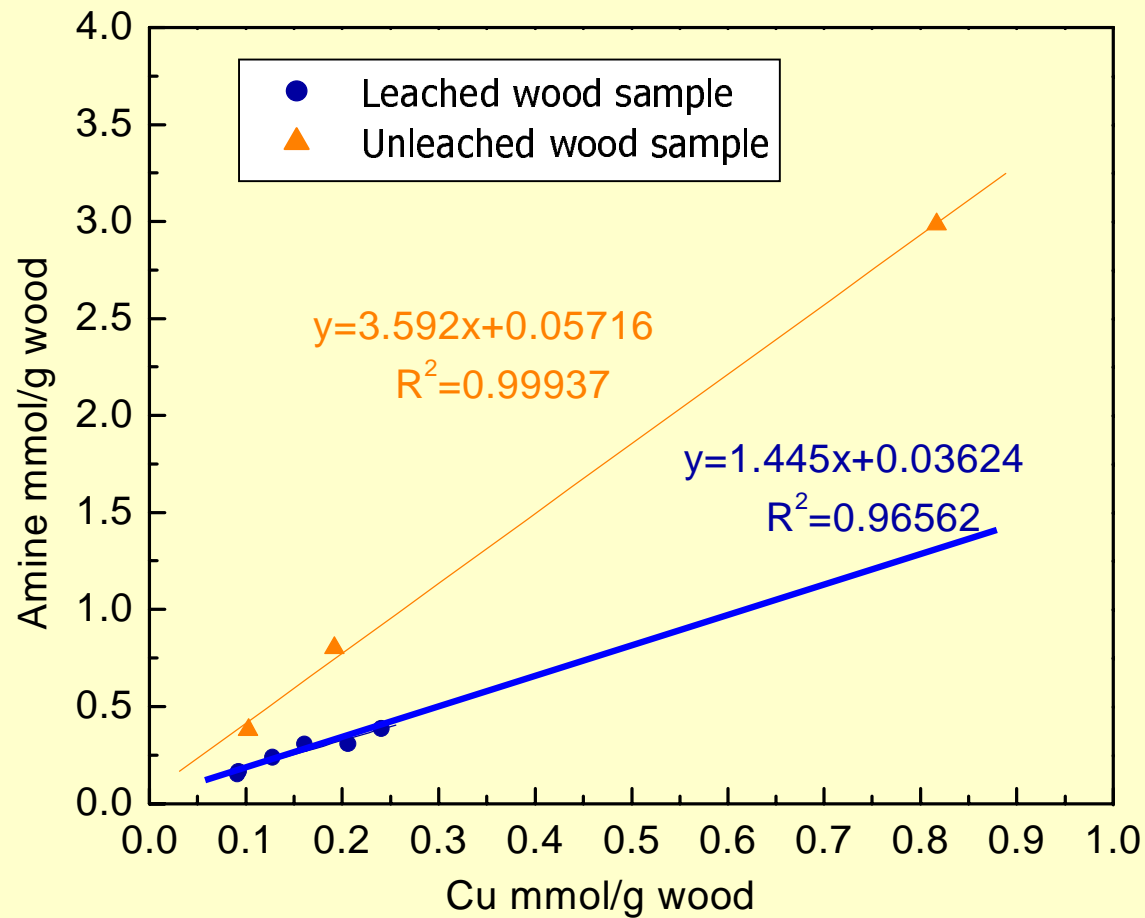


Nitrogen content in leached amine and copper-amine treated wood

Treatment	N in the block (mmol/g wood)	
	Water leaching	Buffer leaching
MH	0.282	0.207
en	0.260	0.232
Cu-MH	0.299	0.196
Cu-en	0.171	0.241

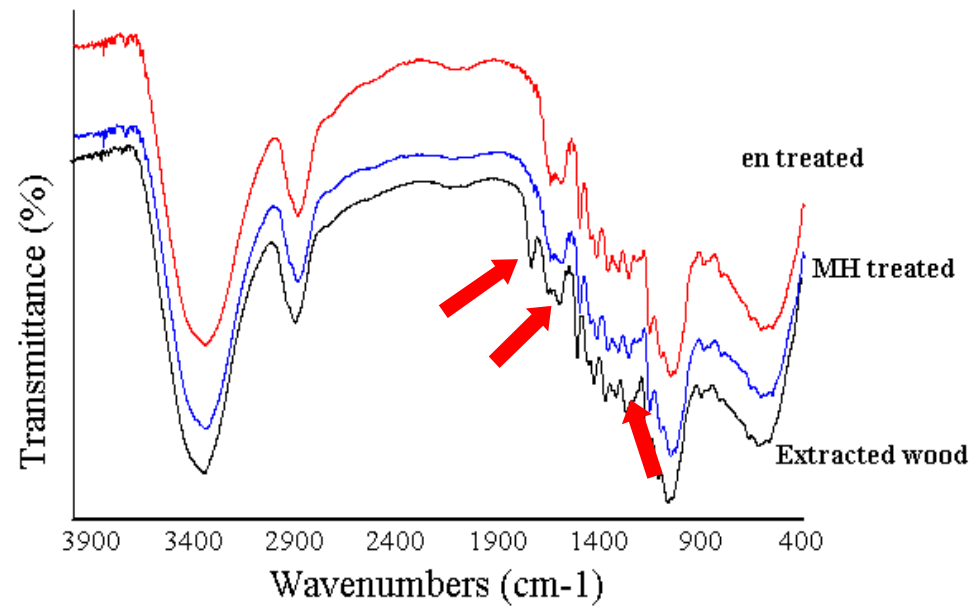


Amine to copper mole ratio in unleached and leached copper monoethanolamine treated wood



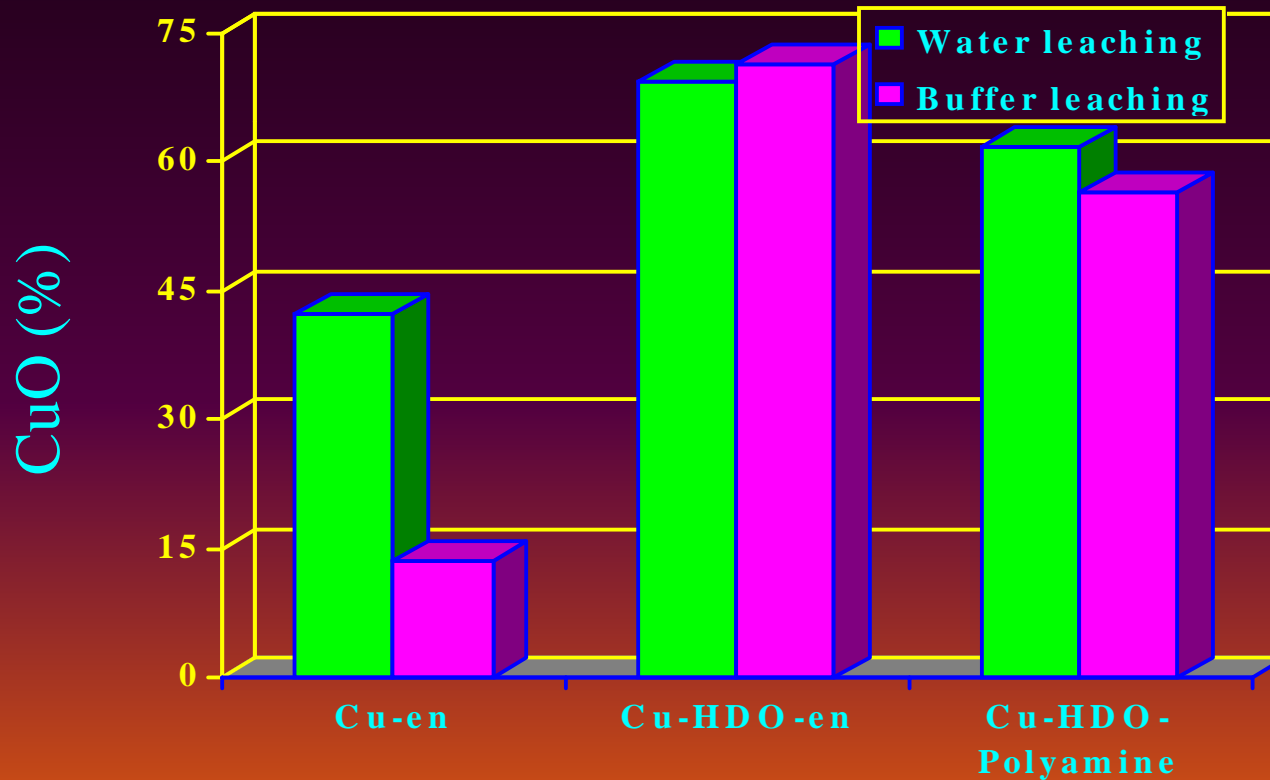


Amine treated wood



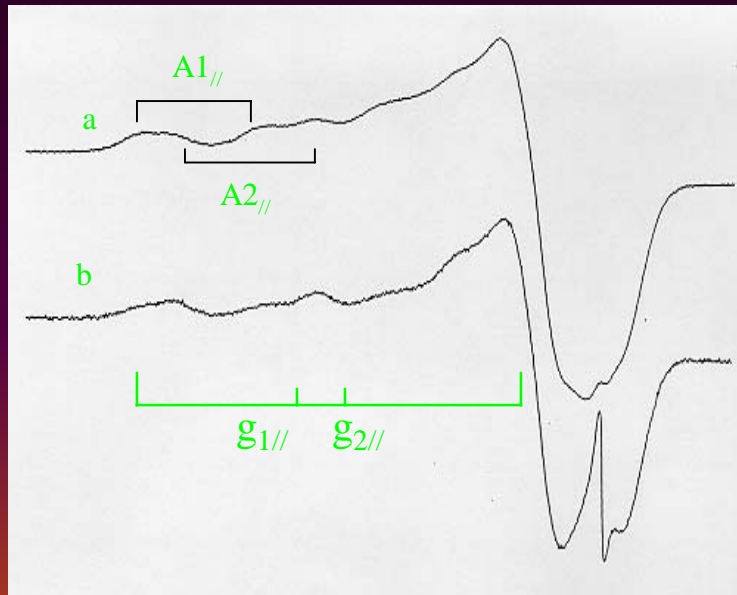


Influence of co-biocide on resistance of copper to leaching from treated wood



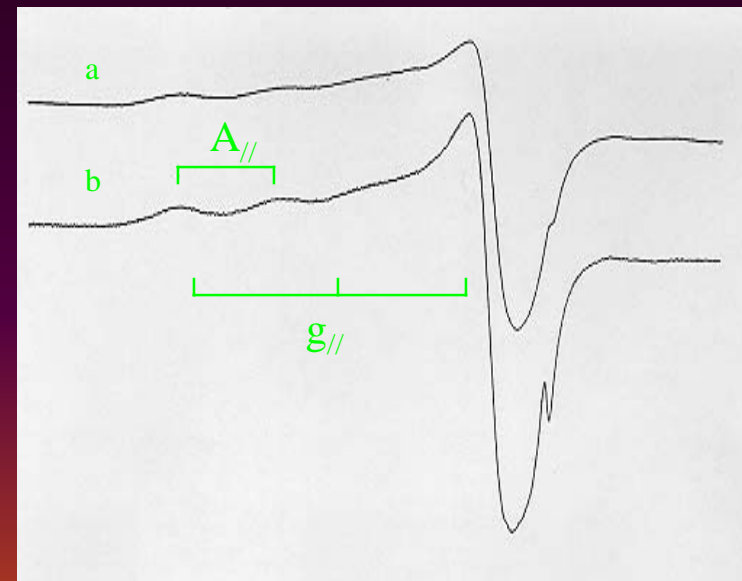


ESR - copper spectra of treated wood



Cu-en treated

a: water leaching;

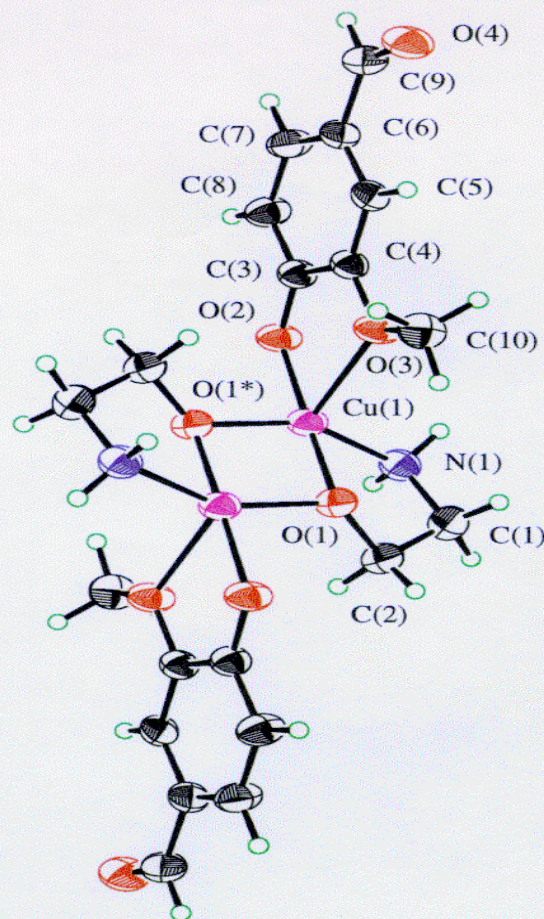


Cu-MEA treated

b: buffer leaching



Crystal structure of ethanolamine.vanillato.copper(II)





Fixation of amine copper systems

Copper likely fixes to:

CELLULOSE?	No
HOLLOCELLULOSE?	No?
LIGNIN?	Yes
EXTRACTIVES?	Yes



So what do we know?

- **Ammoniacal- and amine-copper treatments result in solvent wood reactions which retain solvent bound to wood.**
- **Amine(or ammonia)-wood, copper amine (or ammonia)-wood and copper wood complexes complexes are formed during fixation.**
- **The formation and nature of these complexes strongly influences leaching of copper.**



and....

- **Heating of ammoniacal copper treated wood reduced fixation, while increasing ammonia content in the solution increased fixation.**
- **Heating of amine copper treated wood can accelerate fixation.**
- **Increasing the amine to copper ratio can increase leaching**



and lastly

- **The addition of co-biocides can reduce copper leaching.**
- **Changing the amine can greatly affect copper fixation.**
- **Copper-amine reacts primarily with lignin and extractives, but not with cellulose.**



Acknowledgements

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QUESTIONS

