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COPPER NAPHTHENATE-TREATED SOUTHERN PINE POLE STUBS IN FIELD EXPOSURE: PART I--GRADIENT & BIODETERIORATION ANALYSIS 12 YEARS AFTER TREATMENT

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COPPER NAPHTHENATE-TREATED SOUTHERN PINE POLE STUBS IN FIELD EXPOSURE: PART I--GRADIENT & BIODETERIORATION ANALYSIS 12 YEARS AFTER TREATMENT[1]

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ABSTRACT

Naphthenates have been used for the preservation of timber and cellulose since their original identification in Russia in the early 1880's as part of a series of petroleum characterizations. Later work in the development of copper naphthenate as a heavy-duty preservative for poles led to the development of various treating cycles similar to other oil-borne systems. Recent work concerning the post treatment steam conditioning of copper naphthenate treated southern pine has determined that some amorphous copper naphthenate is converted to a crystalline cuprous oxide. In small laboratory tests, this was later determined to be less efficacious than copper naphthenate. This paper reviews the performance of actual pole-diameter stubs placed in a high hazard location containing both termites and potential for early decay attack. Various treating cycles were used to treat the pole stubs in this test including various post-treatment conditioning methods.

Keywords: poles, copper naphthenate, southern pine, performance, efficacy, preservative, steam conditioning, post-treatment steaming, fixation

INTRODUCTION

Copper naphthenate (CuN) has been documented as being a very effective wood preservative (2, 3, 6, 8, 9, 13) . When the U.S. Environmental Protection Agency reviewed all the major wood preservatives, including pentachlorophenol (penta), creosote, and the inorganic arsenicals, manufacturers of CuN began to actively promote the chemical as a viable alternative to pesticides. Although efforts to use CuN as an extender for creosote began during the war effort of the 1940's due to a shortage of creosote, widespread use of CuN has occurred only within the last decade. Efforts were made within the American Wood-Preservers' Association (AWPA) to have standards for specific commodities for wood treated with CuN as early as the mid-1980s (1).

The treatment of poles with CuN began commercially in the late 1980s. For a variety of reasons, early failures of CuN-treated poles were experienced by utilities.

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Recent publications in the literature have indicated that, in small scale laboratory tests, samples of southern pine wood that have been treated with CuN in P-9 Type A oil, undergo a change from amorphous CuN to crystalline cuprous oxide (11, 12). At low retentions, this conversion to cuprous oxide in small laboratory samples has been as much as 50% of the available copper. The extent to which this is anything but a surface phenomena has yet to be shown. Additional tests have shown that CuN has a more biologically active form of copper than many other copper complexes or copper salts, with the exception of oxine copper (5). As a result of the changes noted in small laboratory tests and the incidence of early failures of poles in service, the executive committee of the AWPA issued the following instruction to Subcommittee P-3 Organo and Organometallic Preservatives: "Review, with particular emphasis on the effects of pre- and/or post-steaming on the efficacy of CuN preservative systems, including degradation of CuN into possible less-efficacious forms of copper" (7). The purpose of this study is to detail our experience with pole-sized material in exterior exposure. Hopefully, this research will answer some of the practical concerns posed by producers and users of treated poles.

METHODS AND MATERIALS

In 1987, pole sections treated with CuN (4) were placed in storage in an above-ground environment as well as placed in ground contact in a high decay, high termite attack area (AWPA Hazard Zone 4) near Starkville, MS. Data and conditions of these pole stubs have not previously been reported since their installation over 12 years ago. Many of the pole stubs in this test were exposed to steaming conditions, either pre-steaming for conditioning purposes, post-steamed for aesthetic reasons, or a combination of these two steaming conditions. Other variables included in these pole stub tests were initial conditioning method (air-dried or steam-conditioned), varying solution temperature conditions, and use of a final fixation/expansion bath (10). Details of the treating and conditioning processes and procedures can be found in the literature (4). A summary of the treatment details is given in Table 1.

Selected trees of loblolly pine (*Pinus taeda* L.) were cut, bucked into nominal 8-ft pole stubs and immediately debarked, and cut into matched 4-ft sections for use in this study. Nominal pole stub diameter was eight inches.

Table 1. Processing variables and materials used.

Variable	Description
Initial conditioning	Steam-conditioned, Air-dried
Treatment cycle	Rueping: 30 psig initial air; 150 psig maximum pressure; Final vacuum >24 in Hg; Treating temperature varied (ambient to 200 F)
Preservative	8% (as Cu) copper naphthenate (CuN) concentrate
Solution	0.8% (as Cu) CuN in No. 2 fuel oil meeting AWPA specifications for P9 type A solvent except for penta solvency
Final conditioning	None, Steam flash +vacuum; Fixation (expansion) bath+vacuum

After cooling overnight, each 4-ft pole stub was bored to the pith on third points around the circumference of the stub at the mid-point and 1-ft from the end of each stub. Borings were segmented into the following zones for analysis: 0.0-0.5, 0.5-2.0, 2.0-3.0, and 3.0-4.0 inches from the surface. Similar zonal segments from all stubs in a charge were combined for copper analysis by X-ray fluorescence spectroscopy (AWPA Standard A9). The data were cross-checked by atomic absorption (AA) spectrometry (AWPA Standard A11) using wet ashing procedures (AWPA Standard A7). In December 1987, half of the treated pole stubs were placed 18 inches into the ground while the remainder were placed horizontally on treated 4x4s in above-ground exposure. In 1999, selected pole stubs were bored and reassayed using AA spectroscopy. Poles representing the extremes in the treated population were chosen. For pole stubs placed in ground contact, four borings were taken at quarter-points mid-way between the ground line and the stub top and four additional borings were taken mid-way between the ground line and the butt end of the stub. For stubs exposed above ground, four borings were taken at approximately mid-length. One boring from each position was reserved for future testing while the three from each location were separated into the 0-0.5 in, 0.5-2.0 in, and 2.0-3.0-in zones for assay. The three cores for each zone and location were combined for assay. All pole stubs, whether assayed or not, were physically examined for signs of decay by visual inspection, sounding, and probing.

RESULTS AND DISCUSSION

The combinations chosen for evaluation are given in Table 2. The steam-conditioning represents the most severe initial conditioning step, while the fixation cycle and steam flash cycles represent the extreme in post-treatment conditioning.

None of the cores taken exhibited any signs of biodeterioration, Sounding and probing of all the pole stubs (42 in ground contact, 42 in above-ground exposure =84 total) failed to indicate any decay including colonization by soft rot fungi. Heavy checking in the above-ground portions of most of the pole stubs placed in ground contact was noted. However, no colonization by wood-destroying fungi was evident. The same was true for attack by insects. No termite or beetle activity was noted. The only insect activity was some fiber pull by wasps for nesting material.

Table 2. Processing parameters for pole stubs analyzed for preservative content.

Initial Conditioning	Final Conditioning	Treatment Temperature (F)	Number of Stubs Evaluated	
			Ground contact	Above-ground
Air-dried	Vacuum only	Ambient	2	2
	Fixation +vacuum	Ambient	2	2
	Steam+vacuum	180	2	2
Steam-conditioned	Vacuum only	Ambient	2	2
		200	5	3
	Fixation+vacuum	Ambient	2	2
		140	6	7
	Steam+vacuum	180	2	2

Preservative gradients and copper losses for air-dried (AD) stubs in ground contact are shown in Figures 1-3. Gradients in the above-ground (AG) and below-ground (BG) portions of the exposed stubs are compared with the original gradients obtained immediately after treatment. Copper losses in both zones are shown by bars. Loss data for CuN by treatment combination can be found in Table 3. Both the initial gradients for AD stubs and those after exposure were relatively flat and linear. Copper loss across the outer three inches in the AG portion of the air-dried stubs averaged 35% for stubs with no final conditioning, 30% for stubs which were steamed after treatment, and 7% for stubs undergoing a final fixation cycle. In the BG portion of the stubs, the loss values were 38%, 34%, and -4% for no post-treatment conditioning, final steaming, and fixation, respectively. The negative value represents a gain in preservative, most probably from movement by gravity from the top portion of the stub and/or radial movement from the interior of the pole stubs. These data suggest that the incorporation of a fixation cycle at the end of the pressure period may enhance the resistance to leaching.

Table 3. Copper losses by assay zone, conditioning methods, and location.

Conditioning		Treatment Temperature (F)	Location	Assay Zone Radial Mid-point (in)			Average Across Outer 3.0 inches
Initial	Final			0.25	1.25	2.50	
				Copper Loss (pcf)			
				Copper Loss (% of original)			
Air-dried	Fixation	Ambient	Above Ground (AG)	0.0075	0.0009	0.0046	
				9.7%	1.4%	13.3%	7%
			Below Ground (BG)	-0.014	0.0290	-0.0222	
				-18.1%	45.7%	-63.4%	-4%
			Stacked (ST)	0.0084	0.0157	0.0132	
				10.8%	24.7%	37.7%	21%
	Steam	180	AG	0.0303	0.0152	0.0273	
				26.9%	18.4%	58.1%	30%
			BG	0.0605	0.0207	0.0007	
				53.8%	25.1%	1.5%	34%
			ST	0.0386	0.0091	0.0115	
				34.3%	11.0%	24.5%	24%
	None	Ambient	AG	0.0489	0.0216	0.0179	
				41.8%	25.3%	36.1%	35%
			BG	0.0678	0.024	0.003	
				58.0%	28.1%	5.9%	38%

Table 3. Copper losses by assay zone, conditioning methods, and location.

Conditioning		Treatment Temperature (F)	Location	Assay Zone Radial Mid-point (in)			Average Across Outer 3.0 inches
Initial	Final			0.25	1.25	2.50	
				Copper Loss (pcf)			
				Copper Loss (% of original)			
			ST	0.0354	0.0109	0	
				30.3%	12.8%	-3.3%	18%
Steam-conditioned	Fixation	140	AG	0.1005	0.0185	0.0245	
				36.8%	17.4%	44.2%	33%
			BG	0.2187	0.0434	0.009	
				80.2%	40.8%	15.4%	62%
			ST	0.1429	0.0173	0.0103	
				54.9%	17.7%	21.3%	42%
		Ambient	AG	0.0874	-0.0033	0.014	
				39.2%	-3.4%	17.6%	24%
			BG	0.1795	0.0304	0.0101	
				80.5%	31.1%	12.6%	55%
			ST	0.1009	0.0063	0.0172	
				45.3%	6.5%	21.4%	31%
	Steam	180	AG	0.0746	0.0013	0.0220	
				31.3%	1.3%	26.5%	23%
			BG	0.1846	-0.0031	-0.0141	
				77.6%	-3.2%	-17.0%	40%
			ST	0.0855	0.0006	0.0277	
				35.9%	0.6%	33.4%	27%
	None	200	AG	0.0797	-0.0100	0.0106	
				29.9%	-10.3%	22.6%	20%
			BG	0.2012	0.0115	-0.0061	
				75.5%	11.9%	-13.0%	50%
			ST	0.1104	0.0002	0.0108	
				43.3%	0.2%	19.4%	30%
		Ambient	AG	0.0587	0.0135	0.0026	
				30.9%	13.4%	11.0%	24%

Table 3. Copper losses by assay zone, conditioning methods, and location.

Conditioning		Treatment Temperature (F)	Location	Assay Zone Radial Mid-point (in)			Average Across Outer 3.0 inches
Initial	Final			0.25	1.25	2.50	
				Copper Loss (pcf)			
				Copper Loss (% of original)			
			BG	0.1678	0.0627	-0.0094	
				88.3%	62.0%	-39.0%	70%
			ST	0.0867	0.0193	-0.0109	
				45.6%	19.1%	-45.4%	30%

The copper gradients shown (Figure 4) are very similar to those for penta with the penta gradients being slightly steeper in the original outer assay zones. The inner assay zone portions of the gradients were nearly identical in slope. Losses in both systems averaged 35% over the outer three inches of the pole stubs. In the below-ground portions of the pole stubs (Figure 5), penta had depleted more (66%) than CuN (38%). Trends for the BG gradients were similar to those found above-ground. Thus, with air-dried stock, no negative effects of post-treatment conditioning on CuN retention or gradient shape were observed. Preservative depletion for CuN was similar to or less than that for penta.

Gradients for steam-conditioned stock are shown in Figures 6 and 7. The effect of treating temperature on the preservative gradient is what was expected. Higher temperature yields better treatment. However, other than the initial steepness for the 200 F gradient (Figure 6), little practical difference in gradient shape is noted between the two temperatures after exposure.

Copper loss in the outer three inches averaged 24% and 30% for the ambient treatment temperature in the AG and BG portions of the stubs, respectively (Figure 7). Corresponding average losses for the material treated with heated preservative were 20% and 50%. Post-treatment steaming had no deleterious effect on the shape of the gradient (Figure 8). Copper losses for the above- and below-ground sections after exposure were 23% and 40% (Figure 8), certainly within the range found for stubs undergoing no final conditioning (see Figs. 6, 7, Table 3).

Gradients for material fixed post-treatment (Figures 9, 10) showed the same trends with initial treating temperature as material with no post-treatment conditioning. Gradient shape was consistent with material treated using heated preservative and no final conditioning. Copper losses for material treated at 140 F and fixed after treatment averaged 33% above-ground and 62% below-ground (Figure 9). Comparisons between gradients for steam-conditioned stubs treated with CuN and penta are shown in Figures 11 and 12. Similar trends as previously discussed for air-dried stock are shown. Copper losses of 20% and 50% for the above-ground and below-ground portions of exposed CuN-treated stubs compare favorably with the corresponding penta values of 51% and 57%.

The relationship of copper loss to original copper retention is shown in Figure 13 for the outer two inches below ground for all poles assayed. A linear relationship was found and differs from the exponential relationship found for penta (14). Implications of this observation will require additional study.

When comparing AD stubs with SC stubs, the following general trends were noted. Air-dried gradients were generally flatter than ones for SC stock, but the magnitude for SC stubs was two to two and one-half times greater than that for AD stubs. Depletion (% loss) was of the same order of magnitude regardless of initial seasoning employed.

Little has been said for the stubs placed in horizontal above-ground exposure. For most combinations, copper loss lies between the values found in above- and below-ground portion of stubs in ground contact.

CONCLUSIONS

This study has shown that there is little practical difference in the gradients obtained and copper loss between steam-conditioned and air-dried stock. Air-dried gradients tended to be flatter but of lower magnitude when compared to steam-conditioned stubs. While differences exist among gradients and copper losses for different combinations of initial seasoning and final conditioning, no deleterious effects on the gradient, copper loss, or performance in field exposure were noted. Steam-conditioned southern pine treated with CuN which has been final conditioned by either a steam flash or expansion (fixation) bath performs in a manner similar to that of penta. No fungal colonization or insect attack was noted for any of the 84 southern pine pole stubs inspected after 12 years of exterior exposure in ground contact or above-ground storage in a high biodeterioration hazard zone.

While this study does not directly answer the question of the form of copper arising as a result of pre- and/or post-treatment steaming CuN-treated poles, it does provide direct evidence that steaming has no deleterious effect on the performance of CuN-treated poles in ground contact. In that regard, this study answers the concerns posed in the AWPA. In spite on any copper reduction which may or may not occur at the surface of the pole, all combinations in this study have performed extremely well.

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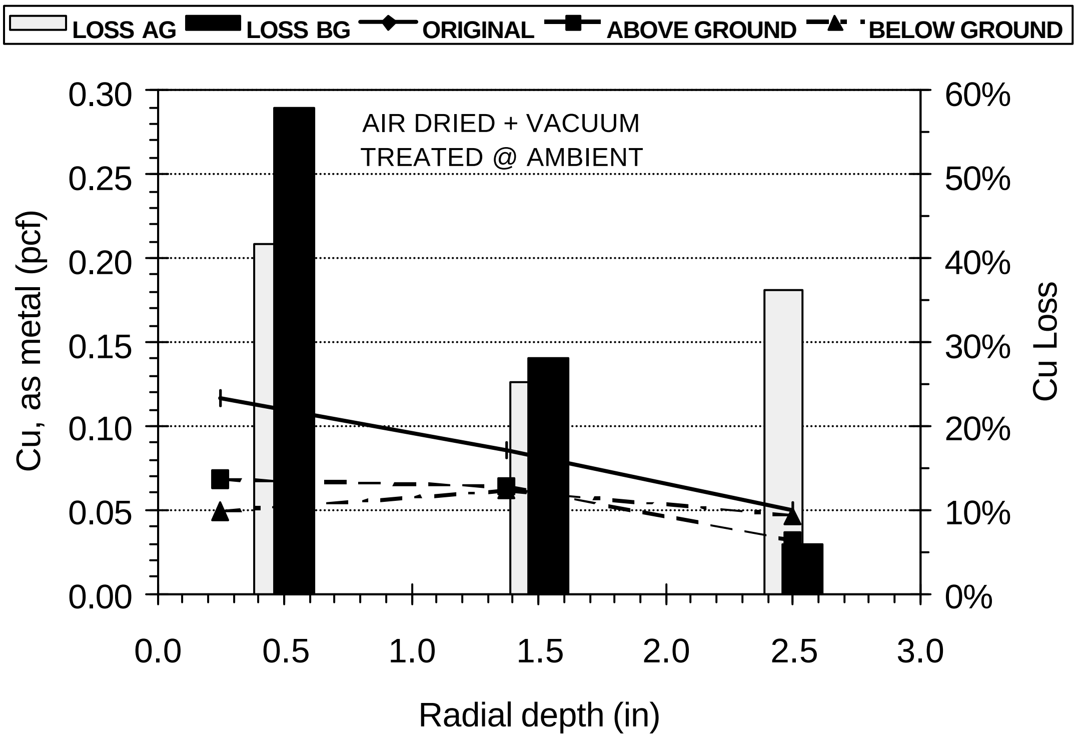

Figure 1. Above-ground (AG) and below-ground (BG) gradients and copper loss by zone for CuN-treated air-dried stubs with no final conditioning after 12 years in ground contact.

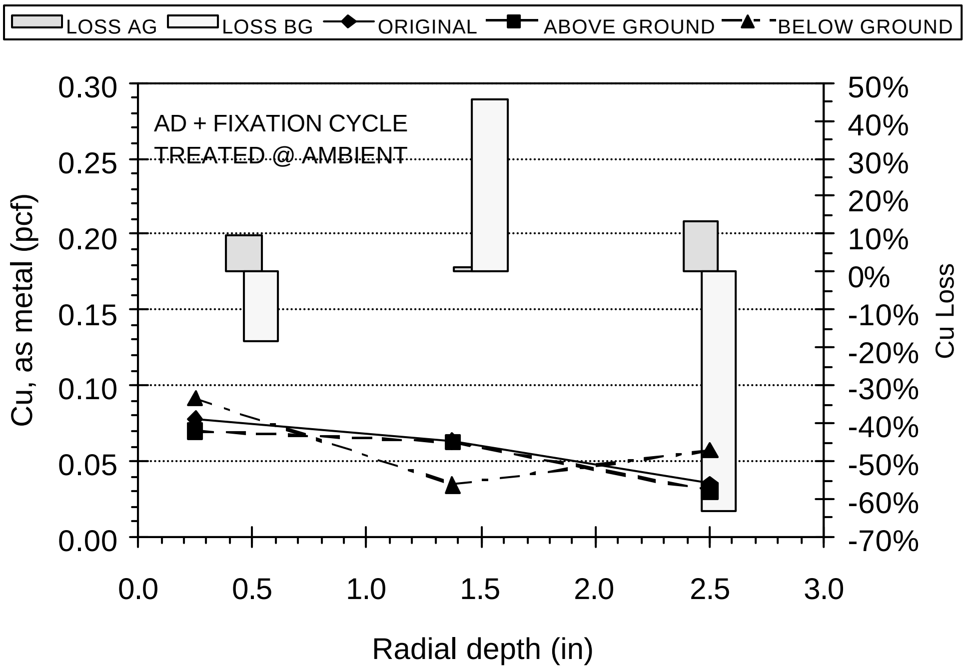

Figure 2. Above-ground (AG) and below-ground (BG) gradients and copper loss for CuN-treated air-dried stubs undergoing a final fixation cycle after 12 years in ground contact.

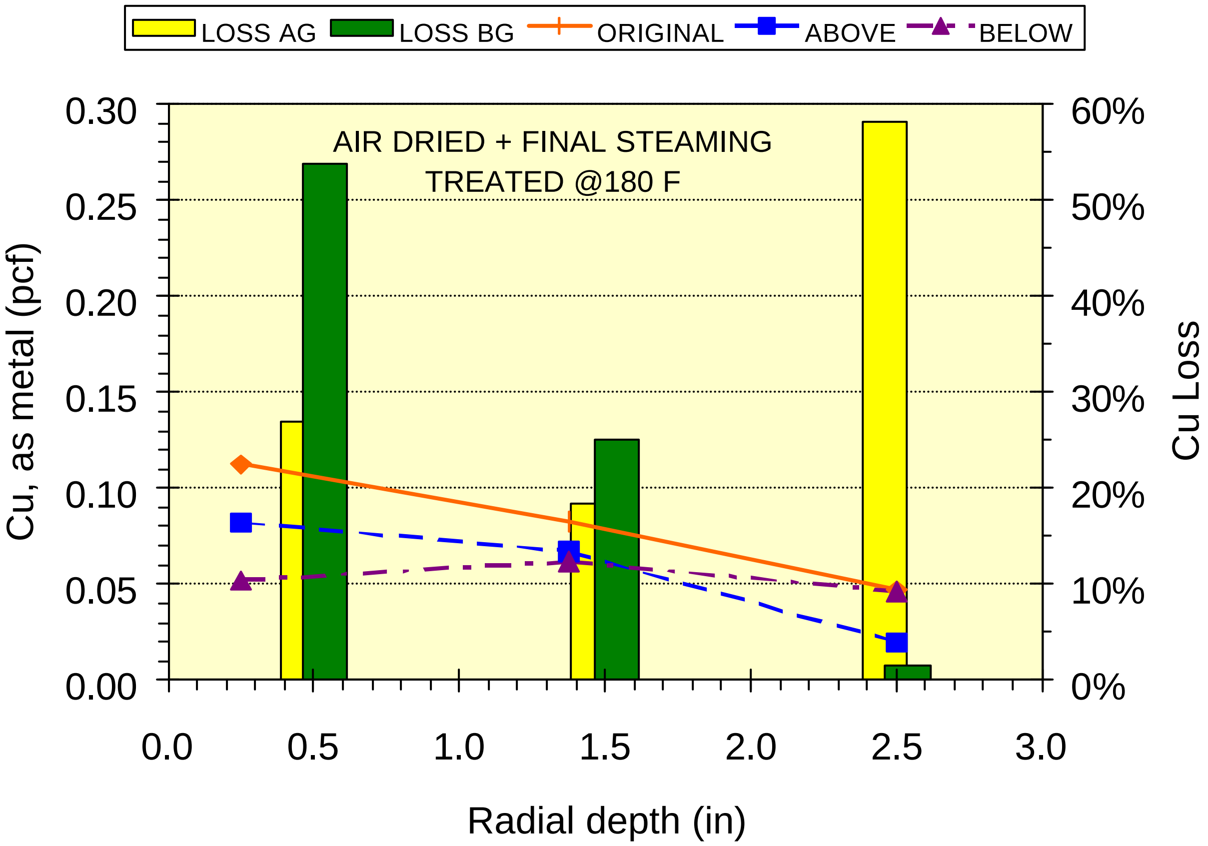

Figure 3. Above-ground (AG) and below-ground (BG) gradients and copper loss by zone for CuN-treated air-dried stubs undergoing a final steaming cycle after 12 years in ground contact.

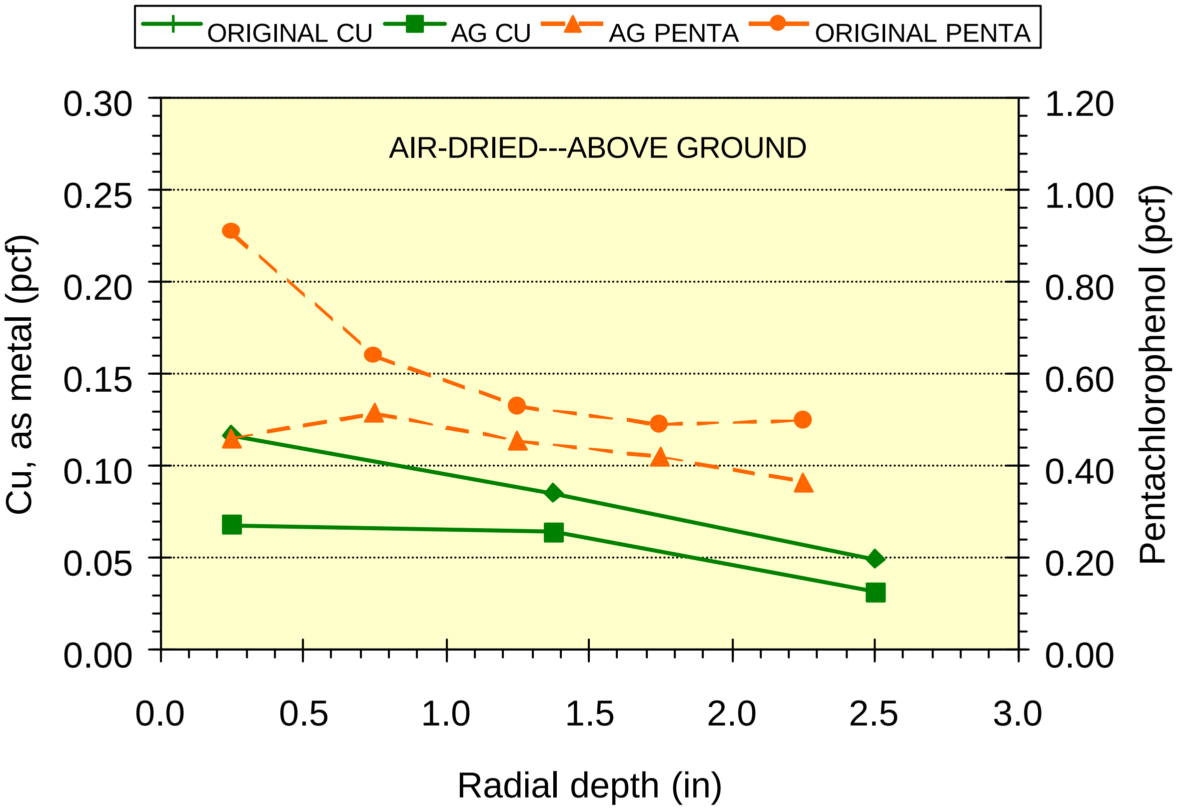

Figure 4. Comparison of above-ground (AG) CuN for air-dried pole stubs after 144 months exposure to those published for penta after 97 months of exposure (14).

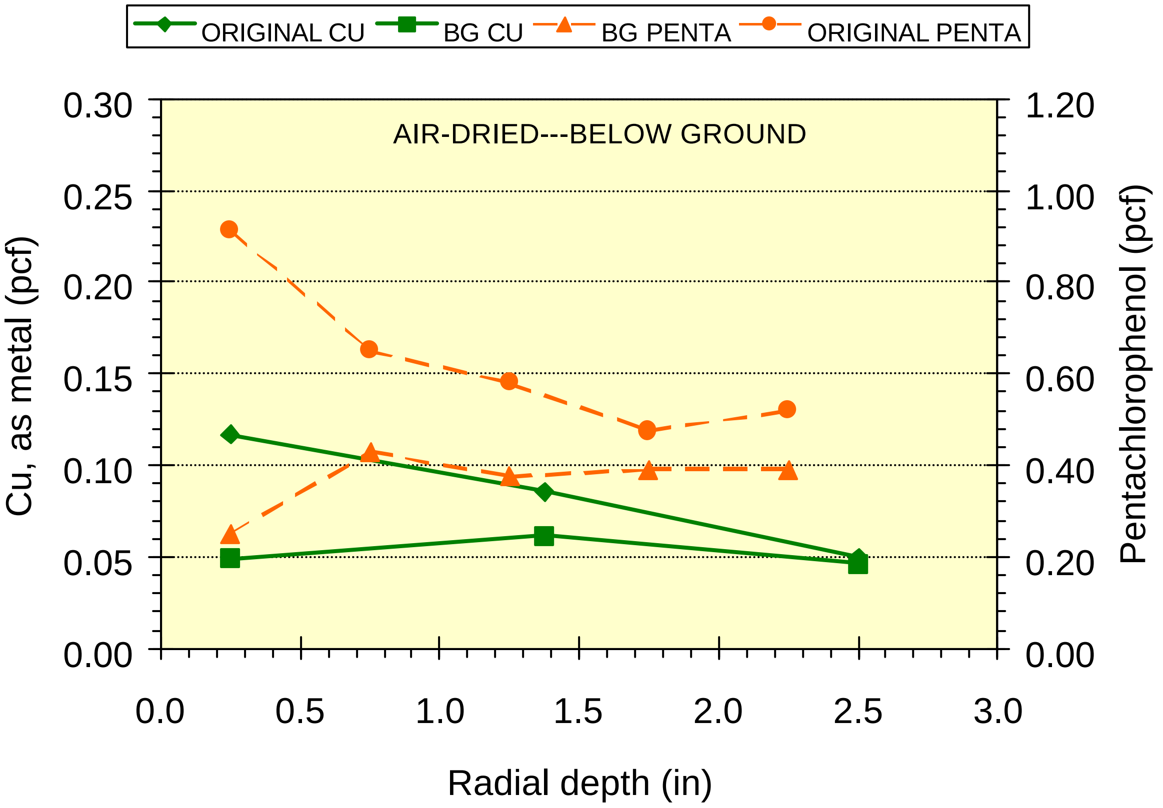

Figure 5. Comparison of below-ground (BG) CuN for air-dried pole stubs after 144 months exposure to those published for penta after 97 months of exposure (14).

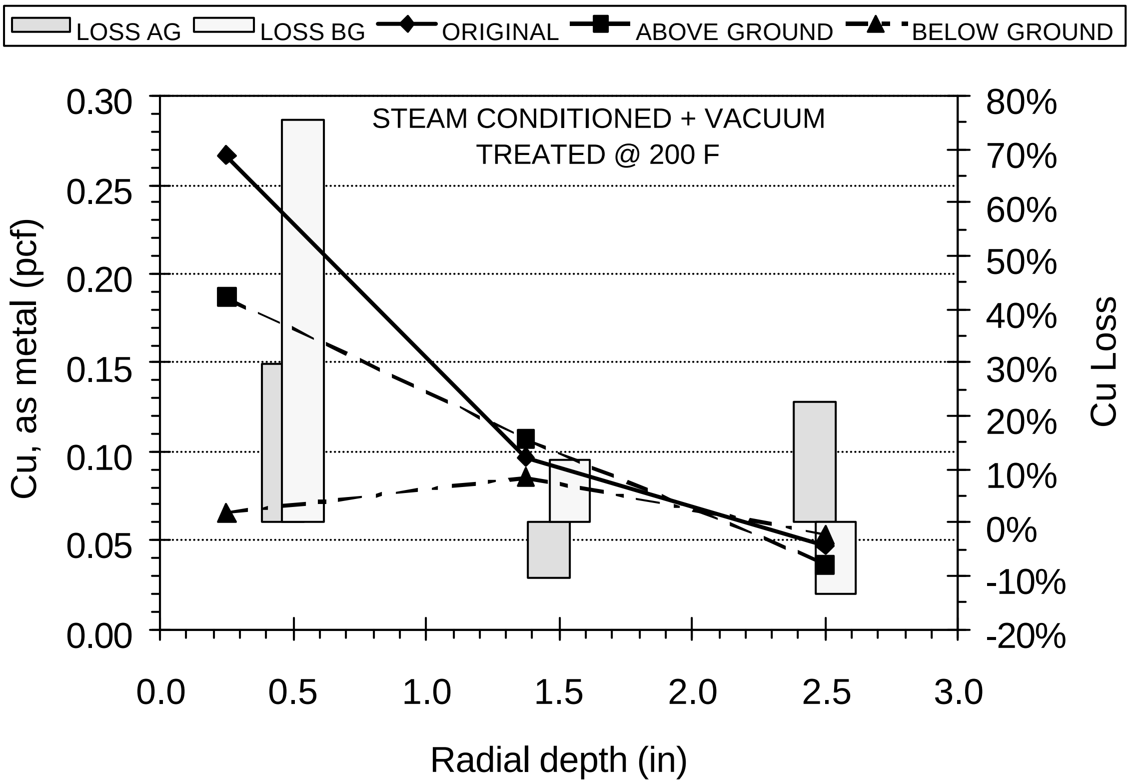

Figure 6. Above-ground (AG) and below-ground (BG) gradients and copper loss by zone after 12 years in ground contact for steam-conditioned stubs treated at 200° F with no final conditioning.

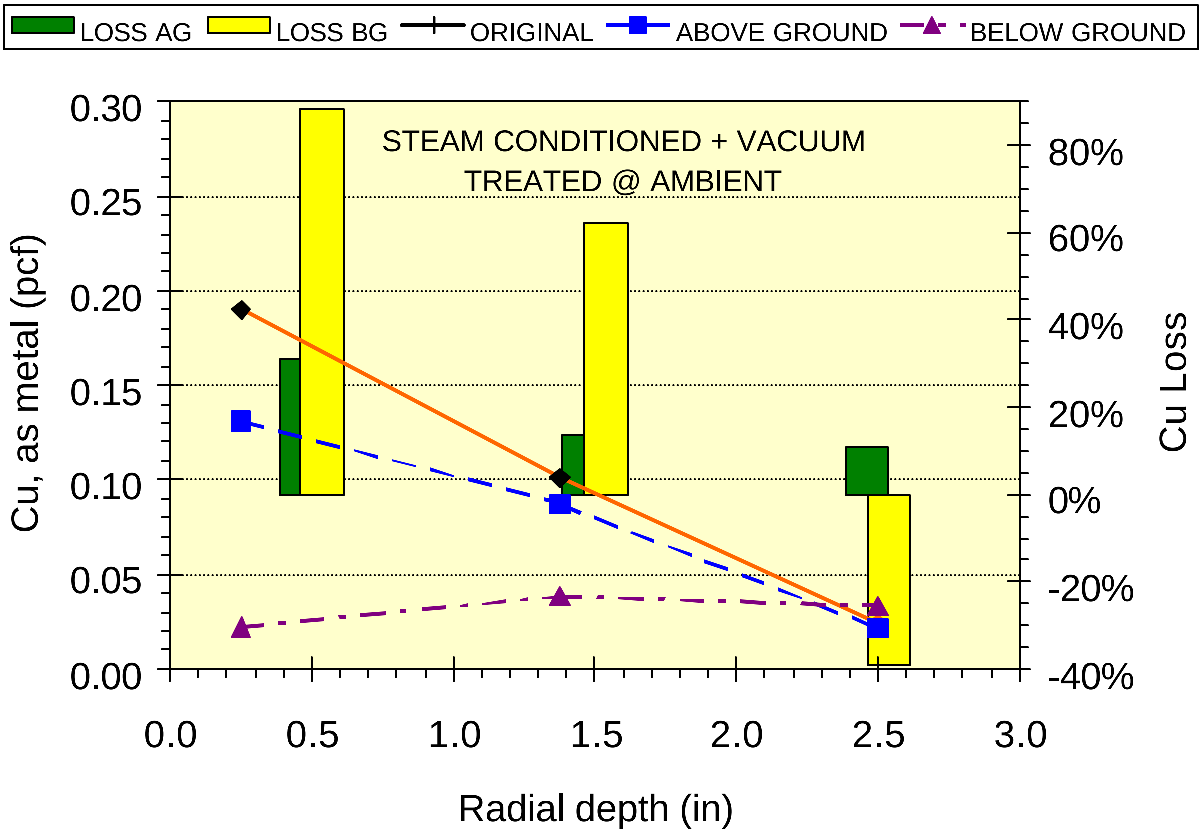

Figure 7. Above-ground (AG) and below-ground (BG) gradients and copper loss by zone after 12 years in ground contact for steam-conditioned stubs treated at ambient with no final conditioning.

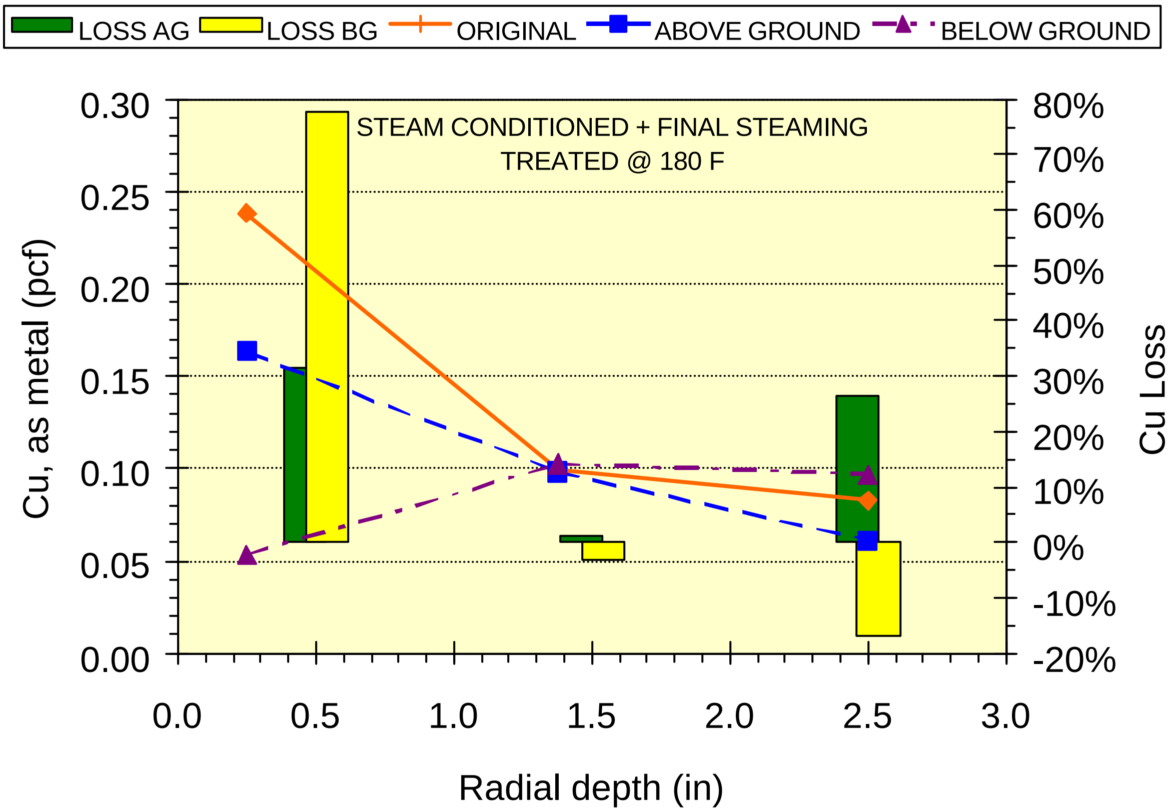

Figure 8. Above-ground (AG) and below-ground (BG) gradients and copper loss by zone after 12 years in ground contact for steam-conditioned stubs treated at 180° F and steamed after treatment.

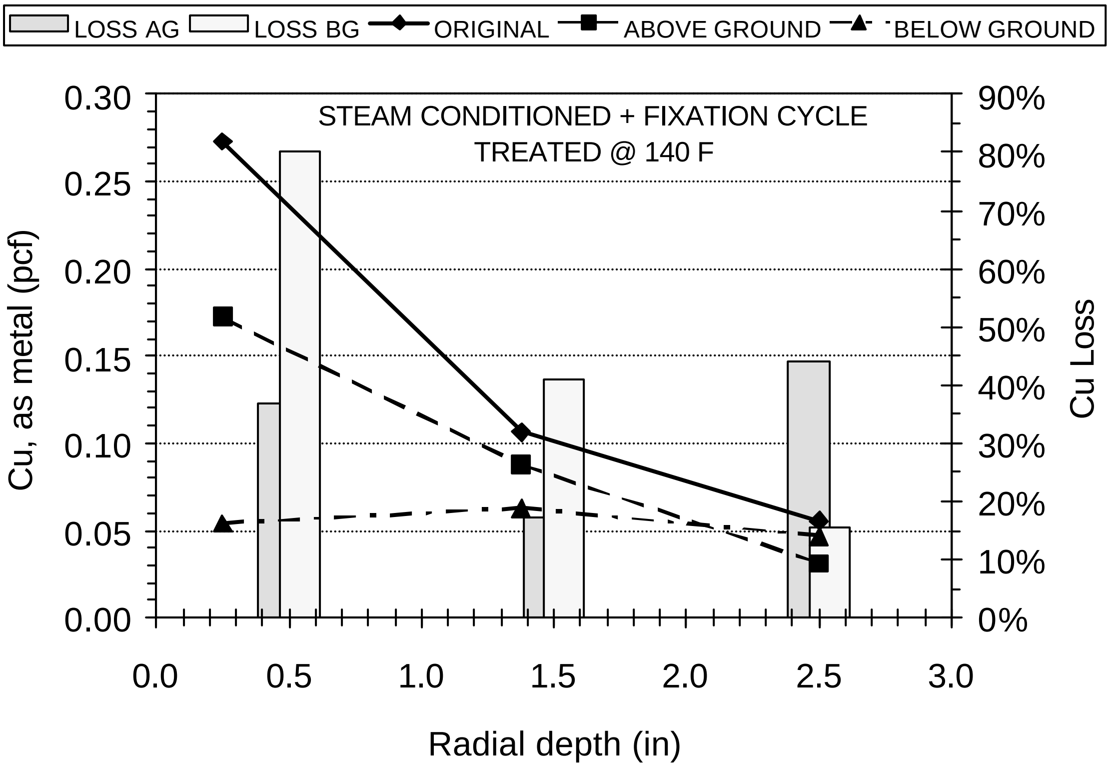

Figure 9. Above-ground (AG) and below-ground (BG) gradients and copper loss by zone after 12 years in ground contact for steam-conditioned stubs treated at 140° F and fixed after treatment.

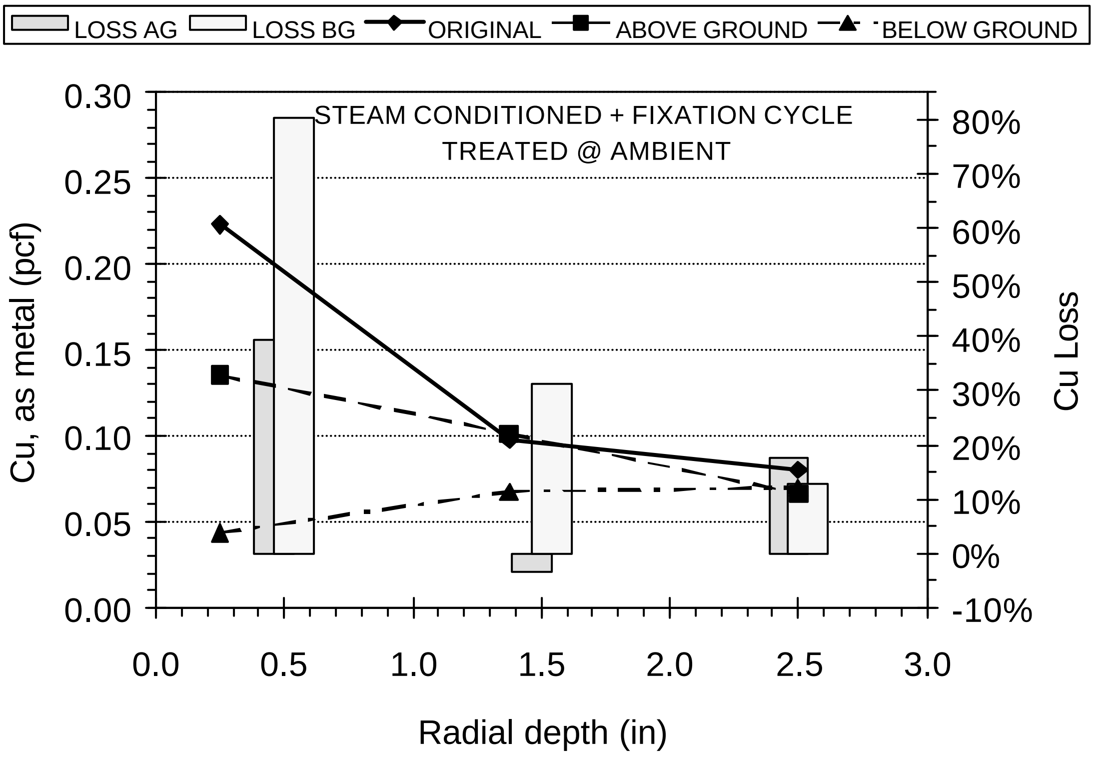

Figure 10. Above-ground (AG) and below-ground (BG) gradients and copper loss by zone after 12 years in ground contact for steam-conditioned stubs treated at ambient and fixed after treatment.

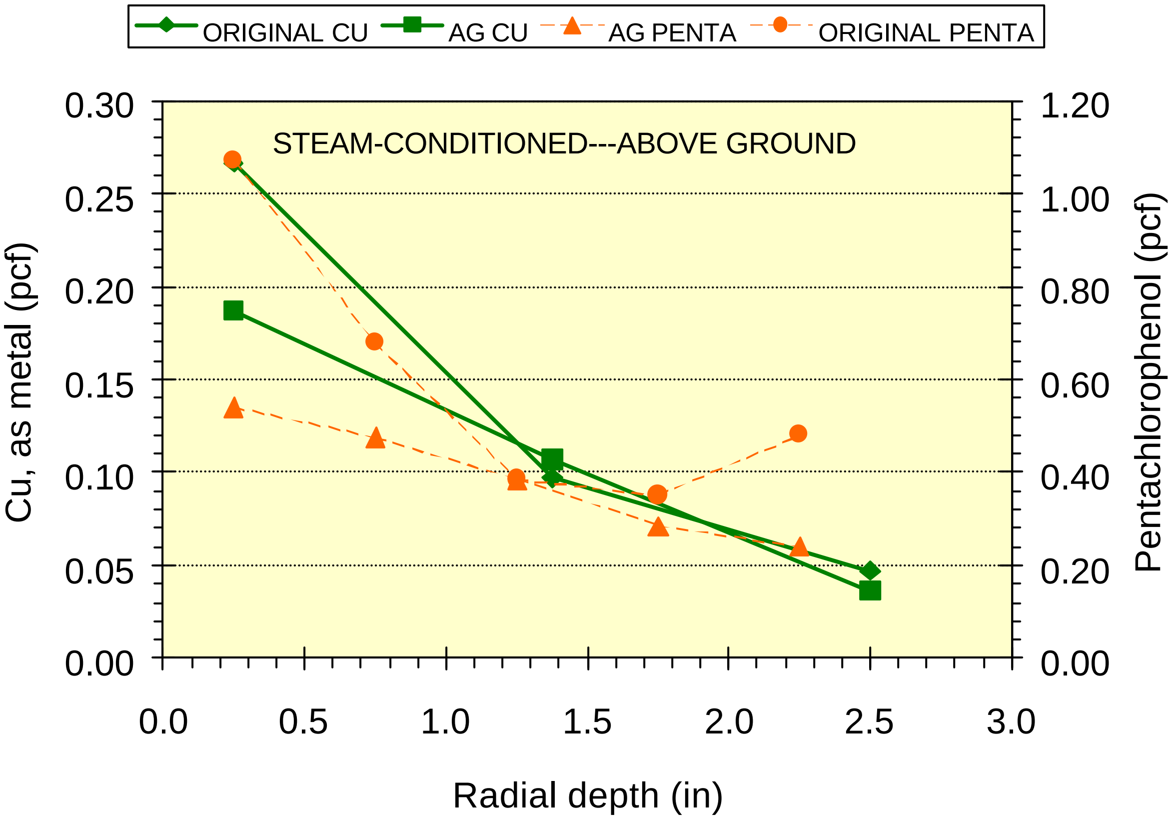

Figure 11. Comparison of above-ground (AG) CuN for steam-conditioned pole stubs after 144 months exposure to those published for penta after 97 months of exposure (14).

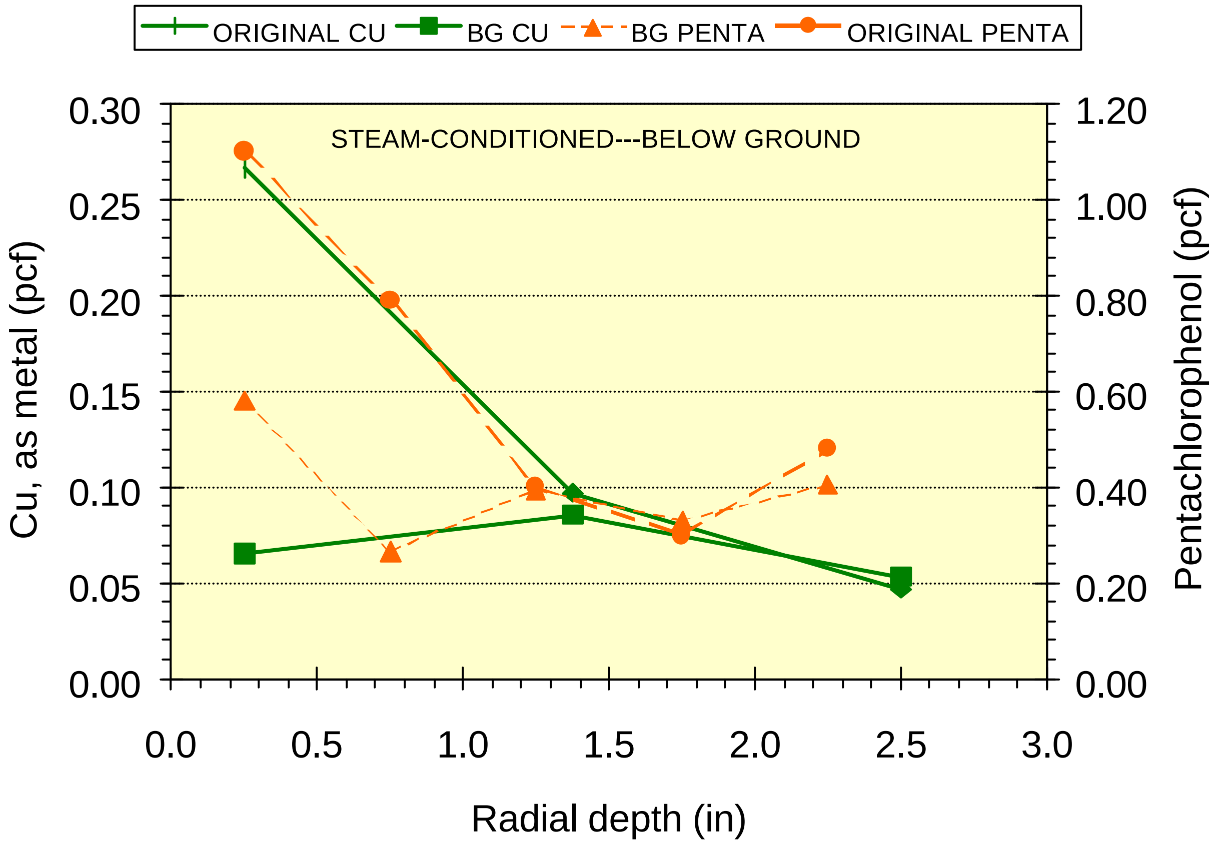

Figure 12. Comparison of below-ground (BG) CuN for steam-conditioned pole stubs after 144 months exposure to those published for penta after 97 months of exposure (14).

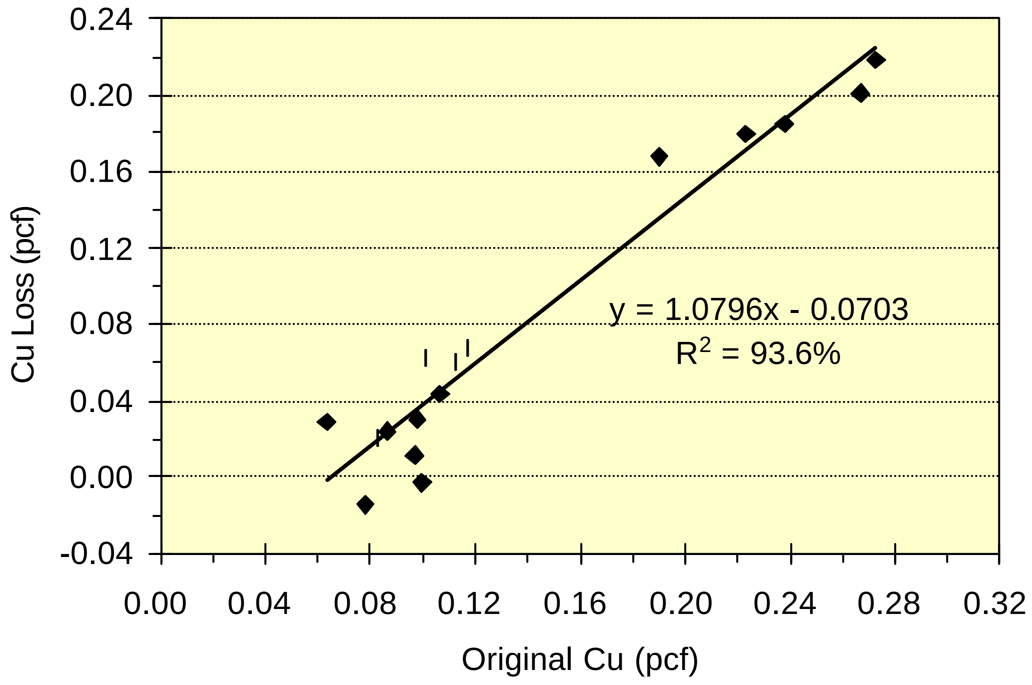

Figure 13. Average copper los below-ground in the outer two inches of CuN-treated pole stubs as a function of original copper concentration.