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The Future of Remedial Wood Preservative Technology in Canada – Performance Characteristics of a Compressed Dazomet Stick For The Control of Internal Wood Utility Stick For The Control of Internal Wood Utility Pole Decay

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Introduction

There has traditionally been 3 methylisothiocyanate based fumigants commercially used for the control of internal fungal decay in wood utility poles. They are:

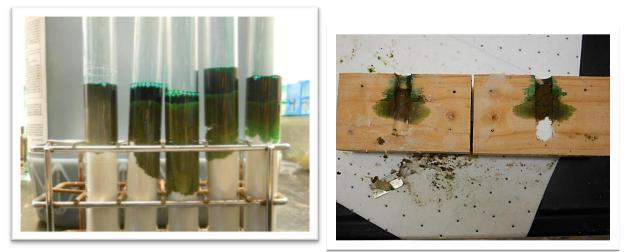
- <u>Metam Sodium</u> The earliest of the methylisothiocyanate based fumigants and was commercially introduced in the late 1970's. Metam sodium is a liquid formulation that contains 33.0% methylisothiocyanate. Metam Sodium is currently the only wood pole fumigant registered for use in Canada.
- <u>MITC-FUME®</u> Commercially introduced in the late 1980's, MITC-FUME is 97% methylisothiocyanate in a solid melt form and is packaged in sealed aluminum tubes, each containing 30 grams of fumigant. MITC-FUME® is the only solid melt form of methylisothiocyanate that is currently available commercially. MITC-FUME® is also the only wood pole fumigant that is packaged in a ready-to-use delivery system that is registered with the US EPA as a pesticide.
- <u>Granular/Powdered Dazomet</u> Introduced in the late 1990's, granular/powdered dazomet is the most recently commercialized methylisothiocyanate based fumigant. Dazomet is 98-99% tetrahydro-3,5-dimethyl-2H-1,3,5,thiadiaznie-2-thione and decomposes within a utility pole to release methylisothiocyanate. Under ideal conditions, dazomet decomposes to methylisothiocyanate at a theoretical maximum conversion rate of approximately 45%. Furthermore, as a means to accelerate the decomposition to methylisothiocyanate, the EPA product labels for dazomet allow the addition of a copper solution at the time of fumigant application.

The performance of dazomet has been well documented by researchers since its introduction. Multiple studies conducted by the Oregon State University Utility Pole Research Cooperative (OSU-UPRC) have demonstrated the ability of dazomet to deliver fungitoxic level of methylisothiocyanate in the treatment zone of wood utility poles in as little as 1 year following application and persist for as long as 12 to 15 years.^(1,2,3,4,5,7,8)

Osmose has verified these positive long-term performance characteristics in multiple tests including a multiyear field test established in New York on pentachlorophenol treated southern pine poles. ^(9,10) This extensive field testing has also confirmed that the addition of a 2% copper solution to dazomet enhances methylisothiocyanate release.

Following the commercial introduction of dazomet almost 20 years ago, there has been no real advancement in fumigant technology for the wood utility pole market and metam sodium remains the single registered pole fumigant in Canada. While granular dazomet has been shown to be an effective fumigant, there are potential risks of worker exposure from dusting and wind-blown product during application. There are also potential risks of environmental release from overfilling application holes or accidental tipping of containers. Dosing accuracy is also a concern. Accurate dosing to application holes is important to ensure that the pole is receiving the prescribed amount of chemical to afford optimal protection against the action of decay fungi. In addition, filling treatment holes with granular or powdered dazomet limits the efficiency of copper accelerants. When filled with dazomet, copper penetration is generally limited to the outer 2-3 inches of the treatment hole, effectively limiting the copper-dazomet interaction to a small fraction of applied material.

The behavior of copper-based accelerants in dazomet treatment holes has been studied by the OSU-UPRC. It was reported that when mixing dazomet and copper naphthenate in test tubes the copper naphthenate tended to soak into the upper portion of the dazomet, leaving the zone below devoid of any copper accelerant (see photo below).⁽⁶⁾ Researchers also evaluated the penetration characteristics of copper naphthenate through dazomet when applied to treatment holes drilled into dimension lumber. Results showed that the copper naphthenate only penetrated 2-2.5" through the dazomet column (see photo below).



(Photos extracted from the 2015 OSU-UPRC Annual Report)⁽⁶⁾

Recently, Osmose has introduced a new patented fumigant technology (US 9,510,599) to the utility pole market that effectively addresses some of the concerns associated with the granular formulations. This fumigant formulation, commercially known as EZ-FUME[®], utilizes direct

compression technology to generate a solid-stick fumigant. This solid form of dazomet provides for an easy to apply, pre-calibrated dose of fumigant that minimizes worker exposure and essentially eliminates concerns over accidental release into the environment. When applied to application holes, EZ-FUME sticks leave ample room to apply copper accelerants that are capable of penetrating the entire length of the hole providing greatly improved interaction between the copper accelerant and applied fumigant (see Figures 3 and 4 below).

To demonstrate the performance characteristics of the EZ-FUME technology, a comparative field study was initiated at the Osmose Research Field Test Site located in Gainesville, FL on full-size pentachlorophenol treated southern pine pole sections.

Performance Testing

The objective of this study was to evaluate concentrations of methylisothiocyanate at various heights and depths in southern pine pole sections at selected time intervals following internal treatment with the EZ-FUME sticks. It was a further objective of this study to evaluate the performance of the EZ-FUME sticks when incorporating a copper based accelerant. Granular dazomet was included in the study as a control.

Procedural Summary

EZ-FUME Stick Formulation

EZ-FUME contains the following composition of ingredients:

- Methylisothiocyanate, dazomet, (91.14%)
- Inert ingredients, (8.86%)

The inert ingredients formulated into the EZ-FUME stick are a patented combination approved by the US EPA that allows granular or powdered dazomet to be compressed and cohere as a solid body, or stick. Each EZ-FUME stick measures approximately 0.56" in width and depth and is 3.8" in length. This allows for the application of as many as 3 sticks to a standard length application hole of 15 to 18". The width of the stick is also slightly smaller than the typical 7/8" diameter application hole which allows for the addition of a liquid copper accelerant. The EZ-FUME stick weighs 25.1 grams and contains 23.3 grams of active dazomet. Thus, the application of 3 sticks per treatment hole is equivalent to the commonly specified application dose for granular dazomet of 70 grams.

Southern Pine Pole Sections

A total of sixteen, 10' long southern pine pole sections were used in this study. The pole sections were cut from full-length Class 4-40' new poles pressure treated with pentachlorophenol in an AWPA P-9 Type A solvent. Each pole stub was labeled for ease of identification during subsequent inspections.

Fumigant Application Procedures

In January 2014 the 16 southern pine pole sections were treated using the following fumigant formulations and accelerant:

- **EZ-FUME stick:** Product obtained from commercial production and identified as Batch # BAK 03-118.
- Granular Dazomet: Product obtained from a commercial sample of DuraFume II.
- **Dazomet Accelerant:** Product obtained from a commercial batch of Hollow Heart CB. Hollow Heart CB is a liquid concentrate that contains 5% copper as Cu and 12.5% sodium borate (DOT). When diluted according to the product label, the ready-to-use formulation contains 2.0% copper as Cu and 5% DOT as active ingredients.

Four of the pole sections were treated with 226 grams of EZ-FUME (210 grams of dazomet) without accelerant following the procedures specified on the product label. This involved the application of 3 sticks to each of three 7/8" diameter by 15" to 17" long holes drilled at a 45° angle in a counter clockwise spiral pattern beginning at groundline and progressing upwards 8" and 120° (see Figure 1). The EZ-FUME sticks were preweighed in the laboratory to confirm dosage and applied to each treatment hole by simply dropping them in the holes (see Figure 2).

Four additional pole sections were treated with 226 grams of EZ-FUME (210 grams of dazomet) plus the Hollow Heart CB accelerant. The EZ-FUME was applied first, following the same application procedures as described above. Following application of the EZ-FUME, the liquid Hollow Heart CB solution (2% Cu) was added to each treatment hole using a graduated cylinder (see Figure 4). Accelerant was added to refusal which resulted in application rates that averaged 75 ml (2.54 oz.) per hole and that ranged from 50-100 ml (1.69-3.38 oz.) per hole.

Four of the pole sections were treated with 210 grams of granular dazomet without accelerant following the procedures specified on the product label. This involved the application of 70 grams of dazomet to each of three 7/8" diameter by 15" to 17" long holes drilled at a 45° angle in a counter clockwise spiral pattern beginning at groundline and progressing upwards 8" and 120°. The dazomet was preweighed in the laboratory into 70 gram doses and applied to each treatment hole using a glass funnel.

Four additional pole sections were treated with 210 grams of granular dazomet plus the Hollow Heart CB accelerant. The dazomet was applied first, following the same application procedures as described above. Following application of the dazomet, the liquid Hollow Heart CB solution (2% Cu) was added to each treatment hole using a graduated cylinder. Accelerant was added to refusal which resulted in application rates that averaged 23 ml (0.78 oz.) per hole and that ranged from 15-40 ml (0.51-1.35 oz.) per hole.

Following treatment, all fumigant application holes were tightly plugged with an Osmose PlastiPlugTM.

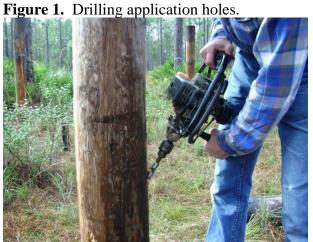


Figure 3. Applied EZ-FUME stick.

Figure 2. Application of EZ-FUME stick.



Figure 4. Application of 2% copper accelerant.



Sampling and Chemical Analysis of Pole Sections

At 12 and 32 months following treatment, chemical analysis samples were obtained from all 16 pole sections by removing three 0.2" diameter core borings perpendicular to the pole and 120° apart at the following four heights:

- 6" below groundline
- 6" above groundline
- 12" above groundline
- 22" above groundline

During the sampling of the poles, care was taken to avoid intersecting the fumigant treatment holes. Three 1.0" segments were then removed from each core at positions corresponding to the following three pole depths:

- 1.0" to 2.0" from the pole surface
- 3.0" to 4.0" from the pole surface
- 4.0" to 5.0" from the pole surface

The three segments from the same pole height and core depth were combined into a composite sample and transferred to a preweighed 4 ml glass vial that was tightly sealed with a cap containing a Teflon insert. Prior to insertion in the vials, each boring segment was further dissected into small discs, 2 to 3 mm in length.

Quantitative Chemical Analysis of Methylisothiocyanate

The vials containing the composite samples were transported to Osmose's analytical laboratory where they were reweighed to determine the total net weight (wet) of the wood samples. Samples were then sent to the Oregon State University Analytical Laboratory where they were extracted with ethyl acetate. Extracts were analyzed for methylisothiocyanate by gas chromatography (GC) and the results were reported back to Osmose.

Results and Discussion

The average concentrations of methylisothiocyanate (*mitc*) measured at various locations in southern pine pole sections sampled at 12 and 32 months following treatment with EZ-FUME or granular dazomet with and without a copper accelerant are summarized in Tables 1 and 2, respectively. These results are graphically presented in Figures 5 and 6.

The effectiveness of the fumigant treatments against decay fungi can be determined by comparing the measured *mitc* levels in the test poles to the minimum threshold level for *mitc* against wood decay fungi. In the 2003 Annual Report of the OSU-UPRC, a minimum threshold level for *mitc* against decay fungi was reported to be $20 \,\mu g$ *mitc* per gram of oven-dried wood, or $20 \,\text{ppm}$ *mitc*.⁽¹⁾

12 Month Results

Overall, the concentrations of *mitc* measured at 12 months following fumigant treatment in the EZ-FUME and granular dazomet treated pole sections were similar at all sampling heights and core depths. This provides direct evidence that the compressed dazomet of the EZ-FUME stick is capable of releasing equivalent levels of *mitc* under the same environmental conditions. This demonstrates that compressing dazomet into a solid body did not negatively impact its ability to decompose to active *mitc*.

The addition of the copper accelerant to the EZ-FUME treatment holes resulted in a marked increase in *mitc* concentrations at all sampling locations 12 months following fumigant treatment.

A similar trend was noted for the granular dazomet, but the benefit of the copper accelerant was less pronounced within and above the treatment zone. This finding supports the theory that a solid body of dazomet allows for increased interaction between the copper accelerant and dazomet within the treatment holes resulting in improved *mitc* conversion.

Fungitoxic levels of *mitc* were detected in all assay zones at 6" above and below groundline and at 12" and 22" above groundline for all fumigant treatments after 12 months of field exposure.

32 Month Results

When compared to the corresponding chemical assay results at 12 months following fumigant treatment, the 32 month results showed a sharp increase in the overall *mitc* concentrations in the EZ-FUME treated pole sections. Similarly, the granular dazomet produced much higher levels of *mitc* at 32 months, but this increase was generally confined to the groundline region of the poles. Higher up the pole, at the 12" and 22" sampling heights, levels of *mitc* remained relatively unchanged for this treatment from 12 to 32 months. While the distribution of *mitc* varied somewhat within test poles treated with the EZ-FUME stick and the granular dazomet, overall *mitc* levels were relatively similar for these treatments after 32 months. This provides further evidence that compressing granular dazomet into a solid body does not negatively impact its ability to decompose to *mitc* during prolonged exposure periods.

The most pronounced increase in *mitc* concentrations from 12 to 32 months was seen in the pole sections treated with EZ-FUME + copper accelerant. In fact, *mitc* concentrations were generally twice that found for the other treatments after 32 months. Levels of *mitc* remained relatively unchanged in pole sections treated with the granular dazomet + copper accelerant from 12 to 32 months. This finding supports the concept that the copper accelerant provides an initial boost when applied to the granular dazomet but the long-term benefit is questionable.

Similar to the 12 month results, fungitoxic levels of mitc were detected in all assay zones at 6" above and below groundline and at 12" and 22" above groundline for all fumigant treatments after 32 months of field exposure.

Health and Safety

In 1992, a field study and associated risk assessment was sponsored by the Empire State Electric Energy Research Corporation (ESEERCO) and performed by O'Brien & Gere Engineers, Inc. (OBG) to evaluate the potential ecological and human health impacts related to the application of five (5) supplemental, or remedial, wood preservatives to in-service utility poles. The field study involved post-application monitoring for active ingredients and biological impacts in a wetland area of the New York State Adirondack Park. The remedial preservatives and principal active ingredients evaluated were OsmoPlastic (fluoride, chromium, creosote); Dursban (chlorpyrifos); WoodFume (sodium methyl dithiocarbamate); Hollow Heart (fluoride, chromium, arsenic); and Cop-R-Nap (copper, naphthenic acid). Each of these remedial preservative technologies was manufactured and/or distributed by Osmose Utilities Services, Inc. (Osmose) at the time of the ESEERCO testing.

The ESEERCO Field Study established that essentially no preservative active ingredients were released to surrounding ground water, surface water or soil in the seventeen (17) month post-treatment sampling period. Researchers concluded that the supplemental utility pole treatments did not cause measurable post-application impacts to Adirondack Park wetlands. Researchers also performed a risk analysis using computer generated estimates of preservative concentrations released from the remedially treated poles. This risk analysis utilized a ground water transport computer model to generate "worst case" estimates of preservative release in ground water at fifteen (15) m downgradient from the pole based on total amounts of applied commercial product. Predicted estimates of active ingredient concentrations were found to be significantly higher than actual measured levels in soil, surface or ground water, yet were still lower than USEPA drinking water criteria. Thus, the modelled analyses further supported the conclusion that the supplemental wood pole treatments did not present a significant health risk to biota or humans.

While Osmose's remedial preservative technologies have been reformulated to be even more environmentally responsible than those evaluated in the 1992 ESEERCO Study, Osmose engaged OBG to perform a risk assessment to establish the potential ecological and human health effects, if any, related to the application of EZ-FUME and Hollow Heart CB.

For this risk analysis, OBG Researchers utilized a ground water transport computer model like that utilized in the ESEERCO Study to generate "worst case" estimates of preservative release in stormwater and groundwater at a fifteen (15) m distance downgradient from the pole. The human exposure scenario assumes that a potable water well is developed at this point and that humans are exposed to Product active ingredients via ingestion, dermal contact, and inhalation. The ecological exposure scenario assumes that aquatic receptors are exposed to Product active ingredients that are discharged to a stream located at this point. Preservative release was also modeled at a three (3) m distance downgradient from the pole to assess the appropriateness of Osmose's recommended Set-Back Distance of three (3) m from bodies of water to mitigate risk to aquatic receptors.

Risk to human receptors from exposure to boron and copper was evaluated using USEPA Regional Screening Levels (RSLs) for tap water. As none of the mitc-based constituents (mitc, dazomet or SMD) were included in the RSL table, a mitc tap water standard was derived herein using existing toxicological literature and RSL methodology. Risk to aquatic receptors from individual constituents was determined by comparing the modeled surface water concentrations to benchmarks derived from two sources: 1) the USEPA's on-line ECOTOX database (acute exposure), and 2) the USEPA Region 3, Biological Assistance Technical Group (BTAG) Freshwater Screening Benchmarks (chronic exposure).

Effect Ratios were also calculated for both human and ecological receptors by dividing exposure point concentrations by the above-described criteria. Ratios greater than one (1) indicate a potential for risk. For Products with more than one active ingredient (Hollow Heart CB), cumulative impacts were evaluated by adding Effect Ratios for that Product.

Predicted potable well concentrations of copper and boron from Osmose's remedial preservative formulation Hollow Heart CB was below the respective RSLs established by the USEPA for tap water. In addition, both individual and cumulative Effect Ratios are all below one (1) for this preservative system. Predicted potable well concentrations of mitc from Osmose's EZ-FUME fumigant formulation was also below the derived RSL for tap water. Again, the individual Effect Ratios are below one (1) for this preservative system.

The predicted surface water concentrations for all active ingredients from Osmose's remedial preservative formulations are below the established USEPA BTAG (chronic exposure) and ECOTOX (acute exposure) benchmarks for aquatic receptors. In addition, the individual and cumulative Effect Ratios are below one (1) by several orders of magnitude for both preservative systems. When the fifteen (15) m distance is shortened to three (3) m in the risk analysis, predicted surface water concentrations remain below BTAG and ECOTOX benchmarks, and individual and cumulative Effect Ratios remain below one (1). These results support the Set-Back Distance of three (3) m from surface water bodies for these remedial preservative formulations to be protective of aquatic receptors.

As with the 1992 ESEERCO Study, predictive estimates of preservative release for this computer modeled risk assessment are conservative. This is particularly true when considering the cautious nature of the USEPA RSL residential tap water exposure scenario of bathing 42.6 minutes/day; drinking 2.5 liters/day; for 350 days/year for 26 years. Even with this conservative approach, predicted surface water and potable well water concentrations remained below the environmental and human health thresholds established by EPA. Based on the results of this risk assessment, it is concluded that supplemental utility pole treatments of EZ-FUME and Hollow Heart CB provide minimal risk to the environment and human health when properly applied.

Conclusions

Chemical analyses of southern pine pole sections 12 and 32 months following fumigant treatment revealed that the release and migration of *mitc* from the pressed EZ-FUME stick was similar to that of the free-flowing granular dazomet. This finding supports the conclusion that a compressed form of dazomet is capable delivering comparable levels of *mitc* to that of granular or powdered dazomet.

Chemical analysis further showed that the addition of Hollow Heart CB enhanced the decomposition of the dazomet for both the EZ-FUME and granular dazomet treatments. This is a significant finding, as little research has been conducted on the benefit of using a water-based copper accelerant. Most, if not all, previous field work has been performed using an oil-based copper naphthenate formulation. However, concerns over VOC content and uncertainties surrounding EPA's classification of naphthenic acid as an inert ingredient have limited the use of these copper containing formulations in recent years. Hollow Heart CB is an EPA registered water-based formulation that is labeled for use as an internal void treatment in wood utility poles or as a copper accelerant for dazomet.

Results suggest that the benefit of the Hollow Heart CB is relatively short-lived when applied to the granular dazomet. This is likely a result of the limited interaction between the copper and dazomet as the liquid accelerant does not effectively penetrate the treatment hole. In contrast, the Hollow Heart CB was found to greatly enhance the production of *mitc* from the EZ-FUME sticks. This finding supports the conclusion that the larger volumes and improved mobility of the copper accelerant within the EZ-FUME application holes enhances the conversion and release of *mitc* from dazomet.

Based on a reported threshold value against decay fungi of 20 ppm, the 12 and 32 month chemical assay results show that the EZ-FUME sticks with or without accelerant provide fungitoxic levels of *mitc* both within and well above the zone of fungiant treatment.

Field performance testing and environmental and human health risk assessment confirm that the EZ-FUME plus the Hollow Heart CB copper accelerant is an environmentally responsible and effective preservative system for the treatment of in-service wood poles in both the US and Canada. Work has been initiated with PMRA to register this remedial wood preservative system that will serve to extend the useful service life of wood poles throughout Canada while providing minimal risk to the environment and human health.

		Average methylisothiocyanate (ppm) at selected heights				
Treatment	Assay Zone	6" Below Groundlin e	6" Above Groundline	12" Above Groundlin e	22" Above Groundline	
EZ-FUME	1.0" - 2.0"	32	74	37	42	
	3.0" - 4.0"	88	67	29	20	
	4.0" - 5.0"	91	77	28	26	
EZ-FUME + 2% Cu Accelerant	1.0" - 2.0"	57	132	138	111	
	3.0" - 4.0"	177	152	78	93	
	4.0" - 5.0"	194	164	39	39	
Granular Dazomet	1.0" - 2.0"	70	57	89	66	
	3.0" - 4.0"	123	40	39	37	
	4.0" - 5.0"	55	51	25	30	
Granular Dazomet + 2% Cu Accelerant	1.0" - 2.0"	48	127	89	86	
	3.0" - 4.0"	78	146	64	42	
	4.0" - 5.0"	109	174	57	51	

TABLE 1. Concentrations of *mitc* at various pole heights and depths in southern pine pole sections sampled at <u>12 months</u> following treatment with the EZ-FUME stick or granular dazomet.

<u>Note:</u> Methylisothiocyanate values reported in this table are an average of 4 pole sections. Values in RED represent fungitoxic levels of *mitc* (≥ 20 ppm).

		Average methylisothiocyanate (ppm) at selected heights				
Treatment	Assay Zone	6" Below Groundlin e	6" Above Groundline	12" Above Groundlin e	22" Above Groundline	
EZ-FUME	1.0" - 2.0"	111	32	54	29	
	3.0" - 4.0"	172	100	167	68	
	4.0" - 5.0"	197	93	117	84	
EZ-FUME + 2% Cu Accelerant	1.0" - 2.0"	137	106	74	36	
	3.0" - 4.0"	374	320	211	72	
	4.0" - 5.0"	379	405	300	145	
Granular Dazomet	1.0" - 2.0"	229	143	44	24	
	3.0" - 4.0"	277	118	61	45	
	4.0" - 5.0"	202	152	63	42	
Granular Dazomet + 2% Cu Accelerant	1.0" - 2.0"	61	72	38	26	
	3.0" - 4.0"	109	129	69	41	
	4.0" - 5.0"	126	150	75	30	

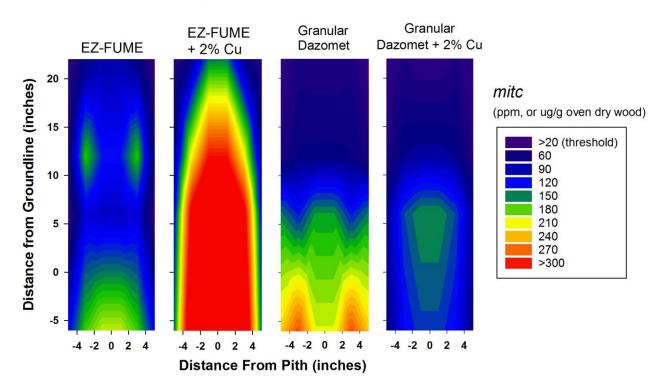
TABLE 2. Concentrations of *mitc* at various pole heights and depths in southern pine pole sections sampled at <u>32 months</u> following treatment with the EZ-FUME stick or granular dazomet.

<u>Note:</u> Methylisothiocyanate values reported in this table are an average of 4 pole sections. Values in RED represent fungitoxic levels of *mitc* (\geq 20 ppm).

EZ-FUME Granular Granular EZ-FUME + 2% Cu Dazomet Dazomet + 2% Cu 20 mitc Distance from Groundline (inches) (ppm, or ug/g oven dry wood) 15 >20 (threshold) 60 90 10 120 150 180 210 5 240 270 >300 0 -5 -4 -2 0 2 4 -4 -2 0 2 4 -4 -2 0 2 4 -4 -2 0 2 4 **Distance From Pith (inches)**

Figure 5. Residual *mitc* levels in penta treated s. pine pole sections <u>12 months</u> following treatment with EZ-FUME or granular dazomet with and without copper accelerant.

Figure 6. Residual *mitc* levels in penta treated s. pine pole sections <u>32 months</u> following treatment with EZ-FUME or granular dazomet with and without copper accelerant.



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