ANALYSIS OF SIMULATED STORM WATER RUNOFF FROM PACKS OF HEM-FIR AND SOUTHERN YELLOW PINE FIXED VIA AMBIENT TEMPERATURE FIXATION METHODS

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Summary

The simulated rain test consisted of eight cycles with each cycle applying about 0.25" (6.4 mm) of rain in a five minute period followed by a five minute drain. Each increment was analyzed for chrome (Cr), copper (Cu) and arsenic (As). The analytical results were then averaged for the total 2" (50 mm) of rain.

Hem Fir

Thirty two packs of both 2" (50 mm) and 4" (100 mm) thick chromated copper arsenate (CCA) treated Hem-Fir (HF) lumber were subjected to a simulated rain test (SRT) to determine the relationship between fixation, time in storage and CCA metals contribution to storm water runoff. Of the 32 packs tested in the simulated rain test, eight tested had a waterproof over wrap (paper wrap) during storage. All eight were SRT tested without the wrap and four of these packs were tested with over wrap . The remaining packs represented ambient fixation times ranging from one day after treatment to 224 days after treatment. The rain tests were conducted in two series. The first series was conducted in March, 1994 and the second series in January, 1995. The ambient temperatures for each series ranged between 30 (-1 °C) and 80 °F (27 °C) and the total rain fall during storage on each series was between 20" (508 mm) and 25" (635 mm). The Cr, Cu, and As concentrations in the SRT runoff from freshly treated packs were 41, 6, and 8 ppm respectively. These values continued to decrease over time and after about three months were reduced to 0.06, 0.15, and 0.12 ppm, respectively. No difference could be detected between packs of wood that were exposed to the elements during the test period and those that were not (i.e. paper wrapped soon after treatment). Paper wrapping substantially reduced the contribution of CCA metals to the simulated rain water.

Southern Yellow Pine

Twenty four packs of both 2" (50 mm) and 4" (100 mm) thick CCA treated southern yellow pine (SYP) lumber and one pack of 3/4" (19 mm) plywood were subjected to the SRT. Of the 24 packs of lumber tested in the SRT, three had been protected from the weather and one had been kiln dried and the remaining packs had been stored, unprotected, in the yard. The 24 packs represented fixation times ranging from eight hours after treatment to 88 days after treatment. The SYP simulated rain tests were conducted in two series. The first series was conducted in August 1994 and the second series in April 1995. The ambient temperatures for the first test series ranged between 70 (21 °C) and 95 °F (35 °C) and the second series ranged between 20 (-7 °C) and 80 °F (27 °C). The total ambient rain fall for the first series was 8" (203 mm) and the second series was 13" (330 mm). The Cr, Cu, and As concentrations in the SRT runoff from freshly treated packs were 44, 5, and 9 ppm respectively. These values continued to decrease over time and after about three months were reduced to 0.15, 0.40, and

0.40 ppm, respectively. No difference could be detected among packs of wood that were exposed to the elements over the test period and those that had been protected from the elements.

1. Introduction

Fixation may be defined as a chemical reaction between chromated copper arsenate (CCA) solution and various wood components. The progress of this reaction may be monitored by testing for the conversion of hexavalent chrome (Cr^{+6}) to trivalent chrome (Cr^{+3}). This reduced form of chrome complexes with arsenic to form highly insoluble compounds in the CCA treated wood. Since this transformation occurs more slowly than the chemical transformation of copper and arsenic, chromium conversion is a valid and conservative measure of total CCA fixation. Many papers have been written on the chemistry of this reaction and several reviews have been published (Anderson, 1990).

Storm water runoff from treating plants is coming under investigation by various state, provincial and federal regulators. The allowable levels of CCA metals in storm water runoff varies by state. For example, in late 1996, the State of Washington will reduce the allowable storm water limits for copper to 18 ppb, chrome to 16 ppb and arsenic will remain at its current level of 360 ppb. Achieving these values will probably require re-evaluating plant operations, adding roofs to protect freshly treated materials and in some cases using accelerated fixation techniques to reduce the concentration of CCA metals available for leaching by rain water.

Little information exists which relates the degree of fixation of CCA metals to the concentration of CCA metals in storm water runoff. In addition to fixation there are steps that can be implemented to reduce stormwater contamination, such as wrapping packs with waterproof paper or storing treated material under roof. The following study was undertaken to evaluate the amount of CCA metals in storm water runoff from packs of CCA treated Hem-Fir and SYP of various ages and levels of fixation.

2. Methodology

A simulated rain test (SRT) was devised to determine the relationship between fixation and CCA metals contribution to storm water runoff from individual packs of CCA treated wood. This test is based on work reported by Zahora *et.al.* (1993).

A test stand was constructed to support a single pack of wood. The stand had a sloped bottom tray that directed the runoff from the pack to a gutter that drained to a single point that allowed for collection of the runoff. An adjustable overhead rig allowed for positioning of two spray nozzles for uniform water coverage. The rain tests were conducted outside but under a roof.

A pressure regulator was used to control the water supply to the spray nozzles and a ball valve was used to turn the sprays on and off. The second series of tests included installation of a rotometer to monitor the water flow during the test. A pressure of 35 psig (241 kPa) resulted in a water flow of 1 gallon per minute (gpm) (3.8 l/min) which is the equivalent to a 2.18 inch (55 mm) rain over a 40 minute period on the surface of a pack of 2x6" - 8' long (29.3 square feet of top surface area) (50 mm x 150 mm x 2.4 m - 2.7 sq.m). The rain test consisted of a five minute spray period followed by a five minute drain period. The run off from each spray/drain period was collected in a calibrated 5 gallon (19 l) bucket. The level in the bucket was recorded, the water was agitated and a sample was taken for analysis. Two buckets (labeled A and B) were used. The bucket not collecting water was rinsed with tap water and allowed to drain before reuse to prevent cross contamination. This procedure was repeated eight times for each test. The charge number was used to identify each pack. The charge number, pack description, individual cycle water volumes, bucket identification and any comments were recorded on individual log sheets. Upon completion of the test procedure the pack was removed and the test rack was washed with water to remove residual drips before positioning the next pack for testing.

After the pack was positioned on the test stand, and before beginning the rain test, ten borings were taken for fixation determination. Distilled water was used to flush the increment borer between each use to prevent CCA cross contamination. Several of these borings were placed on white filter paper and tested with chromotropic acid (AWPA, 1995). Chromotropic acid is colorless but will turn purple to pink in the presence of Cr^{+6} concentrations as low as 15 ppm. The results of this test were recorded as either pass or fail depending on the presence of the purple to pink color. . The remaining borings were used in the Hickson leach test. In this test, a total of 1" (25 mm) of treated wood was obtained with no more than 0.5" (13 mm) of treated wood taken from any one boring. The borings were then placed into a disposable centrifuge tube containing 10 ml of distilled water. The borings were leached for 15 minute with frequent agitation. At the end of the leach period, the borings were removed from the water and stored in a plastic bag. The centrifuge tube, the boring bag, and the filter paper were marked with the charge number, date treated, and date and time sampled.

The samples of water from the rain test and the samples from the fixation leach test were transported to the Hickson Corporation Technical Center for analysis. The solutions were acidified with nitric acid, and analyzed by an Inductively Coupled Plasma Spectrometer (ICP). The borings were dried, weighed, digested in nitric acid and diluted to about 100 ml. The exact weight of the diluted samples were determined and then they were analyzed by ICP. The following calculation was used to determine the percent fixed for each element:

$$\textit{Percent Fixed} = 100 * \left(1 - \left(\frac{\textit{Element Leached}}{(\textit{Element Leached} + \textit{Boring Analysis})}\right)\right)$$

The Hem-Fir packs from storage represented wood treated as long as 224 days, to as recently as one day before the rain testing. The ambient temperatures were in the 30-60°F (-1 to 16 °C) range during the test. Two SRT series were conducted. The first series was conducted during the week of March 22, 1994 and the second series was conducted during the week of January 23, 1995. Figure 6 plots the maximum and minimum temperatures for each test and Figure 7 plots the daily and total rainfall for each test period.

The SYP packs from storage represented wood treated as long as 88 days, to as recently as 8 hours before the rain testing. The freshly treated packs were retained on the drip pad for 48 hours before being moved to the storage yard. Two SRT series were conducted. The first series was conducted during the week of August 31, 1994 and the second series was conducted during the week of April 5, 1995. The ambient temperatures during the first series of tests were in the mid to high 80's (27 °C) and in the mid 60's (16 °C) for the second series. Figure 17 plots the maximum and minimum temperatures for each test and Figure 18 plots the daily and total rainfall for each test period.

2.1 Treatment and Pack Preparation

Since Hem-Fir timbers are normally stored with the sticks in place, the rain tests for these packs of timbers were conducted with the sticks left in the pack and therefore the individual pieces in the pack were not disturbed. Eleven of the Hem-Fir packs had been stored in the field after being paper wrapped. Four of these packs were tested both with and without the paper wrap. The remaining seven packs had the paper wrapping removed before conducting the rain test.

The SYP packs tested were treated to 0.40 pcf (6.4 kg/m3) CCA using a drip free, modified full cell cycle with net treating solution retention in the 12 to 15 pcf (192 - 240 kg/m3) range. Three of the packs tested had been stored under a roof immediately after treatment and one pack of wood tested had been kiln dried prior to testing. One pack of plywood consisting of 33 - 4' x 8' x 3/4" (1.2 m x 2.4 m x 19mm) (sheets separated using 3/16" (5 mm) stickers between each layer was also tested.

3. Results and Discussion

When evaluating the results of the simulated rain test three factors should be noted. First, the packs from storage had been subjected to weeks and in some cases months of outdoor exposure and rain, except for the packs that had been covered with paper wrap. If there had been any surface residue, it would have been washed off during the first few rain storms. Second, while there was reasonably uniform wetting of the top surface of the pack during testing the movement of the water through the pack could not be controlled or predicted. Band tightness, cupping and twisting of the wood, and alignment of the individual pieces of lumber within the pack affect movement of water through the pack and contribute to variability in the amount of metals in the storm water. Third, the amount of water collected during the test depends on the moisture content of the pack and the path the water takes before it reaches the edge of the pack and drains down the side.

Based on the initial calibration of the nozzles each cycle used about 41 pounds (19 kg) of water which totaled about 334 pounds (152 kg) of water for each test. The average water collected from the Hem-Fir Packs was 302 pounds (137 kg) which was about 90% of the applied water. The average water collected from the SYP packs was 89% of the applied water. In general, the water collected during the first one or two spray cycles were the lowest volumes and the balance of the collection was essentially flat. Because the test structure was outside there was a small amount of over-spray during high winds, but it is believed that most of the apparent loss was due to absorption by the wood.

There are many factors that affect the contribution of CCA metals to storm water runoff from packs of lumber. These include surface cleanliness, the potential for CCA treating solution to be trapped between the layers of the pack, incising, retention gradient (including the effect of re-treatment cycles loading the outer surface of the wood with a high level of CCA), tightness of the bands, the use of an overwrap, the natural variability of wood itself and of course the degree of the CCA fixation. Timbers tend to have a rougher surface than nominal 2" lumber that has been surfaced on four sides. This roughness should contribute to trapping more dirt and CCA solution than 2" (50 mm) material. It should be possible to have a relatively well fixed pack of wood contribute a larger metals loading to storm water runoff than a more poorly fixed pack that might have a cleaner surface or less solution trapped between the layers. All of these factors contribute to making the interpretation of data more difficult, though not impossible.

For ease of understanding, the discussion of the results of this test will be broken into six sections. These include a review of:

1) comparison of chromotropic acid test with leach test
2) CCA metals fixation rates
3) individual data
4) average ambient data
5) paper wrapping
6) comparison of SYP and Hem-Fir SRT values

3.1 Comparison of Chromotropic Acid Test With Boring Leach Test

Chromotropic acid is currently the only American Wood Preservers Association (AWPA) recognized test to determine fixation of CCA treated wood and is listed as an approved method by the Canadian Standards Association (CSA). It is a pass / fail test that results in a color change (fail) at about 15 ppm Cr^{+6} which relates to 99.5% conversion of Cr^{+6} to Cr^{+3} at a 0.40 pcf (6.4 kg/m2) retention. Figure 1 relates the percent chrome conversion needed to achieve 15 ppm of Cr^{+6} as a function of retention. A major advantage of the Hickson boring leach test is that it produces a numeric percent element leached that may be used to track the progress of the fixation reaction.

Figure 2 plots the Chromotropic Acid (CA) results as a function of the leach test for combined SYP and hem-fir data. These tests were conducted as part of the simulated rain tests. Figure 3 plots the same data except the scale has been expanded to show the values above 99% fixed.

For this series of tests it was assumed that any one boring failing CA would fail the charge. As can be seen, all borings with chrome fixation levels below 99.2% fail the CA test. The borings above 99.8% pass the CA test. There is a grey area when the concentration of Cr^{+6} is in the 15 ppm range where it is possible to have a single boring fail the CA test but the average leach results (which include multiple borings) indicate a high degree of fixation. This anomaly will be most apparent in refractory species (such as hem-fir) where it requires about six borings to achieve a sample with an equivalent length of 1" (25 mm).

3.2 Comparison of CCA Metals Fixation Rates

A comparison of relative rates of fixation can be made using the combined results of the boring leach tests for both the SYP and hem-fir SRT tests. Figure 4 plots the percent copper fixation as a function of chrome fixation and Figure 5 plots the arsenic fixation as a function of chrome. As can be seen both copper and arsenic appear to fix faster than chrome. When chrome is 90% fixed, both copper and arsenic are about 96% to 97% fixed and when chrome is 95% fixed by the boring leach test copper and arsenic are well over 99% fixed.

3.3 Individual Data

All individual data for all tests have been entered into a database so that values for any test series may be easily obtained. This table also lists the fixation level for chrome, copper, and arsenic as well as the type of storage (ie roof or paper wrap). In general, the analysis of runoff samples from the first two cycles in the SRT resulted in higher metals content than the remaining 6 samples. When a rain event occurs, the leachable metals at or near the surface of the wood are leached by the water. As the rain event progresses, the movement of the leachable metals in the wood is limited by diffusion and therefore their availability to be leached should be greatly reduced.

3.4 Average SRT Data

In the following discussions, the average concentration values of all eight rain cycles for a given pack will be used. Figures 8 through 10 plot the combined average chrome, copper and arsenic concentrations in the runoff from a 2" (50 mm) rainfall for all the Hem-Fir packs. Figures 19 through 21 plot the combined average chrome, copper and arsenic concentrations in the runoff from a 2" (50 mm) rainfall for all the SYP packs.

3.4.1 Comparison of 2" (50 mm) and 4" (100 mm) thick packs

It has been theorized that 4" (100 mm) thick timbers might trap more CCA due to the tendency to have rougher surface. Figures 11 through 13 plot the average chrome, copper, and arsenic concentrations for both 2" (50 mm) and 4" (100 mm) thick Hem-Fir material. Figures 22 through 24 plot the average chrome, copper, and arsenic concentrations for both 2" (50 mm) and 4" (100 mm) thick SYP material. This data indicates that there is no discernable trend between the 2" (50 mm) and 4" (100 mm) packs.

3.4.2 Comparison of Weathered and Protected Packs

Figures 14 through 16 plot the comparative results of run off from Hem-Fir packs that had been exposed to the weather versus packs that had been protected from the elements with a paper wrap directly after treatment but had the wrap removed before the test. Figures 25 through 27 plot the comparative results of SYP packs that had been exposed to the weather and packs that had been protected from the elements immediately after treatment.

If CCA solids were deposited on the wood during treatment, then the protected samples should have a higher metals concentration in the run off then the packs that have been exposed to the weather where residuals would have washed away. The results show that there is no difference between exposed and protected packs. This would indicate that in a well run plant, using clean treating solution, there does not seem to be any residual solids laying on or trapped between the layers that would contribute additional metals to storm water.

3.5 Paper Wrapping

The purpose of these tests is to determine cost-effective ways to reduce the concentration of CCA metals in storm water runoff. One method would be to paper wrap every pack of wood after treatment and before placing it in storage. Four packs of lumber were tested with and without paper wrapping. The paper wrap extended about 5 - 6 inches down the sides of the pack and about one foot down the ends. After completing the SRT on the wrapped pack, the paper was removed and the pack was retested.

Figure 31 plots the results for the four day old packs of lumber which had chrome concentrations between 10 and 15 ppm. The addition of the paper wrap reduced the average chrome concentration to 0.22 ppm. This represents a 98% reduction in the chrome contribution. Figure 32 plots the results for aged packs. These packs were 160 to 200 days old and had chrome concentrations in the 60 to 110 ppb range. Addition of the over wrap reduced these values to 30 to 70 ppb chrome. Figure 33 plots the percent reduction for the CCA metals for this series of tests.

Addition of the protective cover substantially reduces metals in the run off as well as providing protection to the pack from fading and yard dirt and dust.

3.6 Comparison of SYP and Hem-Fir SRT Values

Figures 28 thru 30 compare the concentration of CCA metals in a 2" (50 mm) rainfall for both SYP and hem-fir. As can be seen from Figure 28, SYP reaches a chrome concentration of 0.20 ppm chrome in about 10 days and hem-fir requires about 85 days to reach the same level. The concentrations of copper and arsenic in the simulated rain water are substantially lower than chrome and somewhat more scattered. Initially, the copper values (Figure 29) for Hem-Fir are higher than SYP but after about 20 days the Hem-Fir values cross over the SYP line. Arsenic (see Figure 30) follows a pattern similar to copper except that it required about 40 days for the cross over to occur. These differences are probably due to the difference in ambient temperatures as well as the fixation rates among species .

4. Conclusions

Hem-Fir

The simulated rain test has generated data that describes the contribution of metals from packs of CCA treated Hem-Fir subjected to ambient temperature fixation in the 35° F to 70° F (2 - 21 $^\circ$C) range. After about 80 days of ambient temperature storage it appears that the concentration of CCA metals in the storm water essentially levels off to chrome values between 60 and 100 ppb, copper between 100 and 200 ppb, and arsenic between 80 and 100 ppb. The addition of roofed storage areas will remove some or all of the wood from exposure to rain and will further reduce the average metals concentration in the storm water.

Southern Yellow Pine

The simulated rain test has generated data that describes the contribution of metals from packs of CCA treated SYP subjected to ambient temperature fixation in the 35° F to 90° F range. After about 30 days of ambient temperature storage it appears that the concentration of CCA metals in the storm water essentially levels off to chrome values between 100 and 200 ppb, copper between 30 and 100 ppb, and arsenic in the 50 ppb range.

The addition of roofed storage areas will remove some or all of the wood from exposure to rain and will reduce the average metals concentration in the storm water. Each method to reduce storm water runoff metals concentration has capital, operating and manpower costs associated with it. Using the storm water model a cost / benefit table can be generated for various scenarios and used by treating plant management as a guide for the most efficient use of their capital and manpower to reduce CCA metals in their storm water.

Blending of the storm water from the entire plant site with the runoff from the treated wood storage area is an accepted practice. Figure 20 is a plot of the acres of clean water required to reduce the concentration from treated wood stacks to the proposed State of Washington discharge limits. For example, if there is an acre of treated wood that has an average concentration of 1 ppm chrome then it will require a minimum of about 150 acres of clean dilution water to meet the standard. If the treated wood covers a half acre (.2 ha), a minimum of 75 acres (30 ha) of clean water would be needed. Most treating plants will not have enough unused acreage to provide significant dilution. To meet stringent standards such as those proposed for the State of Washington, a treating plant will have to initiate an aggressive program including some or all of the following items; improved plant cleanliness, erection of roofs, paper wrapping, and accelerated fixation.

The next phase of this project will be to incorporate this data into a storm water management model that will allow a treating plant to predict metals concentration in an outfall based on the actual plant layout.

5. References

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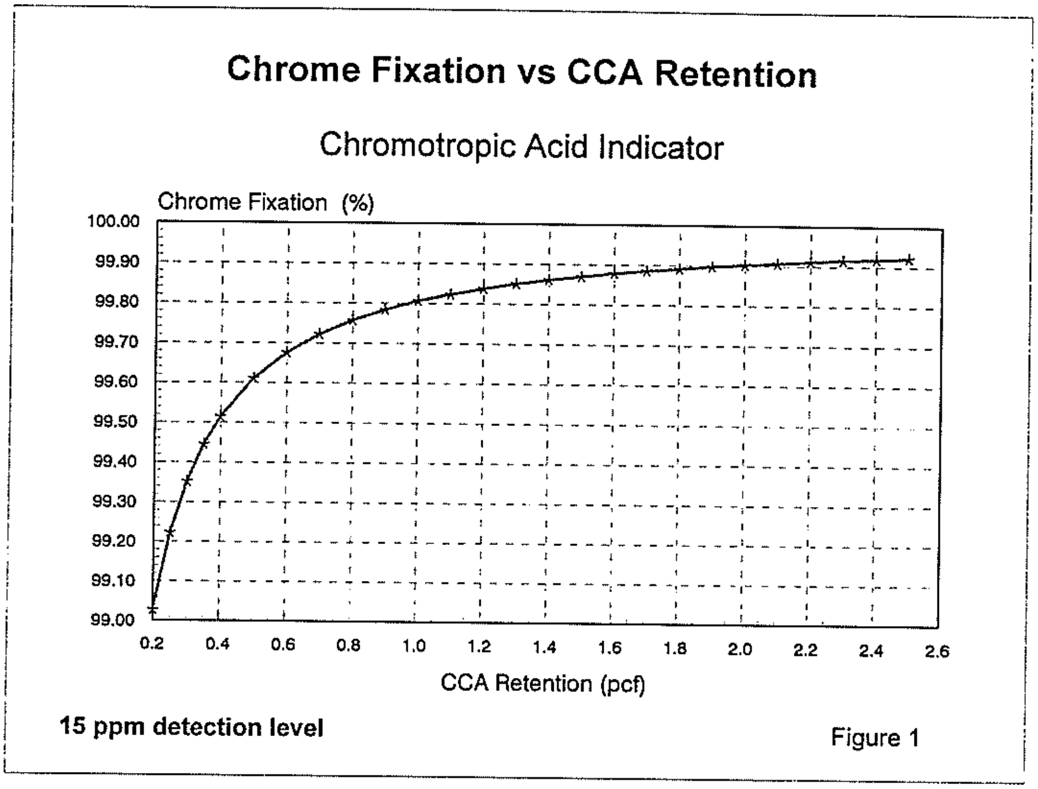

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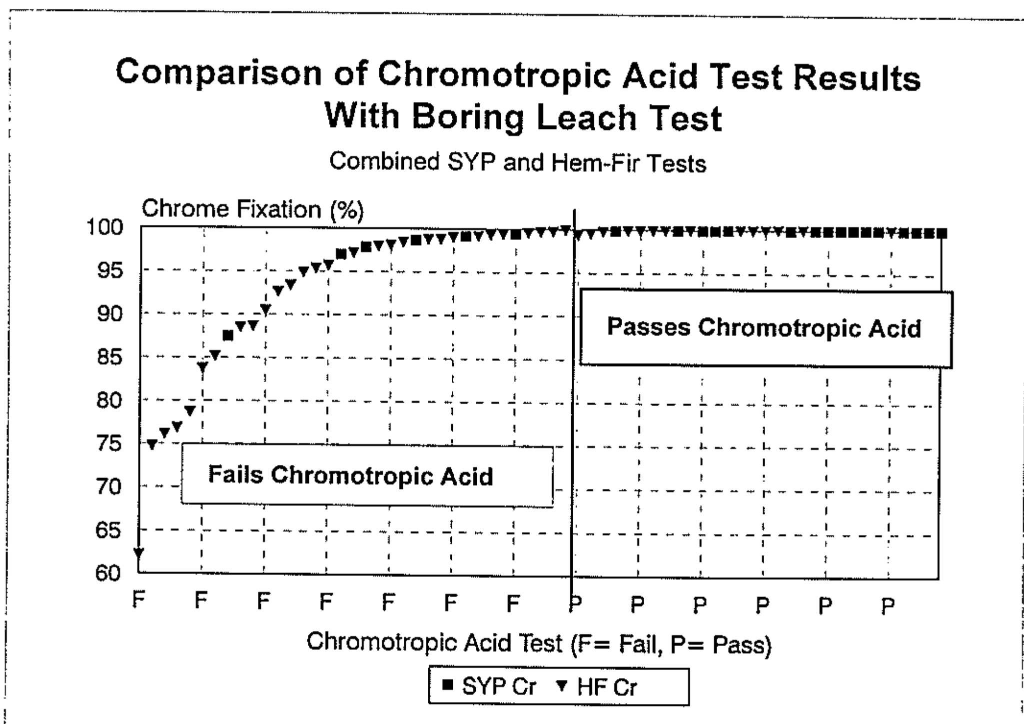

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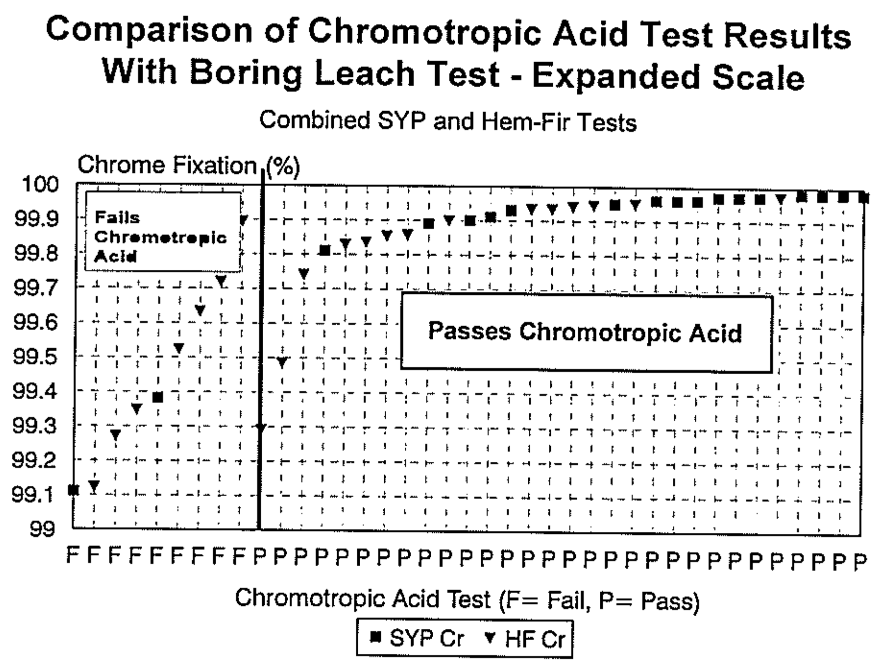

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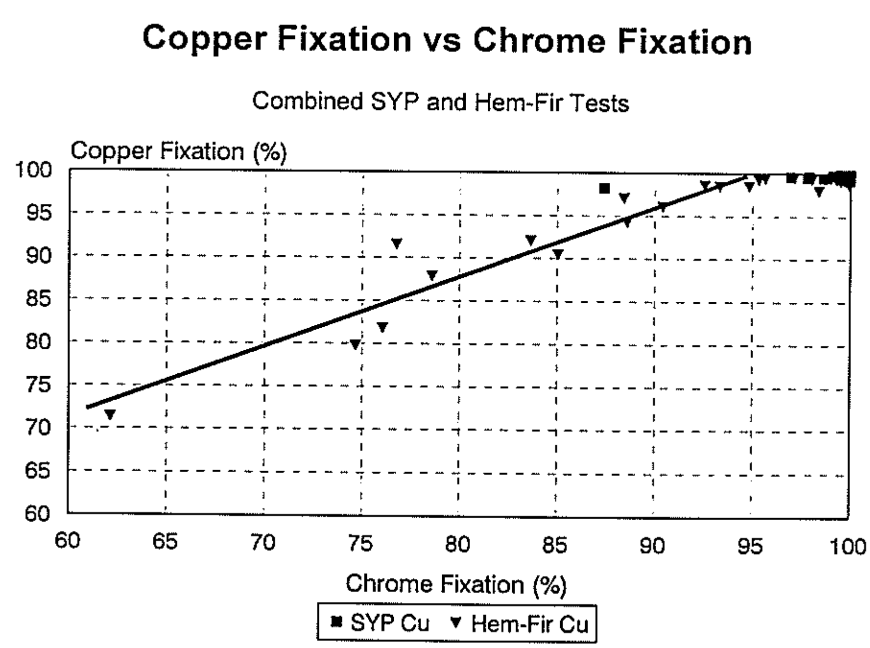

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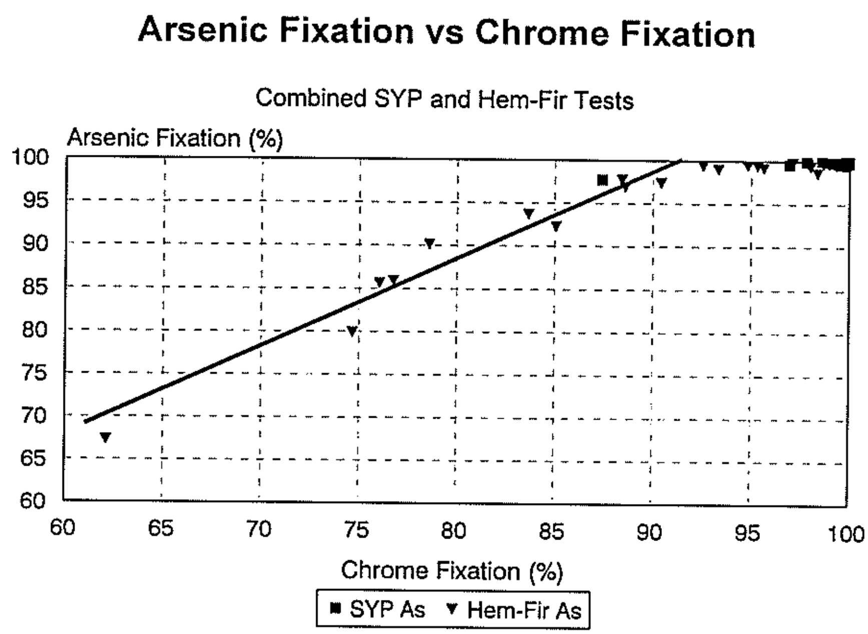

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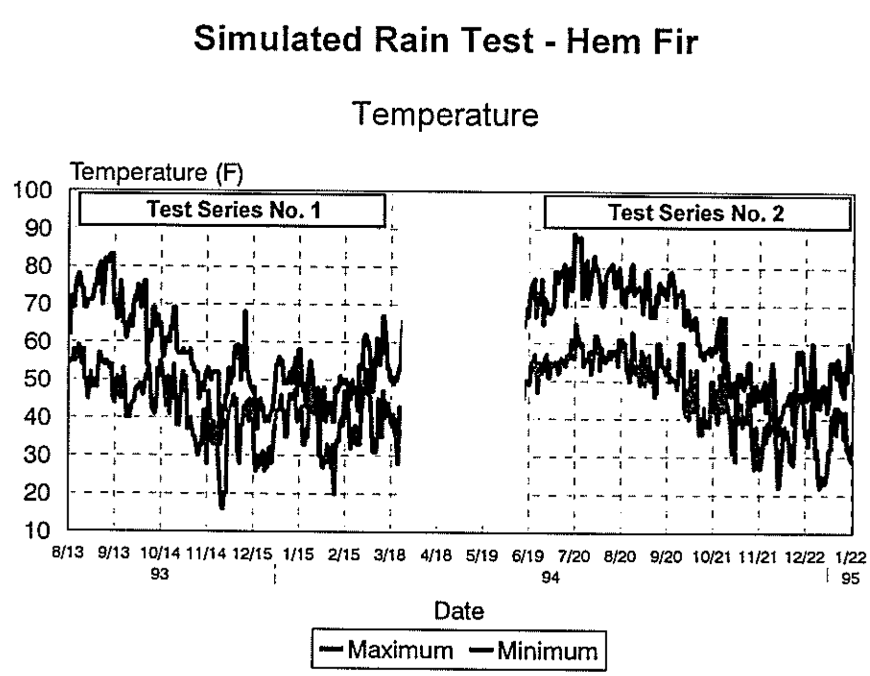

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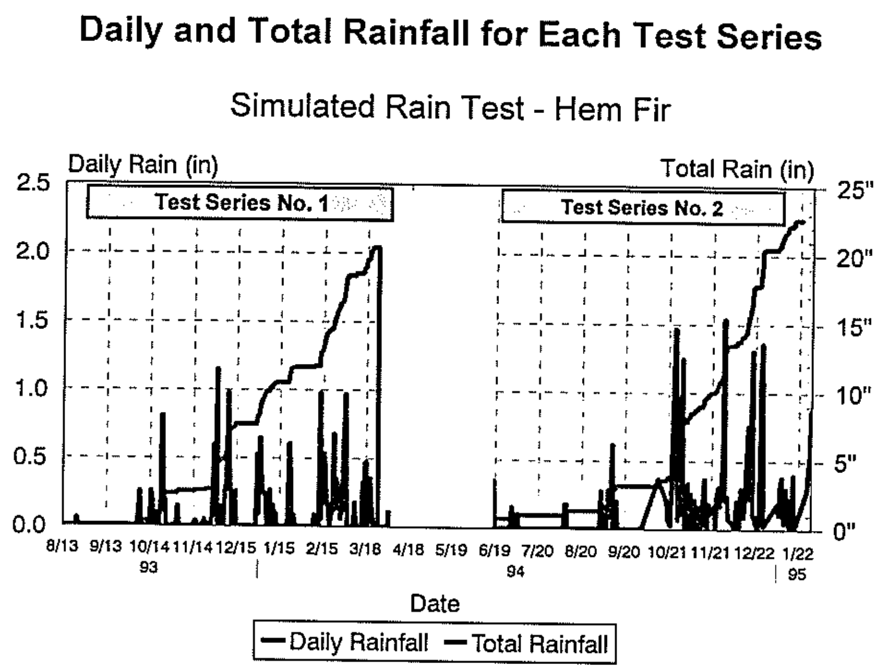

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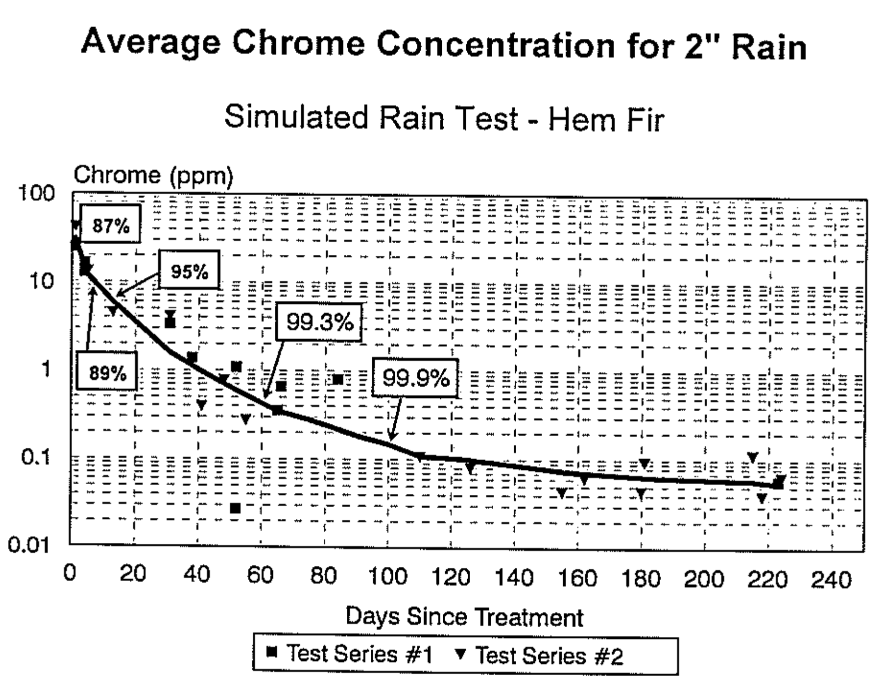

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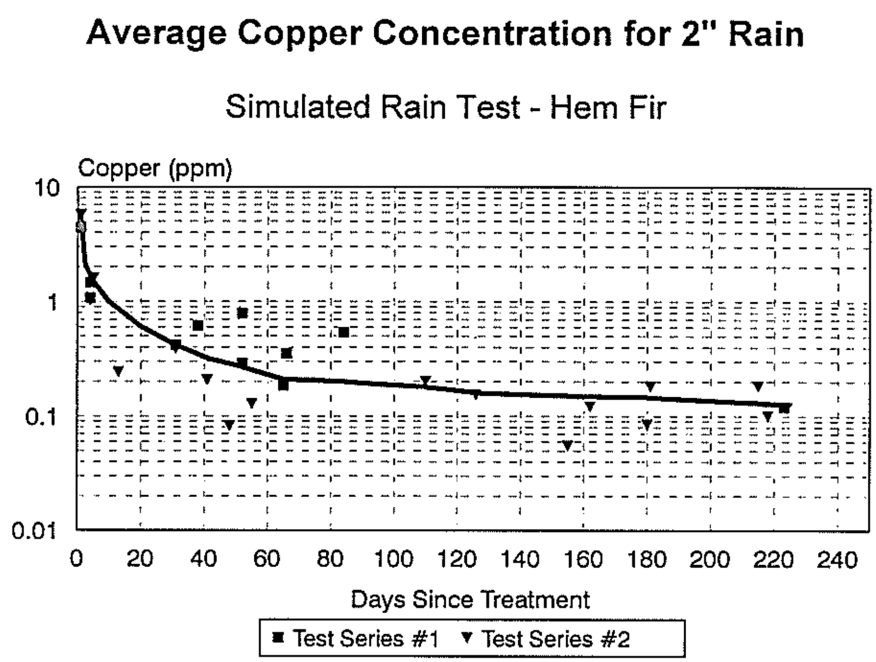

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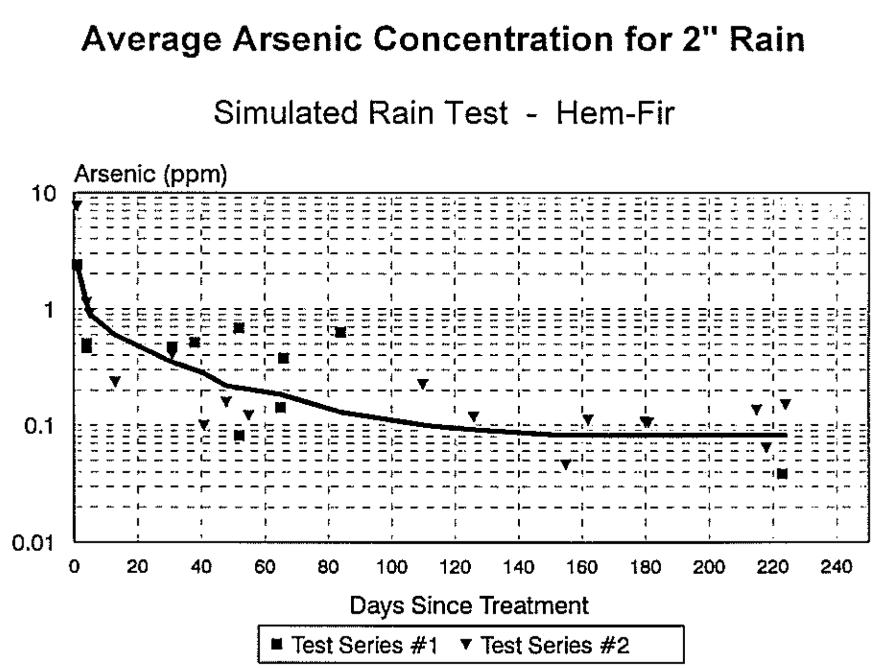

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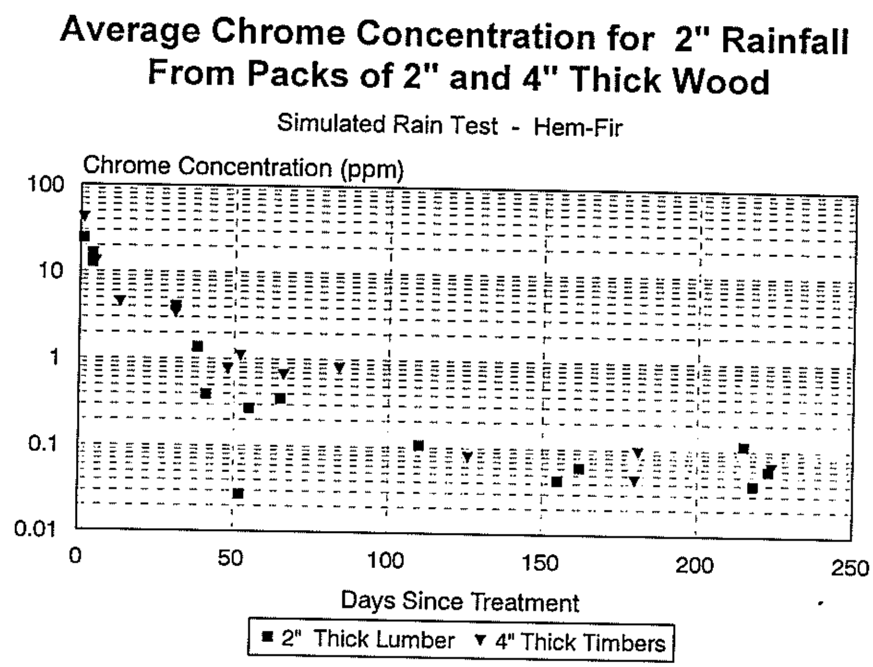

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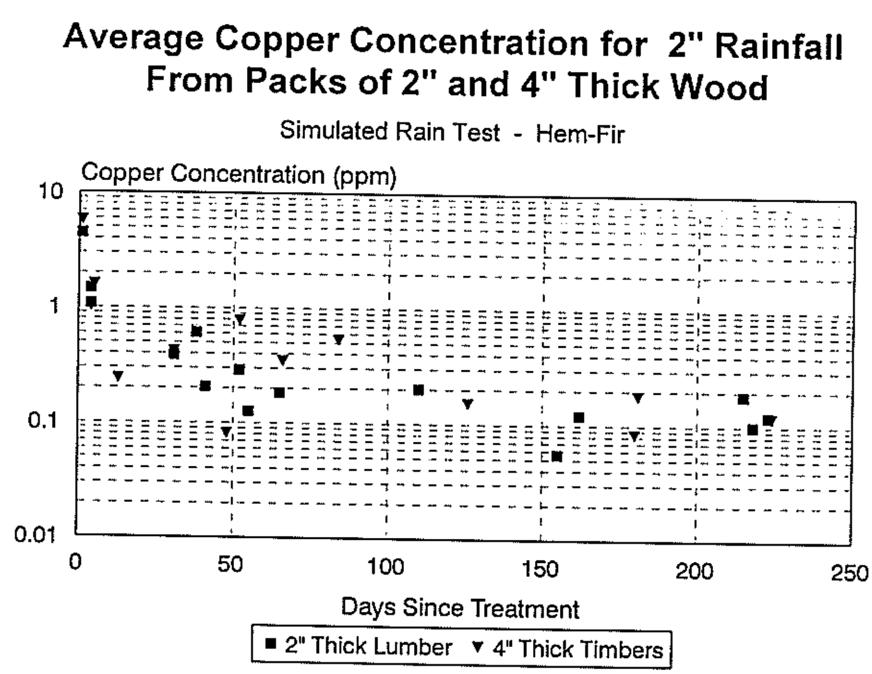

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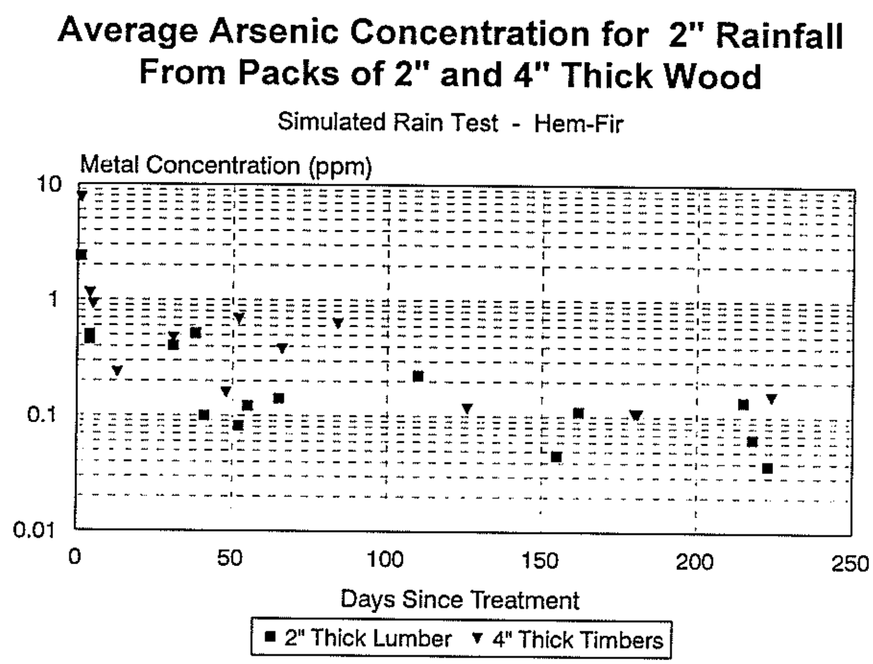

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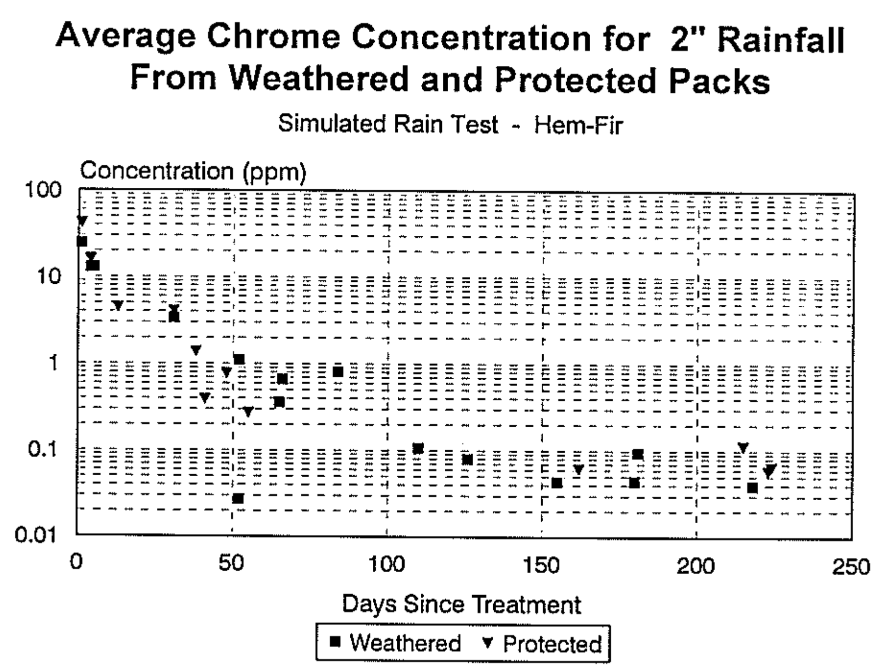

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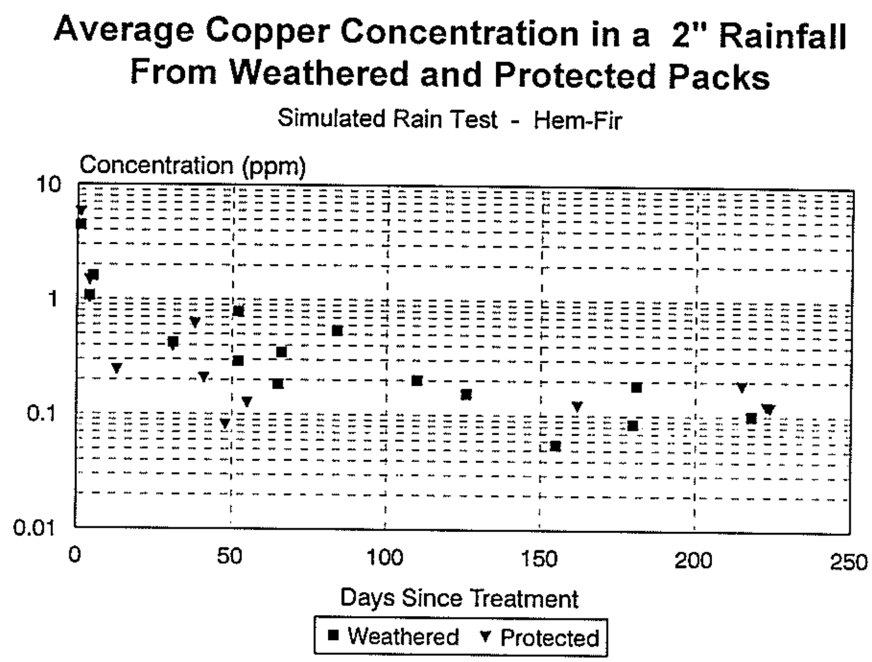

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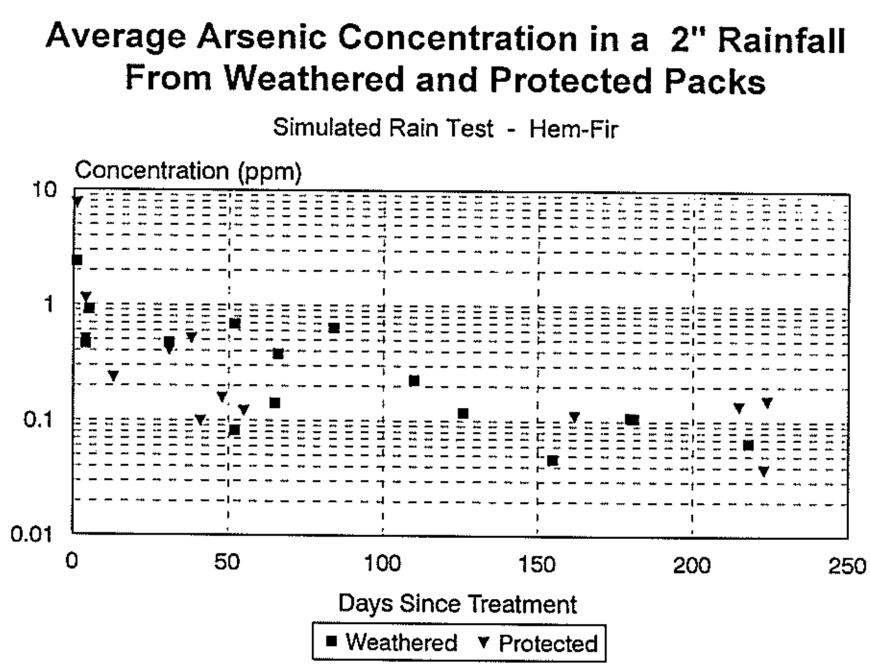

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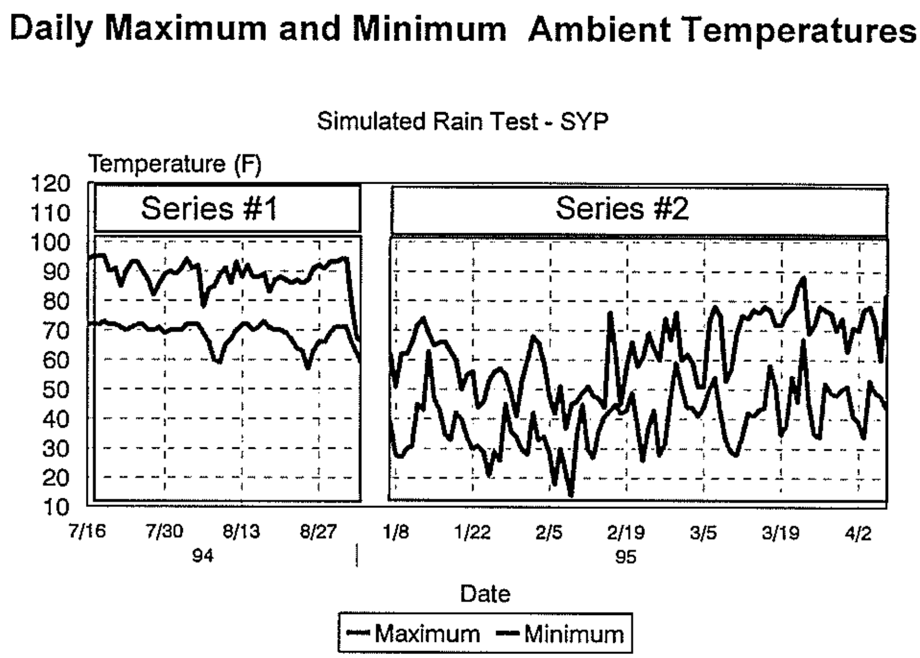

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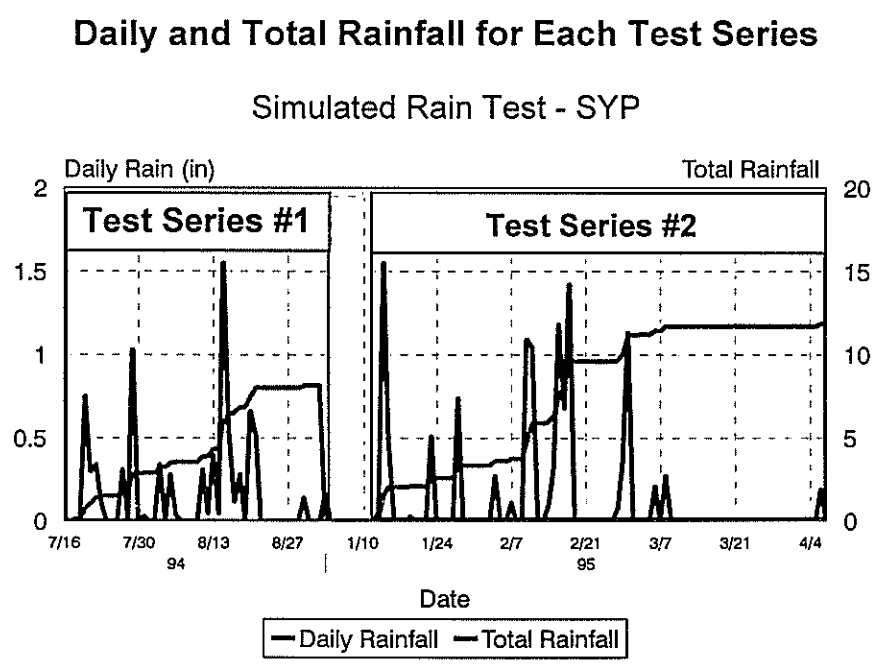

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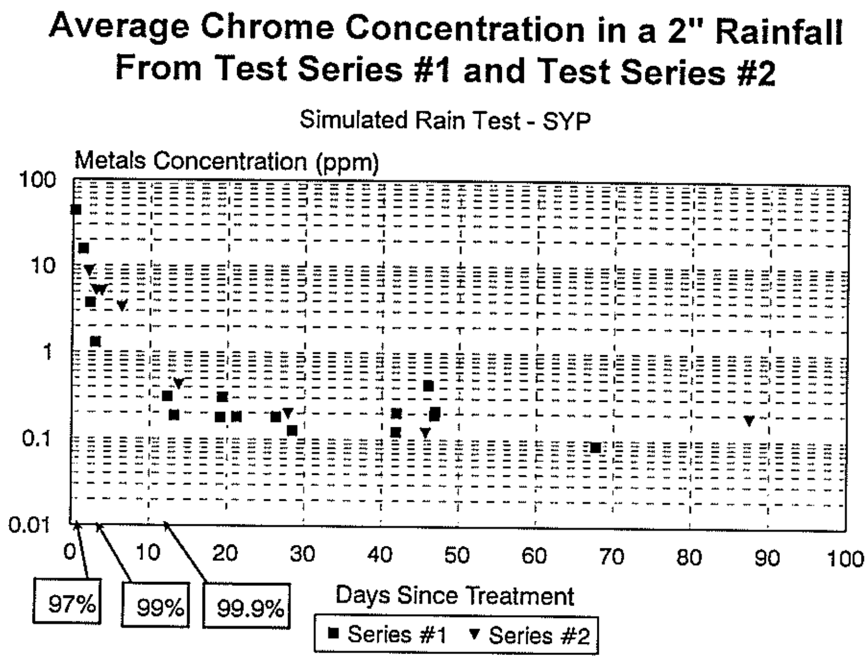

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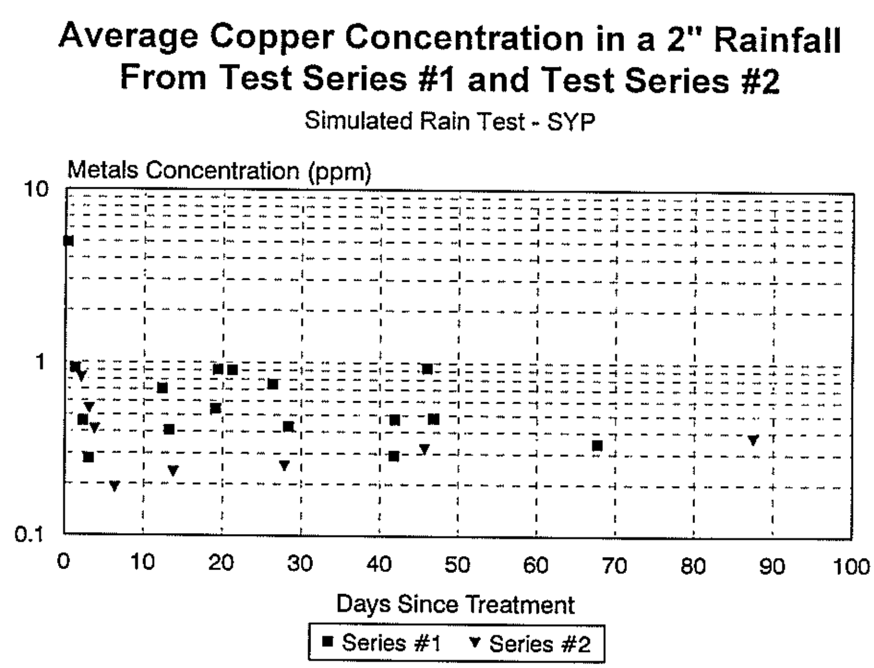

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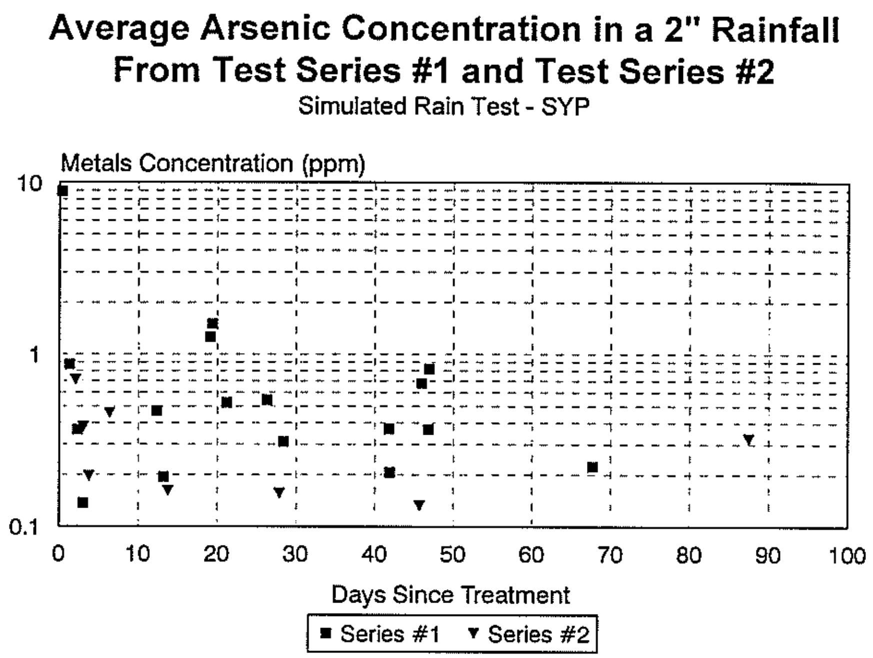

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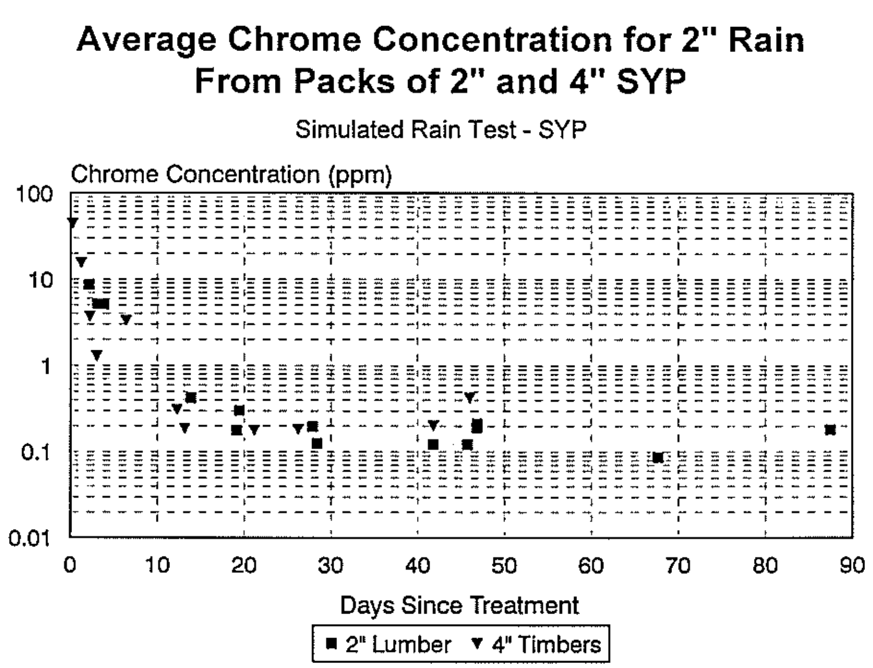

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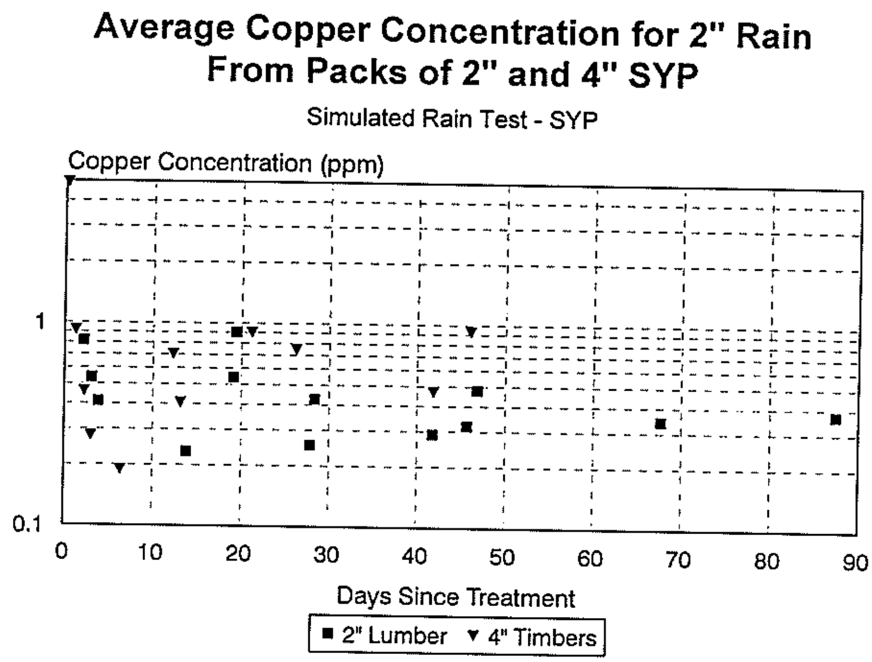

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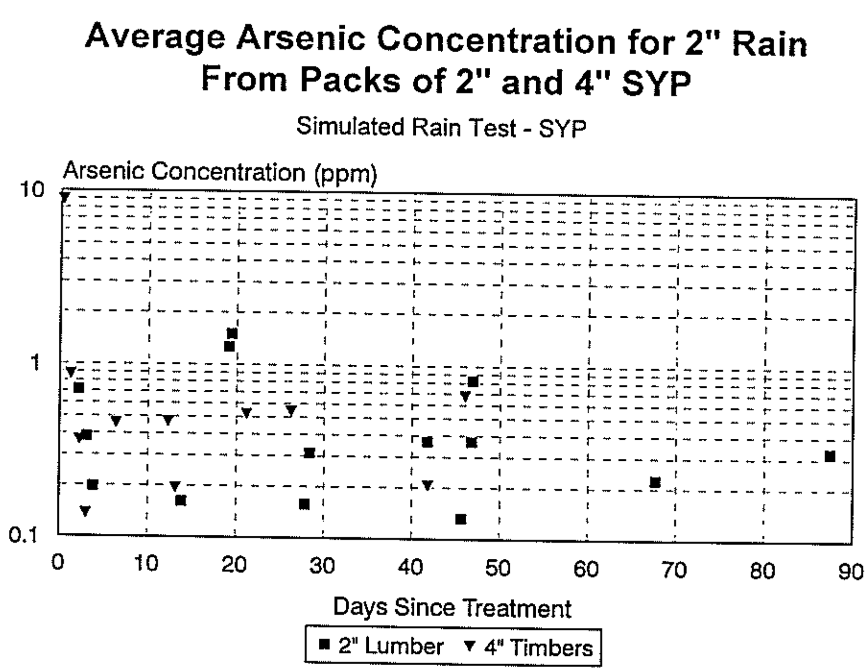

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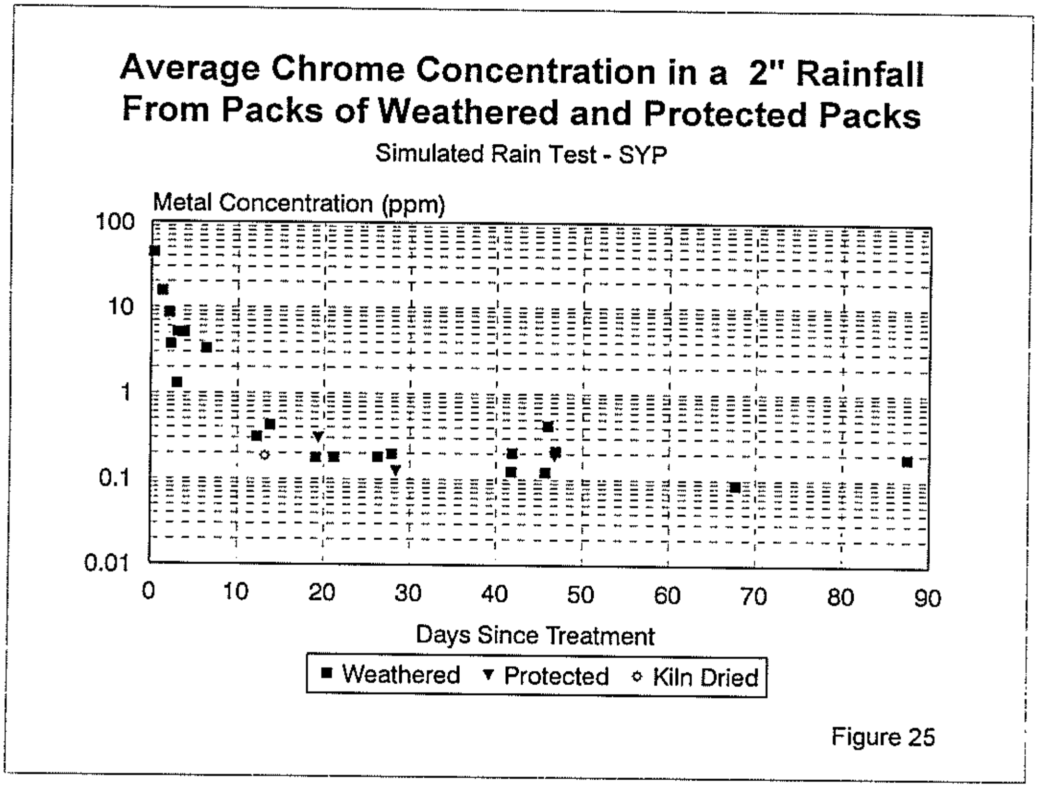


Figure 25

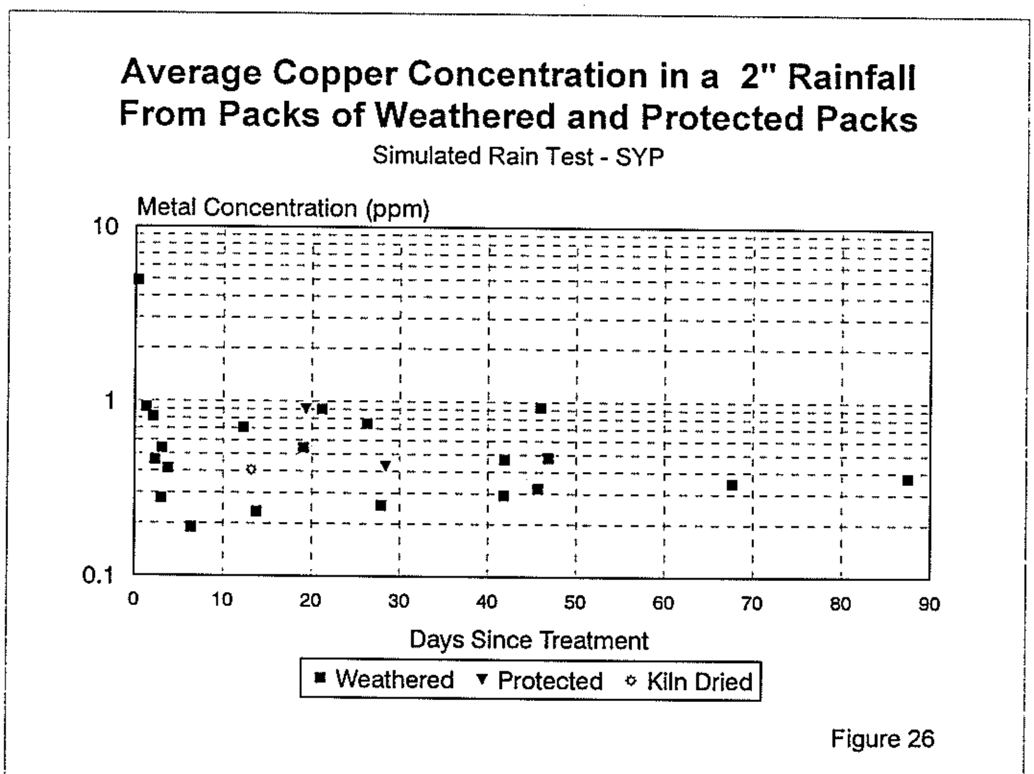


Figure 26

Average Arsenic Concentration in a 2" Rainfall From Packs of Weathered and Protected Packs

Simulated Rain Test - SYP

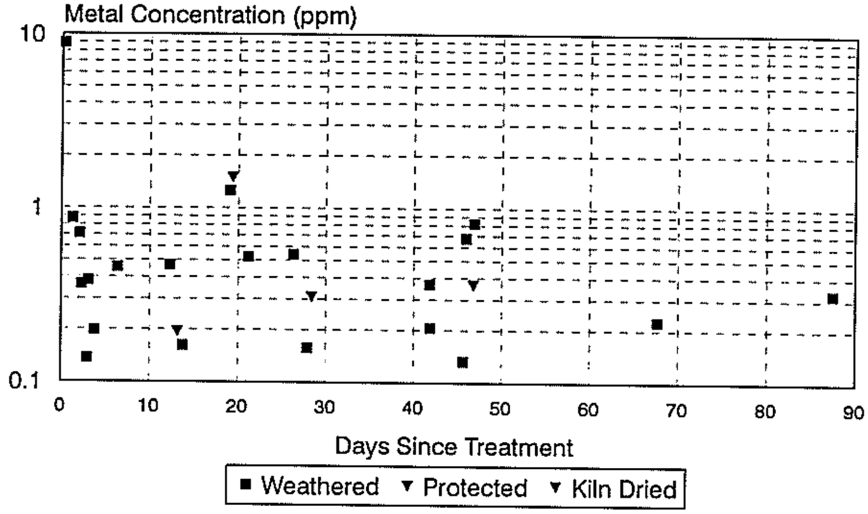


Figure 27

Comparison of Chrome Concentration from Hem-Fir and SYP for 2" Rainfall

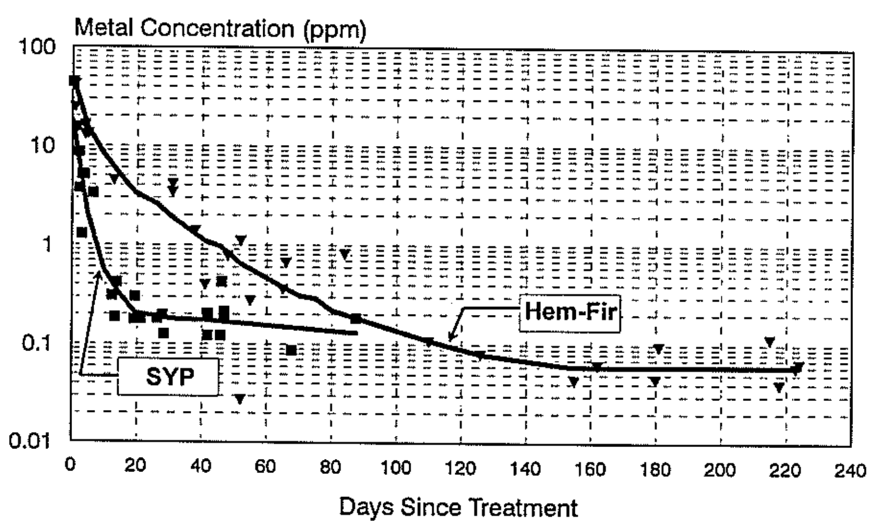


Figure 28

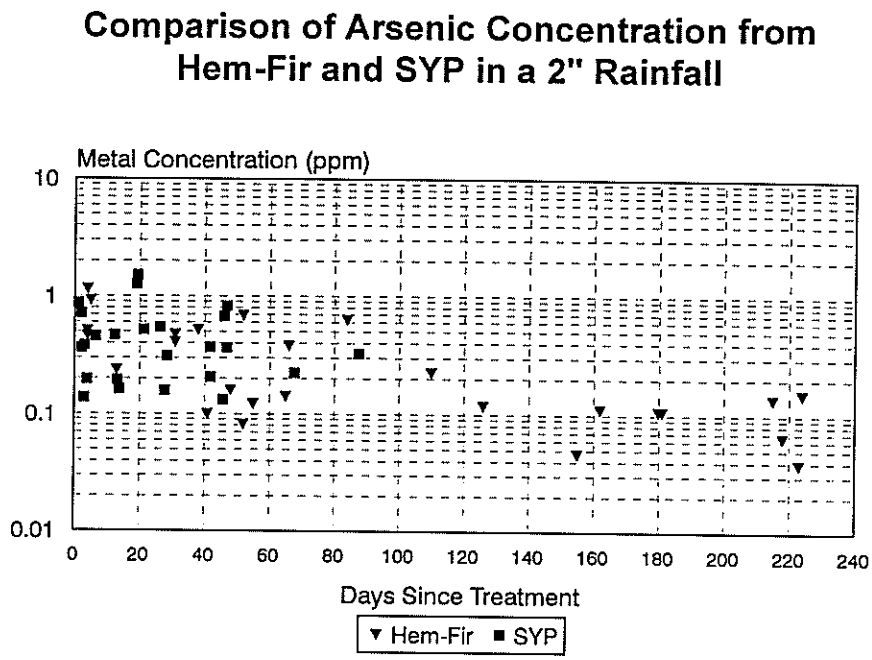


Figure 29

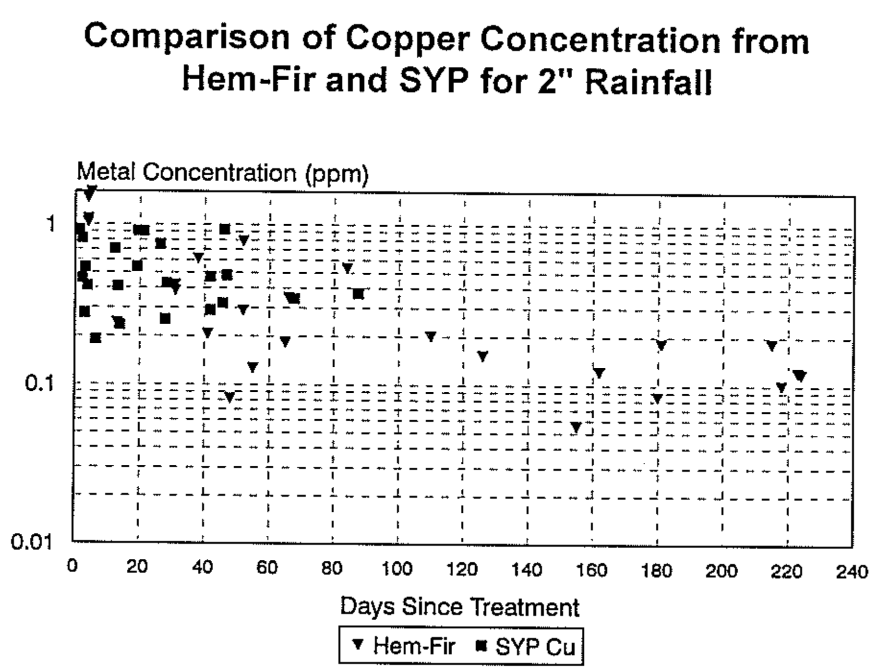


Figure 30

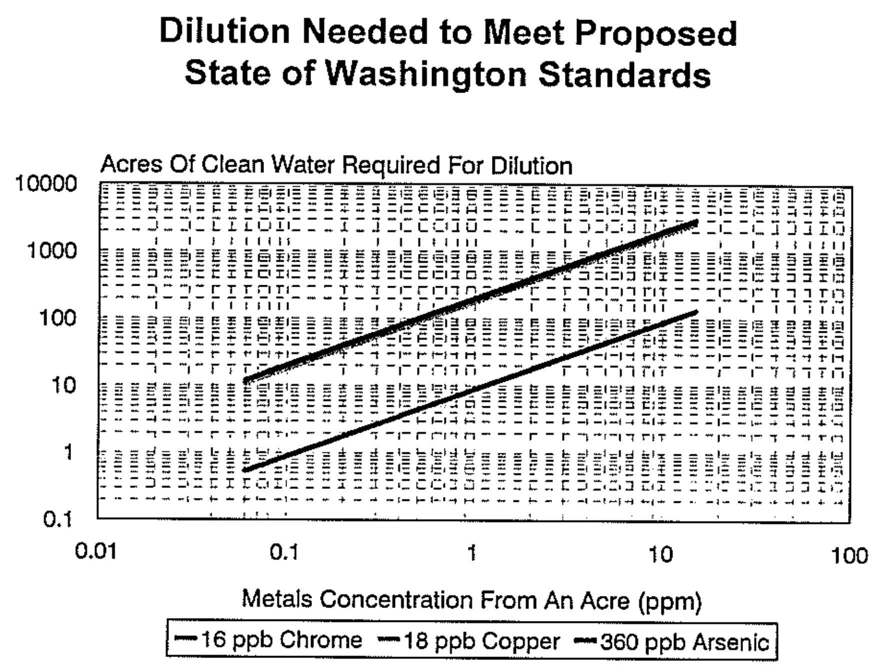


Figure 31

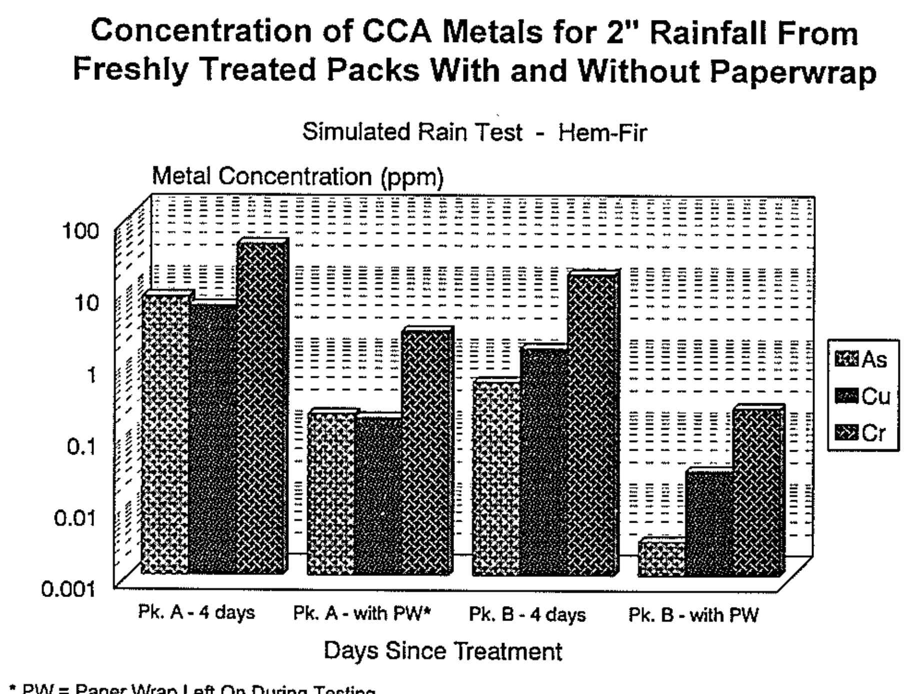
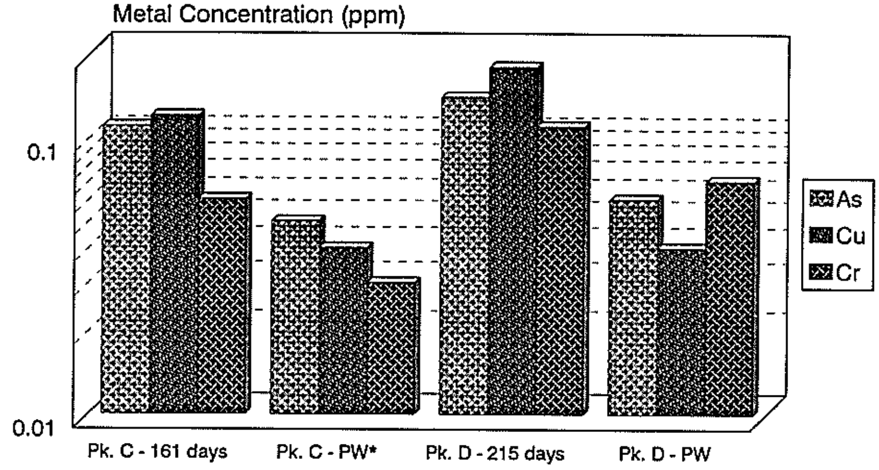


Figure 32

Concentration of CCA Metals for 2" Rainfall From Aged Packs With and Without Paperwrap

Simulated Rain Test - Hem-Fir

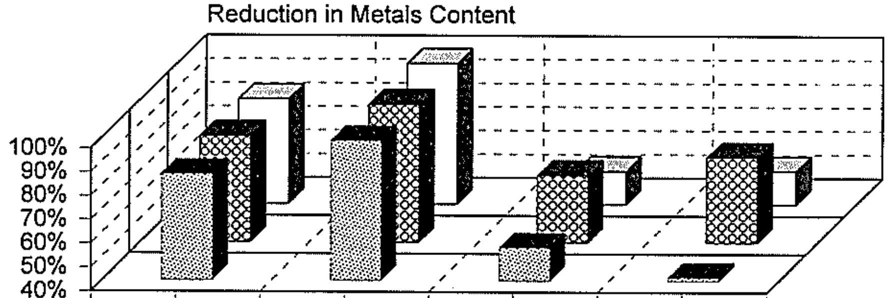


* PW = Paper Wrap Left On During Testing

Figure 33

Comparison of the Percent Reductions in CCA Metals Concentration in a 2" Rainfall Due to Paper Wrap

Simulated Rain Test - Hem-Fir



	3.8 days	4 days	161 days	215 days
Chrome	84%	99%	54%	41%
Copper	85%	98%	68%	76%
Arsenic	84%	99%	54%	54%

Days Since Treatment

Chrome Copper Arsenic

Figure 34