DIFFUSION AND MICRO-DISTRIBUTION OF WOOD PROTECTING CHEMICALS IN THE WOOD CELL WALL

by

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Abstract

This paper summarizes a number of studies on the movement and interaction of water soluble wood protecting chemicals in the wood cell wall. The anatomical characteristics of wood affect the initial distribution of solution in the wood. This in turn affects the rate of equalization of chemicals in the cell wall matrix. In general, softwoods have the greatest rate of equalization, followed by diffuse porous hardwoods and ring porous hardwoods. Adsorption of copper on wood increases with increased pH of the treating solution, consistent with cation exchange onto weak acid groups in wood. The rate of equalization of copper in solid wood is slow compared to the rate of water movement into the cell wall, but in red pine sapwood, complete penetration of the cell wall matrix occurs within a few minutes. In aspen, on the other hand, several days may be required for Cu to be completely distributed and even longer times are expected for other hardwood species. Anions, such as phosphates are substantially excluded from the wood cell walls under normal treating conditions. Performance of fire retardants can be enhanced by conditioning wood to enhance cell wall penetration.

Introduction

When water soluble chemicals are impregnated into the void space of wood, the components of the solution equalize with the wood cell walls according to their chemical and physical properties. If the wood is below its fiber saturation point (FSP) moisture content (about 30%), water diffuses into the cell wall until the wood substance is saturated. This results in an initial concentration of the treating solution in the cell lumens and swelling of the cell walls. This is followed by a drop in concentration as the solutes diffuse into the cell walls. If the solution contains solutes that react in some way with the wood components, the concentration of the solute will drop in accordance with the rate of chemical diffusion into and reaction with the cell wall. This provides a technique for following the rates of diffusion and/or reaction. Free solution is expressed from the wood at various

times after treatment and analysed for the chemical(s) of interest. This has become a common method for monitoring the fixation of chromated copper arsenate (CCA) wood preservatives (e.g., McNamara 1989, Cooper and Ung 1989). Chemicals that do not interact with the cell wall components will diffuse into the bound water in the wood cell walls, depending on the size of the molecules and the distribution of bound water "capillaries" in the cell walls.

The wood cell wall is slightly acidic, due to carboxylic acid groups in the pectin and hemicellulose constituents, phenolic hydroxyl groups in the lignin and other weak acids. When these acids are significantly dissociated (i.e. at high pH's), the cell wall contains negatively charged groups (anions) incorporated or fixed in the cell wall structure. Under these conditions, positively charged solutes (cations) such as copper and quaternary ammonium compounds are adsorbed to the cell wall. Anions, on the other hand, are inhibited from diffusing into the cell walls and should equalize at lower concentrations in the cell wall bound water than in the free lumen solution in equilibrium with it (Donnan membrane effect - Cooper and Roy 1991).

We believe that the performance of wood protecting chemicals may be affected by the distribution of the chemicals in the cell wall matrix. Thus, a series of studies were undertaken to monitor the rates of diffusion and equilibrium distribution of several chemicals in the wood cell walls following vacuum treatment. Several approaches to enhance cell wall penetration of solutes were investigated for their effects on treated wood performance.

Methodology

The effect of wood anatomy on the initial distribution of solution in wood was investigated by following the rates of swelling of dry wood blocks of different species after vacuum impregnation with water (Cooper and Churma, 1990).

The reaction of copper with trembling aspen (Populus tremuloides Michx. and red pine (Pinus resinosa) sapwood, as affected by copper salt and pH and concentration of the treating solution, was quantified by mixing ground wood in various copper solutions until equilibrium was reached and analysing the wood for copper adsorption (Cooper, 1991)

The rates of diffusion and equilibrium distributions of chemicals in the cell walls were determined under various conditions for trembling aspen and red pine sapwood. Wood specimens were vacuum treated with the solution of interest and the free solution in the cell lumens expressed at various times after treatment until equilibrium was reached. The blocks were then squeezed in a hydraulic press to express much of the free solution and the expressed solution analysed by an appropriate method. The times to

50% equalization were estimated for comparison of chemical treatments.

Solutions evaluated included CCA, ammoniacal copper arsenate (ACA), solutions of copper salts, phosphoric acid, monoammonium phosphate (MAP) and diammonium phosphate (DAP).

Limited microanalyses of DAP content in the wood tissue around vessels in aspen was made using a scanning electron microscope (SEM) equipped with an energy dispersive X-ray analysis unit (EDXA). Samples were frozen in a dry ice bath at different times after treatment then freeze dried to stop diffusion of solutes into the cell wall water and analysed by spot analysis with the EDXA unit.

The effects of enhanced cell wall loading of fire retardant solutes on the fire resistance (crib tests), hygroscopicity and dimensional stability of treated wood samples were also evaluated.

Results and Discussion

The rates of swelling of water impregnated wood samples differs greatly among the species evaluated (Fig. 1). Red pine sapwood swells very quickly due to the relatively thin cell walls and good initial distribution of water in the void structure (short diffusion distances). The half swelling time is only 3-4 seconds at room temperature (Table 1). Southern pine also has almost complete cell void saturation (high fractional void volumes (FVV)

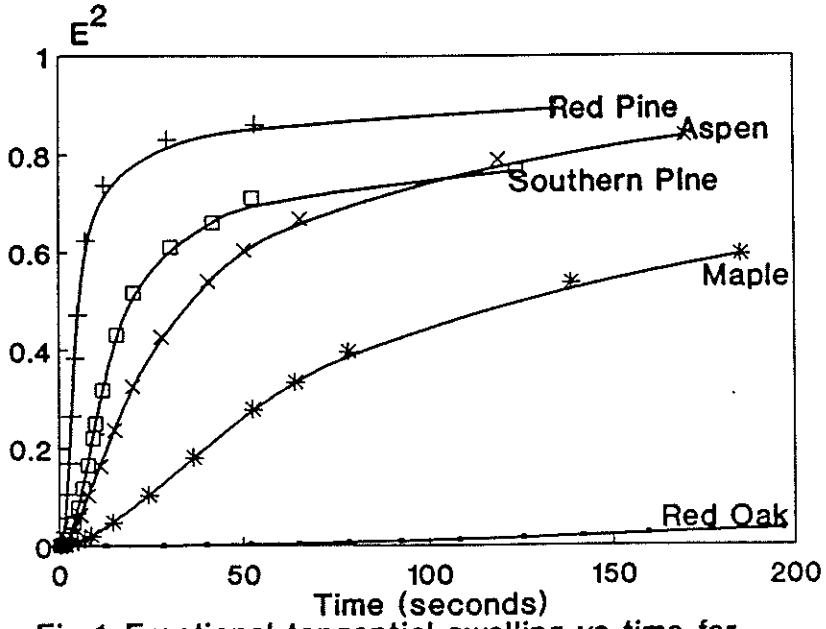

Fig 1: Fractional tangential swelling vs time for various wood species.

Table 1: Rates of swelling for various species (water at room temperature).

Species	Direction	$t_{1/2}$ S	G_b	FVV %	L_e um
Red oak	radial	1550	0.61	41	280
	tangential	940	0.61	54	200
Soft maple	radial	46	0.52	62	50
	tangential	51	0.51	57	44
Aspen	radial	7.9	0.36	60	21
	tangential	12.7	0.35	71	23
South. pine	radial	8.8	0.51	91	21
	tangential	10.8	0.51	88	19
Red pine	radial	3.4	0.39	74	12
	tangential	3.1	0.39	82	10

$t_{1/2}$ - time to 50% of total swelling
G_b - Basic relative density
FVV - Fraction of total theoretical void space saturated with solution after treatment
L_e - Estimated effective diffusion path length, based on published values for diffusion coefficient for water in the cell wall

treated - Table 1) but swells slower than red pine because of its higher relative density, i.e., thicker cell walls. Aspen has a similar density to red pine, but swells slower because the initial penetration of water into the block is confined mainly to the vessel elements, resulting in a lower fractional void volume penetrated and longer diffusion distances. Denser maple swells correspondingly slower and ring porous red oak swells very slowly because of the poor initial distribution of water (mainly in the earlywood vessels).

If the wood protecting chemicals in a solution follow the same pathways as the swelling water, we can expect the same relative effects for solute diffusion and equalization in the cell walls for different species, i.e., slower equalization of solutes in diffuse porous hardwoods and ring porous hardwoods than in softwoods. This effect is the basis of the "micro-distribution" hypothesis for why Eucalyptus and other hardwood species are more prone to softrot degradation than pine species (e.g., Dickinson, 1974).

Copper adsorption on wood increases with increasing copper concentration up to a limiting adsorption (Fig. 2). This limiting value suggests that there are a discrete number of available adsorption sites in the cell wall (i.e., exposed anions). When these sites are occupied by copper ions, no further adsorption occurs. The amount of copper adsorbed is highly pH dependent with higher adsorption at higher pH's.

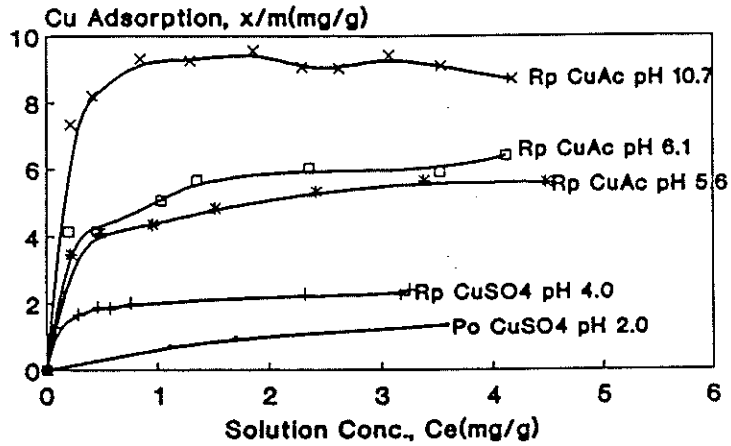

Fig 2: Adsorption of copper on wood - NAA method

This follows from the fact that weak acid groups in wood are more completely dissociated at high pH's. Carboxylic acid groups in pectins and hemicelluloses are expected to be completely ionized at about pH 4 - 5, but less than 10% ionized below pH 2 (Kertesz 1951). The phenolic hydroxyl groups in lignin are significantly dissociated only at pH's greater than 10 (Pu and Sarkanen 1989).

As with water, copper equalizes in the wood cell walls of red pine much faster than in aspen following vacuum treatment (Fig. 3). In fact the effect is even more dramatic, with half equalization times for copper as much as 100 - 200 times greater for aspen than for pine (Table 2) compared to only 4 - 5 times greater for water (Table 1). Thus, distribution of copper in the cell wall matrix of diffuse porous hardwoods may well be inhibited by the longer and more tortuous diffusion paths. In general, the times to equalization of copper in aspen are in the order of 2 - 6 days (e.g., Fig. 3 and 4) and complete distribution of copper in the cell walls may be inhibited if the wood is dried or the preservative fixed before the diffusion is complete. (Note: for CCA fixation at accelerated temperatures, any deleterious effect of

shorter time to fixation will be offset to some extent by the increased rate of diffusion at higher temperatures). These effects should be considered, if hardwoods are to be treated with CCA.

Table 2: Examples of copper diffusion in aspen and red pine under different conditions

Solution	Species	pH	initial Conc. (mg/ml)	FVV	$t_{1/2}$ S
Cu sulfate	TA	2	4.0	46	21000
"	TA	4	4.0	52	9000
"	TA	10.5	4.0	41	2640
"	RP	2	4.0	96	30
"	RP	4	4.0	95	19
"	RP	10.5	4.0	92	22
Cu carbonate	TA	10.5	2.0	75	1090
"	RP	10.5	2.0	83	5
Cu acetate	TA	5.5	2.6	60	775
"	RP	5.5	2.6	64	6
"	RP	10.5	4.2	68	5
ACA-Cu	TA	10.5	3.0	51	550
"	RP	10.5	2.8	63	14

As expected from the copper adsorption results, more copper enters the cell walls when applied in basic solutions than if in acidic solutions (Fig.4).

For CCA solutions, adsorption of Cu, Cr and As components is not a major factor, and concentration changes in the cell lumens are not controlled by solute diffusion, but by rates of reactions with the cell wall components. Thus, the rate of change is much slower at normal ambient temperatures (Fig. 5). Copper and arsenic are removed from the free solution in the lumens faster than the chromium.

Phosphate anions are highly excluded from the cell walls under normal conditions (Fig. 6). This is consistent with Donnan membrane effects; an electric potential is created by the fixed anions in the cell walls that inhibit movement of the mobile phosphate anions. However, if treated wood is held for long periods without drying, some penetration of phosphate does occur in the cell walls (Fig.6).

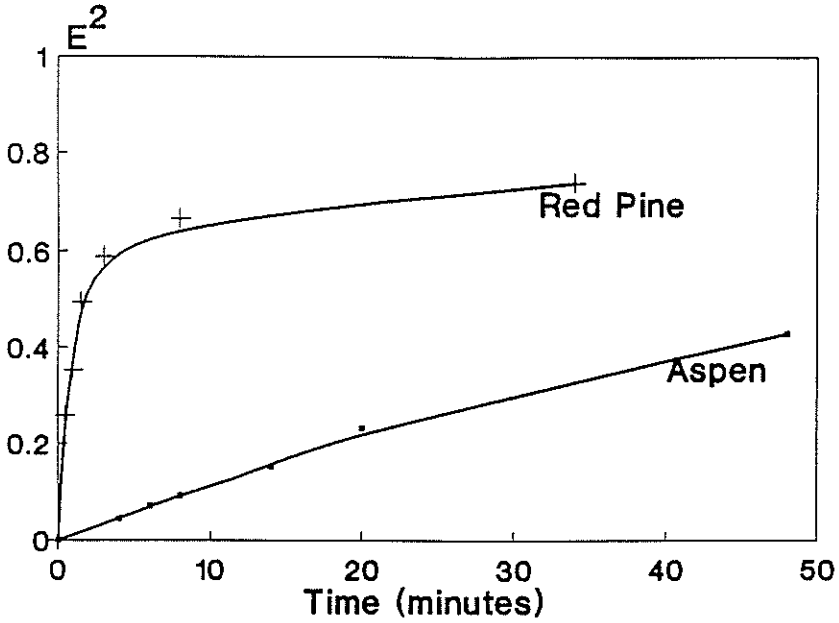

Fig 3: Rates of equalization of copper in aspen and red pine samples
- ACA, 1,720 ppm Cu, 5% MC, pH 10.5
E - Fractional Cu adsorption

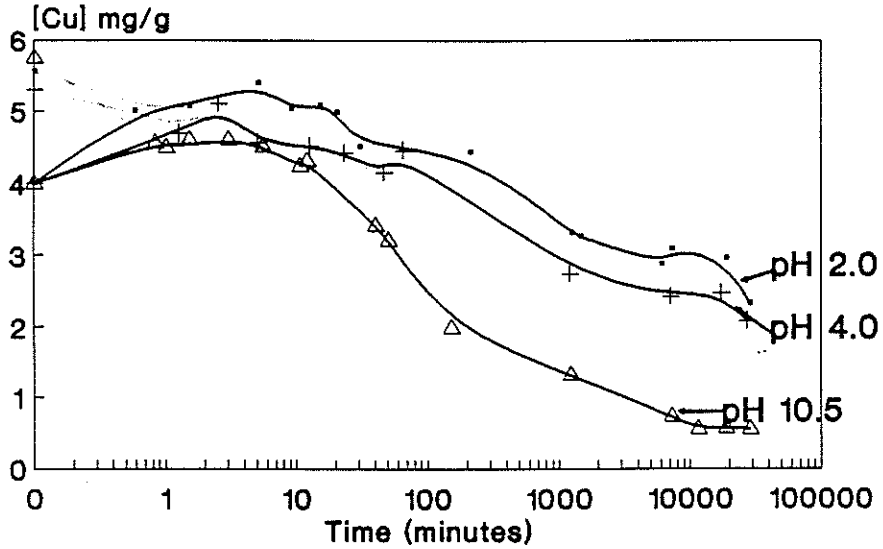

Fig 4: Effect of pH on copper movement into and reaction with the cell wall in aspen
- CuSO4, 4,000 ppm Cu, 10% MC

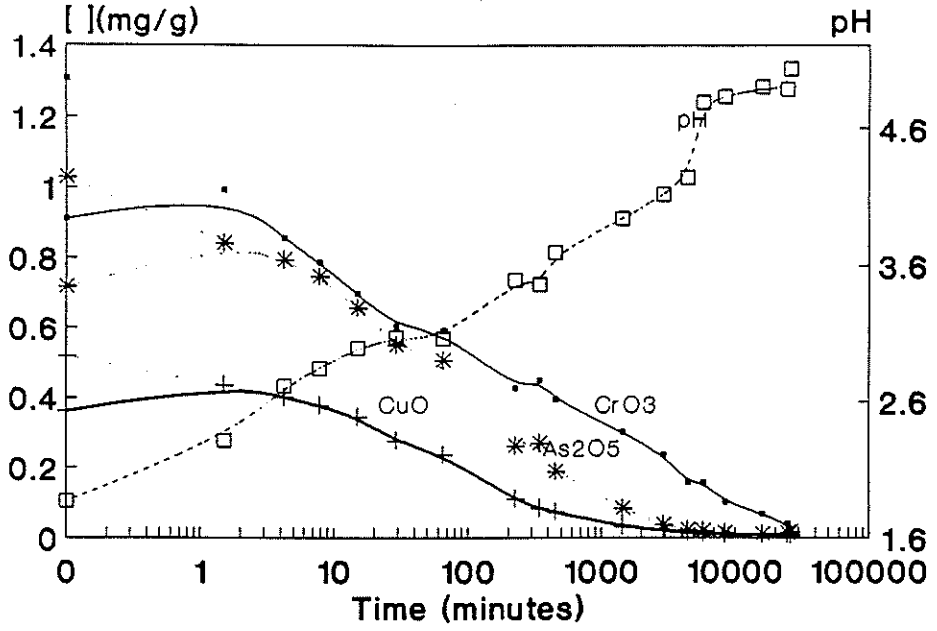

Fig 5: Diffusion and reaction of CCA in aspen wood.

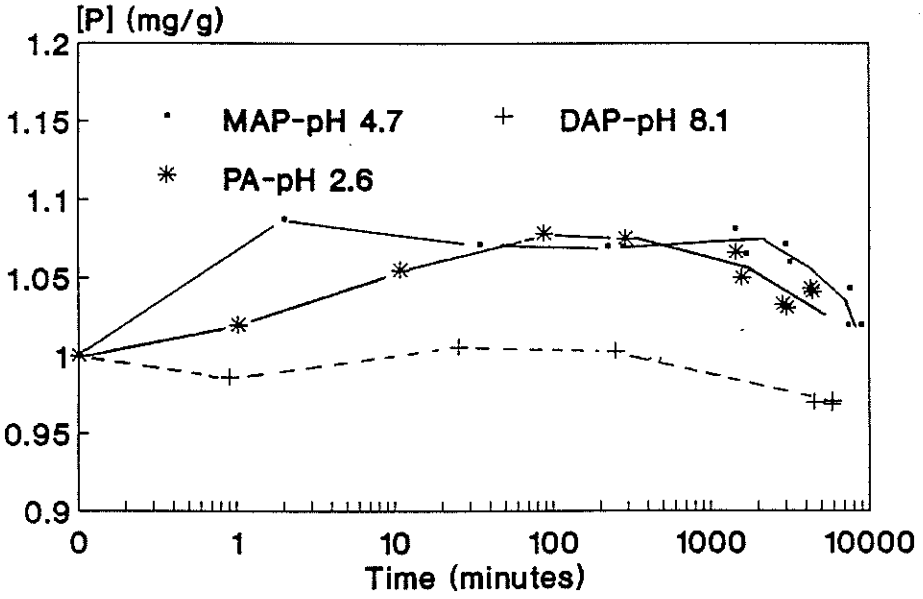

Fig 6: Exclusion of phosphates from wet (MC=28%) red pine.

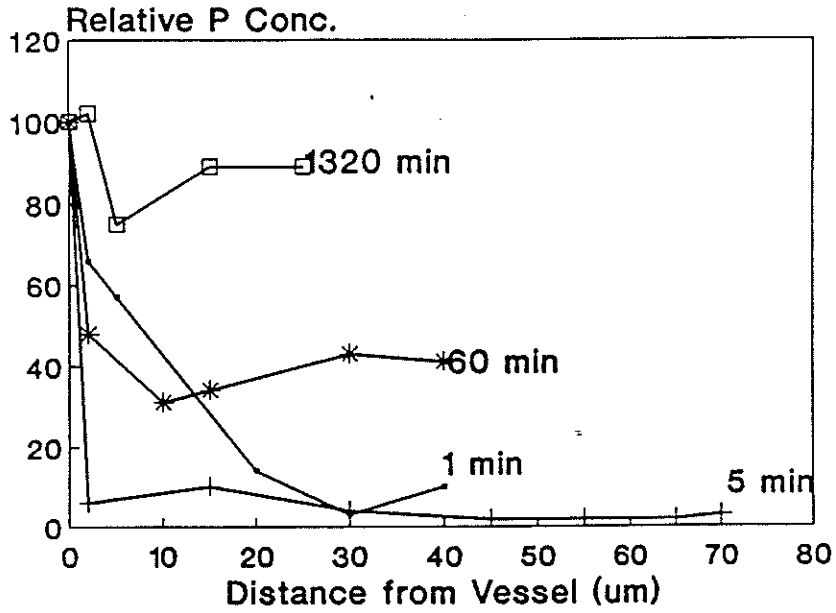

Fig 7: Phosphorous distribution near the vessels of Aspen as affected by diffusion time

SEM/EDXA analysis of wood at various times after treatment shows that the concentration away from the penetrated vessels increases with time and after 23 hours is well distributed through the structure (Fig. 7).

By delaying the drying of phosphate treated wood after treatment to promote cell wall penetration, the fire performance, hygroscopicity and dimensional stability properties can all be improved (Cooper and Holtforster 1991 - Figs. 8, 9 & 10). To gain these benefits, it is important that wood be dried slowly. As the treating solution concentrates in the cell lumens, there is sufficient time for the solute to equalize with the bound water in the cell walls.

Conclusion

A number of factors influence the rate of equalization and equilibrium distribution of wood protecting chemicals in the wood structure following treatment. There is evidence that by paying attention to these factors we may be able to increase the efficiency of chemical treatments.

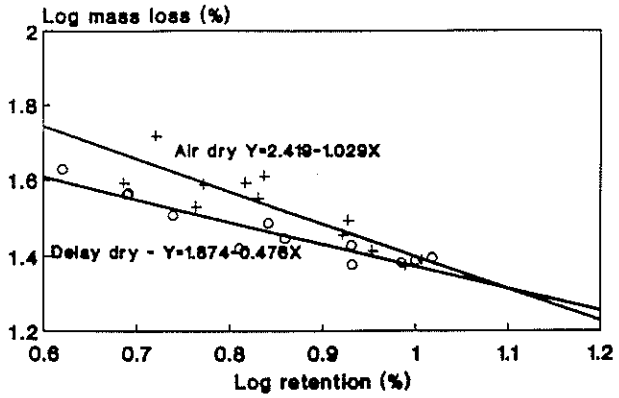

Fig 8: Mass loss vs retention for DAP treated crib specimens at high pH

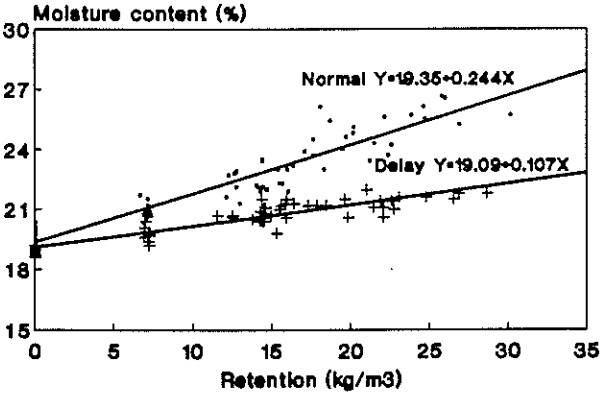

Fig 9: Effect of delayed drying on hygroscopicity of diammonium phosphate treated wood

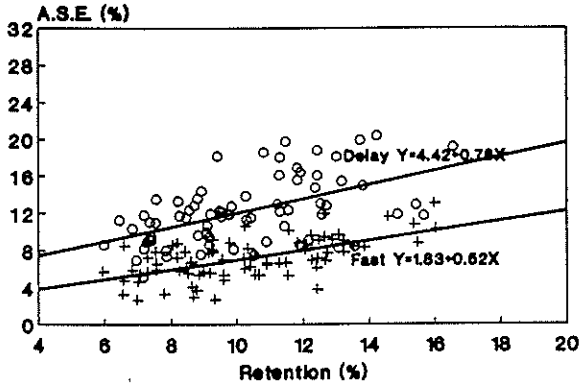

Fig 10: Effect of retention and drying method on anti-shrinkage efficiency (A.S.E.)

References

1. Cooper, P.A. 1991. Cation exchange adsorption of copper on wood. Wood Protection. 1(1):9-14.

2. Cooper, P.A. and R. Churma. 1990. Estimating diffusion path lengths in treated wood. Forest Prod. J. 40(11/12):61-63.

3. Cooper, P.A. and D.N. Roy. 1991. Interaction of anions with the wood cell wall. Manuscript in preparation.

4. Cooper, P.A. and A. Holtforster. 1991. Effects of delayed drying on performance of fire retardant treated wood. Proc. Int. Symp. on Chem. Mod. of Wood. Kyoto. Japan. :184-189.

5. Dickinson, D.J. 1974. The micro-distribution of copper-chrome - arsenate in Acer pseudoplatanus and Eucalyptus maculata. Mat. und Organismen. 9(1):21-33.

6. W.C and Kertesz, Z.I. 1951. The pectic substances. Intersciencs Publishers Inc. New York, London. 628p.

7. McNamara, W.S. 1989. CCA fixation experiments - Part 1. Int. Res. Group on Wood Preserv. Doc. IRG/WP/3504.

8. Pu, Q. and K. Sarkanen. 1989. Donnan equilibria in wood-alkali interactions. Part 1. Quantitative determination of carboxyl-, carboxyl ester and phenolic hydroxyl groups. J. Wood Chem. and Tech. 9(3):293-312.