INTERACTION OF WOOD-PROTECTING ANIONS WITH THE WOOD CELL WALL

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ABSTRACT

Under normal treating conditions, anionic components of wood preservatives and fire retardants, such as arsenates and phosphates, equilibrate at much lower concentrations in the cell-wall bound water than in the free solution in the cell lumens. A degree of anion exclusion is expected in wood due to the Donnan membrane effect. Fixed anions in the wood cell wall are not free to diffuse into the lumens, resulting in limited migration of the mobile anions into the cell wall. The observed exclusion, measured as "solute free water" (δ), decreases with increasing solute concentration, as expected from Donnan exclusion effects. However, the expected pH dependence (increased exclusion with increased pH) is not observed in ammoniacal solutions. In fact, there is an apparent anomalous effect of high cell-wall penetration or reaction with basic solutions containing ammonium hydroxide. Dichromate solutions are more or less depleted from the free lumen solution, depending on the initial pH of the solution as the hexavalent chromium is reduced and fixed to the cell-wall material.

Keywords: Anion exclusion, arsenate, cell wall, chromate, diffusion, Donnan membrane effect, phosphate, *Pinus resinosa, Populus tremuloides,* solute free water.

INTRODUCTION

Negatively charged ions are important components of several wood-treating chemicals. Of most interest in the field of wood protection are the arsenate ($H_2AsO_4^-$) and dichromate ($Cr_2O_7^{-2}$) constituents of chromated copper arsenate (CCA) solutions, the arsenate component of ammoniacal copper arsenate (ACA), and the phosphate ($H_2PO_4^-$, $NH_4HPO_4^-$ etc), sulfate and borate constituents of fire retardants.

Wood substance carries a pH-dependent negative charge due to dissociation of its weak acidic groups. These negatively charged groups (fixed anions) are responsible for wood's weak cation exchange properties (Rennie et al. 1987; Cooper 1991a). The degree of dissociation, and therefore the anionic nature of wood substance, increases with increasing pH of the wood/solution system.

Anionic components of wood-treating solutions should be partially excluded from the wood cell wall by the fixed anionic components of the cell wall (Donnan membrane effect). This effect has been confirmed in commercial cation exchange resins (Kunin 1963), in plant roots and other plant tissues (Dainty and Hope 1959; Jenny 1966), and cellulose products (Farrar and Neale 1952; Pu and Sarkanen 1989, 1991); but few studies have considered anion distribution in wood subjected to commercially important treatments. Exclusion effects may also result from other than electrochemical factors, such as reduced availability of the bound water

for anion solution and physical exclusion from some tiny cell-wall capillaries.

Anion exclusion not only affects the equilibrium distribution of solute in the cell wall, but may also affect the diffusion process and, possibly the efficacy of the treatment (Cooper and Holtforster 1991). Once the factors affecting anion distribution in the wood cell walls are known, it may be possible to maximize performance by selecting conditions that minimize exclusion effects.

Interaction with the cell wall is more complicated with anions that react chemically with the cell-wall substance. The dichromate ion is reduced by contact with wood to insoluble trivalent chromium. Reduction of acidic dichromates is accompanied by an increase in the pH of the system, which may inhibit fixation reactions through exclusion of the anions from the cell walls.

In this study, the movement and equilibrium distribution of several anionic substances were monitored by following the change in solute concentration of free lumen solution, expressed from treated wood at various times following treatment.

Donnan membrane effects

In wood, the interface between the swollen wood cell wall and the free solution in equilibrium with it, i.e., the S_3 cell wall layer-lumen interface, is similar to a semi-permeable membrane, since free ions in the lumen can diffuse across the interface into the cell-wall hydrogel and free ions in the cell wall can diffuse into the lumen; but the fixed anions responsible for wood cation exchange properties cannot leave the cell-wall matrix.

At equilibrium, by definition, the chemical potential of each solute must be equal in the two phases (cell wall and free solution) and they must be so distributed as to maintain charge neutrality in both phases. The chemical potential of an ionic species depends on its chemical activity (i.e., concentration) and electrostatic potential. The charges must be balanced in both phases at equilibrium, and since the fixed anions cannot diffuse into the solu-

tion phase, the number of mobile anions that can enter and remain in the cell wall is restricted. The cations are not restricted in this way except by neutrality requirements. By considering these requirements for equal chemical potentials and net charge neutrality in the two phases, and assuming an ideal solution, the following relationships can be derived (e.g., Briggs et al. 1961). For a treating solution containing only univalent cations and anions, such as for phosphoric acid or arsenic acid treatments where only the first ionization predominates:

$$m^2 = \bar{m}^2 + \bar{m}\bar{m}_w \qquad (1)$$

where m is the molal concentration of free anions in the cell lumen solution, $\bar{m}$ is the molal concentration of anions in the cell wall bound water, and $\bar{m}_w$ is the molal concentration of fixed anions in the cell wall. For divalent cations and anions, the relationship is the same as above. From this equation, it is clear that m is greater than $\bar{m}$, i.e., that the arsenate or phosphate concentration in the wood bound water is lower than in the free solution (anions are excluded from the cell wall). Cation exchange studies on *Pinus resinosa* (Cooper 1991a) indicate that at pH 2, the Cu capacity is about 2 mg/g dry wood and at pH 10.5, about 8 mg/g. Assuming a fiber saturation point (fsp) of 0.35, this corresponds to $\bar{m}_w = 0.18$ moles fixed monovalent anions/kg bound water (molality) at pH 2 and 0.72 molal concentration at pH 10.5. The above relationship is plotted for these $\bar{m}_w$ values in Fig. 1.

In the case of divalent cations e.g., Cu^{++} and monovalent anions e.g., $H_2AsO_4^-$, the relationship is:

$$m^3 = \bar{m}^3 + \bar{m}^2\bar{m}_w \qquad (2)$$

At high pHs, where the second ionization is significant, and univalent cations and divalent anions are present, the equation is:

$$4m^3 = 4\bar{m}^3 + 4\bar{m}^2\bar{m}_w + \bar{m}\bar{m}_w^2 \qquad (3)$$

In all cases, the predicted exclusion is greater at lower anion concentrations in the solution, and at higher fixed anion concentrations in the

wood. Thus, we would expect a greater anion exclusion with low anion concentrations and high pH systems.

Estimation of solute free water (δ)

The distribution of solute between the free solution in the cell lumens and the cell-wall bound water may be expressed as "solute-free water" (δ). δ is the fractional bound water moisture content that is free of solute, assuming that the solute in the remaining bound water is at the same concentration as in the free solution in the cell lumens at equilibrium (C_e) (Aggebrandt and Samuelson 1964; Feist and Tarkow 1967). A δ value >0.0 indicates that solute is excluded from the cell walls.

Consider a wood block of mass m_i (g) at fractional moisture content u_i, fractional fiber saturation point moisture content f and dry mass $m_o = m_i/(1 + u_i)$ (g) which is vacuum-treated with solution at concentration C_i (mg solute/g solution) with a mass pickup of P (g) of solution including PC_i mg of solute. If $u_i <f$, water from the treating solution diffuses into the wood cell walls faster than the solute. This results in an initial increase in anion concentration in the cell lumen solution, followed by a decrease as the anion diffuses into the cell wall. By following the concentration of solution expressed out of wood at various times after treatment, the equilibrium lumen concentration C_e (mg/g), can be determined. At this time, the solute is distributed through a new mass of water, which is approximated by $P + (u_i - \delta)m_o$ (the mass of solute $PC_i/1,000$ in grams in the pickup P is ignored). Then:

$$C_e = \frac{PC_i}{[P + (u_i - \delta)m_o]}$$

$$\text{or} \quad \delta = u_i + \frac{P(C_e - C_i)}{C_e m_o} \quad (4)$$

METHODS AND MATERIALS

Various concentration (w/w) solutions of technical grade phosphate, arsenate, and dichromate were used to treat trembling aspen
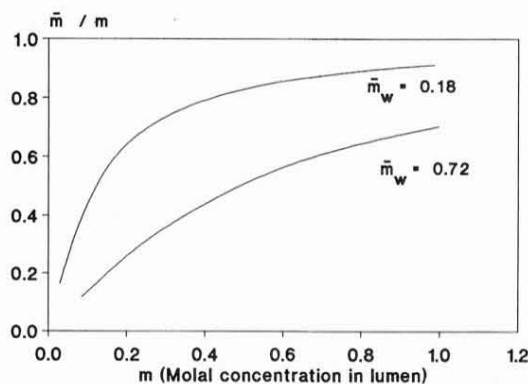
$\bar{m}\ /\ m$

FIG. 1. Theoretical Donnan exclusion of univalent anions accompanied by univalent cations. $[m^2 = \bar{m}^2 + \bar{m}\bar{m}_w]$.

(Populus tremuloides Michx.) and red pine *(Pinus resinosa* Ait.) sapwood samples (Tables 1–3). All aspen samples were from a single 35-year-old tree, and red pine samples from a single pole section. Specimens were 25-mm cubes cut in the radial/tangential/longitudinal planes and equilibrated at low or high relative humidities in a controlled humidity cabinet to produce samples at moisture contents from 5% to 33%. Twenty end-matched specimens were vacuum-treated (24 inches of mercury or 20 KPa absolute pressure Hg for 20 min) in a desiccator at 21 C, removed from the treating solution immediately, and sealed in plastic bags and maintained at 21 C. The equalization of the solutes in wood was followed by an expressing technique. At various times following treatment, specimens were pressed at 63 MPa (10,000 psi) in a small hydraulic press to express 60–70% of the free solution in the wood lumens. After the solute concentration had stabilized (5 to 7 days), five replications were evaluated at equilibrium to estimate the "solute free water" values.

Phosphate treatments included a wide range of concentrations of phosphoric acid (PA) monoammonium phosphate (MAP), and diammonium phosphate (DAP) at a range of pHs applied to wood at low (4–10%) and moderate (25–33%) moisture contents (Table 1). For phosphate treatments, the expressate was analyzed for P content by the molybdenum blue reaction procedure (Kitson and Mellon 1944)

TABLE 1. *Effects of pH, wood species and solution concentration on anion exclusion of phosphates in wood.*

Solution	pH	Species*	Initial conc. (as P) mg/g	Initial conc. (as P) molal	MC %	δ Ave. (SD)
H_3PO_4	2.37	TA	0.100	0.0032	5.7	0.39 (0.032)
H_3PO_4	2.25	TA	0.253	0.0083	6.5	0.30 (0.014)
H_3PO_4	2.10	TA	0.807	0.0260	33.1	0.37 (0.029)
H_3PO_4	2.10	RP	0.838	0.0270	29.6	0.38 (0.013)
H_3PO_4	2.10	RP	0.837	0.0270	8.7	0.27 (0.027)
H_3PO_4	2.60	RP	1.000	0.0323	7.3	0.26 (0.020)
H_3PO_4	2.60	RP	1.000	0.0323	28.1	0.34 (0.007)
H_3PO_4	2.80	RP	4.000	0.1290	6.5	0.28 (0.039)
MAP	4.32	TA	0.100	0.0032	6.5	0.58 (0.041)
MAP	4.32	TA	0.204	0.0066	9.2	0.46 (0.010)
MAP	4.32	TA	0.208	0.0067	32.2	0.61 (0.057)
MAP	4.32	TA	0.250	0.0081	6.0	0.54 (0.045)
MAP	4.30	TA	0.965	0.0311	7.1	0.28 (0.015)
MAP	4.30	TA	0.945	0.0305	24.1	0.24 (0.050)
MAP	4.30	TA	0.965	0.0311	7.1	0.26 (0.024)
MAP	4.20	TA	2.350	0.0759	31.2	0.31 (0.025)
MAP	4.20	TA	2.360	0.0762	8.0	0.19 (0.049)
MAP	5.12	RP	0.208	0.0067	9.9	0.42 (0.051)
MAP	5.12	RP	0.212	0.0068	25.6	0.51 (0.105)
MAP	4.30	RP	0.935	0.0302	9.8	0.30 (0.008)
MAP	4.74	RP	1.000	0.0323	4.4	0.33 (0.043)
MAP	4.74	RP	1.000	0.0323	27.2	0.30 (0.007)
MAP	4.20	RP	2.350	0.0760	9.6	0.31 (0.022)
MAP	4.20	RP	2.310	0.0746	27.9	0.34 (0.018)
DAP	7.60	TA	0.100	0.0032	6.0	0.49 (0.005)
DAP	7.84	RP	0.250	0.0081	6.2	0.43 (0.022)
DAP	7.84	RP	0.250	0.0081	7.7	0.33 (0.007)
DAP	7.60	RP	1.000	0.0323	7.9	0.29 (0.019)
DAP	7.60	RP	1.000	0.0323	28.8	0.25 (0.006)
DAP +NH_4OH	10.3	RP	4.000	0.1290	7.5	0.11 (0.017)

* TA = Aspen; RP = Red pine.

using a Shimadzu uv-visible light spectrophotometer.

Arsenic acid was evaluated at approximately 3,500 ppm (As) with specific solutions adjusted to a range of pHs with ammonium hydroxide, sodium hydroxide, or sodium bicarbonate (Tables 2 and 3). The expressate was analyzed with an ASOMA X-ray fluorescence spectrometer. Standard arsenate solutions ranging from 500 ppm to 4,000 ppm As were prepared with reagent grade As_2O_5 to generate a calibration curve for the ASOMA analysis. Samples were expressed at various times after treatment, and five replications were evaluated at equilibrium for each solution. Solute free

water values were determined as above and statistically compared for each solution by paired t-tests.

Four chromium solutions were prepared at 4,000 ppm elemental Cr from analytical grade chromate compounds to provide a range of pH conditions:

0.46% CrO_3;	pH = 2.02
0.68% $K_2Cr_2O_7$;	pH = 4.32
0.58% $(NH_4)_2Cr_2O_7$;	pH = 4.71
0.74% Na_2CrO_4;	pH = 9.37

All chromate expressate samples were ana-

TABLE 2. *Effect of pH on arsenate anion exclusion in red pine.*

pH*	Initial as concentration		MC %	δ Ave. (SD)	†
	mg/g	molal			
2.0	3.53	0.0473	3.7	0.250 (0.024)	ab
2.6	3.51	0.0471	3.8	0.214 (0.041)	ab
4.0	3.53	0.0473	4.7	0.268 (0.019)	b
4.3	3.47	0.0465	3.2	0.223 (0.020)	a
6.2	3.38	0.0453	4.3	0.206 (0.013)	a
7.9	3.34	0.0447	4.2	0.285 (0.068)	ab
9.0	3.56	0.0477	4.4	0.194 (0.032)	ab
10.0	3.41	0.0457	4.7	−0.104 (0.067)	c
10.1	3.32	0.0445	4.2	−0.179 (0.119)	c
10.8	3.67	0.0492	5.0	−0.416 (0.075)	d
11.7	3.75	0.0503	4.3	−0.218 (0.098)	c

* pH adjusted by addition of NH_4OH.
† Values sharing the same letter are not statistically different at the 0.05 level of confidence.

FIG. 2. Exclusion of phosphoric acid (PA), monoammonium phosphate (MAP), and diammonium phosphate (DAP) in vacuum-treated red pine (MC = 7%).

lyzed with the ASOMA spectrometer. Standard calibration curves were prepared using serial dilutions of the treating solution. The pH of the expressate was also measured by meter at each sampling time.

The changes in solute concentration and pH of the expressed solutions with time were plotted against the logarithm of time to provide an indication of rates of diffusion into or reaction with the cell walls.

RESULTS AND DISCUSSION

Phosphates

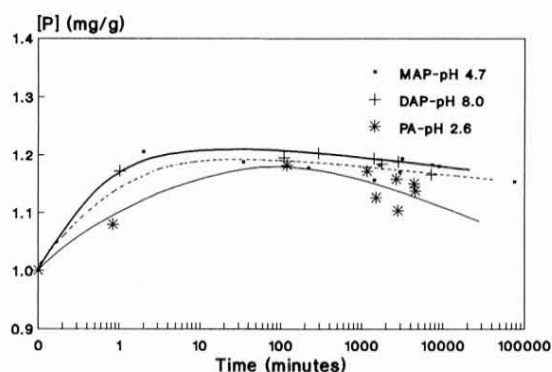Plots of lumen phosphate concentrations vs. time (Fig. 2) for initially dry red pine sapwood,

treated with 1 mg/g phosphate, show that the P concentration in the lumen increased very quickly as water entered the unsaturated cell wall. Furthermore, the phosphate concentration remained high following treatment. This indicates that phosphates were highly excluded from the cell walls. Even in wood with relatively high moisture content (MC = 28%), the concentration increased slightly (Fig. 3) indicating that the fiber saturation point (f) was greater than 0.28 for these samples. The amount of exclusion was not consistently lower for the acidic systems than for the basic ones. This observation runs counter to the Donnan theory, as the basic solution should expose more fixed anions in the wood resulting in greater exclusion. Over a long time frame

TABLE 3. *Effect of base on arsenate exclusion in red pine and aspen blocks.*

Solution	Species	pH		Initial as conc.		δ Ave. (SD)	*
		Initial	Final	mg/g	molal		
H_3AsO_4	RP	2.2	3.1	3.47	0.0465	0.24 (0.04)	a
	TA	2.2	3.2	3.47	0.0465	0.15 (0.04)	b
H_3AsO_4 +	RP	11.0	10.1	3.53	0.0473	−0.58 (0.30)	c
NH_4OH	TA	11.0	10.0	3.53	0.0473	−1.33 (0.23)	d
	TA	10.5	9.7	3.26	0.0437	−0.92 (0.13)	d
H_3AsO_4 +	RP	10.4	6.5	7.30	0.0978	0.21 (0.03)	a
NaOH	RP	10.6	6.0	3.26	0.0437	0.25 (0.02)	a
	TA	10.4	6.6	7.30	0.0978	0.21 (0.03)	a
	TA	10.6	5.8	3.26	0.0437	0.03 (0.00)	e
H_3AsO_4 +	RP	10.5	10.0	2.45	0.0328	0.32 (0.03)	a
$NaHCO_3$	RP	10.6	10.0	3.26	0.0437	0.21 (0.03)	a
	TA	10.6	9.1	3.26	0.0437	0.15 (0.02)	b

* Values sharing the same letter are not statistically different at the 0.05 level of confidence.
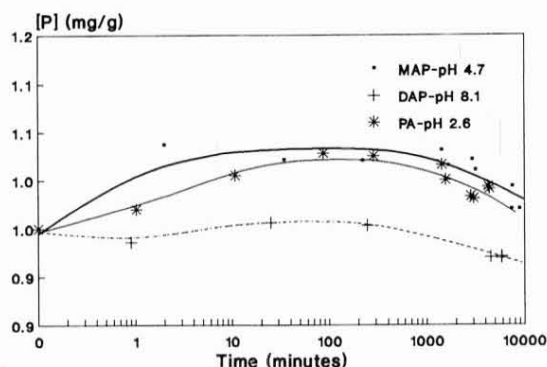
FIG. 3. Exclusion of phosphoric acid (PA), monoammonium phosphate (MAP), and diammonium phosphate (DAP) in vacuum-treated red pine (MC = 28%).

FIG. 4. Effect of pH on exclusion of arsenate in vacuum treated red pine (MC = 4%).

(1,000–10,000 min), there appeared to be a slight drop in cell lumen concentration, suggesting very slow diffusion and equalization of the phosphates into the cell walls. However, even after several days, there was still a considerable exclusion of the phosphates from the cell-wall water.

Depending on the solution concentration and phosphate used, the calculated solute free water ranged from 0.24 to 0.61, indicating that a large proportion of the bound water was effectively phosphate-free (Table 1). These results suggest that the effective fiber saturation point of both species was higher than 0.35 and, in fact, may be 0.60 or higher. This value is much higher than generally accepted f values estimated from the relationship between wood moisture content and physical or mechanical properties (e.g., Stamm 1971). However, solute exclusion measurements tend to provide high estimates of fiber saturation point moisture contents for wood and paper products (e.g., Ahlgren et al. 1972). The discrepancy between values of f obtained by physical estimates and solute exclusion procedures remains unexplained.

The degree of solute exclusion generally increased as phosphate concentration decreased, as predicted by the Donnan equations. For low concentration solutions, the higher pH MAP had greater phosphate exclusion than the phosphoric acid solution, as predicted by the Donnan equations. However, the DAP solution ad-
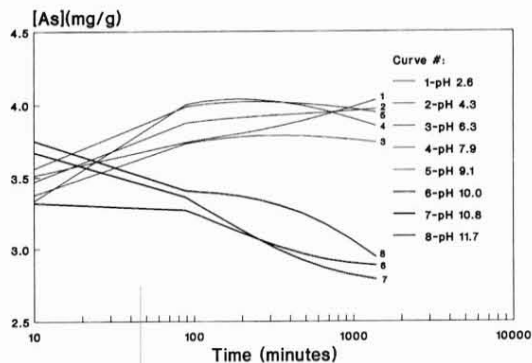
justed to high pH by addition of ammonium hydroxide, had a much greater apparent penetration of phosphate into the cell wall as shown by the low δ value (Table 1). The effects of pH are complicated by two conflicting factors: at high pH, the fixed anion concentration is higher and a greater degree of exclusion is expected; however, at pHs above 7–8, a significant amount of the divalent phosphate ion is present, which is excluded differently than the monovalent anion [e.g., Eq. (3)]. However, the differences in predicted exclusion were not great enough to explain the inconsistent effect of pH on phosphate exclusion.

Exclusion effects appeared to be similar for aspen and red pine. There was no consistent effect of initial wood moisture content on the solute free water.

Conditions that favor reduced exclusion of phosphate from the cell wall, e.g., higher solution concentration and high pH, could result in improved dimensional stability and fire-retardant effectiveness. We have previously demonstrated that delayed drying after phosphate treatment enhances these properties (Cooper and Holtforster 1991).

Arsenates

Solution pH had a great effect on arsenate exclusion from the wood cell-wall matrix for arsenic acid solutions adjusted with ammonium hydroxide. At low pHs, arsenic acid was highly excluded from the cell wall (Fig. 4 and Table 2), but there was no consistent effect of
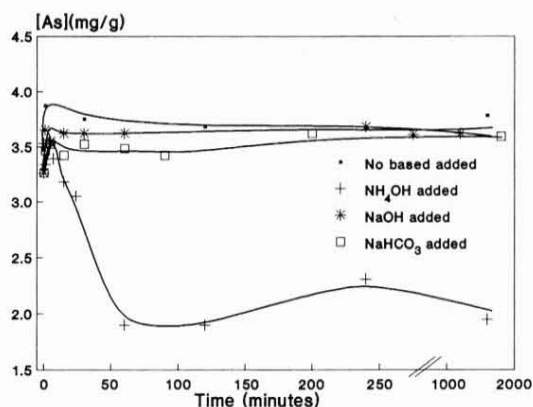
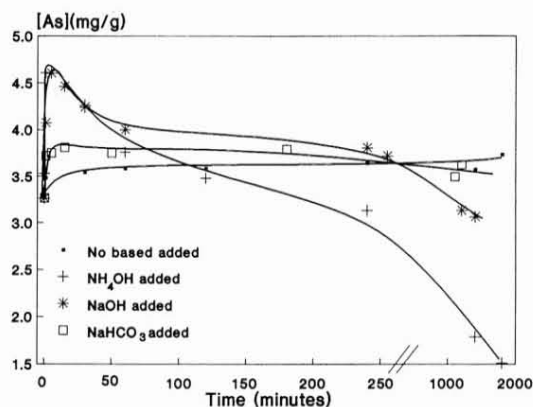FIG. 5.   Effect of addition of base on exclusion of arsenate in vacuum-treated red pine (MC = 10%).

FIG. 6.   Effect of addition of base on exclusion of arsenate in vacuum-treated aspen (MC = 10%).

pH on As concentration in the cell wall below pH = 9. Solute free water values ranged from 0.19 to 0.28 and were similar in magnitude to those for the phosphates at similar concentrations. Some of these values were statistically different from one another, but there was no consistent trend with pH. This lack of pH dependence is contrary to the Donnan theory.

At pHs greater than 10, the free lumen As concentration dropped significantly over the test period (Fig. 4), indicating substantial movement or reaction of arsenate in the cell walls. The calculated cell-wall molal concentration was greater than the free solution concentration, resulting in negative δ values and suggesting a reaction between arsenate and the cell wall at high pHs. However, adsorption studies of arsenate on wood at a range of pHs (Cooper 1991b) show no fixation of arsenate under these high pH conditions; i.e., any "reacted" As is readily removed by the washing process. The higher cell-wall concentrations at high pHs were opposite to the effects predicted by the Donnan equations, indicating that other factors were involved.

To investigate this pH effect further, the equalization of arsenate was compared for pine and aspen samples initially at 10% MC using unadjusted arsenic acid solution and solutions adjusted to pH 10.5 with NH$_4$OH, NaOH, or NaHCO$_3$ (Table 3). As before, the ammonium hydroxide adjusted solution showed a substantial drop in arsenate concentration in the cell lumens with time, while the concentrations in the cell lumens increased with the acidic solution (Fig. 5). The rate of equalization with the cell wall was much faster for the red pine compared to aspen (Fig. 6). This is consistent with the longer diffusion path lengths for aspen (Cooper and Churma 1990), which cause poor initial distribution of solution. Because of the relatively weakly basic nature of this solution, the pH of the cell lumen solution dropped only slightly with time.

With a strong, highly dissociated base (NaOH), the arsenate was as highly excluded as with the acidic system. However, the solution was rapidly neutralized by the wood and the pH dropped rapidly to below 7. With the
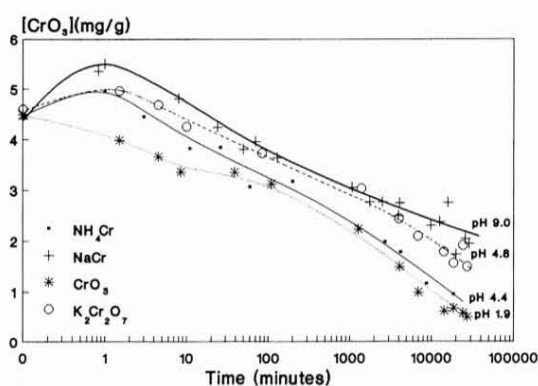

FIG. 7.   Effect of chromate formulation on reduction of chromium in vacuum-treated aspen (MC = 7%).

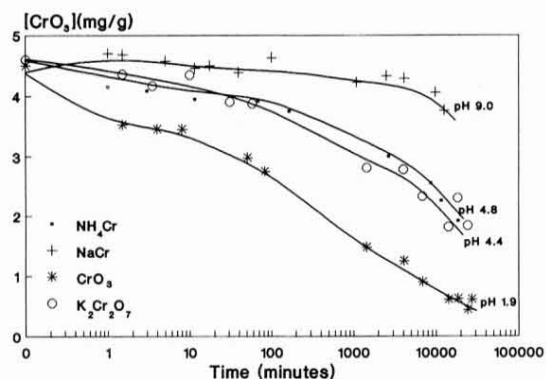　　　　WOOD AND FIBER SCIENCE, JULY 1994, V. 26(3)

FIG. 8. Effect of chromate formulation on reduction of chromium in vacuum-treated red pine (MC = 7%).
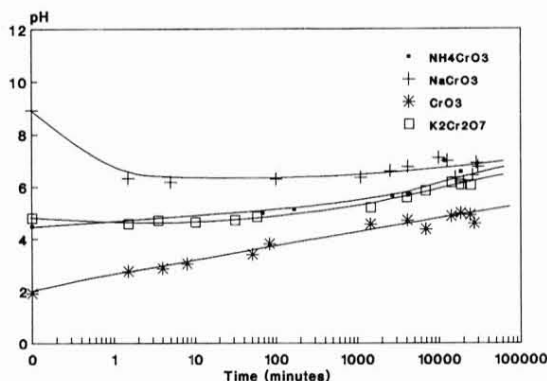

FIG. 9. pH change in chromate solutions expressed from vacuum-treated red pine (MC = 7%).

buffering sodium bicarbonate, the pH remained high, but the arsenate was still excluded from the cell wall.

These results suggest that the arsenate penetration into or reaction with the wood cell-wall matrix is related to the presence of free ammonium hydroxide rather than to the high pH per se. This may be caused by formation of complex coordination compounds between ammonia and arsenate, or perhaps to copper catalyzed formation of amine groups in wood which could serve as anion exchange sites (Shreve 1945), but at this time we are unsure of the mechanism.

Chromate

The chromium concentration of the expressed solutions (expressed as equivalent CrO_3 concentration) dropped with time as the chromium anion entered and reacted with the wood substance (Figs. 7 and 8). The rate of reaction was much greater in the acidic chromic acid solutions and dropped with increasing pH of the solution. This is consistent with the expected oxidation of primary and possibly secondary alcohol groups in wood components, e.g.:

$$3RCH_2OH + 16H^+ + 2Cr_2O_7^{-2} \rightarrow 3RCOOH + 4Cr^{+3} + 11H_2O \qquad (5)$$
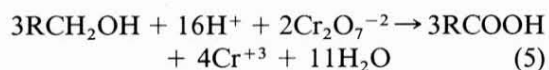
Since the reaction is dependent on the hydrogen ion concentration, the low pH systems re-

acted more quickly and completely. Also, oxidation of organic compounds depends on the active chromium anion species (e.g., Dahlgren and Hartford 1972). At high pHs, the dichromate ($Cr_2O_7^{-2}$) ions predominate, while at higher pHs, $HCrO_4^-$ is dominant. It is possible that the dichromate ion is a more powerful oxidizing agent. The reaction is also a neutralization reaction, and the pH of the expressate from the acidic solutions increased with time of reaction until equilibrium was reached at pH 5 to 7 (Fig. 9). In the basic sodium chromate solution, the pH dropped to a similar value.

In the aspen samples, the chromium content of the expressed lumen solution increased initially in all except the chromic acid solution suggesting exclusion of chromate initially. For the chromic acid solution, there was an instantaneous drop in chromium concentration in the expressed solution as has been observed for CCA treatments (e.g., Cooper and Ung 1992). This is generally attributed to rapid adsorption of hexavalent chromium to the wood cell wall (Dahlgren and Hartford 1972). In time, as the hexavalent chromium is reduced, the soluble chromium concentration in the expressed solution drops. In red pine, the initial reaction was much faster, and the Cr concentration in the lumens dropped by the time of the first reading in all except the basic sodium chromate solution. The eventual extent of reaction was greater in the aspen, especially for

the high pH chromate. This may be due to the lower solution pickup in aspen and therefore higher ratio of wood to chromate for reaction or may result from the different chemical constituents of the two species.

SUMMARY AND CONCLUSIONS

1. Anionic components of wood-protecting chemicals, such as phosphates and arsenates, were highly excluded from the cell-wall water under normal treating conditions. At equilibrium, the solute free water content in the cell wall was usually 20–30%, but was as high as 60%.

2. Generally, the exclusion of phosphate increased with decreasing concentration as predicted by the Donnan equations. However, the expected increased exclusion with increasing pH was observed only in solutions that did not contain ammonia, suggesting that factors other than Donnan effects were involved in the distribution of anions in the cell-wall substrate.

3. There appeared to be limited diffusion of phosphate into the cell wall over a long time frame (several days), suggesting that delayed slow drying of wood after treatment could promote higher cell-wall loadings of the active fire-retardant chemicals.

4. At low pHs, arsenate was also highly excluded from the cell walls with solute free water values of 20–30%. There was no consistent pH effect in the pH range 2 to 9. In solutions made basic (pH > 9) with ammonium hydroxide, an as yet unexplained anomalous effect was observed, with apparent reaction of arsenate with the cell-wall constituents. This effect was not seen in systems made alkaline with other bases.

5. Chromates slowly enter and react with the cell wall. Low pH chromic acid reacted much more quickly and completely with both aspen and red pine than higher pH chromium solutions. While the reaction rate was initially faster in red pine, high pH sodium chromate reacted more completely in aspen.

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