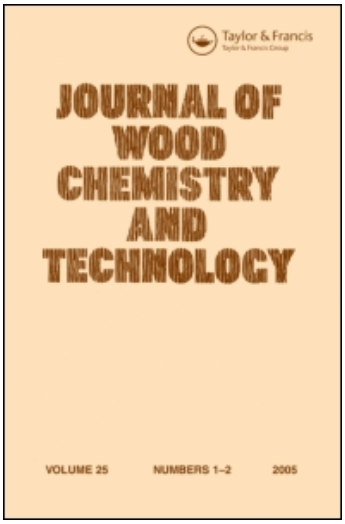


**Journal of Wood Chemistry and Technology**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

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Online publication date: 27 November 2002

**To cite this Article** Yantasee, W. and Rorrer, G. L.(2002) 'COMPARISON OF ION EXCHANGE AND DONNAN EQUILIBRIUM MODELS FOR THE PH-DEPENDENT ADSORPTION OF SODIUM AND CALCIUM IONS ONTO KRAFT WOOD PULP FIBERS', Journal of Wood Chemistry and Technology, 22: 2, 157 — 185
**To link to this Article: DOI:** 10.1081/WCT-120015523
**URL:** http://dx.doi.org/10.1081/WCT-120015523

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JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY
Vol. 22, Nos. 2 & 3, pp. 157–185, 2002



# COMPARISON OF ION EXCHANGE AND DONNAN EQUILIBRIUM MODELS FOR THE pH-DEPENDENT ADSORPTION OF SODIUM AND CALCIUM IONS ONTO KRAFT WOOD PULP FIBERS

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## ABSTRACT

Management of nonprocess element (NPE) accumulation in pulp washing operations requires equilibrium models that predict the distribution of metals between the wash liquor and the pulp fibers. The overall goal of this study was to assess models for predicting the multi-component adsorption of hydrogen ions ($H^+$), sodium ions ($Na^+$), and calcium ions ($Ca^{+2}$) onto bleached and unbleached kraft pulp fibers over a pH range of 2.7–11. As part of this study, binary equilibrium constants for hydrogen and metal ion exchange on carboxylate sites in bleached pulp (0.041 meq/g dry pulp) were measured at 25°C, with $\log K^{Na/Ca} = -1.604 \pm 0.119$, $\log K^{H/Ca} = 0.633 \pm 0.087$, and intrinsic dissociation constant $pK_{io}$ of $3.64 \pm 0.46$. Ion exchange and Donnan equilibrium models

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DOI: 10.1081/WCT-120015523
0277-3813 (Print); 1532-2319 (Online)

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adequately predicted the multi-component equilibrium data for competitive adsorption of $H^+$, $Na^+$, and $Ca^{+2}$ onto bleached kraft wood pulp fibers. The ion exchange model was fully predictive, whereas the Donnan model required that the solution pH be known. At pH 2.7–6, the Donnan model predicted the adsorption of $Na^+$ and $Ca^{+2}$ onto both bleached and unbleached wood pulp fibers better than the ion exchange model. The ion exchange model assumed that residual carboxylate in the pulp served as the only site for the competitive binding of hydrogen and metal ions. In contrast, the Donnan model assumed a non site-specific distribution of metal ions between charged fiber and external solution phases and a carboxylate site specific adsorption of hydrogen ions. Above pH 6, both models failed to predict that the calcium adsorption on unbleached brownstock pulp increased beyond the carboxylate site capacity, suggesting that other functional groups within the brownstock pulp with intrinsic dissociation constant values higher than carboxylate were providing additional binding sites for calcium.

*Key Words:* Donnan; Ion exchange; Nonprocess element; Wood pulp

## INTRODUCTION

A long-term goal of the pulp and paper industry is to reduce the water consumption in pulp mill operations.[1,2] Reduction of water consumption requires the recycle of wash water effluents. The wash water can be passed counter-currently through the bleach plant sequence washers, and then reused in the brownstock washer sequence.[3] Wash effluent reuse results in the build-up of nonprocess elements or NPEs,[4] which have negative impacts on pulp mill operations.[5]

Process models for assessing NPE accumulation and fate in pulp washing operations require equilibrium models that predict distribution of NPE metals between the wash liquor and the pulp fibers. One of the important chemical equilibrium processes underlying NPE distribution in pulp washing operations is the binding of metal cations to residual functional groups on pulp fibers. Kraft pulp fibers contain residual carboxylic acid and phenolic hydroxyl functional groups carried over with non-extracted hemicellulose and lignin fragments that surround the outside surface of

the cellulose fiber.[6] Bleached pulp fibers primarily contain carboxylic acid functional groups, whereas unbleached pulps contain both carboxylic acid and phenolic hydroxyl groups. Carboxylic acids are weakly dissociated, and the carboxylate moiety on pulp ($COO^-$) serves as anionic site for cation exchange, providing one equivalent of cation exchange per mole of functional group on the pulp. The binding of metal ions to wood pulp has been studied by three approaches, including adsorption isotherms,[7–12] ion exchange,[13–16] and Donnan equilibrium.[17–20] However, none of these studies focused on the multi-component, competitive distribution of hydrogen and metal ions onto bleached and unbleached pulps over a broad range of pH. Furthermore, none of these studies developed material balance models to predict multi-component hydrogen ion and metal ion distribution for a given set of process inputs. Finally, none of these studies compared ion exchange and Donnan approaches to prediction of hydrogen and metal ion distribution on bleached vs. unbleached pulp fibers.

Sodium and calcium are often the predominant metals in the fiberline.[4] Furthermore, significant amounts of acid and base are added to the fiberline during the various stages of bleaching (e.g., D-E-D type sequences). The overall goal of this study was to develop and assess predictive models for the multi-component adsorption of hydrogen ions ($H^+$), sodium ions ($Na^+$), and calcium ions ($Ca^{+2}$) onto bleached and unbleached kraft pulp fibers. This present study had three objectives. The first objective was to measure the exchange of metal ions onto bleached pulp fibers for three binary systems, including $Na^+$ exchange onto hydrogen-exchanged pulp, hydrogen ion exchange onto calcium-exchanged pulp, and $Na^+$ exchange onto calcium-exchanged pulp. From these data, binary equilibrium ion exchange constants were estimated. The second objective was to measure the multi-component partitioning of $H^+$, $Na^+$, and $Ca^{+2}$ within the aqueous pulp suspension over a broad pH range of 2.7–11.0. The third objective was to develop and compare ion exchange and Donnan equilibrium models for prediction of the multi-component adsorption of these cations onto bleached and unbleached pulp fibers.

## EQUILIBRIUM MODELS

### Multi-component Ion Exchange Model

Principles of ion exchange processes are described by Helfferich.[24] In this study, these principles were used to develop a multi-component ion exchange model that describes hydrogen ion and metal ion distribution between pulp fiber and solution phases within a well-mixed pulp fiber sus-

pension at equilibrium. This model has three primary assumptions. First, hydrogen and metal ions bind with functional groups on wood pulp fibers by an ion-exchange process. Second, only the carboxylate group serves as the metal ion-binding site. Third, there are no effects of ionic strength, aqueous metal ion speciation, or metal precipitation on the metal ion distribution between the pulp and liquid phases. The model includes equilibrium mass-action expressions for hydrogen and metal ion distribution between wood pulp fibers and solution, an adsorption site balance, material balances for adsorbed metal ions, and a charge balance.

The present system has three cations: hydrogen ($H^+$, species H), sodium ion ($Na^+$, species 1), and calcium ion ($Ca^{+2}$, species 2). For convenience, the carboxylate sites on the pulp are in the calcium-exchanged form. However, specific calculations can be based on any initial ion-exchange form of the pulp. The ion-exchange reactions between $Na^+$ and $H^+$ with Ca-exchanged carboxylic acid sites on the pulp are

$$n_1 Na^+ + Ca \cdot S_2 \overset{K^{Na/Ca}}{\longleftrightarrow} n_1 Na \cdot S + Ca^{+2} \tag{1}$$

$$n_H H^+ + Ca \cdot S_2 \overset{K^{H/Ca}}{\longleftrightarrow} n_H H \cdot S + Ca^{+2} \tag{2}$$

where S represents the carboxylate ($-COO^-$) binding site. For stoichiometric ion exchange of $Na^+$ with $Ca^{+2}$, $n_1 = 2$. Similarly, for stoichiometric ion exchange of $H^+$ with $Ca^{+2}$, $n_H = 2$. The equilibrium mass-action expressions for these binary ion-exchange reactions are

$$K^{Na/Ca} = \frac{[Na \cdot S]^{n_1}[Ca^{+2}]}{[Na^+]^{n_1}[Ca \cdot S_2]} \tag{3a}$$

$$K^{H/Ca} = \frac{[H \cdot S]^{n_H}[Ca^{+2}]}{[H^+]^{n_H}[Ca \cdot S_2]} \tag{3b}$$

The log-log forms of Eqs. (3a) and (3b) are linear

$$\log \frac{[Ca^{+2}]}{[Ca \cdot S_2]} = n_1 \cdot \log \frac{[Na^+]}{[Na \cdot S]} + \log K^{Na/Ca} \tag{4a}$$

$$\log \frac{[Ca^{+2}]}{[Ca \cdot S_2]} = n_H \cdot \log \frac{[H^+]}{[H \cdot S]} + \log K^{H/Ca} \tag{4b}$$

In Eqs. (3a) and (3b), the hydrogen and metal ion concentrations adsorbed on the pulp are expressed on a liquid phase basis. Therefore, in terms of the pulp solid phase, the adsorbed concentrations on the pulp are

$$[\mathrm{H}\cdot\mathrm{S}] = q_{\mathrm{H}}\frac{m_p}{V} \tag{5a}$$

$$[\mathrm{Ca}\cdot\mathrm{S}_2] = q_2\frac{m_p}{V} \tag{5b}$$

$$[\mathrm{Na}\cdot\mathrm{S}] = q_1\frac{m_p}{V} \tag{5c}$$

where $m_p$ is mass of the pulp (g dry pulp); $q_1$, $q_2$, and $q_{\mathrm{H}}$ are the equilibrium amounts of $Na^+$, $Ca^{+2}$, and $H^+$ adsorbed on the pulp (mmol/g dry pulp); $V$ is the volume of metal solution (L). Combination of Eqs. (3) and (5) yields

$$K^{\mathrm{H/Ca}} = \frac{C_2}{q_2}\left(\frac{q_{\mathrm{H}}}{C_{\mathrm{H}}}\right)^{n_{\mathrm{H}}}\left(\frac{m_p}{V}\right)^{(n_{\mathrm{H}}-1)} \tag{6a}$$

$$K^{\mathrm{Na/Ca}} = \frac{C_2}{q_2}\left(\frac{q_1}{C_1}\right)^{n_1}\left(\frac{m_p}{V}\right)^{(n_1-1)} \tag{6b}$$

where $C_1$, $C_2$, and $C_{\mathrm{H}}$ are the equilibrium concentrations of $Na^+$, $Ca^{+2}$, and $H^+$ in solution (mmol/L). The total adsorption site balance in terms of carboxylate equivalents is

$$q_T = \nu_{\mathrm{H}}q_{\mathrm{H}} + q_1\nu_1 + q_2\nu_2 \tag{7}$$

where $q_T$ is amount of carboxylate ($-COO^-$) equivalents on the pulp (meq/g dry pulp). The ion-exchange coefficients for carboxylate ion exchange site are

$$\nu_{\mathrm{H}} = \frac{1\ \text{meq}\ \mathrm{COO^-}}{1\ \text{mol}\ \mathrm{H^+}} \quad \nu_1 = \frac{1\ \text{meq}\ \mathrm{COO^-}}{1\ \text{mol}\ \mathrm{Na^+}} \quad \nu_2 = \frac{2\ \text{meq}\ \mathrm{COO^-}}{1\ \text{mol}\ \mathrm{Ca^{+2}}}$$

In a well-mixed batch adsorption process, the material balance for each metal ion distributed between the aqueous and solid phase is

$$C_{i,o}V_o - C_iV = (q_i - q_{i,o})m_p \tag{8}$$

where $C_{i,o}$ is the initial concentration of metal ion "$i$" in solution (mmol/L), $q_{i,o}$ is the initial amount of metal ion "$i$" adsorbed on the pulp (mmol/g dry pulp), $V_o$ is the initial solution volume (L), and $V$ is the final volume (L). Hydrogen ions adsorbed on the pulp that are released by ion exchange with metal ions can be neutralized by free hydroxyl ions ($OH^-$) in solution. The charge balance in the aqueous phase is

$$\beta_{\mathrm{H}}C_{\mathrm{H}} + \beta_1C_1 + \beta_2C_2 = [\mathrm{Cl^-}] + [\mathrm{OH^-}] \tag{9}$$

where $\beta_{\mathrm{H}} = 1.0$ for $H^+$, $\beta_1 = 1.0$ for $Na^+$, and $\beta_2 = 2.0$ for $Ca^{+2}$. The chloride anion concentration [$Cl^-$] is calculated from sum of all chloride sources (HCl, chloride salts) added to the pulp suspension. The hydroxyl anion concentration [$OH^-$] is calculated from

$$K_w = C_{\mathrm{H}}[\mathrm{OH^-}] \tag{10}$$

where $K_w = 10^{-8}$ (mmol/L)$^2$ at 25°C.[21]

## Material Balance for Multi-component pH Isotherm

In the multi-component pH isotherm adsorption experiments, stock solutions of 25 mM NaOH and 25 mM $CaCl_2$ were incrementally added to hydrogen-exchanged pulp in dilute HCl suspension (Fig. 1) and allowed to equilibrate. The addition of NaOH neutralized $H^+$ in solution to increase the pH. This also allowed $Na^+$ (species 1), $Ca^{+2}$ (species 2), and $H^+$ (species H) to competitively adsorb onto the pulp at a given pH. The material balance on metal ion "$i$" in this stepwise, fed-batch pH isotherm experiment after the $k$th incremental addition of stock metal ion solution is given by

$$\left(C'_{i,o}\sum_k V_{i,k} + C_{i,o}V_o\right) - C_i V = (q_i - q_{i,o})m_p \tag{11}$$

where $C_{i,o}$ is the initial concentration of metal ion "$i$" in solution before addition of NaOH and $CaCl_2$ solutions to the pulp suspension (mmol/L), $C'_{i,o}$ is the concentration of metal ion "$i$" in the stock solution incrementally added to the pulp suspension (mmol/L), $C_i$ is the current concentration of metal ion "$i$" in solution, $q_{i,o}$ is the initial amount of metal adsorbed on the pulp (mmol/g dry pulp), $q_i$ is the current amount of metal adsorbed on the pulp, $V_o$ is the initial volume of liquid in the pulp suspension (L), $\sum_k V_{i,k}$ is the cumulative volume of stock solution for metal ion "$i$" added to the pulp suspension (L), and $V$ is the current cumulative volume of liquid in the pulp

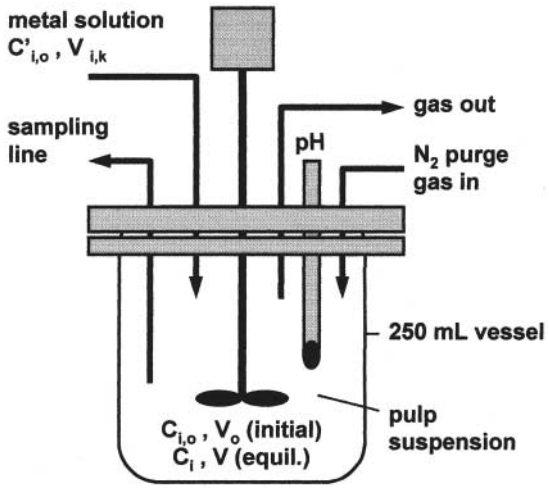


***Figure 1.*** Stirred tank apparatus for fed-batch addition of Na (as NaOH or NaCl) and Ca (as $CaCl_2$) into dilute pulp suspensions.

suspension (L), determined by

$$V = V_o + \sum_k V_{1,k} + \sum_k V_{2,k} \tag{12}$$

The hydrogen ion concentration ($C_H$) in the aqueous phase of the pulp suspension is calculated from a charge balance

$$C_H - \frac{C_H}{K_w} = \frac{1}{V}\left(C_{H,o}V_o + 2C'_{2,o}\sum_k V_{2,k}\right) - C_1 - 2C_2 \tag{13}$$

In Eq. (13), the source of [$Cl^-$] in the system is the sum of the HCl initially in the pulp suspension ($C_{H,o}V_o$) and the cumulative amount $CaCl_2$ added to the pulp suspension.

Equations (6)–(9) for the batch model or Eqs. (6), (7), and (11)–(13) for the fed-batch model represent a system of 6 independent equations with 6 unknowns ($C_H$, $C_1$, $C_2$, $q_H$, $q_1$, $q_2$). This system of nonlinear equations was solved numerically using MathCad version 8.0 (MathSoft Inc., Cambridge, MA).

## Multi-component Donnan Equilibrium Model

The multi-component Donnan equilibrium model described here builds upon earlier work of Towers and Scallan.[17] Donnan equilibrium theory assumes a non site-specific distribution of metal ions between pulp fibers and the bulk solution. The Donnan phase, i.e., the aqueous phase within the water-swollen pulp fibers, contains fixed, anionic (i.e., dissociated) carboxylate (–$COO^-$) sites on the pulp surrounded by positively charged cations (hydrogen and metal ions). Only hydrogen ions specifically bind to the carboxylate sites, and the presence of free carboxylate causes an unequal distribution of metal cations between the Donnan phase and the bulk solution. The distribution constant ($\lambda$) relates the concentration of a free ion in the Donnan phase to its concentration in the external solution surrounding the pulp fibers. Specifically, for hydrogen ions, $\lambda$ is

$$\lambda = \frac{[H^+]_D}{[H^+]_S} \tag{14a}$$

where subscripts $D$ and $S$ denoting the Donnan and external solution phases, respectively. For monovalent metal ions, $\lambda$ is

$$\lambda = \frac{[M_i^+]_D}{[M_i^+]_S} \tag{14b}$$

For divalent metal ions, $\lambda$ is

$$\lambda = \sqrt{\frac{[M_i^{+2}]_D}{[M_i^{+2}]_S}} \tag{14c}$$

where $[H^+]$ is hydrogen ion concentration, $[M_i^+]$ is the concentration of a given monovalent metal ion, and $[M_i^{+2}]$ is the concentration of a given divalent metal ion. Based on the definition of $\lambda$ above, it can be shown that the total concentration of monovalent metal ions $[M^+]_S$ and total concentration of divalent metal ions $[M^{+2}]_S$ in the external solution phase are given by

$$[M^+]_S = \frac{1}{V/m_p + F(\lambda - 1)} T_{M^+} \tag{15a}$$

$$[M^{+2}]_S = \frac{1}{V/m_p + F(\lambda^2 - 1)} T_{M^{+2}} \tag{15b}$$

where $F$ is water content of pulp fibers at the fiber saturation point, equal to 1.4 mL/g dry pulp for Kraft pulps,[22] $T_{M^+}$ is the total molar amount of monovalent metal ions in the external solution *and* fiber phases per unit mass of pulp (mmol/g dry pulp), and $T_{M^{+2}}$ is total molar amount of divalent metal ions in the external solution *and* fiber phases per unit mass of pulp (mmol/g dry pulp). From the fed-batch material balance model defined by Eq. (11), $T_{M^+}$ for NaOH solution addition and $T_{M^{+2}}$ for $CaCl_2$ solution addition are defined as

$$T_{M^+} = \frac{C'_{1,o} \sum_k V_{1,k} + C_{1,o} V_o}{m_p} + q_{1,o} \tag{16a}$$

$$T_{M^{+2}} = \frac{C'_{2,o} \sum_k V_{2,k} + C_{2,o} V_o}{m_p} + q_{2,o} \tag{16b}$$

Towers and Scallan[17] derived the balance for the distribution of metal ions between the Donnan and external solution phases in terms of $\lambda$. Their result is

$$\frac{(\lambda^2 - 1)}{V/m_p + F(\lambda - 1)} T_{M^+} + \frac{2(\lambda^3 - 1)}{V/m_p + F(\lambda^2 - 1)} T_{M^{+2}} + (\lambda^2 - 1)[H^+]_S - \frac{\lambda (S_i/F) K_{io}}{\lambda [H^+]_S + K_{io}} = 0 \tag{17}$$

where $[H^+]_S$ is the hydrogen ion concentration (i.e., pH) in the external solution (mmol/L, equivalent to $C_H$ in Eq. (9)), $S_i$ is the carboxylate binding site concentration in the pulp fiber solid (mmol/g dry pulp, equivalent to $q_T$ in Eq. (7)), and $K_{io}$ is the intrinsic dissociation constant of carboxylic acid functional group on the pulp fibers. To obtain λ, Eq. (17) is solved numerically at a specified $[H^+]_S$ (i.e., the equilibrium pH). The solution yields multiple values for λ. However, the true value of λ is the first root greater than 1.[17] Once λ is obtained, the predicted external concentration of any metal cation is determined by Eqs. (15) and (16). With the external concentration of each metal ion known, the predicted Donnan phase concentration of each metal ion is backed out from Eqs. (14b) and (14c). Finally, the concentration of each adsorbed metal ion on the pulp is determined by

$$q_i = [M_i]F \tag{18}$$

In the Donnan model, the effects of speciation or precipitation on the metal ion distribution between the pulp fiber and external solution phases are neglected.

The Donnan equilibrium model requires the intrinsic dissociation constant ($K_{io}$) for the carboxylic acid functional groups on the wood pulp fibers. First, the Henderson-Hasselbalch equation defines the apparent dissociation constant for weak acids (e.g., carboxylic acid) as

$$pK_{\text{app}} = \text{pH} + \log[(1-\alpha)/\alpha] \tag{19}$$

where $\alpha$ is the degree of ionization of carboxylate, defined by

$$\alpha = \frac{[-\text{COO}^-]}{[-\text{COOH}]} \tag{20}$$

For wood pulp fibers, $pK_{io}$ is related to $pK_{\text{app}}$ by the relationship proposed by Herrington and Petzold[23]

$$pK_{\text{app}} = m\,\text{anti-log}\,\alpha + (pK_{io} - m) \tag{21}$$

Equation (21) is linear with slope $m$ and intercept $pK_{io}-m$. Therefore, $pK_{io}$ can be determined from $\alpha$ vs. pH measurements of the wood pulp fibers.

## RESULTS AND DISCUSSION

### Pulp Functional Group Content

Residual functional group content of bleached (P3, Perox) and unbleached (brownstock) kraft pulps used in this study are presented

***Table 1.*** Functional Group Content of Kraft Wood Pulp (Duplicate Samples)

| Residual Functional Groups | Bleached P3 Pulp ±1.0 S.D. | Bleached Perox Pulp ± 1.0 S.D. | Unbleached Brownstock Pulp ± 1.0 S.D. |
|---|---|---|---|
| Carboxylate (mmol/g dry pulp) | $0.044 \pm 0.0014$ | $0.045 \pm 0.0071$ | $0.055 \pm 0.00035$ |
| Phenolic hydroxyl (mmol/g dry pulp) | $0.0031 \pm 0.00035$ | $0.0022 \pm 0.00011$ | $0.026 \pm 0.00064$ |
| Total (meq/g dry pulp) | $0.047 \pm 0.0018$ | $0.047 \pm 0.0072$ | $0.081 \pm 0.0010$ |

in Table 1. Bleached pulps contained only carboxylic acid functional groups, whereas unbleached pulp contained both carboxylic acid and phenolic hydroxyl groups.

## Titration of Bleached Pulp

Titration measurements for H-exchanged bleached P3 pulp at 25°C are presented in Figs. 2(a) and (b). Figure 2(a) presents the measured final conductivity and pH of the bleached P3 pulp in the dilute HCl suspension (initial pH 2.82) as incremental amounts of NaOH were added, whereas Fig. 2(b) shows the amount of Na adsorbed on the pulp as incremental amounts of NaOH were added. The solution conductivity decreased with NaOH addition as the free $H^+$ in solution was neutralized. At the points where the conductivity was level or increasing, corresponding to pH 4 and above, the $H^+$ adsorbed on the carboxylate sites on the pulp were exchanged with $Na^+$. At pH 10 and above, the molar equivalents of Na adsorbed on the pulp approached the carboxylate functional group content. In the pH range of 4.2–10.2, the equilibrium $Na^+$ concentration ranged from 1.1 to 1.5 mM, with corresponding ionic strength of the same range. The intrinsic dissociation constant for carboxylate functional groups on bleached pulp ($pK_{io}$) was estimated from this portion of the titration data. Values for $K_{app}$ were obtained from Eq. (19) using the data shown in Fig. 2(b), where the extent of ionization ($\alpha$) at a given pH was assumed to be equal the extent of $Na^+$ adsorbed, i.e.,

$$\alpha = \frac{\nu_1 q_1}{q_T} \tag{22}$$

A plot of $K_{app}$ vs. anti-log($\alpha$) for bleached P3 pulp is presented in Fig. 3. From linear regression of this data to Eq. (21), $pK_{io} = 3.64 \pm 0.46$ (±1.0 S.D.)

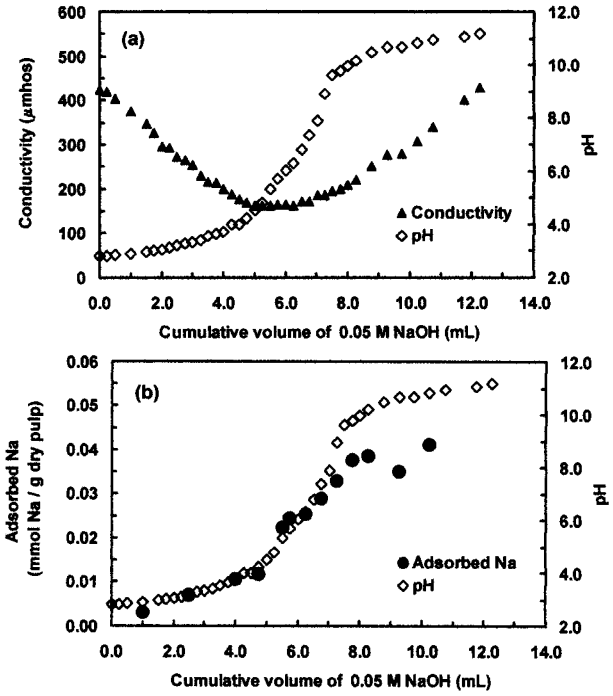


*Figure 2.* Titration of H-exchanged bleached P3 pulp at 25°C. (a) Conductivity and pH; (b) adsorbed sodium (Na).

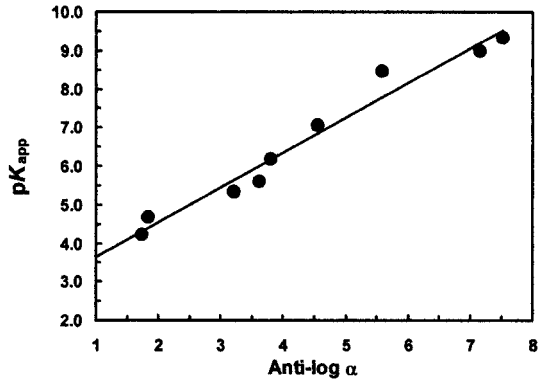


*Figure 3.* Plot of $pK_{app}$ vs. anti-log $\alpha$ for bleached P3 pulp at 25°C, using titration data presented in Fig. 2. From the intercept at anti-log $\alpha = 1$, the intrinsic dissociation constant $pK_{io} = 3.64 \pm 0.46$ ($\pm 1.0$ S.D.); from slope, $m = 0.902 \pm 0.062$ ($\pm 1.0$ S.D.), $r^2 = 0.97$.

and $m = 0.902 \pm 0.062$ ($\pm 1.0$ S.D.) in a background ionic strength of 1.1–1.5 mM. Our results for bleached pulp agreed with previous results of Laine et al.[6] and Räsänen and Stenius,[18] who estimated $pK_{io}$ for unbleached wood pulps from potentiometric titration measurements. In the pH range of 2–8, both investigators found two values of $pK_{io}$ (3.4 and 5.5) for unbleached wood pulp. Laine et al.[6] further proposed that the stronger acid functional group with $pK_{io}$ of 3.4 resulted from uronic acid in hemicellulose and the weaker acid functional group with $pK_{io}$ of 5.5 resulted from residual lignin within wood pulp.

## Binary Ion-Exchange Equilibrium Experiments

The multi-component ion exchange model requires binary equilibrium constants for hydrogen and metal ion adsorption on Ca-exchanged pulp. Two binary adsorption isotherm experiments were conducted at 25°C. The process conditions for each experiment are presented in Table 2. In the first experiment, the adsorption of $H^+$ on Ca-exchanged bleached Perox pulp was measured over pH range of 1.8–5.8 (Fig. 4). Adsorbed Ca was completely displaced below pH 2.5. The distribution plot derived from this data is presented in Fig. 5. In the second experiment, the adsorption of $Na^+$ on Ca-exchanged bleached P3 pulp was measured at a near-neutral pH range of 5.4–6.1 (Fig. 6). The distribution plot derived from this data is presented

***Table 2.*** Process Input Parameters for Binary Ion Exchange Experiments

| Conditions | $H^+$ Exchange | $Na^+$ Exchange |
|---|---|---|
| Temperature | 25°C | 25°C |
| Adsorption time | 2 h | 2 h |
| Pulp type | Ca-exchanged bleached Perox pulp | Ca-exchanged bleached P3 pulp |
| Initial Ca loading on pulp ($q_{2,o}$) | 0.0130 mmol/g dry pulp | 0.0152 mmol/g dry pulp |
| Carboxylate content ($q_T$) | 0.045 mmol/g dry pulp | 0.044 mmol/g dry pulp |
| Wet mass pulp | 3.51 g | 5.40 g |
| Dry mass pulp ($m_p$) | 1.02 g | 1.55 g |
| Final solution volume ($V$) | 50.0 mL | 50.0 mL |
| HCl added ($V_o \cdot C_{H,o}$) | 0.00050–0.50 mmol $H^+$ | — |
| pH range (at equilibrium) | 1.82–5.80 | 5.42–6.12 |
| Metal salt added ($V_o \cdot C_{i,o}$) | — | 0.00964–0.0946 mmol NaCl<br>0.00 mmol $CaCl_2$ |

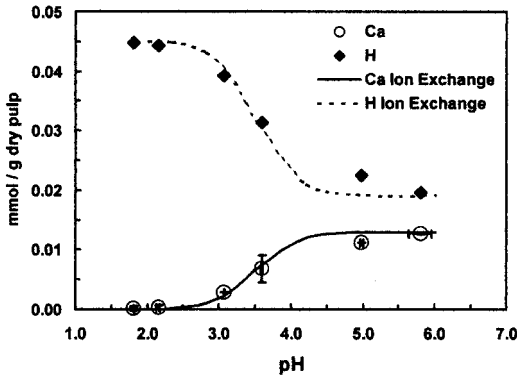


*Figure 4.* Adsorption of $H^+$ onto Ca-exchanged bleached Perox pulp at 25°C. Process conditions are provided in Table 2. Solid lines represent ion exchange model predictions. Error bars on adsorbed Ca and pH are ±1.0 S.D. from triplicate measurements.

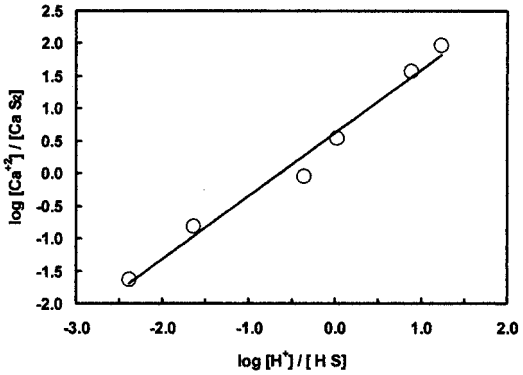


*Figure 5.* Distribution plot for $H^+$ adsorption onto Ca-exchanged bleached Perox pulp at 25°C. Ion exchange parameter estimates are provided in Table 3.

in Fig. 7. The kinetics of this ion-exchange process was rapid, and equilibrium was attained within 5 min (Fig. 8). Furthermore, the total equivalents of adsorbed metal on the pulp were constant, demonstrating that the equivalents of $Na^+$ adsorbed equaled the equivalents of $Ca^{+2}$ displaced.

Ion-exchange equilibrium constants ($K^{H/Ca}$, $K^{Na/Ca}$) and stoichiometric constants ($n_1$, $n_H$) for $H^+$ and $Na^+$ adsorption on Ca-exchanged pulp were estimated by fitting the distribution data shown in Figs. 5 and 7 to Eqs. 4(a) and 4(b) respectively. Parameter estimates are presented in Table 3.

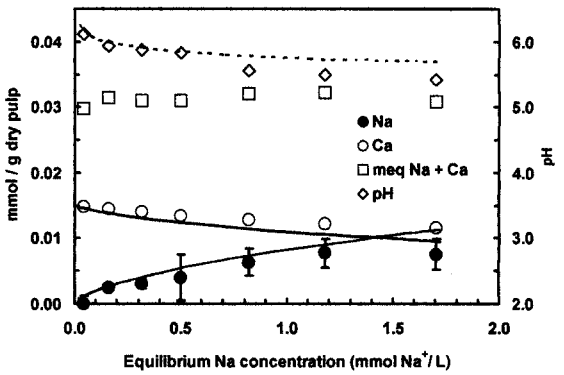


*Figure 6.* Adsorption of $Na^+$ onto Ca-exchanged bleached P3 pulp at 25°C. Process conditions are provided in Table 2. Solid lines represent ion exchange model predictions. Error bars on adsorbed Na are ±1.0 S.D. from triplicate measurements; error bars on adsorbed Ca and pH were within the size of their respective data symbols.

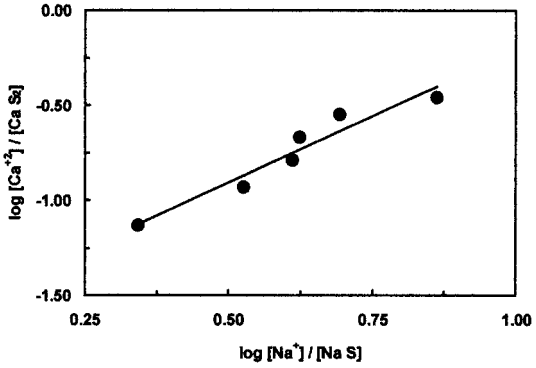


*Figure 7.* Distribution plot for $Na^+$ adsorption onto Ca-exchanged bleached P3 pulp at 25°C. Ion exchange parameter estimates are provided in Table 3.

From the binary equilibrium constant values given in Table 3, the binding affinity for these cations on bleached P3 pulp is

$$H^+ \gg Ca^{+2} \gg Na^+$$

which is the same order associated with weak acid, carboxylate exchangers.[24] This binding preference indicates that $H^+$ is the most strongly bound cation whereas $Na^+$ is the most-weakly bound cation.

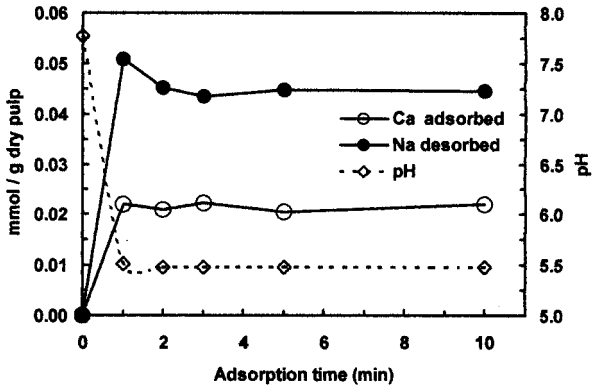


*Figure 8.* Adsorption kinetics of $Ca^{+2}$ onto Na-exchanged bleached P3 pulp at 25°C.

Values for $n_2$ and $n_H$ estimated from data did not match the theoretical ion-exchange stoichiometry constant of 2.0 for Na–Ca exchange and 2.0 for H–Ca exchange. In limited previous studies, Diniz[15] performed potentiometric titration of Ca-exchanged bleached sulfite pulp and determined that $K^{H/Ca}$ was 5.343, which is comparable to this study. Ohlsson and Rydin[13] determined that $K^{Mg/Na}$ was 9.0 and $K^{Ca/Mg}$ was 2.9 on unbleached kraft pulp. From the Triangle rule,[24] their $K^{Na/Ca}$ was 0.0383, which is also comparable to this study.

The ion exchange model was used to predict the pH vs. Ca adsorption data (Fig. 4) and the Na–Ca adsorption data (Fig. 6) using the measured equilibrium constants given in Table 3, the process input parameters given in Table 2, and theoretical values for ion exchange stoichiometry constants ($n_1 = 2.0$ for Na–Ca exchange, $n_H = 2.0$ for H–Ca exchange). The difference between predicted and measured values for Na and Ca adsorption can be attributed to using theoretical vs. fitted values of the ion exchange stoichiometry constants.

## Multi-component pH Isotherms for Sodium and Calcium Adsorption

The pH isotherm specified the amount of sodium and calcium adsorbed on the wood pulp fibers as a function of solution pH in the pulp suspension. Initially, the pulp was in a hydrogen-exchanged form, suspended in a solution of dilute HCl equilibrated to pH 2.7. Then NaOH and $CaCl_2$ solution were added to the pulp suspension. The NaOH

***Table 3.*** Ion-Exchange Binary Equilibrium Constants

| Bleached Pulp | $K$ Definition | Log $K \pm 1.0$ S.D. | $K$ Value (Range) | Estimated $n_i \pm 1.0$ S.D. | Theory $n_i$ | Equilibrium Concentration Range | $r^2$ |
|---|---|---|---|---|---|---|---|
| P3 | $K^{Na/Ca}$ | $-1.604 \pm 0.119$ | 0.0249 (0.0189–0.0328) | $1.39 \pm 0.190$ | 2.0 | 0.16–1.70 mM $Na^+$ 0.033–0.125 mM $Ca^{+2}$ | 0.93 |
| Perox | $K^{H/Ca}$ | $0.633 \pm 0.087$ | 4.29 (3.51–5.25) | $0.97 \pm 0.065$ | 2.0 | 0.006–0.25 mM $Ca^{+2}$ | 0.98 |

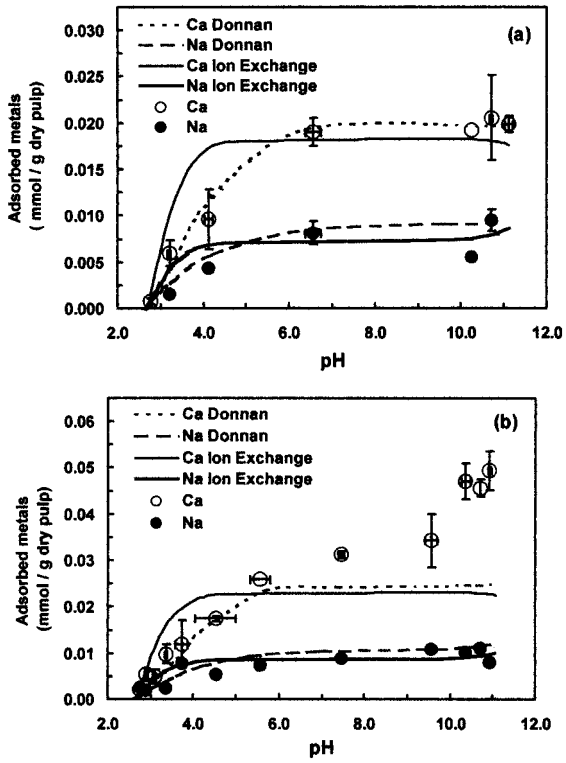


***Figure 9.*** Competitive adsorption of $Na^+$ and $Ca^{+2}$ onto H-exchanged pulp at 25°C. (a) Bleached P3 pulp; (b) unbleached brownstock pulp. Process conditions are provided in Table 4. Solid lines represent multi-component ion exchange model predictions; dotted lines represent Donnan equilibrium model predictions. Error bars on adsorbed Na, adsorbed Ca, and pH are ±1.0 S.D. from triplicate measurements.

solution was used for $Na^+$ addition and $H^+$ neutralization, whereas $CaCl_2$ solution was the sole source for $Ca^{+2}$. Figure 9(a) presents the measured and predicted amounts of $Na^+$ and $Ca^{+2}$ adsorbed on H-exchanged bleached P3 pulp vs. pH at 25°C, and Fig. 9(b) presents the same experiment on H-exchanged unbleached brownstock pulp. Figures 10(a) and 10(b) show the total measured and predicted amounts metal ion equivalents adsorbed on the bleached P3 pulp and the unbleached brownstock pulp, respectively. Process conditions are presented in Table 4. Equilibrium metal ion concentrations are not shown. However, for experiments with the bleached P3 pulp, the equilibrium metal ion concentrations were 0.46 mM Na

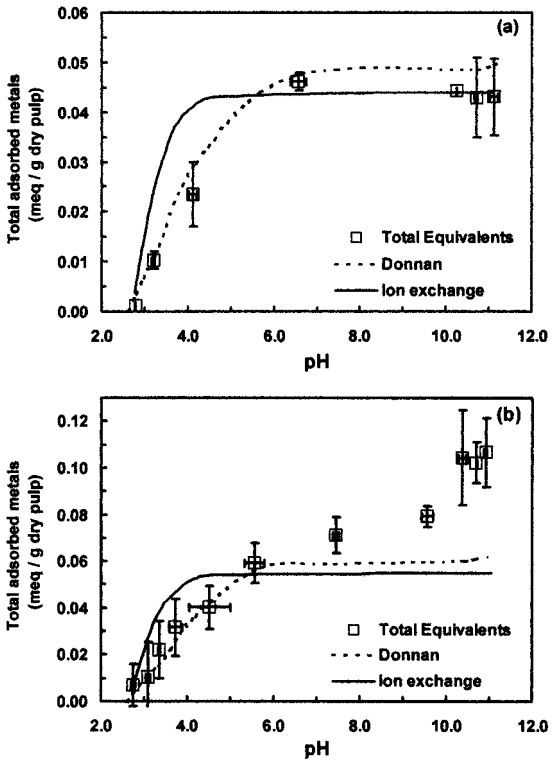


***Figure 10.*** Total equivalents of $Na^+$ and $Ca^{+2}$ onto H-exchanged pulp at 25°C. (a) Bleached P3 pulp; (b) unbleached brownstock pulp. Error bars are ±1.0 S.D. from triplicate measurements.

and 0.46 mM Ca at pH 2.8 (first increment of NaOH and $CaCl_2$ addition), and 4.1 mM Na and 3.5 mM Ca at pH 11.2 (8th increment). Experiments with unbleached brownstock pulp were also within this nominal concentration range.

The metal ion adsorption capacity was a strong function of pH. At pH 2.7, the pulp existed only in the H-exchanged form. As the pH increased from about 2.7 to 6, the amount of $Na^+$ and $Ca^{+2}$ adsorbed on the pulp increased rapidly and then leveled off. The trend was similar for both bleached P3 and unbleached brownstock pulps. However, the metal ion adsorption behavior of the two pulps differed significantly at pH above 8. The bleached P3 pulp possessed carboxylate acid functional groups and a negligible amount of phenolic hydroxyl groups (Table 1). Above pH 8, carboxylic acid functional groups were dissociated, and so the total metal

***Table 4.*** Process Input Parameters for Multi-component pH Isotherm

| Parameter | Bleached Pulp | Unbleached Pulp |
|---|---|---|
| Temperature | 25°C | 25°C |
| Pulp type | HCl-washed Bleached P3 | HCl-washed Brownstock |
| Carboxylate content ($q_T$) | 0.044 mmol COOH/g dry pulp | 0.055 mmol COOH/g dry pulp |
| Dry mass pulp ($m_p$) | 4.95 g dry pulp | 4.95 g dry pulp |
| Initial volume ($V_o$) | 160.0 mL | 160.0 mL |
| Initial metal ion concentration ($C_{1,o}$,$C_{2,o}$) | 0.0 mmol $Na^+$/L<br>0.0 mmol $Ca^{+2}$/L | 0.0 mmol $Na^+$/L<br>0.0 mmol $Ca^{+2}$/L |
| Initial $H^+$ exchange on pulp ($q_{H,o}$) | 0.044 mmol $H^+$/g dry pulp | 0.055 mmol $H^+$/g dry pulp |
| Initial pH/Final pH | 2.67/11.1 | 2.64/10.9 |
| Initial metal loading on pulp ($q_{1,o}$, $q_{2,o}$) | 0.0 mmol Na/g dry pulp<br>0.0 mmol Ca/g dry pulp | 0.0 mmol Na/g dry pulp<br>0.0 mmol Ca/g dry pulp |
| Volume NaOH solution ($V_{1,k}$) | 4.25 mL | 3.0 mL |
| Volume $CaCl_2$ solution ($V_{2,k}$) | 4.25 mL | 3.0 mL |
| Conc. NaOH solution ($C'_{1,o}$) | 25.0 mmol NaOH/L | 25.0 mmol NaOH/L |
| Conc. $CaCl_2$ solution ($C'_{2,o}$) | 25.0 mmol $CaCl_2$/L | 25.0 mmol $CaCl_2$/L |
| Total number of increments ($k$) | 8 | 12 |
| Sample volume | 1.5 mL | 1.7 mL |
| Cumulative NaOH ($C'_{1,o} \sum V_{1,k}$) | 0.900 mmol Na | 0.900 mmol Na |
| Cumulative $CaCl_2$ ($C'_{2,o} \sum V_{2,k}$) | 0.900 mmol Ca | 0.900 mmol Ca |
| Final volume ($V$) | 232.0 mL (no sampling)<br>220.0 mL (sampling) | 232.0 mL (no sampling)<br>211.6 mL (sampling) |



ion equivalents adsorbed on the bleached pulp above pH was approximately equal to total molar equivalent of the carboxylate binding sites. The extent of Na and Ca adsorbed on the bleached pulp was also constant, given the fact that NaOH and $CaCl_2$ were added to the pulp in equal molar amounts (Table 4). Furthermore, $Ca^{+2}$ adsorption was favored over $Na^+$ adsorption.

The unbleached brownstock pulp contained both carboxylate and phenolic hydroxyl functional groups (Table 1). Metal ion adsorption onto the unbleached brownstock pulp increased in two steps. In the first step from pH 2.7 to 6, the extent of both Na and Ca adsorption increased. In the second step above pH 8, the amount of Na adsorbed remained constant whereas the amount of Ca adsorption continued to increase. Above pH 10, the total amount of metal ion equivalents adsorbed exceeded the

carboxylate and phenolic hydroxyl equivalents. The likely reason for this behavior is that the brownstock pulp is a heterogeneous adsorbent. To elaborate, extractive residues may still have been retained in the unbleached pulp, even after acid washing. Therefore, phenolic hydroxyl groups as well as functional groups on these residual extractive residues could potentially serve as binding sites for $Ca^{+2}$ or $Ca(OH)^{+}$. This would be particularly the case for $Ca^{+2}$, which is capable of chelation with a variety of organic moieties.

The pH isotherm experiment was designed to avoid precipitation of $Ca^{+2}$ to calcium hydroxide, $Ca(OH_2)$, and calcium carbonate, $CaCO_3$. The total calcium concentration in the system was very low, varying from only 0.4 to 4.0 mM. Precipitation of $Ca^{+2}$ to $Ca(OH)_2$ at pH 10 was unlikely, as solubility calculations showed that $Ca^{+2}$ did not precipitate at the final $Ca^{+2}$. To prevent $CaCO_3$ precipitate formation, special care was taken to insure that virtually no inorganic carbon was added to the system. First, the pulps were acid washed to remove residual carbonates initially in the wood pulp. Second, all experiments were conducted within a sealed vessel with a nitrogen gas overlay to prevent the introduction of $CO_2$ from the surrounding atmosphere into the system. Details on all of these experimental precautions are provided in the Experimental section.

## Comparison of Ion Exchange and Donnan Equilibrium Predictions for pH Isotherm

The pH isotherms shown in Figs. 9 and 10 were predicted using both multi-component ion exchange and Donnan equilibrium models. The solid lines represent the ion exchange model predictions whereas the dotted lines represent the Donnan model predictions.

Input parameters for the multi-component ion exchange model are presented in Table 4, and binary equilibrium constants for H–Ca and Na–Ca exchange are found in Table 3. Theoretical values for ion exchange stoichiometry constants ($n_1 = 2.0$ for Na–Ca exchange, $n_H = 2.0$ for H–Ca exchange) were also used for model ion exchange model predictions. For the pH isotherm experiments, the starting pulps (bleached P3 or unbleached brownstock) were in H-exchanged form, and so the initial amount of $H^+$ adsorbed on the pulp ($q_{H,o}$) was assumed to be equal to the carboxylate content of a given wood pulp (Table 1). Since the multi-component ion exchange model used binary equilibrium constants estimated from independent binary adsorption experiments (Figs. 5 and 7), the ion exchange model predictions were generated independent of the pH adsorption isotherm data.

The Donnan model required the external solution phase pH at equilibrium. The measured equilibrium pH associated with a given set of $T_{M^+}$ and $T_{M^{+2}}$ values was used. Additional input parameters for the Donnan model are presented in Table 5. The λ values generated from the Donnan equilibrium model are also presented in Table 5.

Both models adequately predicted the competitive adsorption of $Na^+$ and $Ca^{+2}$ on bleached P3 pulp at pH 6–10. In the acid pH range of 2.7–6.0, the Donnan equilibrium model predicted the metal adsorption much better than the multi-component ion-exchange model. The multi-component ion exchange model is based on the specific interaction between free metal ions and metal ions bound to carboxylate sites on the pulp fibers. The interaction of $H^+$ and $Na^+$ with Ca-exchanged pulp may be more complicated than this premise, considering the difference between the measured and theoretical ion exchange constants $n_1$ and $n_H$ (Table 3). In contrast, the Donnan equilibrium model assumed non site-specific distribution of metal ions between the liquid within pulp fibers and in the external solution, with the pH-dependent dissociation of fixed carboxylic acid sites on the pulp fibers determined by the intrinsic dissociation constant $pK_{io}$.

The ion exchange model assumes that the carboxylate functional group in wood pulp serves as the only binding site for metal ions. The single-site model works well for unbleached pulp at pH below 8, where all the phenolic hydroxyl functional groups are still likely protonated, or for bleached pulps, which contain only carboxylate functional groups.

***Table 5.*** Donnan Equilibrium Model Input Parameters for pH Isotherm Prediction

| Parameter | Bleached Pulp | Unbleached Pulp |
|---|---|---|
| Saturation water content of pulp fibers ($F$) | 1.4 mL/g dry pulp | 1.4 mL/g dry pulp |
| Intrinsic dissociation constant for carboxylate site ($K_{io}$) | $10^{-3.644}$ mol/L | $10^{-3.644}$ mol/L |
| Carboxylate content in pulp ($S_i$) | 0.044 mmol/g dry pulp | 0.055 mmol/g dry pulp |
| Equilibrium $H^+$ conc. ($[H^+]_S$) | $10^{-2.67}$–$10^{-11.1}$ mol $H^+$/L | $10^{-2.64}$–$10^{-10.9}$ mol $H^+$/L |
| Total monovalent metal ions ($T_{M^+}$) | 0.182 mmol Na/g dry pulp | 0.182 mmol Na/g dry pulp |
| Total divalent metal ions ($T_{M^{+2}}$) | 0.182 mmol Ca/g dry pulp | 0.182 mmol Ca/g dry pulp |
| λ Range (minimum, maximum) | 1.45–2.64 | 1.46–2.84 |

However, phenolic hydroxyl functional groups, with a nominal $pK_a$ of around 10,[7] are also potential metal ion adsorption sites, particularly at high pH. Therefore, for unbleached pulps, a two-site equilibrium model may be required for prediction of metal ion adsorption at high pH. However, a two-site ion exchange model will require the binary equilibrium constants for $Na^+$ and $Ca^{+2}$ adsorption on H-exchanged phenolic hydroxyl groups in unbleached brownstock wood pulp. Likewise, in order for the Donnan equilibrium model to be extended to unbleached brownstock pulp at high pH, the intrinsic dissociation constant for the phenolic hydroxyl group must be estimated.

## CONCLUSION

Ion exchange and Donnan equilibrium models adequately predicted the multi-component equilibrium adsorption of hydrogen ions ($H^+$) and metal ions ($Na^+$, $Ca^{+2}$) onto bleached Kraft wood pulp fibers. The multi-component ion exchange model was fully predictive, whereas the Donnan model required that the solution pH be specified. At pH 2.7–6, the Donnan model predicted the adsorption of $Na^+$ and $Ca^{+2}$ onto both bleached and unbleached wood pulp fibers better than the multi-component ion exchange model. The ion exchange model assumed that the carboxylate functional groups in the pulp served as sites for the competitive binding of hydrogen and metal ions, whereas the Donnan model assumed a non site specific distribution of metal ions between fiber and solution phases. Above pH 6, both models failed to predict that the calcium adsorption on unbleached brownstock pulp increased beyond the carboxylate site capacity, suggesting that other functional groups within the brownstock pulp with intrinsic dissociation constant values higher than carboxylate were providing additional binding sites for calcium.

## EXPERIMENTAL

### Pulp Samples

Two pulp samples were obtained from the Louisiana-Pacific Kraft softwood pulp mill in Samoa, California. Peroxide bleached pulp (P3) was sampled off the drum of the third stage peroxide bleaching washer on August 15, 1996. Brownstock pulp was sampled off the drum of the second brownstock washer on April 24, 1998. One additional pulp sample was obtained from the Pope and Talbot Kraft softwood pulp mill in Halsey,

Oregon. Bleached pulp (Perox) was sampled off the drum of the final peroxide bleaching stage washer on June 25, 1998.

### Pulp Functional Group Content

The carboxylic acid group content of the pulp was assayed by conductiometric titration[25] and the phenolic hydroxyl group content of the pulp was assayed by oxidation of guaiacyl groups.[26,27] Pulp moisture content was measured by TAPPI Method T-264 om-88 (1988).

### Metal Analysis

Sodium (Na) and calcium (Ca) concentrations in aqueous samples were measured with a Varian ICP Emission Spectrometer (model Liberty 150). The wavelengths for Na and Ca were set at 589.592 and 317.933 nm, respectively.

### Pulp Preparation

Acid washing with dilute HCl to a final pH below 2.0 was used to remove all metal ions initially bound to the mill pulp samples. Initially, the pulp was diluted to ca. 3.0 wt% consistency (30 g dry pulp/L suspension) in deionized/distilled (DI) water, and the suspension heated to 75°C under continuous stirring. Then 1.0 N HCl was added to adjust the pH of the suspension down to 1.6–1.9 under continuous stirring. The suspension was continuously stirred for 30 min at 75°C, and then the pulp was immediately vacuum filtered and washed repeatedly with DI water at 50°C until the pH of washings was constant. This acid-washed pulp was then exchanged with calcium ions. Specifically, acid-washed pulp and 50 mM calcium chloride ($CaCl_2$) solution were mixed to ca. 1.0 wt% consistency (10 g dry pulp/L suspension) at room temperature for 30 min at 25°C. The pulp was then rinsed with DI water until the wash water contained no detectable calcium ions.

To determine Ca content of the pulp after Ca-exchange, Ca was removed from the pulp into solution by adding 0.1 N HCl solution into 2.0 wt% pulp suspension until the final pH was 1.6–1.9. The pulp slurry was continuously mixed for 2 h at 25°C and then vacuum filtered. The acid washing procedure was then repeated. Filtrate samples were analyzed for calcium concentration by ICP. Aqueous filtrate from second acid

washing step contained no Ca, indicating removal of Ca from the pulp was complete. Consequently, the Ca initially adsorbed to the Ca-exchanged pulp was estimated by assuming that all Ca on the pulp was displaced by $H^+$ during the first acid washing step. Specifically, the amount of Ca initially adsorbed ($q_{2,o}$) equaled the amount of $Ca^{+2}$ released by hydrogen exchange

$$q_{2,o} = \frac{C_2 V}{m_p} \tag{23}$$

where $C_2$ is the concentration of $Ca^{+2}$ in the liquid filtrate, $m_p$ is the dry mass of the pulp, $V$ is the total volume of solution after adding the HCl solution, which includes the aqueous solution initially in the wet pulp. The Ca content on bleached P3 pulp after Ca-exchange was $0.0152 \pm 0.0033$ (3 replicates) mmol Ca/g dry pulp. Na-exchanged pulp was prepared similarly, using 50 mM NaCl as the washing solution.

### Sodium Ion Adsorption onto Ca-Exchanged Pulp

The experiments were carried out by contacting the pulp with an aqueous solution of a given metal ion in a 250 mL screw cap Erlenmeyer flask. The sodium metal ion solution was prepared by dissolving its salt (NaCl) in DI water to concentrations ranging from 4.8 to 47.1 mg Na/L (0.21–2.05 mmol Na/L). To begin the adsorption experiment, Ca-exchanged wet pulp of known moisture content was weighed (5.40 g wet basis, 1.55 g dry basis) and added to the flask containing metal ion solution of volume 46.15 mL (total liquid volume 50.0 mL). The flasks were placed in a temperature-controlled orbital shaker and mixed continuously at 160 rpm at 25°C for 2 h, which was sufficient time to attain equilibrium. The total metal concentrations in the initial solution and the final filtrate were measured by ICP. The pH of the solution was also measured. Each adsorption experiment was repeated in triplicate. A control experiment containing only the pulp and DI water was performed to determine if any metal ions were released from the pulp to the DI water. The adsorption capacity of a given metal bound onto the wood pulp ($q_i$, mmol metal ion/g dry pulp) was calculated by

$$q_i = \frac{C_{i,o} V_o - C_i V}{m_p} \tag{24}$$

where $C_{i,o}$ is the initial concentration of metal ion "$i$" in the solution before wet pulp addition, $C_i$ is the final concentration of metal ion "$i$" in the liquid sample, $m_p$ is the dry mass of the pulp, $V_o$ is the initial volume of metal ion solution before wet pulp addition, and $V$ is the final volume of solution at

the end of the adsorption experiment, which includes the aqueous solution initially contained within the wet pulp.

### Hydrogen Ion Adsorption onto Ca-Exchanged Pulp

The experimental procedure for the adsorption isotherm measurements described above was also used to obtain binary H–Ca exchange data on the bleached Perox pulp, with the following modifications. In the H–Ca exchange experiments, dilute HCl solution (0.1, 0.01, or 0.001 M) was added to the Ca-exchanged pulp (3.51 g wet basis, 1.02 g dry basis) in defined aliquots ranging from 0.5 to 25.00 mL for a given flask. The total liquid volume in the suspension in each flask was brought up to 50 mL, which included the water initially in the wet pulp.

### pH Isotherm Experiments

Competitive adsorption of $Na^+$ and $Ca^{+2}$ on bleached and unbleached wood pulps were conducted as a function of pH using the apparatus shown in Fig. 1. The 250 mL vessel was constructed of glass and the Plexiglass headplate was sealed to the vessel with a Viton O-ring. Initially, HCl-washed pulp (15.79 g wet basis, 4.95 g dry basis) was added to 149.16 mL of 2.0 mM HCl and allowed to equilibrate to pH 2.7 at a total liquid volume of 160.0 mL. The pulp suspension in dilute HCl was then loaded into within the glass vessel and then mixed at 150 rpm for 90 min with a 2.5 cm diameter polypropylene marine blade impeller. The vessel was maintained at 25°C within a temperature controlled water bath, and the gas headspace within the sealed vessel was continuously purged with flowing $N_2$ gas (ca. 500 mL/min, 99.999% purity, less than 0.5 ppmv $CO_2$). Then, measured 3.0 mL aliquots of 25.0 mM NaOH and 25.0 mM $CaCl_2$ solutions were added simultaneously to the suspension. The suspension was continuously mixed for 90 min to achieve equilibrium. The solution pH was measured at the end of each step with a pH electrode, and a 1.5 mL sample of the aqueous phase was removed from the pulp suspension for later ICP analysis of Na and Ca concentration. The procedure was repeated to obtain 8–12 equilibrium steps of pH increasing from 2.7 to 11.0. The sodium and calcium concentrations in the aqueous phase samples were measured by ICP. Each pH isotherm experiment was repeated in triplicate. The amounts of Na (species 1) and Ca (species 2) adsorbed on the pulp were calculated from measurements of Na and Ca concentration in the solution samples using Eq. (11).

### Kinetics of Calcium Adsorption onto Na-Exchanged Bleached Pulp

The adsorption of $Ca^{+2}$ onto Na-exchanged bleached P3 pulp was measured as a function of time. The apparatus shown in Fig. 1 was used at the conditions listed in the pH Isotherm Experiments section. Initially, Na-exchanged, bleached P3 pulp (13.50 g wet basis, 4.08 g dry basis) 75.0 mL of 10.0 mmol $CaCl_2$/L solution, and 115.58 mL DI water were loaded into the glass vessel and mixed at 150 rpm to provide an initial Ca concentration of 3.75 mmol Ca/L. Liquid samples (1.5 mL) were removed at 1.0 min intervals for the first 5 min and then at 5.0 min intervals for the next 30 min. Na and Ca concentration in the liquid samples were measured by ICP.

### Titration of Pulp

The titration curve for the bleached P3 pulp fibers was measured. The apparatus shown in Fig. 1 was used at the conditions listed in the pH Isotherm Experiments section. Initially, HCl-washed, bleached P3 pulp (12.06 g wet basis, 3.57 g dry basis) was added to 166.5 mL of DI water in within the glass vessel and then mixed at 150 rpm for 60 min. Next, 2.0 mL of 0.1 M HCl solution was added to the vessel and mixed for another 30 min until the equilibrium pH of the solution in the pulp suspension was 2.8. Increments of 0.25 mL of 0.05 M NaOH solution were added in stepwise fashion to the pulp suspension to increase the pH from 2.8 to 11.2. After each incremental addition of 0.05 M NaOH, the pulp suspension was continuously mixed for 15 min. The solution pH and conductivity were then measured after each 15 min contact time. Conductivity measurements were performed with a Markson conductivity electrode and meter. Selected liquid samples (1.5 mL) were collected and analyzed for Na concentration by ICP. The amount of Na adsorbed on the pulp was calculated by material balance.

## ACKNOWLEDGEMENT

The authors gratefully acknowledge support of this research by the U.S. Department of Energy Agenda 2020 Program under Project #DE-FC07-961D13441.

## NOMENCLATURE

| | |
|---|---|
| $C_{H,o}$ | Initial concentration of $H^+$ in solution (mmol/L) |
| $C_H$ | Final concentration of $H^+$ in solution (mmol/L) |
| $C_{i,o}$ | Initial concentration of metal ion "$i$" in solution (mmol/L) |
| $C_i$ | Final concentration of metal ion in "$i$" solution (mmol/L) |
| $C'_{i,o}$ | Concentration of metal salt solution added to pulp slurry (mmol/L) |
| $F$ | Water content of pulp fibers at the fiber saturation point (mL/g dry pulp) |
| $K_{io}$ | Intrinsic dissociation constant of acidic functional groups wood pulp (mol/L) |
| $K_{app}$ | Apparent dissociation constant of acidic functional groups of wood pulp |
| $K_w$ | Dissociation constant of water at 25°C, $10^{-8}$ $(mmol/L)^2$ |
| $K^{Na/Ca}$ | Binary equilibrium constant for exchange of $Na^+$ on Ca-exchanged pulp |
| $K^{H/Ca}$ | Binary equilibrium constant for exchange of $H^+$ on Ca-exchanged pulp |
| $n_H$ | Ion exchange stoichiometry constant for $H^+$ with respect to Ca-exchanged pulp |
| $n_i$ | Ion exchange stoichiometry constant for metal ion "$i$" with respect to Ca-exchanged pulp |
| $m_p$ | Dry mass of pulp (g dry pulp) |
| $q_T$ | Concentration of carboxylate sites on pulp (meq/g dry pulp) |
| $q_H$ | Adsorbed $H^+$ on pulp (mmol/g dry pulp) |
| $q_{H,o}$ | Initial adsorbed $H^+$ on pulp (mmol/g dry pulp) |
| $q_i$ | Adsorbed metal ion "$i$" on pulp (mmol/g dry pulp) |
| $q_{i,o}$ | Initial adsorption capacity of metal ion on pulp (mmol/g dry pulp) |
| $S_i$ | Total concentration of carboxylate ($-COO^-$) sites on pulp for Donnan model (meq/g dry pulp) |
| $T_{M^+}$ | Total amount of monovalent metals in pulp suspension (mmol/g dry pulp) |
| $T_{M^{+2}}$ | Total amount of divalent metals in pulp suspension (mmol/g dry pulp) |
| $V_o$ | Initial volume of solution, L |
| $V$ | Final volume of solution, L |
| $V_{i,k}$ | Volume of metal salt solution added to pulp slurry at the $k$th incremental addition (mmol/L) |
| $\alpha$ | Degree of ionization of carboxylate acid sites on pulp (mol $COO^-$/mol COOH) |

| | |
|---|---|
| $\lambda$ | Donnan distribution constant |
| $\nu_H$ | Ion-exchange coefficient between carboxylate sites and adsorbed $H^+$ (meq/mol $H^+$) |
| $\nu_i$ | Ion-exchange coefficient between carboxylate sites and adsorbed metal ion "$i$" (meq/mol metal ion) |



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