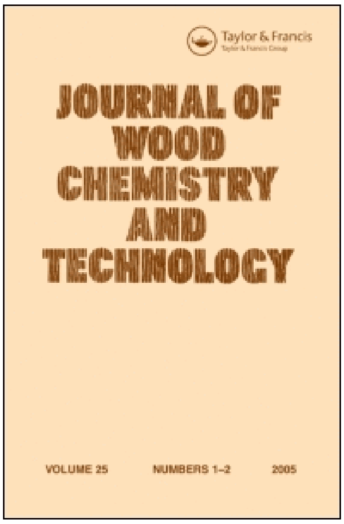

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Ion Exchange of H , Na , Mg^{2} , Ca^{2} , Mn^{2} , and Ba^{2} on Wood Pulp

Alan W. Rudie[a]; Alan Ball[b]; Narendra Patel[c]
[a] Forest Products Laboratory, USDA Forest Service, Madison, Wisconsin, USA [b] Institute of Paper Science and Technology at Georgia Tech., Atlanta, Georgia, USA [c] Madras Saravana Bhavan Restaurant, Decator, Georgia, USA

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Ion Exchange of H^+, Na^+, Mg^{2+}, Ca^{2+}, Mn^{2+}, and Ba^{2+} on Wood Pulp

Alan W. Rudie
USDA Forest Service, Forest Products Laboratory, Madison,
Wisconsin, USA

Alan Ball
Institute of Paper Science and Technology at Georgia Tech., Atlanta,
Georgia, USA

Narendra Patel
Madras Saravana Bhavan Restaurant, Decator, Georgia, USA

Abstract: Ion exchange selectivity coefficients were measured for the partition of metals between solution and pulp fibers. The method accurately models the ion exchange isotherms for all cation pairs evaluated and is accurate up to approximately 0.05 molar concentrations. Selectivity coefficients were determined for calcium and magnesium with each other and with hydrogen, sodium, manganese, and barium. Measurements made at 25°, 50°, and 65°C were used to determine the enthalpy and entropy of the reactions. The data follow the expected linear free-energy relationship. These results can be used to estimate the ion exchange selectivity coefficients for any temperature within the experimental range.

Keywords: Wood fiber, pine, ion exchange, monovalent cations, divalent cations, selectivity coefficients

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Address correspondence to Alan W. Rudie, USDA Forest Service, Forest Products Laboratory, One Gifford Pinchot Dr., Madison, Wisconsin 53726-2398, USA. E-mail: arudie@fs.fed.us

INTRODUCTION

Metals management in the paper industry has been around for a long time, principally to control transition metals in peroxide bleaching of high-yield pulps[1] and control of trace metal buildup in the chemical recovery process through dregs removal and periodic purging or leaching of the precipitator catch.[2,3] The recent interest in alternative bleaching chemicals and in eliminating the bleach plant wastewater stream added a new dimension to the metals management problem. New problems with metals buildup in low effluent elemental chlorine free and closed mills[4,5] have created a need for a much better understanding of metal binding in wood pulp.

There are several approaches to metals control currently employed in closed or low effluent mills. The low pH in an initial chlorine dioxide bleach stage is effective for stripping metals from the pulp. In closed mills and totally chlorine free bleaching (TCF), acid leaching and DTPA chelation have been evaluated under a variety of conditions. These methods successfully remove more than 90% of the divalent cations like manganese, calcium, and magnesium.[6] Strategies employed by low effluent mills include treating this filtrate stream to remove metals[7] or a controlled discharge of sufficient filtrate to control the metals buildup. Under some conditions, the metals remaining in the pulp after treatment can still affect bleaching efficiency and bleach plant operation.[8] Increasing the chelant dose or treatment temperature and extending the treatment time can improve metals removal efficiency to an extent, but on manganese, DTPA doses above 0.2% on pulp, treatment temperatures greater than 75°C, and treatment times beyond 30 min show little incremental gain.[9]

Key technologies required to make the closed mill effort successful are improved and cost-effective metals removal from wood pulp and bleach plant filtrates and improved material balance models to help in engineering and controlling the low effluent mill. Accurate models of metal binding are needed so that mills and engineering firms can estimate the accumulation and distribution of metals in the process and develop solutions that prevent scale formation and bleach chemical decomposition.

Initial efforts to understand metal binding in pulp used solution equilibrium expressions to model the binding behavior.[9] Although these methods can describe the transformation from a bound state to a dissolved state at a pH around 4, they inaccurately express the concentration difference between the internal and external solutions. This produces a concentration error in the equilibrium expression whenever the stoichiometry of the competing ions is different.

Metal binding to wood pulp involves aspects of surface charge (Donnan equilibrium), concentration differences between the solution and fiber, and metal complex formation.[10] Wood pulps typically contain 50–200 mEq/kg of carboxylic acid groups.[11,12] At normal mill pHs, some or all of the acid groups are dissociated. The natural tendency for ions in solution is to diffuse uniformly throughout the solution. Where this is not impeded, it produces a balance of concentrations, ionic strengths, and charge. When one ion is restrained and at a higher concentration than the surrounding solution, complete and uniform distribution of the remaining ions would result in a charge buildup across the barrier (or inside the ion exchange material). The site of the trapped ion attains the charge of that ion and the free solution the opposite charge. Counterions are subsequently attracted to the charged particles, largely balancing the charge of the fixed ionic groups. The net residual charge is the Donnan potential,[13,14] required to maintain the higher concentration of free counterions in the ion exchange particle. So in a cation exchange particle (like the wood fibers) where the trapped functional group is an anion, the resin attains a net negative charge and the solution a net positive charge. This negative charge repels the free anions and attracts the free cations in the surrounding solution. The net result is that the particle becomes enriched in free cations and depleted of free anions. Compared to a simple solution case, the principle of uniform distribution of all constituents has been violated to maintain the charge neutrality (or near charge neutrality) of the ion exchange particle. Therefore, the fiber will collect metal cations whether there is a significant binding potential between the cation and the acid group or not.

Several problems complicate the measurement of chemical bonding in wood pulps. Principal among these is that the effective concentration of bound cations and fixed anions cannot be based on the solution volume because the fixed groups are not free to disperse throughout the solution. Furthermore, this volume is cation dependant, because cations like sodium tend to swell pulps more than calcium or acid.[13,15,16] Secondly, the bound acid group does not exist free of a charge balancing cation, at least in an analytical sense. So it becomes impossible to determine the actual chemical bond formation constants for a metal with a fixed anion because we cannot determine what fraction of a particular cation is in the fiber to balance charge and what fraction is actually bound to sites on the fiber.

Two simplified approaches to modeling the ion exchange process have been applied to wood pulps. Several authors have published reports of efforts to model the ion exchange of pulp using the Donnan theory.[17,18] In Donnan theory, an ion distributes between the internal and external solution according to the relationship:

$$\lambda = \frac{[NR]}{[N^+]} = \sqrt{\frac{[MR_2]}{[M^{2+}]}} \tag{1}$$

where NR and N^+ are the bound and free states respectively of monovalent cation N and MR_2 and M^{2+} are the bound and free states of divalent cation M. The distribution coefficient, λ, is determined experimentally for one metal pair, and according to the Donnan theory, all other cations will partition between the internal and external solutions accordingly. The strength of the Donnan theory is that it handles a wide range of ionic strengths and can largely estimate ion exchange behavior without the need for determining specific ion behaviors. However, where chemical bonding exists between cations and the functional group of the fiber, the Donnan potential and Donnan selectivity are no longer accurate.[14] Because the formation constants of typical NPEs with acetate range over two orders of magnitude,[19] this assumption is clearly not acceptable. An additional limitation of the Donnan approach is that the distribution constant λ is experimentally determined and is anything but constant. At low ionic strengths, it can vary from near 1 to 10^5. At higher ionic strengths, it may only vary by a factor of three.[16] Finally, for wood pulps, protons are not distributed according to the Donnan equilibrium.[17,18] This is because of the reason stated earlier. There is a real and significant "formation" constant for protons with the bound carboxylic acid groups on the fiber. According to Donnan theory, this chemical equilibrium needs to be accounted for in addition to the electrostatic Donnan equilibrium.[14]

SELECTIVITY COEFFICIENTS

A second approach to model ion exchange is quite similar to standard solution equilibrium theory. The chemical equation for a generalized complex formation process for divalent cation M and anion A can be expressed as follows:

$$\mathrm{M^{2+} + 2A^- \longrightarrow MA_2}$$

and

$$\mathrm{K_M = [MA_2]/([M^{2+}][A^-]^2)} \tag{2}$$

where $\mathrm{K_M}$ is the appropriate formation constant.

Similarly, monovalent metal N follows the chemical formation equation,

$$\mathrm{N^+ + A^- \longrightarrow NA}$$

and

$$\mathrm{K_N = [NA]/([N^+][A^-])} \tag{3}$$

Dividing Equation (2) by the square of Equation (3) and replacing $\mathrm{A^-}$ with $\mathrm{R^-}$ to represent the bound anion, one obtains:

$$K_N^M = \frac{[MR_2][N^+]^2[R^-]^2}{[NR]^2[M^{2+}][R^-]^2} = \frac{[MR_2][N^+]^2}{[NR]^2[M^{2+}]} = \frac{K_M}{K_N^2} \tag{4}$$

In ion exchange experiments, $\mathrm{R^-}$ is small (principle of charge neutrality) and can not be easily measured. Having it drop out of the equation is quite convenient. For the case with two divalent cations, the appropriate expression is similar:

$$K_P^M = \frac{[MR_2][N^{2+}]}{[NR_2][M^{2+}]} \tag{5}$$

This ratio is generally called the selectivity coefficient.[20] Choice of concentration units can be molarity, molality, or ionic fractions. A related concept is the thermodynamic equilibrium constant. Where swelling from electrolyte absorption is minor, this is similar to the selectivity coefficient. Two concentration conventions exist for the thermodynamic equilibrium constant, either the use of molal (or molar) activities for both the internal and external solutions or use of molal (or molar) activity for the external solution and ion fraction (or charge fraction) for the ion exchanger or internal solution.[20] The concentration convention adopted for this study is the use of ionic fraction for the ion exchange particle and molar concentration for the solution. The different formalisms give different values of the selectivity coefficient. In the case where ion fraction is used to define concentration in the ion exchanger, changes due to fiber swelling and ion activity of the internal solution are contained in the constant.[20]

The advantage of the thermodynamic equilibrium constant (selectivity coefficient) is that it can describe the metal absorption isotherms and accounts for factors such as complex formation in determining selectivity of one metal over another. As an equilibrium expression, it follows the free energy relationship: $\Delta G = RT\ \ln(K) = \Delta H\text{-}T\Delta S$. On this basis, analysis of $\ln(K)$ relative to $1/T$ should give a straight line with slope $\Delta H/R$ and intercept $\Delta S/R$. This allows estimation of selectivity coefficients at temperatures that were not measured or that are slightly beyond the convenient laboratory measurement range.

This article reports the results of the experimental determination of selectivity coefficients and Gibbs free energy relationships for the cation pairs Ca^{2+}/H^+, Ca^{2+}/Na^+, Ca^{2+}/Mg^{2+}, Ca^{2+}/Ba^{2+}, Ca^{2+}/Mn^{2+}, Mg^{2+}/H^+, Mg^{2+}/Na^+, Mg^{2+}/Ba^{2+}, and Mg^{2+}/Mn^{2+}. Use of these selectivity coefficients to model the accumulation of trace metals in a laboratory bleaching, filtrate recycle experiments,[21] and in modeling the trace metal distribution in a mill bleach plant[22] have been reported previously.

RESULTS AND DISCUSSION

Initial experiments were carried out to evaluate the time needed for the ion exchange process to reach equilibrium. No difference in bound metal was observed for 30-min and 120-min experiments carried out at room temperature, and 30 min was selected for all other experiments. Yantasee and Rorrer have reported that equilibrium is actually reached in less than a minute.[23]

In all cases, the pulp was analyzed for the bound metals. The analyzed metal content was converted to ionic fraction ($x_N = z_N m_N / \Sigma z_i m_i$) where z_N is the charge on cation N and m_N is the content of cation N in moles per unit mass. This assumes that each divalent metal accounts for two acid sites.[11] The initial analysis was carried out by plotting the $\log[NR]/[N^+]$

relative to $\log[MR_2]/[M^{2+}]$ and fitting a straight line using a least squares linear regression. The slope of the regression is the exponent of the terms on the X axis and the zero intercept is Log(K). The result for calcium at pH ranging from 1 to 7 is given in Figure 1. For this case, $K = 6.8$. The coefficient on protons is surprising. From the assumed equilibrium, the exponent on H and HR should be 2. A much better fit is obtained with an exponent around 0.67. Although less elegant than other methods,[18,24] accepting a nonstoichiometric value for the exponent adjusts for the observed deviation from theory. This result is unique to metal exchange experiments with protons; in cation competition experiments between sodium and the divalent metals, the observed exponents are close to the expected stoichiometric value.

Because the use of a linear regression on the log data minimizes the log error rather than the absolute error, and use of the intercept to obtain Log(K) incorporates considerable extrapolation error, the results of this initial analysis usually did not provide an ideal fit to the data. The final step was to manually adjust the selectivity coefficient and exponent to obtain an improved fit. Corrections for the external ion activity and free water contained in the analyzed pulps (*vide infra*) were made at this time. Minimizing the root mean squared error for the data in Figure 1 provides a best fit using an exponent on the proton terms of 0.71 with $K = 3.6$ (Figure 2). Where pulp source had little effect on the selectivity coefficients for ion exchange experiments involving pairs of trace metals, for acid (proton exchange), the exponent and selectivity coefficient varies slightly with pulp source and with temperature. Final analysis was carried out by setting the exponent to 1 and fitting the selectivity coefficient to optimize the fit at the equivalence point where both cations have a charge fraction of 0.5. The values for proton

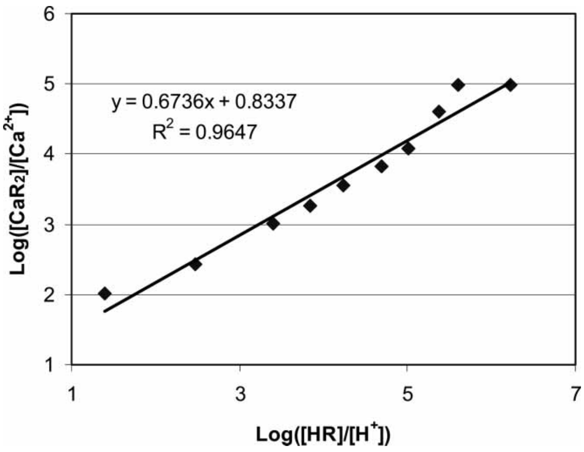

Figure 1. Log plot of the wood pulp ion exchange between Ca^{2+} and H^{+}. The ion fraction of bound protons was obtained by difference.

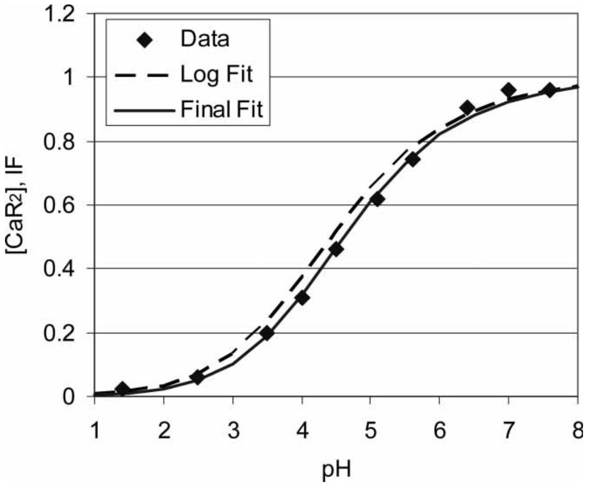

Figure 2. Adjustment of the exponent on proton terms and the selectivity coefficient to minimize the root mean squared error. Dashed curve is the result from the log plot in Figure 1. The solid line is fit to the relationship $3.6 = ([CaR_2][H^+]^{0.71})/([Ca^{2+}][H^+]^{0.71})$.

exchange listed in Table 1 were optimized in this way. For the metal competition experiments, the exponential term was fixed at the integer stoichiometric value, either 1 or 2 and the selectivity coefficient was also optimized relative to a charge fraction of 0.5.

EVALUATION OF BOUND *VERSUS* BULK WATER

In the ion exchange experiments, pulp was isolated by filtration and the resulting pads were pressed between blotters at 90 psig to minimize the amount of water dried with the pulp. In order to determine the internal or bound cation content of the fibers, it is necessary to correct for the amount

Table 1. Selectivity coefficients for calcium exchanged with H^+, Na^+, Mg^{2+}, Ba^{2+}, and $Mn^{2+}$and magnesium exchanged with H^+, Na^+, Ba^{2+}, and Mn^{2+}

	25°		45°		65°	
	Ca^{2+}	Mg^{2+}	Ca^{2+}	Mg^{2+}	Ca^{2+}	Mg^{2+}
H^+	0.75	1.01	0.6	0.8	0.5	0.7
Na^+	1.1	0.9	1.3	1.1	1.5	1.2
Mg^{2+}	5.5		3.5		2.3	
Ba^{2+}	1.6	1.45	2	1.6	2.3	1.9
Mn^{2+}	2.5	1.5	2.0	1.3	1.5	1.1

of free water remaining in the pulps collected for analysis. Several metal competition experiments were analyzed using the two extreme assumptions, either that all water behaves as bulk water or all water remaining after pressing to 90 psig behaves as bound water. The equilibrium point (where the two cations are at equal ionic fraction in the fiber) is relatively insensitive to this assumption. However, considerable error is observed at high ionic strengths with either assumption. The ion exchange experiment and initial estimate of the selectivity coefficient can be used to determine the bound water content experimentally. Using the initial estimate of the selectivity coefficient, the error between the calculated and experimental results can be used to determine how much free water was contained in the fiber, assuming the free water contains the same concentrations of cations as the bulk water. The remaining water in the fiber is then assumed to be bound water subject to anion exclusion and, therefore, contains only adsorbed and chemically bound cations. This analysis measured the average bound water content at 0.31 g/g of fiber with a standard deviation of 0.16 g/g (Table 2). This average value is similar to the amount of bound water in fibers as determined by differential thermal calorimetry (0.25 g/g)[25] and fiber saturation point as defined by Stamm (0.3 g/g).[26]

Metal Competition Experiments

Metal competition experiments were carried out at 25°, 45°, and 65°C. Two sets of experiments were conducted, one using pulp pretreated to exchange the acid groups to calcium counterions and the second using pulp treated to contain predominantly magnesium counterions. For calcium, ion exchange experiments were carried out with sodium, magnesium, manganese, and barium. For magnesium, experiments were carried out with sodium, manganese, and barium. The results of these experiments are reported in Table 1. As stated earlier, the results for calcium and magnesium exchange with acid have all been determined using an exponent on the proton terms

Table 2. Estimate of bound and free water content

Metal	Conc. (M/L)	Analysis (ppm)	Calculated (ppm)	Wet fiber (g)	Bound water (g/g)
Mn	0.01	2045	1592	2.06	0.23
Mn	0.05	4230	1689	2.07	0.15
Mn	0.5	26,250	1728	2.16	0.27
Na	0.05	2000	1389	2.11	0.58
Na	0.5	12,000	1462	2.14	0.22
Mg	0.1	2357	783	2.05	0.40
Ave.					0.31

of 1. The exponent determined by linear regression of the log data varies depending on temperature and the nature of the pulp. A value of 1 appears to be a good compromise for modeling the ion exchange relationship under most conditions and is a necessary compromise to fit the proton exchange selectivity coefficients to the free energy relationship.

An example of the equilibrium isotherm for calcium exchange with magnesium is shown in Figure 3. This graph contains the results of three separate experiments carried out on different unbleached softwood pulps over a period of two years.

As an initial test of the method, several additional cases were included in the magnesium and barium experiments. The selectivity coefficient was determined using the standard procedure with barium added to solution and displacing magnesium. In four extra experiments, both magnesium and barium were added to solution. These results are displayed in Figure 4, where the points represent the analyzed magnesium and barium content of the pulp and the line the calculated equilibrium. The triangles are the data for the added points that were not used in determining the selectivity coefficient. The selectivity coefficient successfully estimated the bound magnesium and barium.

Free Energy

The free energy relationship was determined by plotting the selectivity coefficients as ln(k) against 1/T for the three temperatures. Examples of the linear relationship for calcium exchange with acid, sodium, and barium are shown in Figure 5. A summary table of results for all the ion exchange experiments is given in Table 3.

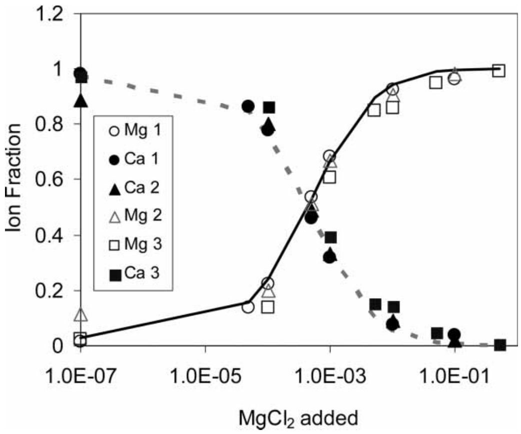

Figure 3. Results of independent wood pulp ion exchange experiments between calcium and magnesium. The experiments used three different unbleached softwood pulp sources.

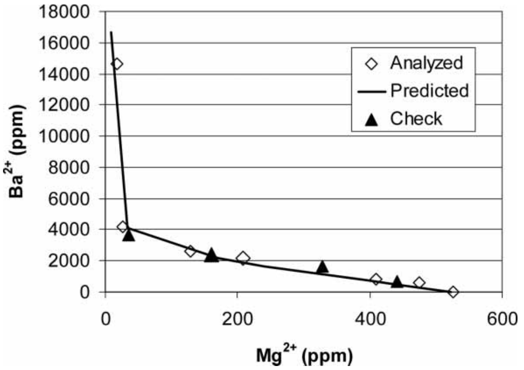

Figure 4. Fit to the experimental data. Solid line is the predicted metal content; diamonds are the experimental data used in determining the selectivity coefficient. Triangles are additional experiments to test the predictive power of the selectivity coefficient.

EXPERIMENTAL

With the exception of Figure 3, all experimental work was carried out with a 22.5 kappa southern yellow pine kraft pulp produced in the laboratory from commercial chips. Identical experiments were carried out with two commercial southern yellow pine kraft linerboard pulps and a commercial 30 kappa grade southern yellow pine kraft. All unbleached softwood pulps demonstrated nearly identical ion exchange behavior (Figure 3) with the sole difference being the variation in acid group content with degree of delignification.

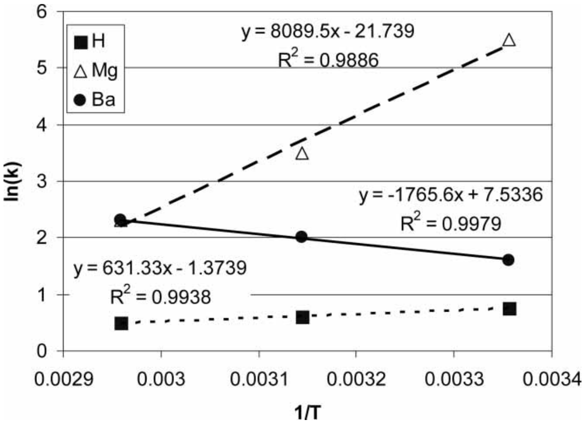

Figure 5. Free energy plots for ion exchange between calcium and magnesium, protons, and barium.

Table 3. Enthalpy and entropy determined from the temperature sensitivity of the selectivity coefficients

1st Metal	2nd Metal	ΔH/R	ΔS/R	R^2	K@297°
Ca^{2+}	H^+	1021.8	3.719	1	0.76
Ca^{2+}	Na^+	−781.2	−2.718	1	1.1
Ca^{2+}	Mg^{2+}	2194.2	5.655	1	5.6
Ca^{2+}	Mn^{2+}	1281.2	3.368	0.99	2.6
Ca^{2+}	Ba^{2+}	−917.0	−3.557	0.99	1.6
Mg^{2+}	H^+	927.2	3.113	0.98	1.2
Mg^{2+}	Na^+	−729.4	−2.357	0.96	0.9
Mg^{2+}	Mn^{2+}	778.8	2.201	0.99	1.5
Mg^{2+}	Ba^{2+}	−675.8	−2.625	0.96	1.4

Pulp Preparation (Ca Case)

Pulps were fractionated on a 100-mesh screen to remove fines. The pulp was then acid washed twice at pH 1.5 and 70°C for 90 min. The pulp was adjusted to pH 7.0 and allowed to set overnight to hydrolyze lactones. It was soaked in 0.01 M $CaCl_2$ (or $MgCl_2$) and the pH adjusted to 8.0. The metal exchanged pulp was washed thoroughly with nanopure water (Resistivity $> 17\,M\Omega$), leached overnight in nanopure water, and thickened to 20% consistency on a Büchner funnel. It was then fluffed and placed in plastic bags for storage.

Ion Exchange Procedure (Acid Exchange)

Experiments were carried out by diluting 10 g (o.d.) pulp to 1 L with either nanopure water or a solution of nanopure water containing the competing metal. The pH was adjusted to target with hydrochloric acid or sodium hydroxide and the sample was mixed for 30 min using a polypropylene stirrer. The sample was dewatered on a Büchner funnel and the pulp pad was pressed to approximately 50% consistency using a TAPPI handsheet press set for 98 psi. Pressed pulps were weighed so the metals content could be adjusted for the dissolved metals in the free water.

Ion Exchange Procedure (Metal Competition)

Metal competition was carried out by suspending 10 g (o.d.) pulp (ion exchanged to either Mg or Ca) in 1 L of nanopure water containing a known molarity of the second metal as a soluble salt. A typical set of experiments tested 5 or 6 molar concentrations ranging from 0.0001M to 0.1 M. For all experiments, the pH was adjusted to 7 with sulfuric acid or sodium hydroxide, and the suspension was stirred at room temperature for 30 min. Pulps were then filtered onto a clean Büchner funnel and pressed between blotters at 98 psig.

The metal equilibrium was determined by analyzing the trace metals in the fibers. In all experiments, the starting pulp was ion exchanged so that nearly all the anionic sites were associated with one metal (usually calcium or magnesium). This was typically the only source of that cation in the experiment. Thus the solution concentration of calcium or magnesium was determined from the loss in adsorbed calcium (or magnesium) relative to the starting pulp. The solution concentration for the competing cation was determined by subtracting the bound cation from the starting solution concentration before the ion exchange. In most sets of experiments, several filtrate samples were also analyzed for metal concentration, and these never showed significant deviation from the values estimated by difference.

Metal analysis was carried out on oven-dried pulps (105°C) that were digested in nitric acid, hydrogen peroxide, and hydrochloric acid and analyzed by ICP emission spectroscopy.[27]

CONCLUSIONS

Selectivity coefficients were calculated and used to measure and predict the partition between solution and fiber for Na, Ca, Mg, Mn, and Ba. The technique was accurate for solution concentrations up to about 0.05 molar at which point the ion concentration in solution exceeded the ion concentration in the fiber, and the fibers begin to absorb additional anions and cations in excess of the ion exchange capacity of the fiber. For the monovalent and divalent cations evaluated, the exchange stoichiometry was close to prediction based on equal anionic and cationic charges in the fiber. However, for the case of acid competition with calcium, it was necessary to adjust the exponent on bound and solution protons in the selectivity coefficient expression to obtain a good fit to the experimental data.

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