

**CLOSED MILL OPERATION: AN ANALYSIS OF COMPETITION FOR PULP BINDING SITES**

**Project F017**

**Report 1**

**to the**

**MEMBER COMPANIES OF THE INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY**

**January 13, 1998**

INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY

Atlanta, Georgia

CLOSED MILL OPERATION: AN ANALYSIS OF COMPETITION FOR PULP BINDING SITES

Project F017

Report 1

A Progress Report

to the

MEMBER COMPANIES OF THE INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY

By

Alan W. Rudie

January 13, 1998

## ABSTRACT

The ion exchange selectivity coefficient has been evaluated for determining the partition of metals between solution and pulp fibers. Under the controlled conditions of the experiments, the method accurately models the ion exchange isotherms for all binary pairs evaluated and is accurate up to approximately 0.05 molar concentrations. Selectivity coefficients have been determined for the calcium/hydrogen, calcium/sodium, calcium/magnesium, magnesium/barium, and magnesium/manganese cases. Cation saturation levels are close to what is predicted by stoichiometry, but in several cases, there is a slight - about 10% - difference between metals. It is thought that this may be caused by the formation and slow hydrolysis of lactones during the ion exchange experiments. In addition, there is evidence for different types of ion exchange sites in calcium exchange with protons and sodium. Because this only appears with the ion exchange processes comparing monovalent cations with divalent cations, a good explanation is close proximity of some acid groups resulting in a chelating effect with multivalent metals, and repression of the second pKa for the acids in the associated groups.

## INTRODUCTION

Metals management in the paper industry has been around for a long time, principally related to control of transition metals in peroxide bleaching of high-yield pulps.<sup>1</sup> The recent interest in alternative bleaching chemicals and in eliminating the bleach plant wastewater stream has added a new dimension to the metals management problem. The problem with metals buildup and inorganic scale formation on process equipment in low effluent and closed mills<sup>2,3</sup> has 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 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 manganese, calcium, and magnesium, but only about 50% of iron.<sup>4</sup> Strategies employed by low effluent mills include treating this filtrate stream to remove metals and reuse of the filtrate in the bleach plant or in brown stock washing,<sup>5</sup> 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.<sup>6</sup> 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 minutes show little incremental gain.<sup>7</sup>

Key technologies required to make the closed mill effort successful are improved and cost-effective metals removal from wood pulp, cost-effective metals removal from filtrates, and improved material and energy balances 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.<sup>7</sup> Although these methods can describe the transformation

from a bound state to a dissolved state at a pH around 4, the observed transition behavior is much slower than predicted using chemical theory for homogeneous systems. In particular, a homogeneous solution equilibrium model does not predict the residual bound metal accurately at pH values around 3 and 5 (Fig. 1).

A solution equilibrium calculation for metal binding to pulp requires solving the acid dissociation constant for the acid functional groups in pulp (generally assumed to be carboxylic acids) and the formation constant equation for the metal with the acid binding site.

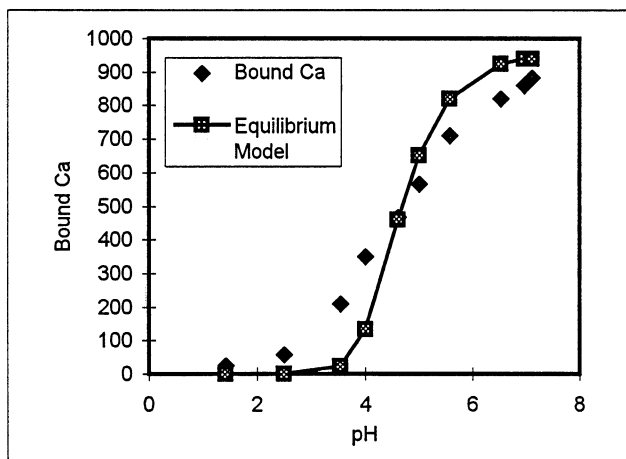
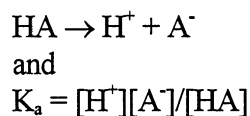


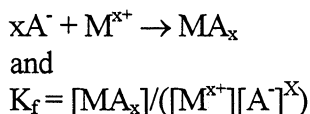
Figure 1. Solution equilibrium model for calcium binding to wood pulp.

The chemical theory for acid equilibria in homogeneous solutions generally abides by the following chemical and mathematical equations:



where  $A^-$  is the conjugate base of acid  $HA$ , and  $K_a$  is the appropriate acid dissociation constant.

The metal binding follows the chemical formation equation,



where  $K_f$  is the formation constant for the counterion with the dissociated fiber bound anion. Figure 1 shows an acid base Calcium formation equilibrium calculation using this solution equilibrium approach. Clearly this method fails to match the data near a pH of 3 and around a pH of 5.

Laine et al. claim this acid/base behavior of pulp is evidence for two different carboxylic acid functional groups, one at a  $pK_a$  of 3.3-3.5 and the second with a  $pK_a$  above 5.<sup>8</sup> The two-acid model gives a slight deflection from the experimental data at a pH around 4, so they also invoke an electrical double layer/capacitance effect to completely explain their results. The Laine approach increases the complexity and has yet to provide a credible source for the second ion exchange site, that can account for as much as 30% of the total sites.

Metal binding to wood pulp is a complex process that involves aspects of surface charge (electrical double layer), Donnan Equilibrium (concentration differences between the solution and fiber), and metal complex formation. Under most conditions, wood fibers carry a negative charge, generally attributed to the presence of acid groups in the fiber. The existence of this negative charge is the

impetus for the myriad of wet-end chemicals and surface-active agents used to improve retention and formations on the paper machine. The presence of this charge also affects metal binding, because the metal cations are attracted to the negatively charged fibers, and the higher the charge on the cation, the greater the surface attraction. The acid groups in the pulp have three major sources. The Xylan (arabino-xylan) portion of the wood hemicellulose contains side chain 4-O-methyl-D-glucuronic acids,<sup>9</sup> which have a C<sub>6</sub> carboxylic acid functional group. End groups on cellulose and hemicellulose contain carboxylic acid functional groups, and residual lignin contains a number of carboxylic acid functional groups. Typically, carboxylic acids have a pKa between 4 and 5, but this can vary significantly depending on the presence of other electron donating or withdrawing groups, and proximity to other acid functional groups. The pKa reported for glucuronic acid is considerably lower, at 3.3.<sup>8</sup> At normal mill pH's, some or all of the acid groups are hydrolyzed resulting in a negatively charged fiber. However, the principle of electroneutrality cannot be violated; the negatively charged acid sites must have associated with them an equal number of positive charges, either protons or metal cations, and the net surface charge is but a small portion of the total acid content of the fiber.<sup>10</sup> (The principle of electroneutrality does not prevent the formation of a surface charge; it simply states that the number of anionic sites and associated cations is equal within analytical limits.) Therefore, the fiber will collect metal cations whether there is a significant binding potential between the cation and the acid group or not. Furthermore, there does not have to be a direct bond between cations and the specific charge sites. If other functional groups within the fiber matrix provide a more suitable ligand, the metal will bind to it preferentially. Technically, like the various cations, the acid groups serve only to maintain electroneutrality. Specific binding sites, quantities, and preference for one cation relative to all the others are largely unknown.

In dealing with a heterogeneous system such as a wood pulp slurry, several potential problems become apparent. Principal among these is that the effective concentration of bound acid [HA] and conjugate base [A<sup>-</sup>] cannot be based on the solution volume because these functional groups are not free to disperse throughout the solution. Secondly, as stated above, the chemical entity A<sup>-</sup> does not exist on an analytical scale, it is always associated with an appropriate cation to balance the charge. For example, one does not isolate the chloride anion from chemical solutions, it is always obtained as a salt where the charge of the chloride anions is balanced by a suitable cation such as sodium or calcium. In this sense, a wood fiber is an analytical entity; it also must maintain charge balance, and the dissociated anions must be balanced by appropriate cations either within the fiber or in the electrical double layer surrounding the fiber. The difficulty this presents is that there will always be a measurable equilibrium between a metal, or protons and the fiber, but that equilibrium can be driven by the electrostatic effects, and may not represent the ability of the metal to compete against other metals for sites on the fiber.

The Donnan theory was developed to explain ion distribution across a semipermeable membrane where one or more ions were excluded because of size or membrane selectivity.<sup>11</sup> The theory can consider effects of neutral materials, dissolved ions, and salts. With salts, where complete dissociation cannot be assumed, the theory must include the use of appropriate solution equilibrium constants to correctly calculate solution concentrations and ionic strength. In the Donnan theory, one or more ionic constituents are trapped to (or in) a portion of the system. This can be caused by a semipermeable membrane, or ionic groups confined to a swollen polymer such as an ion exchange resin. The natural tendency is for each constituent 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, complete and uniform distribution of the remaining ions would result in a charge buildup across the barrier (or inside the ion exchange resin), with the site of the trapped ion attaining the charge of that ion, and the free solution the opposite charge. This charge difference is the Donnan Potential. So in a cation exchange resin (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 in the surrounding solution, and attracts the free cations in the surrounding solution. The net result is that the resin 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 resin.

A second feature of the ion exchange resin also violates the principle of uniform distribution of all ions. The resin has a fixed ionic strength, dictated by the distribution or concentration of ionic groups in the resin. Under most conditions, this ionic strength differs from that of the surrounding solution, and is often considerably higher. This typically results in diffusion of water into the resin to reduce the ionic concentration and bring it into balance with the surrounding solution.<sup>12</sup> In a typical kraft pulp, the acid content is between 50 and 100 meq/kg; on a molar basis, 0.05 to 0.1 Molar. Under typical conditions, the fiber absorbs a considerable amount of water, 1 to 2 grams of water per gram of fiber.<sup>13</sup> If the Water Retention Value is considered to be the amount of water absorbed by the fiber to dilute the ion concentration, this reduces the acid group concentration to 0.02 to 0.04 Molar. At high solution pH, the acid group content, concentration, and ion exchange behavior must also account for the phenolic contribution from lignin.

When the ionic strength of the solution equals or exceeds the ionic content of the fiber and "bound" water, the behavior of the resin changes.<sup>14</sup> At this point, there is no longer a driving force to absorb water, and the fibers begin to shrink or deswell. Also at this point, the driving force that repels mobile anions is reduced, the Donnan Potential disappears, and the fiber begins to absorb anions and cations in approximately equal amounts.<sup>13</sup>

The attraction of the resin for cations and repulsion of anions can be calculated from the Donnan Potential, which is dependent on the charge of the cations (or anions), ion exchange capacity of the resin, solution conductivity, solution concentrations, and the degree of swelling of the ion exchange resin. Multivalent counterions are attracted more strongly, and absorbed selectively over monovalent counterions. Concurrently, multivalent co-ions (ions with the same charge as the functional group of the matrix) are repelled more strongly than monovalent co-ions.

The strength of the Donnan theory is that it handles a wide range of ionic strengths, and can largely calculate ion exchange behavior from first principles, without the need for determining specific ion behaviors. The disadvantages include:

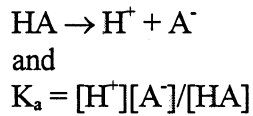
1. The calculations are based on concentrations of free ions. Where bonding exists between the functional group of the resin and cations in solution, the Donnan Potential and Donnan selectivity break down.
2. The distribution constant  $\lambda$  is experimentally determined and is anything but constant. 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 3.<sup>13</sup>
3. As concluded by Rasanen and Stenius, protons are not distributed according to the Donnan

Equilibrium.<sup>15</sup>

Recent articles by Towers and Scallan<sup>16</sup> and Rasanen and Stenius<sup>15</sup> support the Donnan theory in that the results appear to explain the differences in behavior of monovalent, divalent, and trivalent metals, but these results still have considerable error in the pH regions from 3.0 to 3.5 and around pH 5.

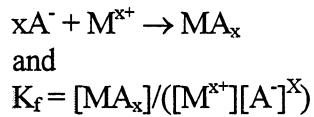
### Selectivity Coefficients

A second approach to explain ion exchange is quite similar to standard solution equilibrium theory. Using again the acid equilibrium with Ca,



where  $\text{A}^-$  is the conjugate base of acid HA, and  $K_a$  is the appropriate acid dissociation constant.

The metal binding follows the chemical formation equation,



As stated earlier, one problem with the solution equilibrium approach is that the concentration of ion exchange sites and bound cations cannot be considered as their solution concentration, but must be based on the respective concentrations or activities in the fiber. Combining the acid dissociation and formation equations and replacing  $\text{A}^-$  with  $\text{R}^-$  to represent the bound anion, one obtains:

$$K_H^M = \frac{[\text{MR}_x][\text{H}^+]^x[\text{R}^-]^x}{[\text{HR}]^x[\text{M}^{x+}][\text{R}^-]^x}$$

where the coefficient  $x$  represents the number of ion exchange sites occupied or neutralized by the metal. Usually, this will balance the respective charges, but in the case of trivalent metals, and in some cases with divalent metals, the cation can enter the fiber with associated anions and under these conditions, may account for fewer sites.

Several features of this equilibrium expression make it attractive. The term  $\text{R}^-$  drops out of the expression. Because  $\text{R}^-$  (anionic sites that do not contain a directly bound or solvated but still fiber bound cation) is small (principal of charge neutrality), it cannot be easily measured. Having it drop out of the equation is quite convenient. Secondly, for monovalent cations, the concentration basis for MR and HR becomes immaterial. This allows one to ignore bound water and exclude effects from fiber swelling. The corresponding process considering competition between two metals is

$$K_M = [\text{MR}_a]/([\text{M}^{a+}][\text{R}^-]^a)$$

$$K_N = [NR_b]/([N^{b+}][R^-]^b)$$

$$K_N^M = \frac{[MR_a][N^{b+}]^{a/b}}{[NR_b]^{a/b}[M^{a+}]}$$

where M and N are now the two metals, and a and b are their assumed valencies and corresponding stoichiometries. Although the concentration of dissociated anionic sites always cancels in this approach, the concentration issues of the bound (absorbed) and free solution ions only cancel for a = b.

This ratio is generally called the selectivity coefficient.<sup>17</sup> Choice of concentration units can be Molarity, Molality, or ionic fractions. The numerical value for the selectivity coefficient is dependent on the choice of concentration. There are two common conventions for concentration scales, use of molal scales for both the solution and resin, assuming some state for pore liquid in the resin, or using a molal scale for the solution and ionic fraction (rational scale) for the resin. Using ionic fraction for the resin simplifies the mass balance equation for the resin, and has been selected for this study. The advantages of the selectivity coefficient is that it can describe the metal absorption isotherms, and allows for factors such as complex formation in determining selectivity of one metal over another. With appropriate considerations, the selectivity coefficient can be used to determine the thermodynamic equilibrium constants for ion exchange, which should be readily incorporated in Free Energy Minimization programs for predicting equilibrium metals distributions.

The disadvantages of the selectivity coefficient are

1. The use of several concentration bases for determining selectivity coefficients makes it more difficult to use values collected from multiple sources.
2. The assumption that anions are effectively excluded from a cation exchange resin is only accurate at low ionic strength. At high ionic strength (above the nominal 0.02 Molar ionic strength of the wood fiber), all ion exchange sites can be assumed to be occupied, and the conditions that maintain anion exclusion are negated.

## EXPERIMENTAL

### Pulp Preparation (Ca Case)

Pulps are fractionated on a 100-mesh screen to remove fines, and acid washed twice at pH 1.5 and 70°C for 90 minutes. The pulp is then soaked in 0.01 M CaCl<sub>2</sub> and the pH adjusted to 7.0. The metal exchanged pulp is washed thoroughly with nano-pure water (Resistivity > 17 MΩ), leached over night in nano-pure water, and thickened to 20% consistency on a Buchner funnel. It is then fluffed and placed in bags for storage.

### Ion Exchange Procedure (Acid Exchange)

Experiments were carried out by diluting 10 OD grams of pulp to 1 liter with either nano-pure water, or a solution of nano-pure water containing the competing metal. The pH was adjusted to target with hydrochloric acid, or sodium hydroxide, and the sample mixed for the specified time period using a U-shaped polypropylene stirrer. The sample was dewatered on a Buchner funnel and the pulp pad pressed to approximately 50% consistency using the TAPPI handsheet press set for 98 psi. Pressed pulps were weighed so the metals content could be adjusted for dissolved metals.



Pulps in the calcium form were treated at various pH levels for either 30 or 120 minutes to determine the effect of treatment time on the residual metals. A third experiment was carried out in 1 M NaCl to collapse the electrical double layer, and reduce the capacitance and fiber swelling effects on metal desorption.

### Ion Exchange Procedure, Metal Competition

Metal competition was carried out by suspending 10 OD grams of pulp (ion exchanged to one of the two metals of interest) in 1 liter of nano-pure water, containing a known Molarity of the second metal as a soluble salt. A typical set of experiments tests 5 or 6 molarities ranging from 0.0001M to 0.1 molar. For all experiments to date, pulps were adjusted to pH 7 with HCl (or sulfuric acid) or TMAH, and were stirred at room temperature for 30 minutes. Pulps were then filtered onto a clean Buchner funnel and pressed between blotters at 98 psig.

Pulps were dried at 105°C; digested in nitric acid, hydrogen peroxide, and hydrochloric acid; and analyzed by ICP Emission Spectroscopy.<sup>18</sup> Filtrates were generally not analyzed, and have been calculated by difference. All metal analyses for the starting pulps and ion exchange experiments are listed in the Appendix.

### Calculations

Two procedures have been evaluated for data analysis. The wet, pressed samples typically weighed 20 to 25 grams, giving 10 to 15 grams of water still adsorbed by the fiber. One assumption is that this water has the same mineral content as the free water surrounding the fibers, so-called bulk water. For the case of removing calcium from pulp with acid, the free proton concentration is obtained from pH, and the bound proton concentration can be obtained by difference once the bound calcium is calculated (assuming charge neutrality of the fibers). If  $Ca_i$  is the initial calcium content of the fibers,  $Ca_A$  is the analyzed calcium content of the fiber,  $Ca_f$  the bound calcium content, (expressed as moles per 10 grams of fiber),  $[Ca]$  the solution concentration of calcium in moles per liter, and  $w$  the wet weight of fiber in kg. True bound calcium content can be calculated as follows.<sup>19</sup>

$$[Ca] = (Ca_i - Ca_A) / (1 - w)$$
$$Ca_f = Ca_A - (w - 0.010)[Ca]$$

With this assumption, when evaluating metal competition, both metals need to be adjusted for the adsorbed water. The calculation of the dissolved and bound concentrations of the competing metal is the same, with the exception that the initial metal content ( $Ca_i$ ) is now the number of moles of the added metal. This is not required in the acid removal experiments because the pH meter gives the activity (Molarity) of protons.

An alternative assumption is viable for the remaining water after pressing. The wet pads typically weighed between 20 and 25 grams, near the water retention value and in the same range as the typical < 7 nm pore volume of kraft pulps as measured by inverse size exclusion chromatography.<sup>20</sup> At issue is how much of this water is bound and subject to the anion exclusion effect of the negatively charged fibers, and how much is bulk water with the same concentration of dissolved ions as the surrounding solution. The water within the electrical double layer is affected by anion exclusion, and the associated metals can be considered bound. Assuming all the water is bound water and subject to anion exclusion offers the second choice for data analysis. In this case, the bound metal is the same as the analyzed metal and there is no adjustment. The solution concentrations are calculated directly by difference.

As an initial guess, acid group content was taken as the starting metal content assuming two acid groups for divalent metals. This value was normally adjusted later because initial pulps always contained other metals that could participate in the ion exchange process. For example, in the Ca exchange experiment with acids and with magnesium, the initial calcium content was 970 ppm, and 169 ppm sodium. This corresponds to acid sites of 48 meq/kg using just the calcium analysis, and 55 meq/kg using both. After the initial analysis was completed, the selectivity coefficient was used to calculate the expected bound metal contents. If the predicted equilibrium level of bound metal was below the analyzed level, the number of acid groups was adjusted to minimize the error. When this was necessary, the adjustment always required a slight increase in acid groups which never exceeded 10%.

## RESULTS AND DISCUSSION

The experiments with Ca were quite extensive and were used to establish the procedures. There was very little difference in the bound metal level between the 30-minute and 120-minute experiments, and it has been concluded that 30 minutes is sufficient for most work (Fig. 2).

In all cases, pulp was analyzed for bound calcium. Analyzed calcium was converted to ionic fraction basis by converting ppm to moles per 10 g. This value times two (to account for the charge) divided by the starting number of acid sites per 10 grams gives the ionic fraction of calcium (fraction of acid sites neutralized by calcium). Free calcium was taken as the difference between the starting calcium and measured bound calcium *vide supra*. The starting calcium in ionic fraction was 1, so (1 - the calculated ionic fraction) times the number of acid sites per 10 grams gives the amount of free calcium. Divide this by 2 to convert from equivalents to moles. Because 10 grams of pulp were used in one liter, this is the solution Molarity of the calcium. 1 minus the bound calcium ionic fraction is also the bound proton content. The solution proton content is taken directly from pH, ( $10^{-\text{pH}}$ ).

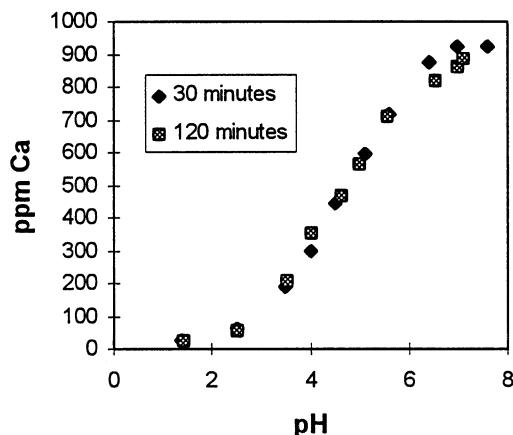


Figure 2. Evaluation of equilibration time.

The  $\log[\text{CaR}_2]/[\text{Ca}^{2+}]$  and  $\log[\text{RH}]/[\text{H}^+]$  are calculated and fit to a straight line using a least squares linear regression. The slope of the regression is the exponent of the terms on the X axis in the selectivity coefficient (a/b), and the zero intercept is Log K. The result for calcium at pH ranging from 1 to 7 is given in Fig. 3. Also in Fig. 3 is the same calculation assuming the water after pressing is subjected to anion exclusion and contains no additional metal ions. The  $R^2$  for the concentration adjusted case is 0.995, for the anion exclusion case, 0.993. This is not considered conclusive for either case. For this case,  $K_{\text{H}}^{\text{Ca}} = 30$  to 80, depending on the model used. 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 0.6 (1/1.7).

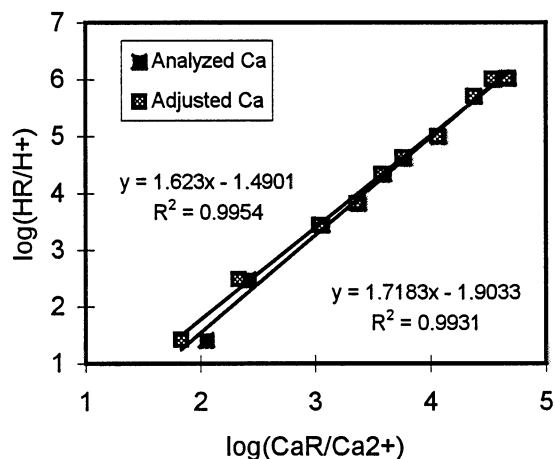


Figure 3. Calculation of log k for calcium and acid.

Because the use of the log scales minimizes the log error and extrapolation back to zero to obtain  $\text{Log}(k)$  incorporates considerable error, the results of the initial analysis were used to calculate the expected calcium under the experimental conditions. This usually did not provide the best fit to the data, and the selectivity coefficient and exponent need to be tuned manually to obtain an

improved fit. For the Calcium/acid experiment, the final exponent on hydrogen is 0.61, and the selectivity coefficient is 10. This result is shown in Fig. 4. It should be noted that use of an exponent of 0.61 will provide a similar fit to the data using solution molarities for the bound anions and cations, as well as the dissolved cations.

The experiments carried out in 0.1 N NaCl all gave less than 50 ppm adsorbed Ca. At this concentration of ionic strength, the sodium competes effectively for the binding sites and displaces calcium from the fiber.

### Evaluation of Bound vs. Bulk Water

Several metal competition experiments were analyzed using the two extreme assumptions, that all water behaves as bulk water, or all water behaves as bound water. The results for the Ba Mg exchange case are shown in Fig. 5 where the y axis gives the analyzed or adjusted bound metal concentration. Using the assumption that all water is bulk water results in a concentration adjustment that produces a negative value for bound metal at high solution concentrations. Using the assumption that all water is bound water and subject to anion exclusion produces a smooth equilibrium isotherm with a bound metal content near 1 (ion fraction).

### Metal Competition Experiments

Room temperature metal competition experiments have been completed for calcium with sodium, magnesium and barium, and magnesium with barium and manganese. These results are reported in Table 1, and the selectivity coefficient fit to selected experimental results is shown in Figures 6 through 10. One problem that has been observed in several cases is that the equilibrium metal absorption capacity of the metals are slightly different. For example, with pulp in the calcium form ion exchanged with magnesium, the initial acid group content estimated from the calcium and magnesium analysis is 47.9 mmole/kg. Estimated from the equilibrium calcium and magnesium content at 0.01 M magnesium, it is 56 mmoles/kg. None of the other metals analyzed (V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Al, Cd, Sr, Ba, Na, and K) show any significant change.

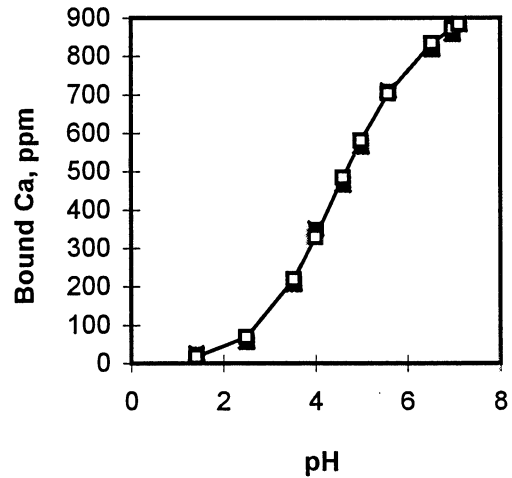


Figure 4. Bound calcium calculated relative to observed bound calcium.

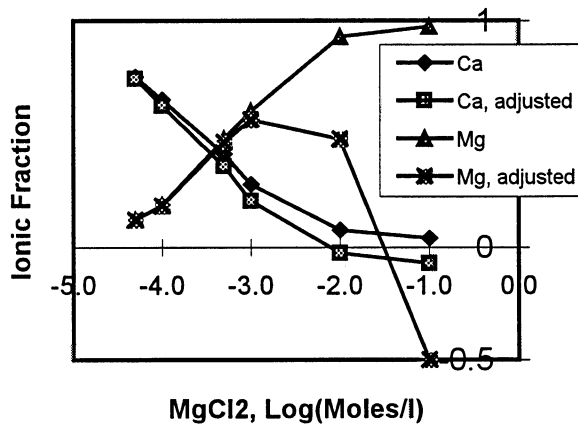


Figure 5. Mole fraction of calcium and magnesium assuming remaining water is bound, or bulk water.

For sodium exchange with calcium (Fig. 5), the initial ion exchange capacity estimated from calcium and sodium is 54 mmoles/kg, and the final ion exchange capacity is 59 mmoles/kg. This effect has been reported previously by Wilson who observed an average 8% increase in acid groups measured by calcium absorption and a 5% increase by magnesium absorption relative to the acid groups measured with sodium absorption.<sup>21</sup> Wilson's observation is credited by Ohlsson and Rydin to the use of carbon dioxide as the acid for removing the sodium, and they do not report a difference in equivalent absorption levels for sodium, magnesium, or calcium.<sup>22</sup>

Table 1. Format: horizontal is bound metal in the numerator, vertical is bound metal in the denominator. The value in brackets is the coefficient on the bound metal in the denominator.

		$M_1$					
	$k_{M_2}^{M_1}$	H	Na	Mg	Ca	Mn	Ba
	H	1			10 (0.61)		
	Na		1		10		0.5(2)
$M_2$	Mg			1	0.71	0.56	0.9
	Ca	0.1 ((1.6))	0.10	1.4	1		0.9
	Mn			1.8		1	
	Ba		2(0.5)	1.1	1.1		1

Use of CO<sub>2</sub> is not an explanation in this case because of the different technique used to estimate the acid group content. Lactone formation does offer a potential explanation. Lactones should form at the low pH of the acid treatment step used to remove metals.<sup>21</sup> They begin to hydrolyze at neutral pH, but may not hydrolyze at a fast enough rate to result in complete saturation with the starting metal.

Some evidence of this exists. In nearly all experiments, there is a significant background of sodium. Sodium is ubiquitous, and is the most likely cation to adsorb to the pulp as lactones hydrolyze and new acid groups form after the metal saturation step of the procedure. Under the low concentrations in the deionized water, it is not likely to displace divalent cations, so its presence neutralizing 10% of the ion exchange sites is most easily explained by lactone formation and hydrolysis. By the time the metal competition experiments are started, the pulp has been in a neutral condition for a minimum of 48 hours. Wilson shows lactone hydrolysis as being incomplete after 20 hours at a pH of 7.8.<sup>21</sup> Because the pulps in these experiments were neutralized to pH 7.0, and stored in the cold room at 4°C, the lactone hydrolysis would be even slower. This is consistent with a small increase in acid group content over the course of the experiments, particularly if the experiments are consistently carried out working from dilute

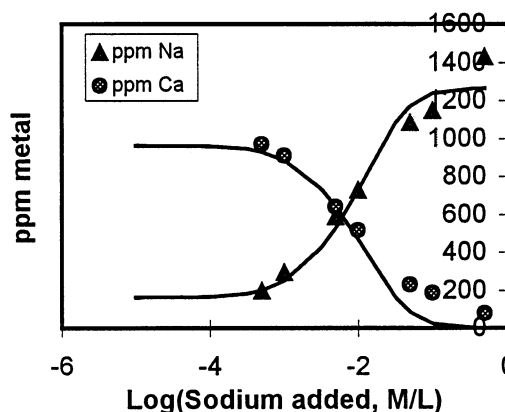


Figure 6. Replacement of calcium with sodium.

solutions to more concentrated ion exchange solutions. This has largely been the case in the reported experiments. An alternative explanation is that there are functional groups that serve as a ligand for one metal, but not for the other metal in the competition experiment. Because of ion exclusion, these functional groups must release protons on metal binding, or they will not result in an increase in sites. In the case of calcium replacement by sodium, this explanation requires that sodium have a higher affinity for the functional group than calcium. This is unlikely, and this possibility is not considered tenable in this case. It is, however, a potential source of problems with other metals.

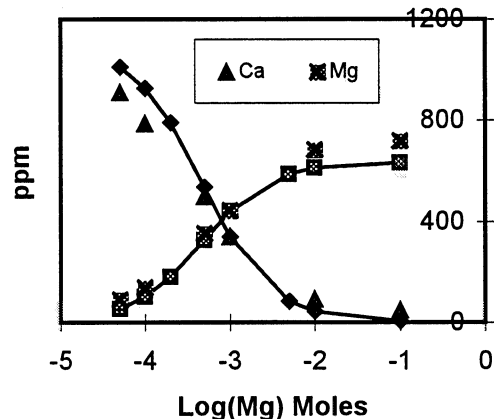


Figure 7. Calcium replacement by magnesium.

The possibility of more than one ion exchange site is, however, supported by the results of the sodium/calcium competition. In this case, the log log plot is not linear, and the fit of the experimental data to actual data in Fig. 6 is rather poor. First, as plotted, the selectivity coefficient underpredicts the calcium content at low solution sodium concentrations and over-predicts the sodium content at high solution sodium concentrations. This is the opposite of the lactone issue discussed above. Secondly, although the calculated curve fits the experimental data reasonably well at low solution sodium content, the calcium prediction is low by 150 ppm at 0.05 and 0.1 molar sodium. This has also been reported previously by both Ohlsson and Rydin for magnesium vs. sodium,<sup>22</sup> and Ampulski for calcium vs. sodium.<sup>23</sup> In the calcium/sodium exchange case reported by Ampulski, (for bleached northern kraft pulp) the thermodynamic equilibrium constant (selectivity coefficient adjusted for ion activities) drops from 52 at a cation concentration of 0.6 mmolar, to 1.3 at 0.032 molar cation concentration. It also rises from 1.3 to around 52 when the calcium ionic fraction on pulp drops below 0.1 (at the 0.032 molar salt concentration). (Note, Ampulski's values are defined in terms of equivalent fraction in both the fiber and solution and are not directly comparable to the results reported in this paper.) The results shown in Fig. 6 are similar to the high salt concentration data, showing an increase in the selectivity for calcium when the ionic fraction drops below 0.2. These results are easiest to understand in terms of different ion exchange sites. For example, two carboxylic acid groups close together have a chelating effect that would provide a stronger binding environment for calcium than would a single acid group.

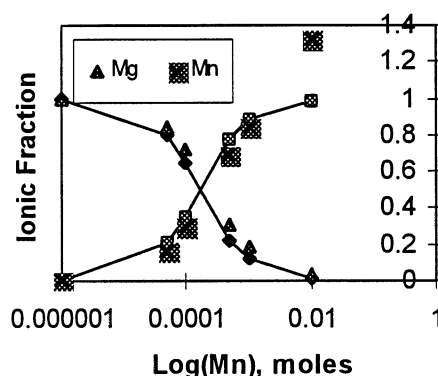


Figure 8. Magnesium replaced by manganese.

Examples of the equilibrium isotherms are given for Ca/Mg (Fig. 7), Mg/Mn (Fig. 8), and Mg/Ba (Fig. 9). For the manganese and barium cases, the y axis has been changed to ion fraction because of the large difference in atomic weights of the metals. There is little evidence of a tightly bound metal in any of these experiments, but none would be expected if the source of the stability is a chelating effect and the metals are all divalent as is the case in these experiments.

The manganese and barium exchange cases with magnesium point out a limitation of the ion exchange theory for describing the metal absorption isotherms. At high ionic strength, when the ionic strength of the bulk solution approaches the ionic strength of the fiber and bound water, anion exclusion fails and additional cations and anions can enter the fiber, exceeding the measured acid content. Unfortunately, the ionic strength of the first two stages in the bleach plant and the brownstock washers is in this range, so it is necessary to understand this effect in order to accurately predict the partition of cations between the solution and fiber in the fiberline.

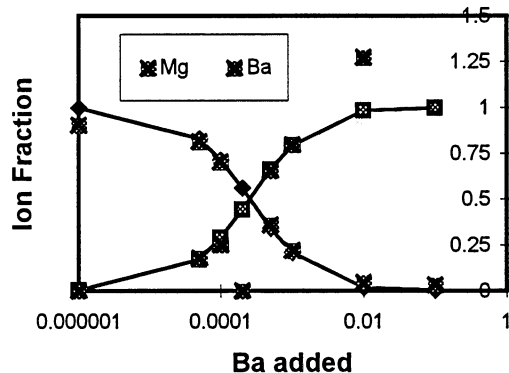


Figure 9. Replacement of magnesium by barium.

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 Fig. 10, where the points represent the analyzed magnesium and barium content of the pulp, and the straight line the calculated equilibrium. The large squares are the data for the added points that were not part of the measurement of the selectivity coefficient. The selectivity coefficient has successfully estimated the bound magnesium and barium under all conditions except solution barium contents greater than 0.01 moles per liter, where the method is known to break down.

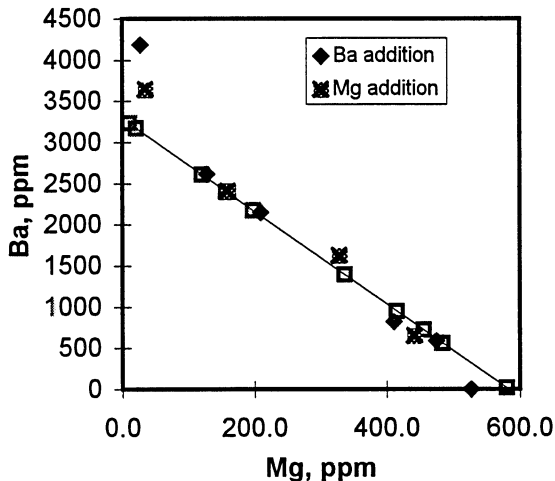


Figure 10. Fit of data to predicted concentrations is good when both metals are added.

## CONCLUSIONS

Selectivity coefficients have been calculated and used to measure and predict the partition between solution and fiber for Ca, Mg, Mn, and Ba in binary metal competition experiments. The technique is accurate for solution concentrations up to about 0.05 molar at which point the ion

concentration in solution exceeds 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 is close to prediction based on equal anionic and cationic charges in the fiber. However, for the case of acid competition with calcium, it has been necessary to adjust the exponent on bound and solution protons in the selectivity coefficient expression to obtain a good fit to the experimental data. This is thought to be due to the presence of more than one type/pKa of acid group, or acid groups in close proximity where there is an interaction that affects the pKa's. This later option also explains a deviation of the calcium exchange with sodium at low bound calcium levels. Additional research comparing the exchange of divalent with monovalent metals should provide additional albeit circumstantial evidence for this explanation.

## **REMAINING WORK**

1. Complete the metal competition experiments for the remaining metal pairs.
2. Evaluate the deviation from the equilibrium relationship at high ionic strength.
3. Evaluate the influence of temperature on selectivity coefficient, and determine the thermodynamic equilibrium constants and Free Energy for the ion exchange reactions.
4. Evaluate the influence of phenolic groups and high pH on the ion exchange.
5. Evaluate lactones as a source of the change in acid group content.

## **ACKNOWLEDGMENTS**

Technicians Alex Shaket, Narendra Patel, and Alan Ball have all contributed to the experimental work of the project and I am grateful for their effort and diligence in conducting the experiments. I would like to thank the members of the Chemical Pulping Project Advisory Committee and Dr. Earl Malcolm for periodic reviews of the project and helpful discussions in establishing and refining the experimental approach. I need to thank Dr. Paul Wollwage (Weyerhaeuser Corp.) who initially brought up the problem with lactones, and for this suggestion, I am in his debt. Funding for this project is provided by the Member Companies of the Institute of Paper Science and Technology.





0.1 17.8 14642 32.5 11.7 15.8 7E-06 0.0338 0.0011 4.922 0.0989 0.0002 2.2082 1.6968

Pulp in Mg form, exchanged with Mn

10 grams pulp, 1 liter water

Mg 526.5 mg/kg 43.333 meq/kg  
Total mono and divalent cations 47.358 meq/kg

MnCl2 M/L	Mg	Mn	Ca	Na	Fe	acid sites / liter				MgR2 Ch.frc	MnR2 M/L	MnR2 Ch.frac	[Mn2+] M/L	[Mg2+] M/L	Log(MgR/Mn) log(MgR/Mn)	
						MnCl2 M/L	MgR2 mg/kg	MnR2 mg/kg	MgR2 M/L							
0	526.5	0.664	54.5	53	8.96	0	526.5	0.664	0.0002	1	1E-07	0.0006	1E-07	1E-10	10	3.6642
5E-05	449	213	51.6	56.7	10.1	5E-05	449	213	0.0002	0.8528	4E-05	0.1791	1E-05	3E-05	4.4272	4.2037
0.0001	381.5	368.5	44.6	55.7	14	0.0001	381.5	368.5	0.0002	0.7246	7E-05	0.3098	3E-05	6E-05	4.0843	3.9742
0.0005	165.5	874	27.7	58	9.2	0.0005	165.5	874	7E-05	0.3143	0.0002	0.7348	0.0003	0.0001	3.3255	3.3336
0.001	98.85	1068	23.4	66.3	10.2	0.001	98.85	1068	4E-05	0.1877	0.0002	0.8979	0.0008	0.0002	3.0281	3.0472
0.01	15.45	1674.5	26	76.7	9.55	0.01	15.45	1674.5	6E-06	0.0293	0.0003	1.4077	0.0097	0.0002	2.1447	2.162
0.1	1	5816.5	21.4	37.6	16.8	0.1	1	5816.5	4E-07	0.0019	0.0011	4.8899	0.0989	0.0002	0.9436	1.6939

## REFERENCES

- Dick, R.H., and Andrews, D.H., "The bleaching of groundwood pulp with peroxide, the influence of certain metals on bleach response," *Pulp and Paper Magazine of Canada*, **62**(3): T-201 - T-208(1965).
- Donovan, D.A., "A review of the closed-cycle mill operating experience at Great Lakes Forest Products Limited, 1977-1985," *TAPPI Closed Cycle Mill Monograph*, TAPPI Press, Atlanta, 1994.
- O'Brien, J., "A visit to SCA Graphic Sundsvall AB Ostrand pulp mill," *Paper Age*, **112**(10): 10-12(1996).
- Bouchard, J., Nugent, H.M., and Berry, R.M., "A comparison between acid treatment and chelation prior to hydrogen peroxide bleaching of kraft pulps," *Proceedings, 1994 International Pulp Bleaching Conference*, pp. 33-39.
- Caron, J.R., and Delaney, G., "Initial learnings from the BFR demonstration," *Proceedings, 1997 TAPPI Minimum Effluent Mill Symposium*, TAPPI Press, 1997, pp. 73-78.
- Lapierre, L., Paleologou, M., Bouchard, J., and Berry, R., "The limits of metal removal from kraft pulp by acid treatment," *Proceedings, 1996 International Pulp Bleaching Conference*, pp. 515-517.
- Bryant, P.S., and Edwards, L.L. "Manganese removal in closed kraft mill bleach plants," *Tappi J.*, **77**(2): 137-148(1994).
- Laine, J., Buchert, J., Viikari, L., and Stenius, P., "Characterization of unbleached kraft pulps by enzymatic treatment, potentiometric titration and polyelectrolyte adsorption," *Holzforschung*, **50**(3): 208-214(1996).
- Timell, T.E., "Wood Hemicelluloses: Part 1," *Advances in Carbohydrate Chemistry, Vol 19*, Wolfrom, M.E., ed., Academic Press, New York, 1964, pp. 247-300.

10. Helfferich, F., *Ion Exchange*, Dover Publications, Inc., New York, 1995, pp 7 and 267. (Note, this is a republication of the original English text published by McGraw-Hill Book Co. Inc., New York, 1962.)
11. Helfferich, F., *Ion Exchange*, Dover Publications, Inc., New York, 1995, p. 135.
12. Helfferich, F., *Ion Exchange*, Dover Publications, Inc., New York, 1995, pp. 100-102.
13. Grignon, J., and Scallan, A.M., "Effect of pH and neutral salts upon the swelling of cellulose gels," *J. Applied Polymer Science*, **25**: 2829-2843(1980).
14. Helfferich, F., *Ion Exchange*, Dover Publications, Inc., New York, 1995, p. 217.
15. Rasanen, E., and Stenius, P., "The sorption of Na<sup>+</sup>, Ca<sup>++</sup>, Mg<sup>++</sup>, and Mn<sup>++</sup> on cellulose fibers: prediction and analysis of sorption equilibrium with electrostatic models," *Proceedings, 1997 International Symposium of Wood and Pulping Chemistry*, 94-1-5(1997).
16. Towers, M., and Scallan, A.M., "Predicting the ion exchange of kraft pulps using the Donnan Theory," *J. Pulp and Paper Science*, **22**(9): 332-337(1996).
17. Helfferich, F., *Ion Exchange*, Dover Publications, Inc., New York, 1995, pp. 153-154.
18. Procedure based on a nitric acid, hydrochloric acid, hydrogen peroxide digestion procedure from Solid Waste 846, method 3050.
19. Note, this estimate is accurate to about 1%. More correctly,  $[Ca] = (Ca_r - Ca_f) / (1 - w + 0.01)$ , and the concentrations are determined by simultaneous solution of the two equations.
20. Berthold, J., and Salmén, L., "Effects of mechanical and chemical treatments on the pore size distribution in wood pulps examined by Inverse Size Exclusion Chromatography (ISEC)," *J. Pulp and Paper Science*, **23**(6): J245-253(1997).
21. Wilson, K., "Determination of carboxyl groups in cellulose," *Svensk Papperstidning*, **69**(11): 386-390(1966).
22. Ohlsson, A., and Rydin, S., "Washing of pulps, Part 2. The sorption of Na, Mg and Ca on kraft pulp," *Svensk Papperstidning*, **78**(15): 549-522(1975).
23. Ampulski, R.S., "the equilibrium for the Na/Ca ion-exchange reaction on bleached northern softwood kraft pulp," *Nordic Pulp and Paper Research Journal*, **4**(1): 38-41(1989).



