

## THE EXCHANGE AND REMOVAL OF THE METAL CATIONS IN PULPS

**G.V. Laivins and A.M. Scallan**

Pulp and Paper Research Institute of Canada  
570 Blvd. St. Jean, Pointe Claire, Quebec H9R 3J9

### ABSTRACT

Metal cations modify the optical and mechanical properties of pulps and in pulp mills can have adverse effects on such parameters as corrosion rate and recovery furnace temperature. With today's emphasis on recycling effluents and on tighter control of all operations, there is a need for quantitative theory predicting the uptake of cations by pulps and the build up of cations in process liquors.

A variation of the Donnan Equilibrium Theory was recently developed to describe the partitioning of cations between the fibres and the liquor in a pulp suspension [1]. In this report we extend use of the theory to examine the ion-exchange of pulps from saturation with one cation to saturation with another. Theoretical predictions are closely duplicated by experiments using sodium, magnesium and lanthanum as model cations of different valencies. Pulps readily exchange cations even with very dilute solutions, preferentially taking up and most tenaciously holding the higher valency cations. Consequently, the replacement of high valency cations by monovalent cations requires higher concentrations of the replacement ion than for the reverse exchange. The differing tenacities by which cations are held are also shown during acid washing of pulps. Upon progressively lowering the pH of a suspension of pulp in mixed ionic form, monovalent, divalent and trivalent cations are successively released and replaced by hydrogen ions. The implication of these results for the "acid washing" of pulps is discussed.

1. Towers, M. and Scallan, A.M., *Predicting the Ion-exchange of Kraft Pulps using Donnan Theory*, J. Pulp and Paper Sci., Sept. (1996).

## INTRODUCTION

The papermaking properties of pulps are sensitive to the nature of the metal ions that they contain. The tensile strength, for example, is enhanced the lower the valency of the metal ions, and this may be understood from a knowledge of the effects that the metal ions have on the swelling and hence the plasticity of the fibres (1). The ions are for the most part held within the fibre walls as counter-ions of the acidic groups and, in order to study their effects on a laboratory scale, it is often necessary to ion-exchange a pulp from the mixture of counter-ions usually present to one particular ionic form. On an industrial scale, ion-exchange is not normally done deliberately but can occur incidentally on exposure of fibres to pulping liquors, bleaching liquors and wash waters.

The metal cation composition of a pulp can affect its response to chemical reactions such as bleaching. In the case of bleaching by hydrogen peroxide, for example, some ions such as iron and manganese are detrimental while others such as magnesium are beneficial (2). The roles of the ions in bleaching are interpreted in terms of their interference with the chemistry of decomposition of the reagent. Prior to bleaching on either a laboratory or industrial scale, it is often required to remove certain cations from a pulp and this is again often done by ion exchange. A frequent approach to remove detrimental cations (and incidentally all other cations) is to wash the pulp with mineral acid. This converts the weak carboxylic acid groups from the salt form to hydrogen form, thus releasing the metal counter-ions and permitting them to enter the wash water.

While the general principles of ion-exchange are understood, the procedure is applied in a qualitative way. Pulps are exposed to arbitrary concentrations of a salt or an acid for a certain time and are then washed. No attempt is made to predict the extent of exchange and this remains largely unknown until measured by chemical analysis. Without guidance from theory, it is probable that excessive quantities of chemicals are applied and these require washing away. In the case of an exchange with acid, a low pH combined with a high temperature can damage the fibres by acid hydrolysis (3).

Lack of a quantitative handling of ion-exchange has been the result of the absence of a general yet readily-applicable mathematical treatment of the phenomenon. This however has changed recently with the publication of papers based on Donnan Equilibrium Theory in which a sound but simple solution of the equations is given which is applicable to systems containing ions of multiple valencies (4,5). In this paper, we will use this theory to examine the ion-exchange of a pulp from one ionic form to another paying particular attention to cases where there is a valency change and cases in which the objective is ion removal by acid washing. The theory is tested by experiments involving model mono-, di- and tri- valent ions. These are sodium, magnesium and lanthanum. Lanthanum was chosen because, at this stage of investigation, we wished to examine how a simple trivalent element behaved and not to complicate matters with the more complex chemistry of such elements as iron and aluminium.

## **THEORY**

The condition for a Donnan Equilibrium to exist is that at least one ionic species within an aqueous system is confined to only one part of that system. Water-swollen pulp fibres have an ionic nature coming from the dissociation of acidic groups that are chemically bound to the lignocellulose gel within the fibre walls. These acidic groups are not, of course, present in the solution external to the fibre wall. Thus, in a suspension of pulp fibres, there exists the fundamental condition for a Donnan Equilibrium. Under the acidic to weakly alkaline conditions considered in this paper, the dissociating groups are the carboxylic and sulphonic acids.

The principal feature of the Donnan Equilibrium is that the presence of the bound ionized groups causes an uneven distribution of every mobile ionic species between the fibre-wall solution and the external solution. This takes place according to a single distribution constant ( $\lambda$ ). However, the nature of the dependence of a particular ion on  $\lambda$  varies with the charge and valency of the ion. Thus, in a system such as we will study, containing different valency cations but only monovalent anions, the basic description of the Donnan Equilibrium is:

$$\lambda = \frac{[H^+]_f}{[H^+]_s} = \frac{[M^+]_f}{[M^+]_s} = \sqrt{\frac{[M^{2+}]_f}{[M^{2+}]_s}} = \sqrt[3]{\frac{[M^{3+}]_f}{[M^{3+}]_s}} = \frac{[I^-]_f}{[I^-]_s} \quad (1)$$

where H represents the hydrogen ion,  $M^+$ ,  $M^{2+}$ ,  $M^{3+}$  represent any mono-, di-, or tri- valent cation and  $I^-$  represents any monovalent anion. The brackets  $[ ]_f$  and  $[ ]_s$  denote the concentrations of the species present inside the fibres and in the external solution respectively. The equation has some interesting features. The ratios of ionic concentrations for all monovalent cations are equal to one another and to a constant  $\lambda$ . The ratios of ionic concentrations for all divalent cations are equal to one another and to  $\lambda^2$ . For the anionic species similar relationships exist but the inverse ratios are involved. Clearly, if one calculates the distribution constant ( $\lambda$ ) for a given set of conditions, it is possible to determine the distribution of every mobile ionic species between the fibre-wall solution and the external solution.

While Equation 1 expresses the Donnan Equilibrium in its best known form, the equation usually needs manipulation in order to obtain a form which can be applied to a specific application. In recent papers (4,5), it was shown that by taking into account the other chemical equilibria and mass balances which must be satisfied, Equation 1 could be transformed into an expression for the distribution constant in terms of the measurable parameters of a pulp suspension. The expression expanded to include trivalent cations is:

$$\frac{3(\lambda^4-1)}{V+F(\lambda^3-1)} \sum M^{3+} + \frac{2(\lambda^3-1)}{V+F(\lambda^2-1)} \sum M^{2+} + \frac{(\lambda^2-1)}{V+F(\lambda-1)} \sum M^+ + (\lambda^2-1) \cdot [H^+]_s - \sum \frac{\lambda(C_i/F)K_i}{\lambda[H^+]_s + K_i} = 0 \quad (2)$$

where  $V$  = total volume of water in the suspension (L/kg),

$F$  = water content of the fibre wall (L/kg),

$\Sigma M^{3+}$  = total amount of trivalent cations in system (mol/kg),

$\Sigma M^{2+}$  = total amount of divalent cations in system (mol/kg),

$\Sigma M^+$  = total amount of monovalent cations in system (mol/kg),

$C_i$  = amount of type  $i$  acidic groups in pulp (mol/kg), and

$K_i$  = dissociation constant of type  $i$  acidic groups (mol/L);

all the quantities in these definitions being expressed on the basis of a kg dry weight of pulp.

Initially appearing to be complex, the equation is readily derived and breaks down to a term for each group of cations of the same valency, a term for the hydrogen ion concentration and a term for the acidic groups. Obviously, if cations of a particular valency are not present, the corresponding term in the equation reduces to zero. Once substituted with appropriate values of the parameters, the equation is solved for  $\lambda$  by numerical means (6).

Having determined  $\lambda$ , the concentrations of any metal cation within the fibre wall can be calculated from the total amount of the cation in the system, use of the Donnan ratios (Equation 1) and mass balance considerations as shown previously (4).

To permit comparisons of the cation content of a pulp with its acidic group content, the results of all cation contents will be presented in meq/kg dry pulp. This is obtained by multiplying the concentration of ions in the fibre wall found by the above calculations (meq/L) by the water content of the fibre wall (L/kg). The result would be the equivalent of the cation content of the fibres if they were drained just free of external liquor and then, with only the water within the fibre wall remaining, they were oven dried.

## EXPERIMENTAL

### Pulps

The starting material for most experiments was an unbleached kraft pulp of 48% yield produced from black spruce wood. A chemi-mechanical pulp (CTMP) also from black spruce wood was used for one experiment that is reported.

The carboxylic acid group content of the kraft pulp was 106 meq/kg dry pulp as determined by conductometric titration (7). Using the same procedure, the carboxylic and sulphonic acid group contents of the CTMP were found to be 96 and 195 meq/kg, respectively.

### **Preliminary Ion Exchanges**

Prior to the study of the kinetics of ion exchanges, samples of pulp were converted to different cationic forms by arbitrary procedures previously established (8). In the light of the findings of the present study, it is clear that concentrations of reagents used for some of these initial exchanges were unnecessarily high.

The hydrogen form of a pulp was prepared by diluting the pulp to 0.5% consistency with 0.1 M hydrochloric acid and stirring for 30 min. The suspension was drained and then washed several times with deionized water. This acidification and washing was repeated once more.

The magnesium form of a pulp was prepared from the hydrogen form by treatment with 0.1 M magnesium chloride at 0.5% pulp consistency and sufficient sodium hydroxide to raise the pH to 9. Following extensive washing with deionized water, the pulp was found to contain 98 meq/kg magnesium and a negligible amount of sodium.

The sodium form of a pulp was prepared from the hydrogen form by merely adding sufficient 0.1 M sodium hydroxide to neutralize the acidic groups in the pulp sample.

Finally, the ion-exchanged pulps were filtered to high consistency and flakes of the pulps were allowed to air-dry for ease of weighing and handling.

### **Fibre Saturation Points**

The levels of swelling of the kraft pulp (fibre saturation points or FSPs) were determined by the solute exclusion procedure using dextran, with a molecular weight of  $2 \times 10^6$ , as the excluded molecule (9). The swelling of

the pulp, as reswollen from air-dry form, was found to be 1.15, 1.10, 1.00 and 0.77 L/kg (water/solid) in sodium, magnesium, lanthanum and hydrogen forms respectively. In theoretical calculations of ion exchange, the average FSP of original and target ionic forms was assumed to be a sufficiently accurate value for all stages of the exchange.

### **Ion-exchange Studies**

In a typical experiment, a 5 g (oven-dry weight) sample of air-dry pulp in suitable ionic form was dispersed in about 300 mL of deionized water in a 1 L polyethylene jar. Next, an aliquot of the target metal cation (in the form of sodium chloride or hydroxide, magnesium chloride, lanthanum nitrate or hydrochloric acid) was added, followed by sufficient deionized water to bring the total volume of water in the suspension to 500 mL. The suspension was stirred for 30 min using a plastic coated impeller and was then filtered to separate a sample of the external solution. On the filtrate, sodium and magnesium were determined by atomic absorption and lanthanum by ICP emission spectrometry. The concentration of cation found in the external solution ( $[M^{n+}]_s$ , meq/L) was then coupled with the total amount of the metal ion initially present to calculate the cation content of the water-swollen fibre wall which, in terms of meq/kg dry pulp, is given by the expression  $\{M^{n+}-(V-F) \cdot [M^{n+}]_s\}$ .

For each ion-exchange process studied, a series of such experiments was carried out in which the amount of the target cation was varied.

## **RESULTS AND DISCUSSION**

The objective of this work was to examine how well the Donnan Theory predicts the progress of ion-exchange of pulps from one pure ionic form to another. Each procedure examined had therefore an experimental and a theoretical aspect and, although the details of these are given in the Theoretical and Experimental sections, it would seem fitting to summarize them prior to presenting the results.

Many of the parameters of the experimental procedure were kept constant throughout this work. Thus, for most experiments, the starting material was

5 g of the same unbleached kraft pulp. To the pulp, known aliquots of metal salts or hydrochloric acid were added before dilution to a final volume of 500 mL. Once equilibrium was established, a sample of the external liquor was isolated and analyzed. From the measurement, the cation contents of the fibres were calculated.

Following a series of experiments examining the partitioning of an ion for different levels of addition, the parameters of the experiments were substituted into Equation 2 for evaluating  $\lambda$  and thence the theoretical amount of each ion within the fibre walls. The basic parameters entering Equation 2 were  $V = 100$  L/kg,  $C = 0.106$  mol/kg,  $K_a = 10^{-4}$  mol/L. The level of swelling used,  $F$ , was the average of the swelling levels of the initial and final cationic forms. It is an indication of the power of the theory that all theoretical lines in the figures are from such basic calculations - they are not "fits to the experimental data". Equation 2 is most directly applicable to examining the effect of progressive acidification. For other types of ion exchange, additional calculations are required; these will be discussed as they arise.

### **Introduction of Cations into Pulps**

Figure 1A shows the ion-exchange of the pulp from hydrogen to sodium form resulting from a series of experiments in which increasing amounts of sodium hydroxide were added to the pulp in hydrogen form. This exchange is important as it occurs during the titration procedure used for the determination of the acidic groups in pulps (7). Due to this importance and the simplicity of the system in terms of the limited number of types of ions present, the exchange has already been subjected to investigations involving the Donnan Equilibrium (10,11).

Since both the total amount of sodium and the hydrogen ion concentration in the system change during the addition of sodium hydroxide, Equation 2 may not be applied directly. However, the term for sodium may be substituted out of the equation. First, the total sodium may be taken out by use of an expression based on mass balance considerations:



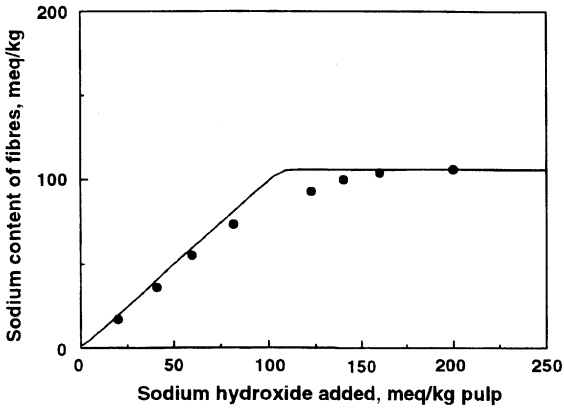


Figure 1A. Conversion of stock pulp from hydrogen to sodium form. Points refer to experimental results and curves to theoretical calculation.

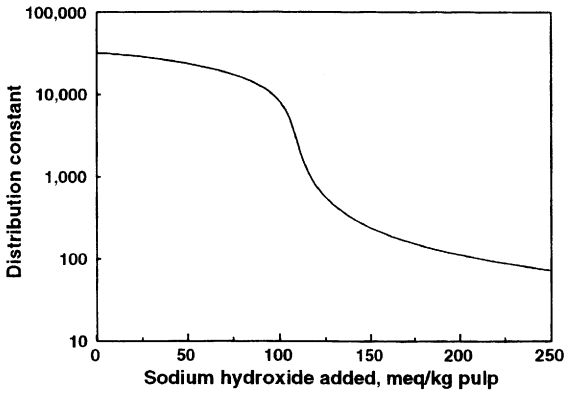


Figure 1B. The theoretical value of the distribution constant,  $\lambda$ , accompanying the exchange from hydrogen to sodium form.

$$[M^+]_s = \frac{M^*}{V + F(\lambda - 1)} \quad (3)$$

where  $[M^+]_s$  is the concentration of sodium in the external solution. Then, we may use the following equation based on the condition of electrical neutrality in the external solution:

$$[M^+]_s + [H^+]_s = [OH^-]_s \quad (4)$$

The final equation for  $\lambda$  is as follows and is identical to that previously derived for this particular case (10):

$$\frac{(\lambda^2 - 1)K_w}{[H^+]_s} - \sum \frac{\lambda(C_i/F)K_i}{\lambda[H^+]_s + K_i} = 0 \quad (5)$$

where  $K_w$  is the ionic product of water. Finally, having found the distribution constant at a given pH, it is used in conjunction with Equations 1, 3 and 4, to back calculate the sodium in the fibre wall and the sodium hydroxide necessary to achieve the postulated pH. A series of such calculations provided the theoretical curve in Figure 1A.

At the start of titration, the distribution constant is very high and virtually all added sodium ions enter the fibre-wall (Figure 1B). Once the amount of sodium hydroxide added is of the order of the acidic group content of the pulp and these groups are neutralized, then the value of  $\lambda$  begins to drop and the additional alkali largely enters the external solution. This leads to a plateau region in sodium retention by the fibres which gives the plot the appearance of a Langmuir isotherm. Several authors have remarked upon this, discussed their results on ion retention by fibres in terms of "adsorption" and indeed have applied a Langmuir type equation to their data (12-16). We believe such an approach is misleading since the tendency is then to think in terms of a mechanism of adsorption onto surfaces rather than of a Donnan Equilibrium between a gel and an external liquid. As we will show a number of times in this text, the plateau levels of retention of ions correspond to the number of ions required to satisfy the acidic groups. On the other hand there is no direct evidence of the association of ion retention with the formation of a monolayer.

### Changing the Cationic Form of Pulps

The application of the theory to exchanges of a pulp from saturation with one metal cation to another may be illustrated with the interconversion of sodium and magnesium forms. The experimental pH we observed in these experiments was in the range 7 to 10. In this pH range and in the presence of appreciably quantities of other ions, pH has only a minor influence on  $\lambda$ . For theoretical calculations, a fixed pH of 7 and a fixed quantity of the original cation were introduced into Equation 2 which was then evaluated at a series of increasing addition levels of the target cation.

Figure 2A shows the loss in sodium and gain in magnesium within the fibre-wall following addition of 120 meq/kg of sodium hydroxide to the hydrogen-form pulp and then the addition of increasing amounts of magnesium chloride. A feature of the plot, throughout low addition levels, is that the total number of equivalents of sodium and magnesium cations associated with the fibres remains constant as previously noted by other workers (17). The total number of equivalents of cations corresponds to the number of carboxylic acidic groups. Thus, the magnesium cation appears to satisfy two ionized acidic groups and not just one "because of its inability to span between acidic groups". This is in agreement with the earlier conclusion of Sjöström et al. (18). Thus, rather than thinking of an acidic group as satisfied by a particular cation, it is better to consider all the acidic groups collectively satisfied by a soup of cations. Going from moderate to high addition levels of magnesium chloride results in a build up of magnesium ions inside the fibres beyond the number of ions required for neutralization. In this region of high ionic strength, the Donnan Equilibrium is becoming a less significant effect, i.e., the value of  $\lambda$  is close to unity and the added cations accumulate at similar rates in the interior and exterior solutions.

The replacement of the monovalent sodium ions by a divalent cation such as magnesium is relatively easy; the exchange is 80% complete when the ratio of the number of equivalents of magnesium cations added is equal to the acidic group content. Thus, the pick up of magnesium ions by the pulp is almost stoichiometric in these experiments and, indeed, a variation of

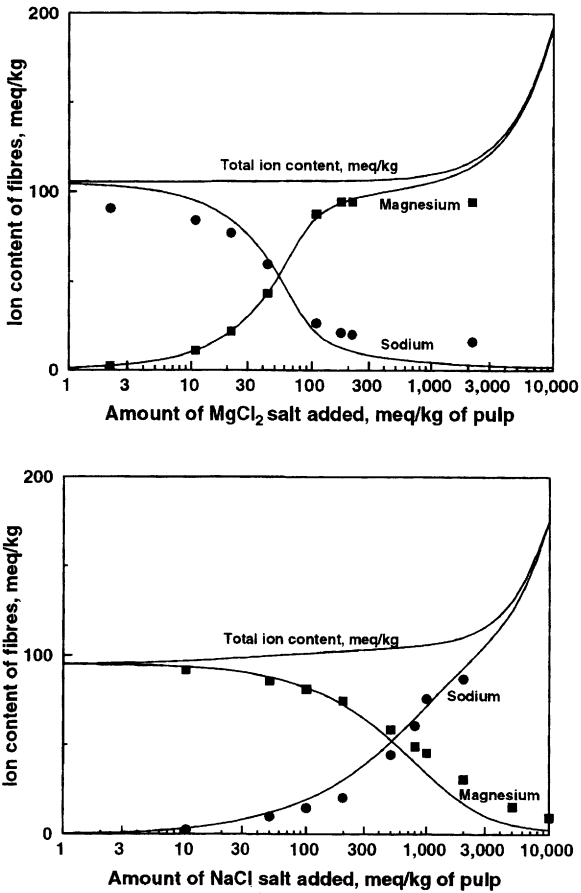


Figure 2A and 2B. Interconversion of sodium and magnesium forms of pulp with experiment (points) closely following theory (curves). While the process is reversible, higher addition levels of sodium are required to displace magnesium from the pulp than for the reverse process.

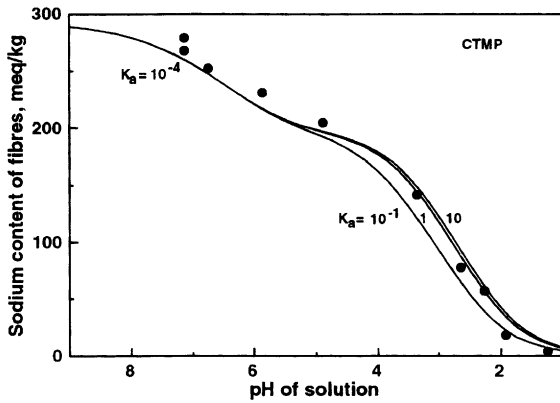
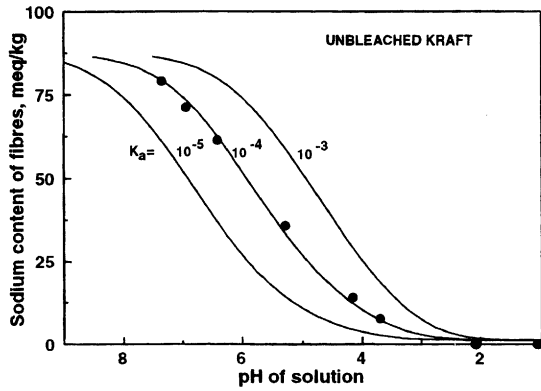
magnesium ion exchange has, in the past, been used to determine the acidic group content of pulps (19).

Figure 2B shows the reverse exchange resulting from the addition of sodium chloride to the pulp in magnesium form. As is seen, both theoretical and experimental results are similar in form to Figure 2A as the lower valency cation replaces the higher valency one. However, a striking difference is the range of salt addition over which the exchange of ions occurs. For a given degree of exchange, the magnesium/sodium exchange requires addition levels which are more than an order of magnitude higher. In other work, we have observed that sodium may even replace lanthanum but this time even higher concentrations are required. The preference of pulps to retain different valency cations originates from the nature of the Donnan Equilibrium (Equation 1) and the direct, square root or cube root dependency on the distribution constant ( $\lambda$ ).

### **Removal of Sodium Ions by Acid Washing**

Figure 3A shows the exchange of the unbleached kraft pulp from sodium back to hydrogen form using hydrochloric acid. Initially  $\lambda$  is very high and virtually all the sodium is within the fibre wall. As the pH of the pulp suspension is brought down, the bound acidic groups start to protonize,  $\lambda$  falls and the fibres release sodium ions into the external solution. It is seen that the experimental behaviour of the ions closely follows predictions particularly when a dissociation constant for the acidic groups of  $10^{-4}$  mol/L is assumed. This is in agreement with the value proposed by others (14,20).

A special type of pulp of interest at the moment is chemimechanical pulp and the removal of metal ions from this pulp prior to peroxide bleaching can be important. Chemimechanical pulps possess sulphonic acid in addition to carboxylic acid groups. Since the Donnan theory is readily adaptable to considering any number of types of acidic groups, we extended our investigation to the removal of ions from a CTMP. Figure 3B shows the change in the amount of sodium in the fibre-wall of a sulphite pulp with acidification. For the theory, the experimentally determined carboxylic and sulphonic acid contents of 96 and 195 meq/kg were used



Figures 3A and 3B. Displacement of sodium from the sodium forms of an unbleached kraft (3A) and a chemimechanical pulp (3B) by acidification. Experiments (points) so closely follow the predicted trends (curves) that they may be used to obtain estimates of the dissociation constants of the acidic groups.

along with a dissociation constants of  $10^{-4}$  for the carboxylic groups and various estimates for the sulphonic acid groups. These values led to a "sigmoidal shaped" curve which has been reported as typical of equilibria involving synthetic ion-exchange resins containing two ionizing groups (21). For the sulphonic acid groups the  $K_a$  appeared to lie between 0.1 and 1.0 mol/L. The release of sodium ions as the pH is lowered occurs in two stages as first the carboxylic groups and then the sulphonic groups lose their cations to the external liquor but, as is seen in the figure, the experiments, while generally agreeing with theory, did not show the inflection point quite as well. Attempts have been made in the past to base the determination of strong and weak acid contents on magnesium release versus pH (7).

Complete removal of ions from a pulp in these types of experiment cannot be effected since the removal of ions stops once the value of  $\lambda$  tends to unity and the ions become equal in concentration in the internal and external solutions.

#### **Removal of High Valency Cations by Acid Washing**

Figure 4 shows a theoretical calculation of the release by acidification of mono-, di-, and trivalent cations from a pulp in each pure ionic form. The model pulp was considered to have a carboxylic content of 100 meq/kg, a swelling level of 1.0 L/kg pulp and to contain only the specified metal cation. All the curves have similar shape but are shifted to lower ranges of pH with increasing valency. Thus, as its valency is increased, a cation shows increasing resistance to removal and, for example, by acidifying to pH 6.0, a pulp with monovalent ions would release half of its ions while a pulp in trivalent form would lose less than 10% of its ions.

While it is of interest from a fundamental point of view to consider the dislodgement of cations from a pulp in which all the cations are of the same type, pulps most often contain a variety of cations. To simulate this situation, we have produced a pulp with a mixture of cations. This was done using our stock pulp in hydrogen form to which was added first an aliquot of sodium hydroxide (100 meq/kg) to ionize the acidic groups. This was followed by aliquots of lanthanum nitrate (32 meq/kg) and

magnesium chloride (37 meq/kg). Amounts were chosen so as to attempt to produce a pulp with an approximately equal number of equivalents of each of the three cations within the fibre wall.

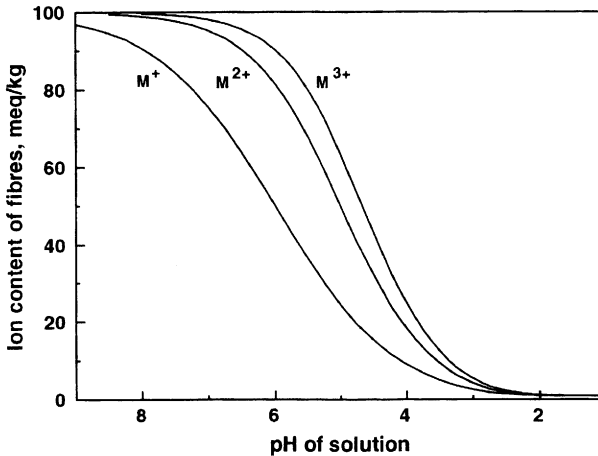
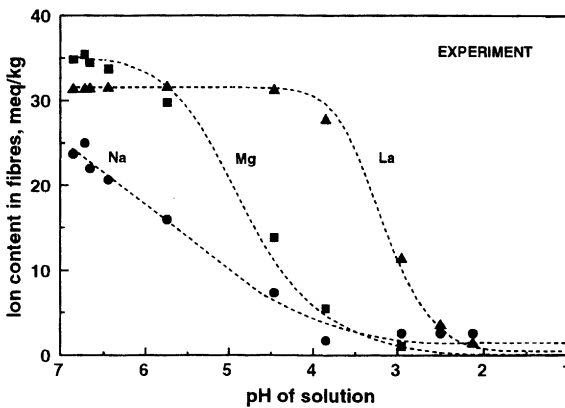
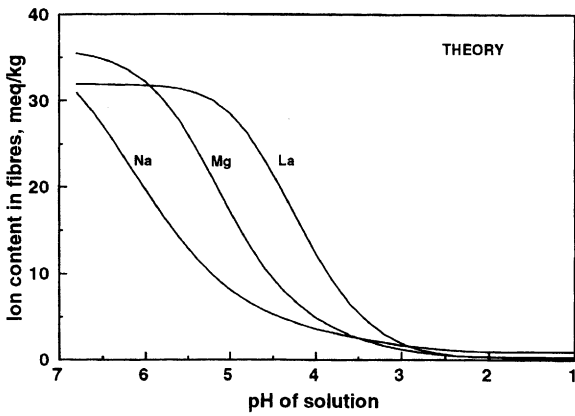


Figure 4. Theoretical plots of the acid displacement of cations of different valencies from pulps in pure ionic forms. The higher the valency of the cation, the lower the external pH required for a given degree of removal.

Figures 5A and 5B show theory and experiment for the acid induced releases of each of the three cations from the pulp. Firstly, it is observed that the attempt to introduce the three cations into the pulp in approximately equal proportions was successful. Secondly, it is seen that the shapes of the experimental curves and their ordering are in accord with theory. An obvious deviation is the release of lanthanum which appears to require a higher acidity for its removal than calculated - we have no ready explanation for this. A further feature of the plot is that at low pH, the curves for the magnesium and lanthanum drop below that for the sodium ion. This is simply due to the fact that at low pH, where there is no Donnan effect, the differing residual amounts of each cation reflect merely the differing initial amounts added to the pulp suspension.





Figures 5A and 5B. Experimental observations on the displacement of a mixture of cations from a pulp by acidification follow closely predicted trends. Although there is some overlap, the cations are released in order of valency with the lowest valency cations being released first.

In a companion paper to this one, similar experiments examined the natural cation content of a kraft pulp as a function of pH and excellent agreement between experiment and Donnan Theory was observed for the simultaneous removal of sodium, calcium, magnesium and manganese (4).

## CONCLUSIONS

We have shown that the introduction of cations into pulps, their exchange to other species and their removal by acidification closely follow the predictions of Donnan Equilibrium Theory.

An understanding of the removal of ions by moderately acidic solutions is provided by the theory - the basic phenomenon affected by pH is the dissociation of the acidic groups which in a kraft pulp appear to have a  $pK_a$  of 4. At sufficiently low pH (pH 2), the acidic groups are not dissociated and the basic condition for a Donnan Equilibrium does not exist; the cations are then equal in concentration in internal and external solutions. Since there is generally a large excess of the latter, most of the cations are then outside the fibres. In a batch-type operation where the objective is to remove ions, the external liquor should then be drained away. Fresh acid liquor should be added to bring about another equilibrium and draw more of the residual ions out of the fibre. Washing with water following an acid treatment and filtration can be less effective than expected as it may lead to re-entry into the fibre wall of some ions from the residual wash water due to a rise in the pH. Finally, it should be said that the theory presented is for metals in ionic form. If the metal is not in a soluble ionic form then it will not behave as we have described - there are indications that iron is such a metal and is not always readily removed by acid washing (22).

## ACKNOWLEDGEMENT

The authors wish to thank J. Sfigakis for the careful experimental work he carried out in connection with this paper.

**REFERENCES**

1. Scallan, A.M. and Grignon, J., The Effect of Cations on Pulp and Paper Properties, *Svensk Papperstidn.*, 82(2), 40 (1979).
2. Anderson, J.R. and Amini, B., Hydrogen Peroxide Bleaching, in "Pulp Bleaching, Principles and Practice", C.W. Dence and D.W. Reeve Eds., TAPPI Press, Atlanta, p. 411 (1996).
3. Lapierre, L., Bouchard, J., Paleologou, M. and Berry, R.M., The Limits of Metal Removal from Kraft Pulp by Acid Treatment, Pulp and Paper Report No. 1191, *Paprican* (1995).
4. Towers, M. and Scallan, A.M., Predicting the Ion-exchange of Kraft Pulps using Donnan Theory, *J. Pulp Paper Sci.*, 22(9), 332 (1996).
5. Been, J. and Oloman, J.W., Electrical Conductivity of Pulp Suspensions Using Donnan Equilibrium Theory, *J. Pulp Paper Sci.*, 21(3), J80 (1995).
6. Noggle, J.H., *QuickBASIC Programming for Scientists and Engineers*, CRC Press, Boca Raton, Florida, p. 57, (1992).
7. Katz, S., Beatson, R.P. and Scallan, A.M., The Determination of Strong and Weak Acidic Groups in Sulphite Pulps, *Svensk Papperstidn.*, 87(6), 48 (1984).
8. Katz, S., Liebergott, N. and Scallan, A.M., A Mechanism for the Alkali Strengthening of Mechanical Pulps, *Tappi*, 64(7), 97 (1981).
9. Stone, J.E. and Scallan, A.M., The Effect of Component Removal upon the Porous Structure of the Fibre Wall of Wood, Part 2., Swelling in Water and the Fiber Saturation Point, *Tappi*, 50(10), 496 (1967).

10. Grignon, J. and Scallan, A.M., The Effect of pH and Neutral Salts Upon the Swelling of Cellulose Gels, *J. Appl. Polym. Sci.*, 25, 2829 (1980).
11. Scallan, A.M., Katz, S. and Argyropoulos, D.S., The Conductometric Titration of Cellulosic Fibres, in "Cellulose and Wood", C. Schuerch Ed., John Wiley, New York, p 1457 (1989).
12. Fogelberg, B.C. and Fugleberg S., A Study of Factors Influencing the Amount of Residual Alkali in Sulphite Pulp, *Paperi ja Puu*, 45(12), 675 (1963).
13. Rosen, A., Adsorption of Sodium Ions on Kraft Pulp Fibres During Washing, *Tappi*, 58(9), 156 (1975).
14. Hartler, N. and Rydin, S., Washing of Pulps: Part 1. Equilibrium Studies, *Svensk Papperstidn.*, 78(10), 367 (1975).
15. Grähs, L.E., Displacement Washing of Packed Beds of Cellulose Fibres. Part 2. Analysis of Laboratory Experiments, *Svensk Papperstidn.*, 79(3), 84 (1976).
16. Trinh, D.T. and Crotogino, R.H., Sodium Equilibrium in Kraft Pulp Washing, *J. Pulp Paper Sci.*, 13(3), J93 (1987).
17. Ohlsson, A. and Rydin, S., Washing of Pulps: Part 2. The Sorption of Na, Mg, and Ca on Kraft Pulp, *Svensk Papperstidn.*, 78(15), 549 (1975).
18. Sjöström, E., Enström, B. and Haglund, P., Ion Exchange Properties of Pulps: Part 2. Note Concerning the Reaction Between Divalent Cations and Carboxyl Groups, *Svensk Papperstidn.*, 68(6), 186 (1965).
19. Sjöström, E. and Haglund, P., Studies of Factors Affecting the Determination of Carboxyl Groups in Cellulose, *Svensk Papperstidn.*, 64(11), 438 (1961).

20. Holmbom, B., Molecular Interactions in the Wet End of Papermaking, Proc. International Paper and Coating Chemistry Symposium, p. 97, Ottawa (1996).
21. Selke, W.A., Mass Transfer and Equilibria, in "Ion Exchange Technology", F.C. Nachod and J. Schubert Eds., Academic Press Inc., New York, Chapt. 4, (1956).
22. Devenyns, J., Desprez, F., Troughton, N. and Plumet, L., Metals Control in TCF Bleaching: Implications for Kraft Bleaching Sequence Design, in "Proceedings 1994 Pulping Conference", TAPPI Press, Atlanta, p. 381 (1994).

# Transcription of Discussion

## **The Exchange and Removal of the Metal Cations in Pulp**

*Anthony M Scallan, Principal Scientist, Paprican, Canada*

*Arthur Ragauskas, Associate Professor, IPST, USA*

Have you a comment on an adjacent issue that is frequently mentioned in the bleaching literature that there are tightly bound ions and that if you take them out of solution and put them back in they are not bound in the same way?

*Tony Scallan*

The Donnan Equilibrium Theory applies to a system when the metal salts in a system are completely ionised. If there are serious deviations from what Donnan Equilibrium predicts, then you can say that there is something else happening other than complete ionisation such as a complex formation or a precipitate. We have made pulps in completely aluminium form and taken all that aluminium out with sodium chloride. You can almost do the same thing with ferric iron. However, with practical pulps there are occasions when some of the metals won't shift. Sodium and calcium will always move but you can get resistant iron and aluminium and it must be that they are present in some other form other than an ionised salt. For example you can have a trace of clay which will give you aluminium content without any ions.

*Dr Theo van de Ven, Director, Paprican/McGill, Canada*

It looks as though at the end of the experiment after exchanging calcium to magnesium and then magnesium by sodium, you have more sodium than at the beginning can you explain this?

*Tony Scallan*

Yes, I assume you are referring to Figures 2A and 2B where to the right of these figures we have added a large amount of electrolyte and the concentration in the wall goes way up. Actually, when you have a large amount of electrolyte you squash the Donnan effect and the large amount is equally distributed between the wall and external solution. Thus the difference in pH between inside and outside can be quelled by adding a 0.1N sodium chloride; this has been recommended for many years when doing a pH titration.

*Professor Borge Steenberg, KTH PMT, Sweden*

This was absolutely the best presentation on the Donnan Equilibrium I have ever heard. I would have given the same lecture but I would have told them it is not the concentrations but the activities in the equation and that is the key problem because nobody knows the internal volume in order to be able to determine the activity coefficients. The activity coefficients of electrolytes in the outer solution are easily determined but those that are inside - we do not know what they are. This has been a standard problem in all Donnan specifications over the 66 years since Donnan got the Nobel Prize for this equation.

*Tony Scallan*

You are quite right and I am quite right. The Donnan Equilibrium may be derived from thermodynamics and you are right that one should use activities instead of concentrations. However, as I have stressed, the lines I have shown in the graphs calculated from theory, using concentrations, fit the experimental data very closely. One of the reasons could be that in the Donnan Equation you are always dealing with ratios and perhaps the constants to convert concentrations to activities cancel out to some extent.

*John Waterhouse, Senior Associate Scientist, IPST, USA*

The water content of the cell wall is going to change due to the osmotic stresses that are generated, but I think you used an average value. What kind of changes are you getting?

*Tony Scallan*

As we change the pH or we change the amount of salt in these experiments the fibre saturation point will change somewhat and, we often know to what extent. But it would just complicate the situation to make corrections. What I am showing you here is the result of taking an average value and it is sufficiently good. Taking a corrected value for each pH would be more laborious but would improve the agreement between theory and experiment.

*Peter Englezos, Associate Professor, University of British Columbia, Canada*

When we calculate activity coefficients they are indeed non ideal . However, the non ideal model agrees very well with your ideal model and there are several reasons for that. We have presented a paper at CPPA meeting in Whistler this Spring, you have to use activity coefficients starting from the electro chemical potential but the model is such that the predictions of the ideal and the non ideal model are in the end exactly the same.