METAL CATIONS

Retention mechanism of metal cations in recycled and never-dried pulps

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ABSTRACT

Linerboard and never-dried kraft pulp were used in cationic soaking experiments. Chloride salts of calcium, sodium, and barium were added to the slushed pulps. Pulps were dewatered, and the water samples were analyzed for metals content with inductively coupled plasma (ICP). When the cation levels were compared, barium showed a much higher concentration in the pulp than did calcium and sodium. Apparently, the cations are retained by an ion-exchange mechanism.

Application:

Optimize washing steps to maintain the strength properties of recycled fiber.

METAL CATIONS OCCUR NATurally in wood, and they can be added inadvertently during the papermaking process. Even in trace amounts, metal cations can affect paper properties *(1, 2)*. Changes in virgin fiber quality, the movement to chlorine-free bleaching, and the increased use of recycled fibers have focused attention on the effects that metal cations have on many paper grades *(2)*.

Multivalent cationic metals reduce fiber swelling by compressing the electrostatic double layer *(1)* or by lowering the osmotic pressure arising from cationic movement *(2)*. The loss in swelling hinders bonding and leads to a weaker sheet. A better understanding of the mechanism for cation retention would help in the effort to reduce the quantity of metal ions and improve paper strength.

MECHANISMS RETENTION

Some metal cations affect the tensile strength properties of paper more strongly than do others. Metal cations undermine paper strength by degrees, depending on which metal cations are at work. If the effects could be isolated, each species of metal cation would impact the sheet strength as follows, in going from the weakest sheet to the strongest sheet *(2, 3)*: $Fe^{3+} > Al^{3+} > H^{+} > Ba^{2+} > Mg^{2+} > Ca^{2+} > NH_4^{+} > Na^{+}$. In other words, iron has the greatest effect on tensile strength, and sodium is the least detrimental.

In an aqueous medium, metal cations are retained in pulp by one of two mechanisms. In one mechanism, the metal cations are exchanged with acidic functional groups; in the other, molecular complexes are formed.

Ion exchange mechanism

Potential sites for ion exchange include carboxylic acid groups, phenolic acid groups, and lignosulfonic acid groups. Kraft pulps contain carboxylic acid and phenolic acid groups, while sulfite pulps also have lignosulfonic acid groups. In general, the exchange can be represented by Eqs. 1 and 2:

$$R\text{–}COOH \leftrightarrow R\text{–}COO^{-} + H^{+} \quad (1)$$

$$R\text{–}COO^{-} + M^{+} \leftrightarrow R\text{–}COOM \quad (2)$$

The following expression defines the acid dissociation value K:

$$K = [R\text{–}COO^{-}][H^{+}]/[R\text{–}COOH] \quad (3)$$

The range of K varies depending on the nature of the organic R group. For carboxylic acid groups, the constant K commonly falls in the range of 10^{-3} to 10^{-4}, while the value is 10^{-9} for phenolic groups. Thus, carboxylic acid groups dissociate at pH 3–4, while phenolic acid groups do not dissociate at a pH lower than 9. Consequently, within the papermaking pH range of 4.5–8.5, the carboxylic acid functional groups are dominant in providing the sites for ion-exchange.

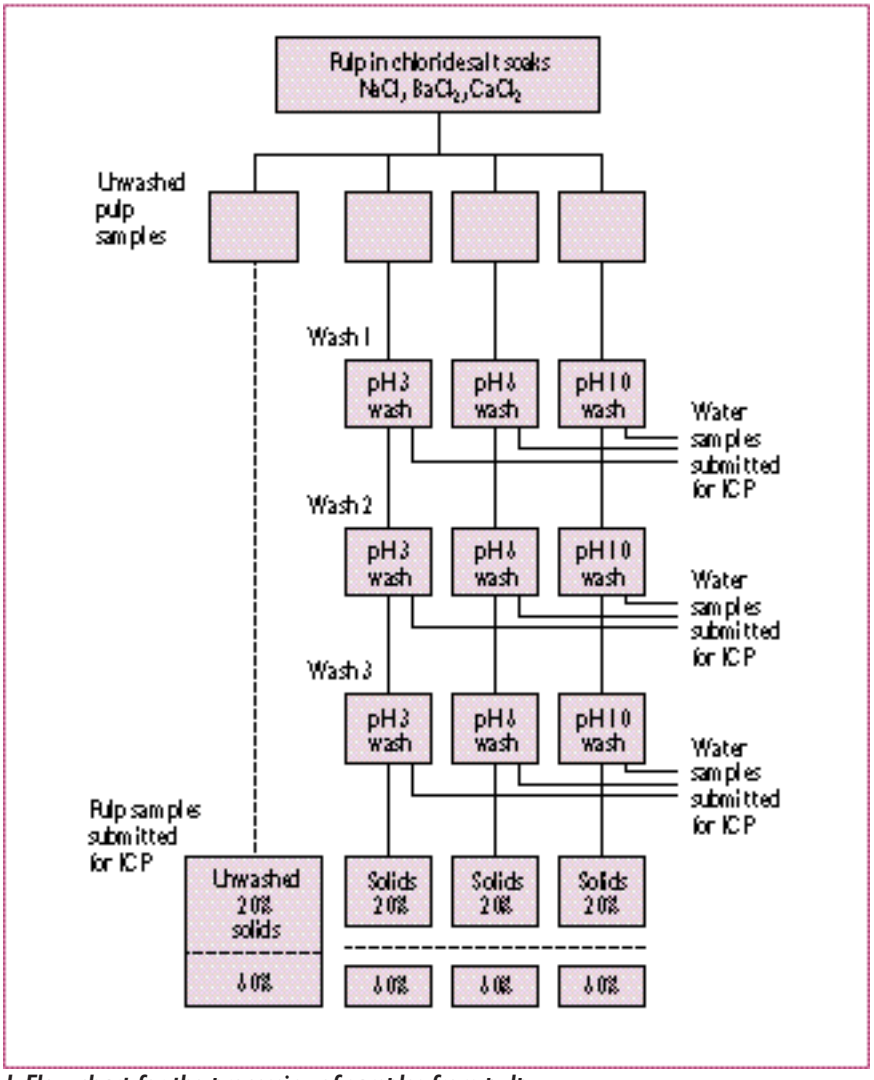
The number of carboxylic acid ion-exchange sites that are available varies in wood chips, in different pulps, and in the same pulp at different kappa numbers. The number of sites has been measured at pH 8 in previous studies *(1, 2)*.

Complex formation mechanism

Multivalent metal cations may also form complexes within the pulp. A pulp with complexed cations requires a lower pH for deionization than do pulps with ion-exchanged cations. The reason is that the complexes are more tightly bonded than the ion exchangers. Although adjusting the pH is effective in removing ion-exchanged cations, an entirely different chemistry is often more effective in removing complexes.

BACKGROUND

Aluminum and calcium are cations commonly found in paper. Aluminum is a trivalent cation known to form complexes in pulp *(4)*. At pH 4.4–4.8, it forms a polynuclear species that bonds more tightly than an ion-exchanged cation. Aluminum is added at noticeable levels in the



1. Flow chart for the processing of samples from pulp

wet ends of many paper machines, and the result is a high cation content in the paper in ensuing cycles.

Calcium, a divalent cation, is often present in the paper machine wet end as part of the mill water system. Calcium bonds to the pulp as an ion-exchanged cation. Significant recycled fiber content decreases paper strength. The presence of cations is one reason that paper made from recycled fibers forms a weaker sheet *(3)*.

There are other reasons that paper made from recycled fibers is weaker than paper made from virgin fibers. During the drying of first-generation papers, fiber hornification occurs as the fiber walls shrink and form internal and external hydrogen bonds. In water, paper made from hornified fibers loses strength as a result of less bonding. The fibers never fully swell to reverse the effects of hornification. Some reports indicate that the addition of hydroxide ions to a pulp slurry causes the fibers to swell and recover much of the original bonding potential of the virgin fibers *(5–8)*.

Freeland studied the effect of caustic soaking treatment on the strength properties of recycled paper *(5)*. His study included the effects of different cations associated with the hydroxide. Handsheets were formed after treatments with the various hydroxides. Barium hydroxide led to the weakest sheet, ammonium hydroxide gave rise to a sheet of intermediate strength, and sodium hydroxide treatment led to the strongest sheet.

In addition, barium seemed to remain with the pulp at much higher concentrations than would have been expected by the mechanism of ion-exchange with acidic groups. Freeland measured the barium to have remained in the pulp at a concentration of 7870 ppm. A possible explanation for the apparently high barium content is the formation of complexes. We attempted to reproduce those results and expand upon them to elucidate the interactions between barium and pulp.

EXPERIMENTAL PROCEDURE

Two pulps were used in the cation soaking experiments: linerboard and never-dried kraft pulp that consisted of hemlock and fir. The linerboard pulp had a kappa number of 85, and the kraft pulp had a kappa number of 35. These two pulps were used to illustrate any contrasting effects caused by differences in hornification or variation in kappa number.

To avoid possible interactions with preexisting cations, both pulps were washed with sodium hydroxide, hydrochloric acid, and ethylene diamine tetraacidic acid chelation treatments to remove trace metals and generate cation-free pulps. **Figure 1** shows the flow chart by which we processed the samples from each pulp. The cation-free pulps (30 g oven-dry weight) were soaked for 20 h in 2.5 L of separate barium, calcium, or sodium chloride salt solutions at 2 mmol/L. After the soaks, pulps were dewatered. The pulps were either left unwashed or treated with triplicate washes. Separate samples were washed with water at different levels of pH. The washwater samples were collected and analyzed for metals content.

Pulp samples were dewatered with a Buchner funnel. A part of each sample was submitted for metals analysis, and a part of each

remaining sample was further dewatered with a Carver press before being submitted for metals analysis. Free cations not adsorbed by the pulp could be readily displaced by pressing *(9)*. Any cations that remained after pressing were bound to the pulp through the mechanism of ion exchange or the formation of complexes.

Metals analysis was performed at the University of Washington by inductively coupled plasma (ICP) with an ICAP 61E VAC system (Thermo Jarrell Ash Corp.). The pulps were prepared for ICP analysis as outlined by EPA method 3050, "Acid digestion of sediments, sludges, and soils." Nitric acid and hydrogen peroxide were used to digest the pulp, which was then refluxed with hydrochloric acid. The ICP measurements of the level of cation in unwashed pulp showed expected values when compared with previously reported data *(1, 2, 6, 9)*. Duplicate runs of washwater showed ICP measurement errors of less than 1%.

Material balances to track cation movement do not fully account for the amount of cation added to the system. **Table I** presents the material balances for cations in the linerboard pulp tested. The values shows cation levels added to pulp slurries (cation in) and cation levels leaving the system (cation out), as measured by ICP.

Of the 688.8 mg of barium charged to the system, only 464.5 mg was measured leaving the system. In the calcium soak, material balances accounted for more than 90% of the added calcium. Surprisingly, the sodium material balance showed an increase of 10% in sodium after soaking.

A source of experimental error for the barium soak may lie with the dewatering techniques. Water was removed by pulling the pulp through the Buchner funnel across a filter paper. Some barium in the water may have remained on the filter paper. This development would have decreased the amount of barium measured in washwater but would not have affected the amount of barium in the pulp.

A source of experimental error with the sodium balance appears in the data for the cation-free pulps. The pulps soaked with barium or calcium showed low, uniform levels of sodium, although no sodium was expected. This concentration accounts for most of the excess sodium, which explains the increase in total sodium. Small amounts of sodium were also added by the alkaline washing; but those amounts were relatively insignificant.

Material balances of the never-dried fibers also showed variations, as shown in **Table II**. The amount of cation remaining with the pulp appears reasonable when compared with the results of other researchers *(1, 6)*. Apparently, difficulties arose with the balances in the washwater values.

	Barium	Calcium	Sodium
Cation charged	688.8	203.2	121.9
Water out			
Soak water	245.82	131.6	90.24
Acid washwater	21	7.34	6.36
Neutral washwater	3.7	1	0.85
Alkaline washwater	3.1	1.1	1.47
Pulp out			
Unwashed pulp	50.27	14.6	11.38
Acid washed	22.25	5.21	0.33
Neutral washed	57.52	9.87	13.82
Alkaline washed	60.84	13.75	10.38
Total cation out	464.5	184.5	134.8
Difference	224.3	18.7	–12.9

I. Cation flow for linerboard pulp, mg

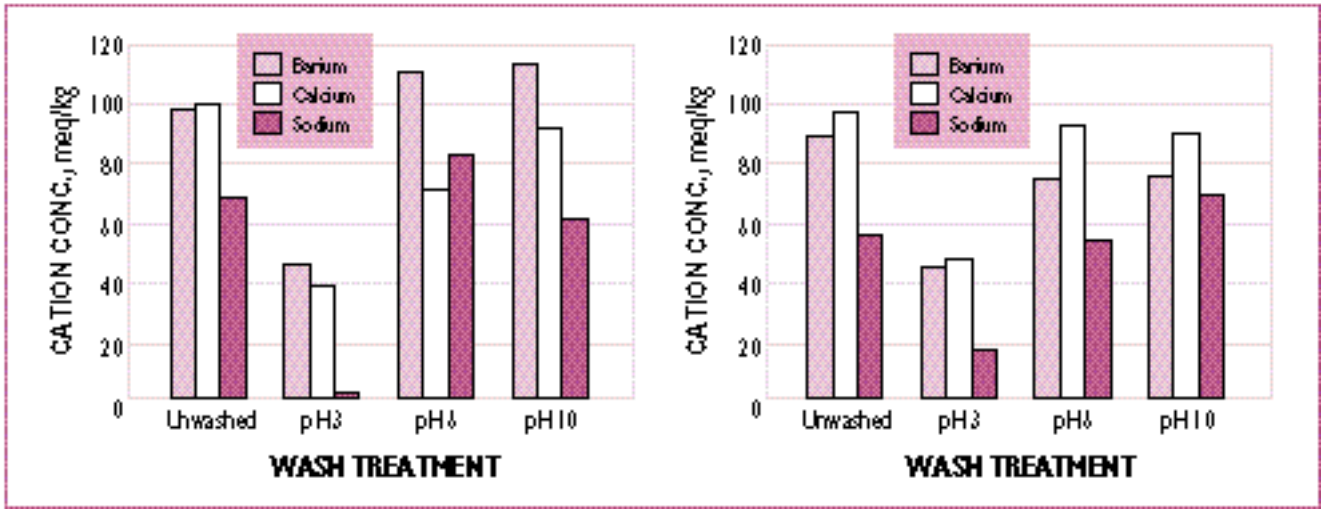
	Barium	Calcium	Sodium
Cation charged	1860	403.1	236.9
Water out			
Soak water	286.7	316.71	325.9
Acid washwater	10	2.6	4.77
Neutral washwater	12.5	1	2.46
Alkaline washwater	10.1	1.1	2.81
Pulp out			
Unwashed pulp	37.01	6.69	3.46
Acid washed	0.02	0	0.23
Neutral washed	20.77	2.93	4.88
Alkaline washed	19.02	2.33	3.64
Total cation out	396.1	333.4	348.2
Difference	1463.9	69.7	-111.3

II. Cation flow for kraft never-dried pulp, mg

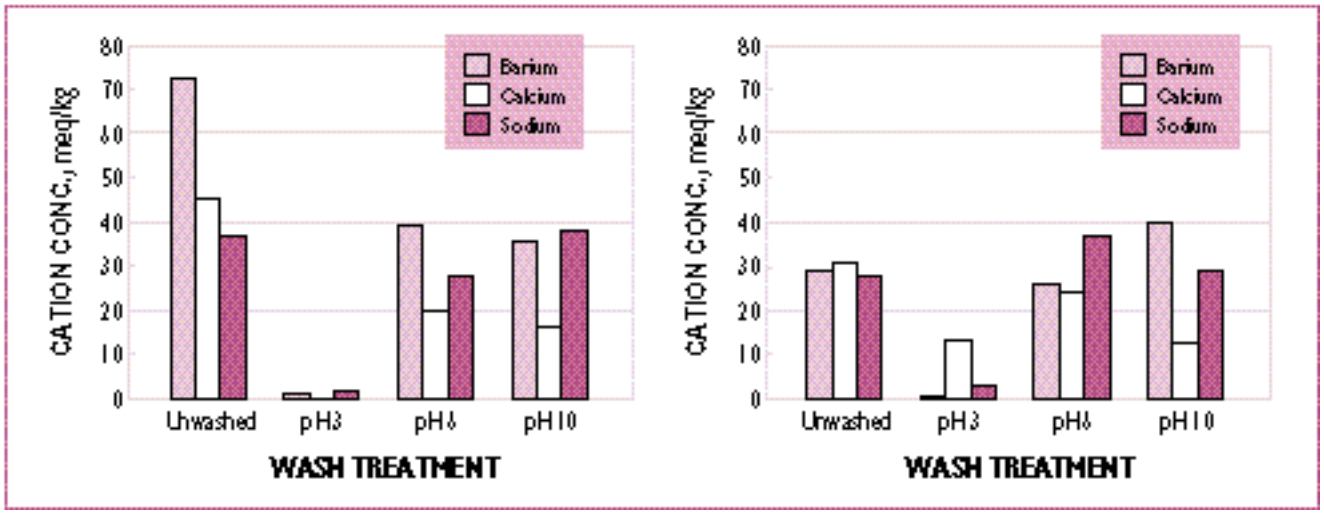
RESULTS AND DISCUSSION

Linerboard pulp

Figure 2 shows cation levels in recy-



2. Cation concentrations in recycled pulp after dewatering with a Buchner funnel (left) and after dewatering in a Buchner funnel and then the Carver press (right)

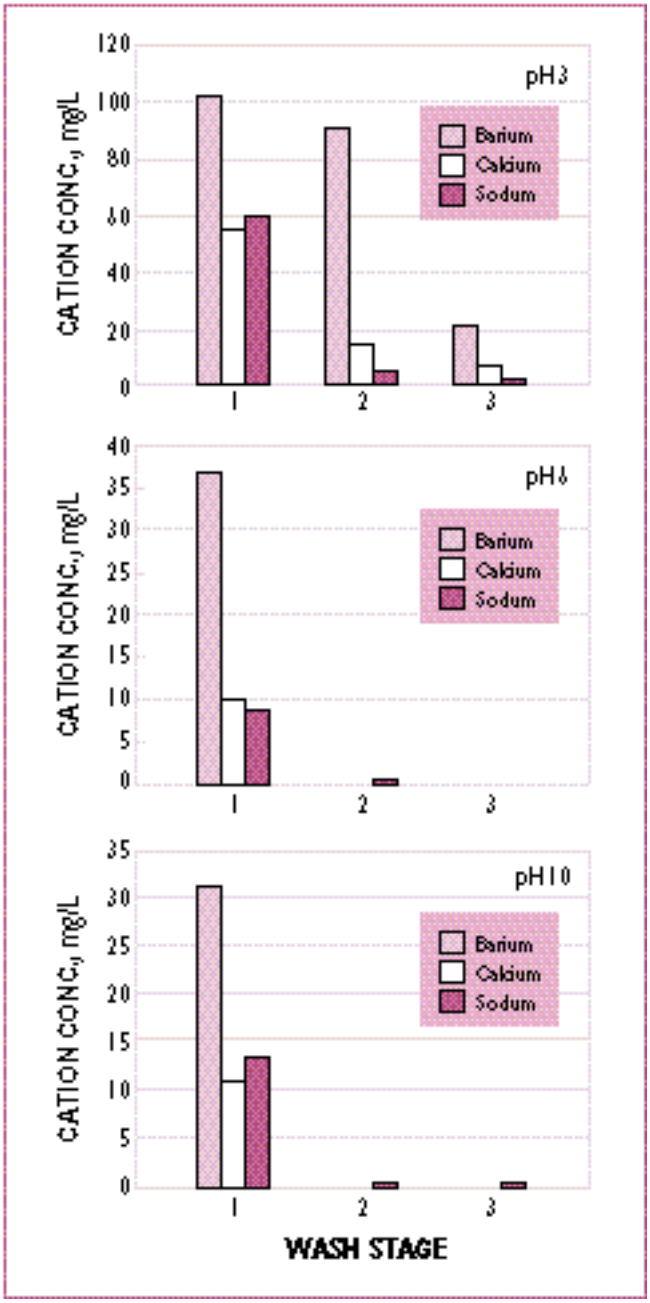


4. Cation concentrations in never-dried pulp after dewatering with a Buchner funnel (left) and after dewatering in a Buchner funnel and then the Carver press (right)

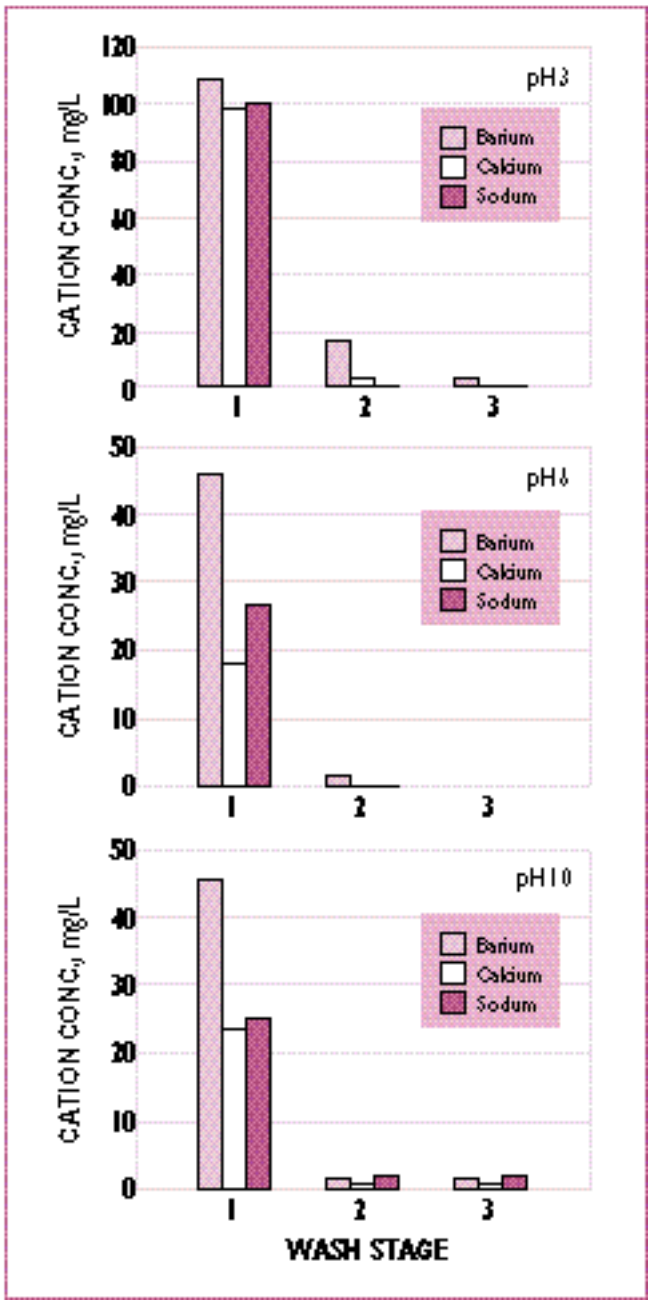
cled pulp after dewatering with the Buchner funnel in the graph on the left and after dewatering with the Buchner funnel and then the Carver press in the one on the right. The ICP measurements were converted to milliequivalents per kilogram to account for variations in particle charge and molecular weight *(2, 6, 10)*. These graphs show the cation levels in units of meq/kg. The wash treatment is indicated on the abscissa in keeping with the flow chart of Fig. 1.

In the graph on the left, for dewatering with the Buchner funnel alone, the first group of data shows that the cation levels of unwashed pulps reached 100 meq/kg. According to Lindstrom and Carlsson *(1)*, a pulp with a kappa number of 90 that is tested at pH 8 will have an acidic group content of 135 meq/kg. Pulps with higher kappa numbers tested at a higher pH have more acidic groups available. The pulp we tested had a kappa number of 85, and it was treated at a lower pH. Consequently, the available acidic group content would be somewhat less than 135 meq/kg. Sodium, the monovalent cation, adsorbed to a lower level in the pulp; it was not retained as readily as the divalent cations.

The other three data groups (at pH 3, 6, and 10) show how the variable pH of the washwater affected the cation levels. With acid washing in water at pH 3, all the pulps showed significant decreases in cation quantities. The cation levels of divalent pulps did not drop as severely as that of the sodium pulp, a result that had been observed previously *(5)*. The barium quantities did not decrease after the pulp was washed with water of pH 6 and again with water of pH 10. The



3. Linerboard pulp: cation concentrations in samples of acid, "neutral," and alkaline washwater



5. Never-dried pulp: cation concentrations in samples of acid, "neutral," and alkaline washwater

amount of calcium decreased after the washing stages at pH 6 and pH 10, while the level of sodium varied. The size of the cations may have slowed the mass transfer, which could explain why more barium remained in the pulp.

On the right side of Fig. 2 are presented the cation levels in the recycled pulps after pressing. The pulps were pressed to approximately 60% solids, which should be enough to displace free cations. The acid-washed pulps did not show a decrease in cations after pressing, because all of the easily displaced cations that may be removed by pressing had already been removed by the acid wash.

Barium-soaked pulps washed in water at pH 6 and at pH 10 showed the greatest decrease in cations after pressing. Barium cations were removed in similar quantities from both washes. Although these cations did not wash out with the Buchner funnel, they could be pressed out with excess water. Calcium-soaked pulps and sodium-soaked pulps washed in water at pH 6 and at pH 10 did not show cation decreases after pressing. This result may have been related to accessibility, meaning that smaller cations were penetrating pores more effectively than the larger barium was penetrating.

KEYWORDS
Barium chloride, calcium chloride, cationic compounds, cations, ion exchange, kraft pulps, linerboards, metals, never-dried fibers, reclaimed fibers, recycling, soaking, sodium chloride, swelling.

Or, it may be that the free cations had already been washed out.

Results of ICP analysis of cation concentrations in the linerboard pulp washwater are shown in **Fig. 3**. Aliquots of 100 mL were used in the wash sequences. The data in the top graph show the successive removals of cations after each acid washwater stage. The net amount of cation available to be removed decreased after each wash. As acid washing displaced the cations held by the pulp at ion-exchange sites, these cations showed up in the washwater.

Much less cation was removed in "neutral" and alkaline washwaters, as the middle and bottom graphs show. Cations held by ion exchange were not displaced at the pH of either of these washes. For pulp soaked with alkaline washwater, a small amount of sodium remained in the water from the sodium hydroxide used to adjust the pH.

Kraft never-dried pulp

The second raw material we considered in the cation soak treatments was a kraft never-dried pulp with a kappa number of 35. This pulp was soaked at higher concentrations of chloride salt, at 5 mmol/L rather than 2 mmol/L.

After soaking and dewatering with the Buchner funnel, the initial unwashed barium-soaked pulp sample had a barium content of 70 meq/kg, as shown in **Fig. 4**. On the other hand, calcium- and sodium-soaked pulps showed cation levels close to 40 meq/kg. Lindstrom and Carlsson suggest an acidic group level close to 70 meq/kg for pulp at a kappa number of 35 *(1)*. This value coincides with the content for barium, but the difference is substantial between the value of 70 meq/kg and the approximate value of 40 meq/kg for calcium and sodium. The difference indicates that not all of the available acidic sites are occupied by these cations.

After acid washing, practically all the cations were removed from the pulps. As the pH drops, cations at ion-exchange sites dissociate and are replaced by hydrogen ions. The "neutral" and alkaline washes also removed significant amounts of the divalent cations, barium and calcium. The amounts removed by washwater of higher pH appeared to be free cations readily displaced from the pulp. Only a slight amount of sodium was removed after the neutral wash; the amount of sodium slightly increased after the alkaline wash. After pressing, the initial unwashed pulps showed a uniform cation decrease to 30 meq/kg (Fig. 4, right graph). The cations behaved in similar fashion.

Cations were most effectively removed from never-dried pulps by acid washing, as the three graphs show in **Fig. 5**. Only a trace amount of cation appeared in the second and third washes, and virtually no cation showed up in the final pulp. Cation levels in neutral and alkaline washwaters were half as high as those in the acid washwater. Since more cation remained in the final pulp, the washes of higher pH were not effective at removing cations.

CONCLUDING REMARKS

Freeland's data showed a barium content of 7870 ppm, or 114 meq/kg. Our results showed a barium level of 6800 ppm. After applying the correction factors for weight and charge, the final barium content was 100 meq/kg in linerboard of kappa no. 85. This value lies well within the range of 75–140 meq/kg for the ion-exchange mechanism.

After the pulp was washed, barium and calcium behaved as cations that are bonded similarly. They both showed trends expected with ion-exchange bonding, in which acid washing thoroughly displaces the cations present in the pulp.

Neutral and alkaline washing had little effect on any of the linerboard pulps. When excess monovalent or divalent cation was applied to the never-dried pulp, adsorption was regulated by the available exchange sites on the pulp and the affinity of the cations for the pulp. **TJ**

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