MECHANISM OF RETENTION OF METAL CATIONS IN LINERBOARD AND NEVER-DRIED PULPS

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ABSTRACT

Even trace amounts of metal cations, which are naturally present in wood, can affect paper properties. We examined the effect of barium, sodium, and calcium on paper made from linerboard and virgin kraft fibers. Soaking the fibers in a caustic solution improved tensile and stiffness properties of the paper. Caustic soaking seems to minimize the effects of hornification by improving the fibers' capability to swell and bond. However, strength was not improved when the pulp was treated with barium cations. When the cation levels were compared on the basis of parts per million, barium showed a much higher concentration in the pulp than did calcium and sodium, possibly indicating the formation of a complex; on a milliquivalents per kilogram basis, the cations were retained in similar fashion. The cations appear to be retained by an ion-exchange mechanism.

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INTRODUCTION

Metal cations are present naturally in wood or can be added during the papermaking process. Their presence in even trace amounts can affect paper properties (1,2). Changes in virgin fiber quality and the movement to ECF/TCF bleaching along with increased use of recycled fibers have all focused attention on the quantity and effect of metal cations on many paper grades (2). Multivalent cationic metals at levels typical for many paper grades reduce fiber swelling by compressing the electrostatic double layer (1) or by lowering the osmotic pressure attained with cationic movement (2). The loss in swelling hinders bonding and leads to a weaker sheet. The cation affects tensile strength properties according to the following sequence (from weaker to stronger sheets) (2,3):

$Fe^{+3} > Al^{+3} > H^{+} > Ba^{+2} > Mg^{+2} > Ca^{+2} > NH_4^{+} > Na^{+}$

Significant recycled fiber content further decreases paper strength. Consequently, improved understanding of the mechanisms for cation retention may help achieve the maximum desired paper properties.

In an aqueous medium, metal cations are retained in pulp by two mechanisms: ion exchange with acidic functional groups or complex formation. 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

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

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

The following expression defines the acid dissociation value K:

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

The range of K varies depending upon the nature of the R-group. For carboxylic acid groups, K commonly falls in the range of 10^{-3} to 10^{-4}, while for phenolic groups the value is 10^{-9}. Thus, carboxylic acid groups dissociate at pH 3 to 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 provide the dominant ion-exchange sites. The number of carboxylic acid ion-exchange sites available in wood chips and in different pulps, including kraft pulps at varying kappa numbers, has been measured at pH 8 in previous studies (Tables I and II).

Table I. Acidic Group Content of Raw Materials[a]

Material	Acidic group content (meq/kg)	Total metals (meq/kg)
Cotton	8	8
wood chips	—	91
Refiner pulp	93	82
Kraft (66% yield)	350	271
Kraft (52% yield)	140	189
Sulfite (54% yield)	222	158

[a]Reference (2).

Table II. Acidic Group Content of Kraft Pulps With Different Kappa Numbers[a]

Percent yield	Pulp kappa number	Acidic group content (meq/kg)
—	Bleached kraft	25
47	38	74
52.8	85	—
53.5	90	135
61.8	130	155
66	145	170

[a]Reference (1).

In addition to ion-exchange bonding, multivalent metal cations may also form complexes within the pulp. Pulps with complexed cations require a lower pH for deionization than do pulps with ion-exchanged cations because the complexes are more tightly bonded than are ion-exchangers. Although pH adjustment is effective at removing ion-exchanged cations, an entirely different chemistry is often more effective at removing complexes.

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 wet end of many paper machines, resulting in 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. It bonds to the pulp as an ion-exchanged cation. The presence of cations is one reason why paper made from recycled fibers forms a weaker sheet (3).

There are other reasons why paper made from recycled fibers is weaker than sheets made from virgin fibers. During 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 strength properties of recycled paper, including the effect of different cations associated with the hydroxide (5). Results showed that barium hydroxide formed the weakest sheet, ammonium hydroxide a sheet with intermediate strength, and sodium hydroxide the strongest sheet. Similar results appear in the literature. However, barium seemed to remain with the pulp at much higher levels than expected by ion-exchange with acidic groups. It was measured to remain in the pulp at a level of 7,870 ppm. A possible explanation for the apparently high barium content is the formation of complexes. In the work reported here, we attempted to reproduce those results and expand upon them in order to describe barium and pulp interactions.

EXPERIMENTAL PROCEDURE

Linerboard and never-dried hemlock/fir kraft pulp were the two pulps used in the cation soaking experiments to contrast effects resulting from hornification and variation in kappa number. The linerboard pulp had a kappa number of 85 and the kraft pulp a kappa number of 35. To avoid possible interactions with pre-existing cations, both pulps were washed with a series of sodium hydroxide, hydrochloric acid, and EDTA chelation treatments to remove trace metals and generate cation-free (CF) pulps. Figure 1 shows the flow chart used to process samples from each pulp. The CF pulps (30 g ovendry weight) were soaked for 20 h in 2.5 L of separate barium, calcium, or sodium chloride salt solutions at 2 Mmol/L concentration. After the soaks, pulps were dewatered and either left unwashed or treated with triplicate washes. Separate samples were washed with water at variable levels of pH. The washwater samples were collected and analyzed for metals content.

Pulp samples were dewatered with the Buchner funnel. A part of each sample was submitted for metals analysis, and a part of the 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 either water associated with the pulp, complex formation, or an ion-exchange mechanism.

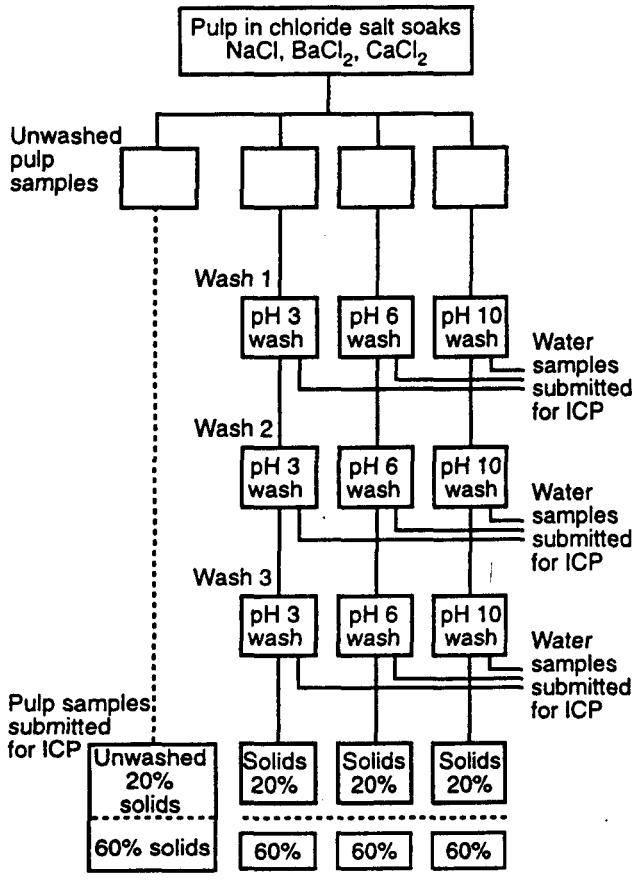

Fig. 1 Flowchart for processing samples from pulp.

Metals analysis was performed at the University of Washington by inductively coupled plasma (ICP) with an ICAP 61E VAC system (Thermo Jarrell Ash Corporation). 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.

Material balances to track cation movement throughout the experimental procedure do not fully account for the cation added to the system. Tables III and IV show cation levels added to pulp slurries (cation in) and cation levels leaving the system (cation out), as measured by ICP.

Duplicate runs of washwater showed ICP measurement errors of< 1%. The ICP measurements of the deionized water used in soaking and washing showed nondetectable levels of cations. Of the 688.8 mg barium charged to the system, only 464.5 mg was measured leaving the system (Table III). The ICP measurements of the level of cation in unwashed pulp showed expected values when compared with previously reported data (1,2,6,9). A source of experimental error may lie

Table III. Cation Flow in Linerboard Pulp Slurry

Cation type	Cation level (mg)	Pulp condition	Pulp level (mg)
Barium soak			
Barium in	688.8		
Barium out	464.5		
Water *out*		Pulp *out*	
Soak water	245.82	Unwashed pulp	50.27
Acid washwater	21.0	Acid washed pulp	22.25
Neutral washwater	3.7	Neutral washed pulp	57.52
Alkaline washwater	3.1	Alkaline washed pulp	60.84
Calcium soak			
Calcium in	203.2		
Calcium out	184.5		
Water *out*		Pulp *out*	
Soak water	131.60	Unwashed pulp	14.6
Acid washwater	7.34	Acid washed pulp	5.21
Neutral washwater	1.0	Neutral washed pulp	9.87
Alkaline washwater	1.1	Alkaline washed pulp	13.75
Sodium soak			
Sodium in	121.9		
Sodium out	134.8		
Water our		Pulp *out*	
Soak water	90.24	Unwashed pulp	11.38
Acid washwater	6.36	Acid washed pulp	0.33
Neutral washwater	0.85	Neutral washed pulp	13.82
Alkaline washwater	1.47	Alkaline washed pulp	10.38

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, which would have decreased the amount of barium measured in washwater, yet not have affected the level of barium in the pulp. In the calcium soak, material balances of the calcium accounted for more than 90% of the added calcium. The sodium material balance showed an increase of 10% after soaking. A source of experimental error with the sodium balance appears in the CF pulps. The pulps soaked with barium or calcium showed low, uniform levels of sodium, although none was expected. This is not a major level of sodium, but it does account for most of the excess sodium. Hence, the total sodium increase in material balances can be explained. Small amounts of sodium were also added by the alkaline washing; however, these amounts were relatively insignificant.

Table IV. Cation Flow in Never-Dried Pulp Slurry

Cation type	Cation level (mg)	Pulp condition	Pulp level (mg)
Barium soak			
Barium in	1,860		
Barium out	396.1		
Water *out*		Pulp *out*	
Soak water	286.7	Unwashed pulp	37.01
Acid washwater	10.0	Acid washed pulp	0.02
Neutral washwater	12.5	Neutral washed pulp	20.77
Alkaline washwater	10.1	Alkaline washed pulp	19.02
Calcium soak			
Calcium in	403.1		
Calcium out	337.9		
Water *out*		Pulp *out*	
Soak water	316.71	Unwashed pulp	6.69
Acid washwater	2.6	Acid washed pulp	0
Neutral washwater	1.0	Neutral washed pulp	2.93
Alkaline washwater	1.1	Alkaline washed pulp	2.33
Sodium soak			
Sodium in	236.9		
Sodium out	348.2		
Water *out*		Pulp *out*	
Soak water	325.90	Unwashed pulp	3.46
Acid washwater	4.77	Acid washed pulp	0.23
Neutral washwater	2.46	Neutral washed pulp	4.88
Alkaline washwater	2.81	Alkaline washed pulp	3.64

Material balance of the never-dried fibers also showed variations (Table IV). The amount of cation remaining with pulp appears reasonable when compared with work by other authors (1,6). Difficulties with the balances appear to have arisen in washwater values.

RESULTS AND DISCUSSION

The ICP measurements for each cation were converted to milliquivalents per kilogram to account for variations in particle charge and molecular weight (2,6,10). Figure 2 shows cation levels in recycled pulp after dewatering with the Buchner funnel. The abscissa describes the wash treatment of the pulp after chloride soaking, while the ordinate shows the cation level. The legend indicates the type of chloride salt used in each soaking procedure. The first group of data (leftmost) shows the cation levels of unwashed pulps reaching 100 meq/kg. As Table II indicates, pulp with a kappa number of 90 tested at pH 8 will have an acidic group content level of 135 meq/kg. Pulps with higher kappa numbers tested at a higher pH have more acidic groups available. The pulp tested here 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 in Figure 2 show how the variable pH of the washwater affected the cation levels. With acid washing in pH 3 water, all the pulps showed significant decreases in cation levels. The cation levels of divalent pulps did not drop as severely as that of the sodium pulp, a result which had been observed previously (5). The barium levels did not decrease after washing the pulp with pH 6 and pH 10 water. The level of calcium decreased after the pH 6 and pH 10 washing stages, while the level of sodium varied. The mass transfer may have been slowed by the size of the cations, which could explain why more barium remained in the pulp.

Figure 3 shows the cation levels in the recycled pulps after pressing. The pulps were pressed to approximately 60% solids, which should displace free cations. The acid-washed pulps did not show a decrease in cations after pressing. 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 pH 6 and pH 10 water 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- and sodium-soaked pulps washed in pH 6 end pH 10 water did not show cation decreases after pressing. This may have been related to accessibility (smaller cations penetrating pores more effectively than did the larger barium) or to the fact that the free cations had already been washed out.

Results of ICP analysis of cation concentration in the linerboard pulp washwater are shown in Figures 4 to 6. One-hundred-milliliter aliquots were used in the wash sequences. The data in Figure 4 show successive removal of cations after each acid washwater stage. The net amount of cation available to be removed decreased after each wash. Acid washing displaced the cations held by the pulp at ion-exchange sites; cations so displaced appeared in the washwater. Much less cation was removed in "neutral" and alkaline pH washwaters (Figs. 5 and 6), as shown previously. Cations held by ion exchange were not displaced by the pH in these washes. For pulp soaked with alkaline washwater, the washwater continued to contain sodium (Fig. 6). The small amount of sodium was simply from the sodium hydroxide used to adjust the pH.

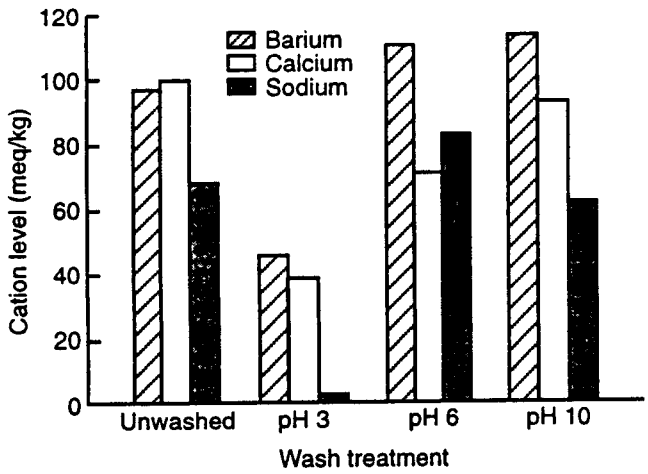

Fig. 2. Cation level in recycled pulp after dewatering with Buchner funnel.

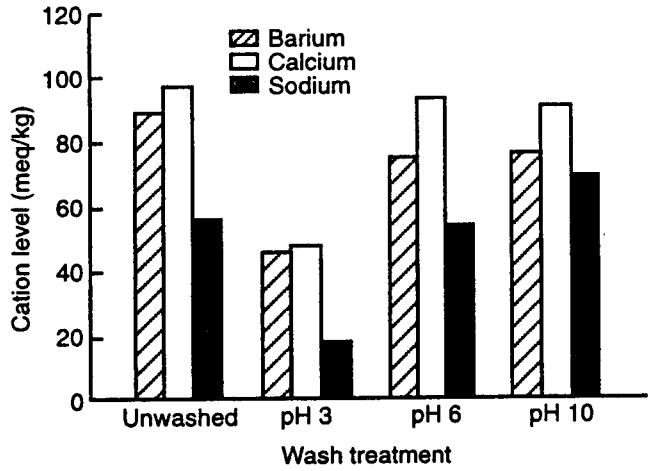

Fig. 3. Cation level in recycled pulp after dewatering in Carver press.

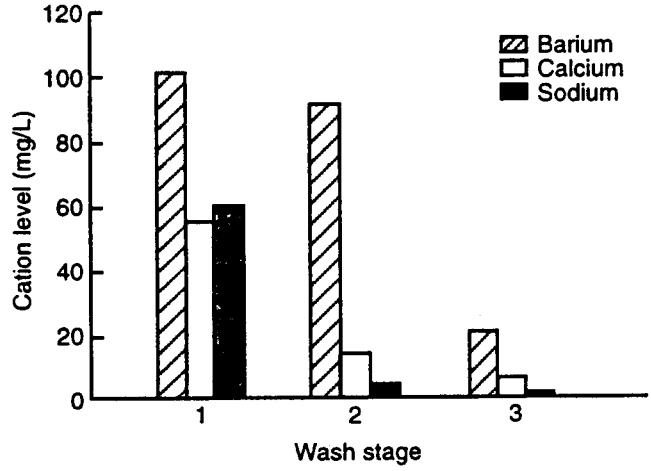

Fig. 4. Cation concentration in acid washwater of linerboard pulp.

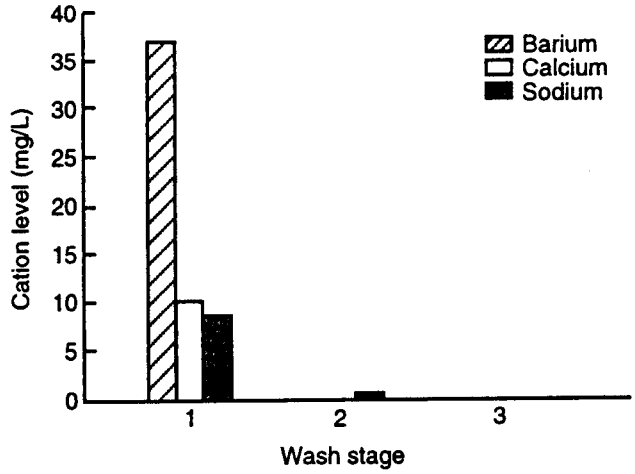

Fig. 5. Cation concentration in "neutral" washwater of linerboard pulp.

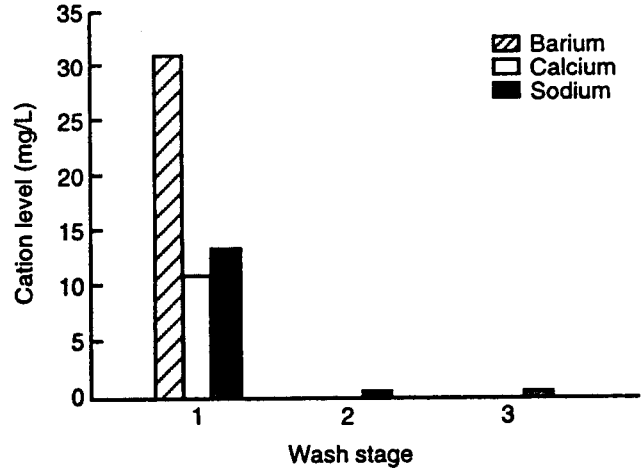

Fig. 6. Cation concentration in alkaline washwater of linerboard-pulp.

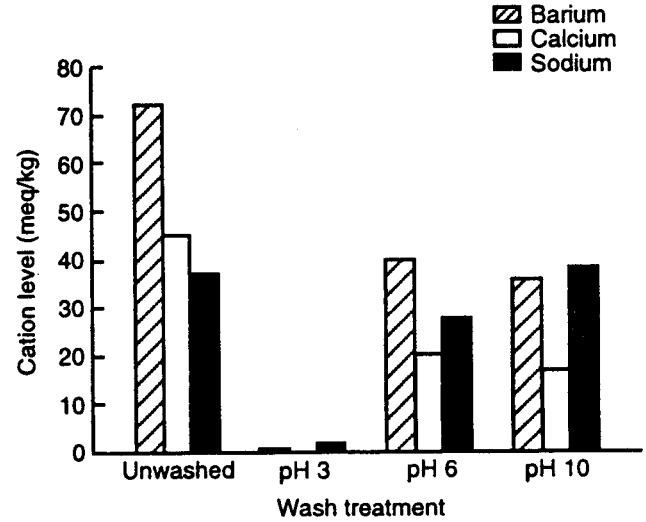

Fig. 7. Cation level in never-dried pulps after dewatering with Buchner funnel.

The second raw material 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 a level of 5 Mmol/L rather than 2 Mmol/L. From the literature, the acidic group content decreases as the kappa number decreases. After soaking and dewatering with the Buchner funnel, the initial unwashed barium-soaked pulp sample had a barium content of 70 meq/kg, whereas calcium- and sodium-soaked pulps showed respective cation levels close to 40 meq/kg (Fig. 7). The literature suggests an acidic group level close to 70 meq/kg for 35 kappa pulp, implying that not all the available acidic sites are occupied by the cations. After acid washing, practically all the cations were removed from the pulps. When the pH is lowered, cations at ion-exchange sites will dissociate and be replaced by hydrogen ions. The "neutral" and alkaline washes also removed significant amounts of the divalent cations, barium and calcium. The amounts removed by higher pH washwater 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. 8). The cations behaved in similar fashion.

Cations were most effectively removed from never-dried pulps by acid washing; only a trace amount of cation appeared in the second and third washes and virtually no cation in the final pulp (Figs, 9-11). 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 higher pH washes were not effective at removing cations.

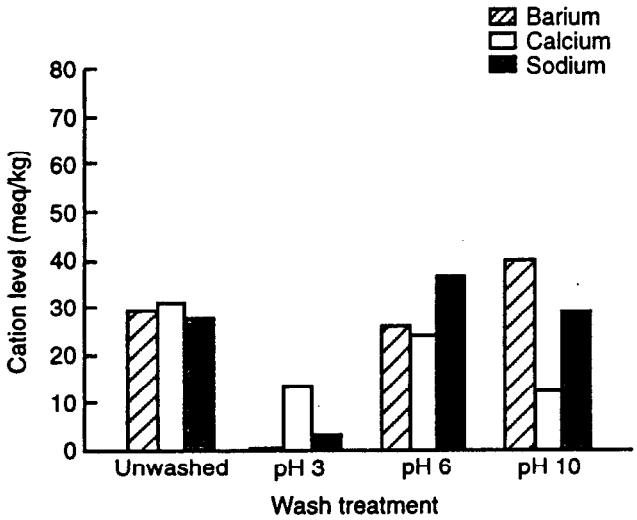

Fig. 8. Cation level in never-dried pulps after dewatering in Carver press.

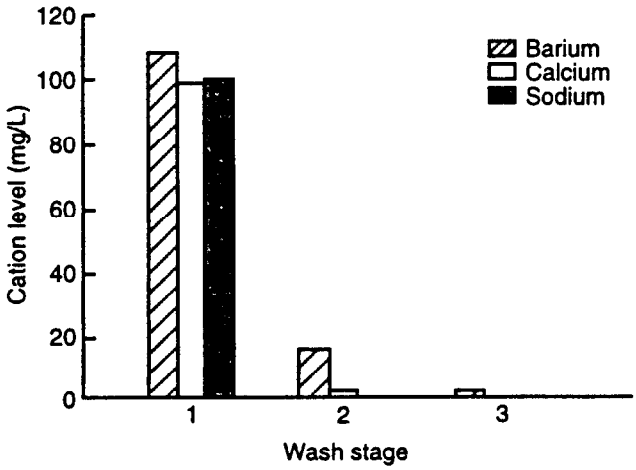

Fig. 9. Cation concentration in acid washwater of never-dried pulp.

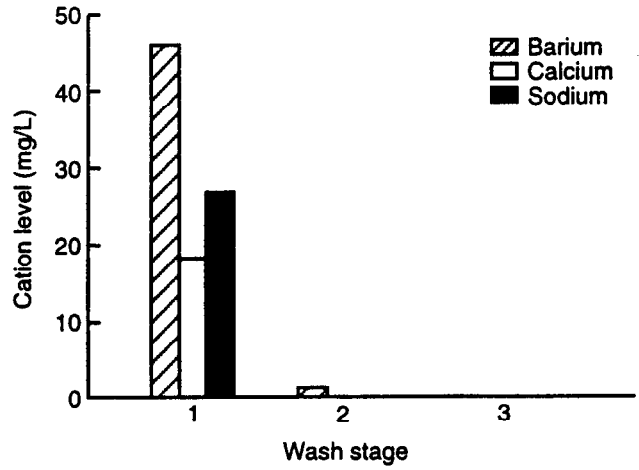

Fig. 10. Cation concentration in "neutral" washwater of never-dried pulp.

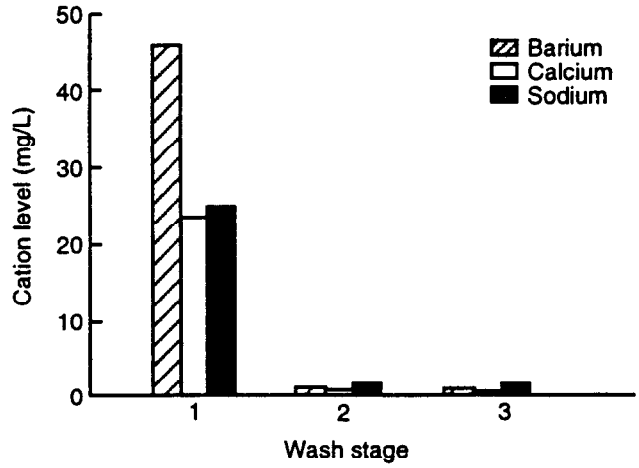

Fig. 11. Cation concentration in alkaline washwater of never-dried pulp.

CONCLUDING REMARKS

Freeland's data showed a barium content of 7,870 ppm, or 114 meq/kg. Our results showed a barium level of 6,800 ppm. After applying the correction factors for weight and charge, the final barium content in linerboard with a kappa number of 85 was 100 meq/kg, well within the expected ion-exchange range of 75 to 140 meq/kg. After the pulp was washed, barium and calcium behaved as similarly bonded cations. 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.

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ISBN 0-89852-657-4
TP 010589/96
Printed in the United States ofAmerica