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Factors influencing retention behavior of aluminum compounds on handsheets*

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Abstract Handsheets were prepared with aluminum sulfate under various conditions of pulp suspension, and factors influencing retention behavior of aluminum components on the handsheets were studied on the basis of their aluminum contents. When deionized water was used in the handsheet-making process, aluminum contents in the handsheets had a plateau level of 0.7 mg/g in the range of 1%–8% $Al_2(SO_4)_3$ addition levels on dry weight of pulp. On the other hand, when tap water was used aluminum contents increased up to 5.6 mg/g, increasing the $Al_2(SO_4)_3$ addition levels to 8%. The high aluminum contents in the handsheets are explained in terms of pH and the presence of calcium ions from the tap water used. Cationic aluminum species, which are formed from aluminum sulfate added to pulp suspensions, are primarily adsorbed on pulp fibers by electrostatic interactions with carboxyl groups in the pulp, competing with OH^- ions in water. These aluminum components, once adsorbed on pulp fibers by ionic interactions, are not removed from the fibers by extending the stirring time of the pulp suspensions.

Key words Aluminum sulfate · Paper · Retention · Wet-end · Pulp fiber

Introduction

Aluminum compounds such as aluminum sulfate have been widely used as wet-end additives under not only acidic but also alkaline conditions in practical papermaking. It is well known that aluminum components have complicated structures and correspondingly various ionic properties in water, depending on the pH and other factors.[1–7] Some hypotheses concerning retention mechanisms of aluminum compounds added to pulp suspensions have been advocated.[8–14] In these reports, the behavior of aluminum components in pulp suspensions was often explained on the basis of the results obtained in experiments using various aluminum compounds and deionized water (or distilled water) under equilibrium conditions. For practical papermaking, however, various inorganic and organic substances are present in papermaking water as the white water circulation proceeds, and the adsorption of aluminum components on pulp fibers must occur under dynamic conditions rather than equilibrium.

A previous paper reported a study on the adsorption behavior of some low- and high-molecular-weight aluminum compounds on handsheets. It was found that retention behavior of the aluminum components is sensitively influenced by their chemical structure, the pH of the pulp suspensions, and the presence of fines fraction in the pulp. Furthermore, aluminum flocs are formed between cationic aluminum species and OH^- ions in pulp suspensions and are entrapped in pulp fiber mats by the filtration effect.[15] More detailed studies are, however, necessary for clarifying overall adsorption mechanisms of aluminum compounds on pulp fibers in practical papermaking.

In this study handsheets were prepared with aluminum sulfate using deionized or tap water under various conditions of pulp suspensions, and factors influencing retention behavior of aluminum components on the handsheets were studied on the basis of their aluminum contents. Furthermore, the roles of carboxyl groups of pulp in the aluminum retention were studied using pulps having various structures at their carboxyl groups.

Materials and methods

Materials

Commercial bleached hardwood kraft pulp was beaten to 450 ml Canadian Standard Freeness with a PFI mill. Car-

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boxyl content of this beaten pulp was 60 μEq/g. Fines-free pulp was obtained in 85% yield by removing the fines fraction in the above beaten pulp according to the TAPPI test method.[16] A carboxyl group-blocked pulp was prepared by amidation of carboxyl groups in the beaten pulp with methylamine and water-soluble carbodiimide at pH 4.75.[17,18] More than 95% of carboxyl groups present in the original pulp were converted to nonionic methylamide groups by this methylamidation.[17,18] Pulps having different counter ions at the carboxyl groups were prepared by ion exchange from the original beaten pulp using a diluted HCl, $Ca(OH)_2$, or NaOH solution,[19] followed by washing thoroughly with deionized water. These pulps, with structures of pulp-COOH, pulp-COONa, pulp-$COOCa^+$, and pulp $CONHCH_3$, were subjected to handsheet making without drying. Aluminum sulfate (Wako Chemicals, Tokyo, Japan) and polyaluminum silicate sulfate (PASS) (Nihon Keikinzoku, Shizuoka, Japan) were used as wet-end additives.[15] Other chemicals used were of pure grade (Wako).

Handsheet production

To clarify the effects of inorganic or organic compounds present in tap water on the retention behavior of aluminum compounds on pulp fibers, certain amounts of calcium chloride, magnesium chloride, sodium sulfate, oxalic acid, and/or sodium oxalate were added to deionized water. The pulp was then added to the water followed by $Al_2(SO_4)_3$ for preparing handsheets. The pH of water without the pulp and of the pulp suspensions were controlled by adding a diluted HCl or NaOH solution. A filtered tap water was prepared by passing the tap water through a cellulose nitrate membrane filter having 0.1 μm pore size (Advantec Toyo, Tokyo, Japan).

Handsheets were prepared according to the procedure reported in a previous paper.[15] For removing aluminum compounds physically retained on pulp fiber mats, repetition of water-feeding, agitation, and drainage in the cylinder of the handsheet machine was carried out on some pulp suspensions.[15] The wet-pressed handsheets were dried at 20°C and 65% relative humidity (RH) for more than 1 day.

Analyses

An X-ray fluorescence analyzer (XFA) (MESA-500; Horiba, Kyoto, Japan) was used for determining the aluminum contents in the handsheets under the conditions reported previously.[15]

Results and discussion

Retention behavior of aluminum components on handsheets

Figure 1 shows aluminum contents in the handsheets prepared from pulp suspensions with aluminum sulfate using tap water, filtered tap water, and deionized water. As reported in the previous paper, when tap water is used for the handsheet making aluminum contents increase with increasing addition levels of aluminum sulfate to pulp suspensions.[15] The handsheets had higher aluminum contents when the filtered tap water was used than with the nonfiltered tap water. Fine solid impurities, which are present in tap water and removable by filtration, led to a partial impediment to aluminum retention on pulp fibers, probably because of adsorption of aluminum components on the impurity fractions to some extent and the loss by drainage during the handsheet making process.

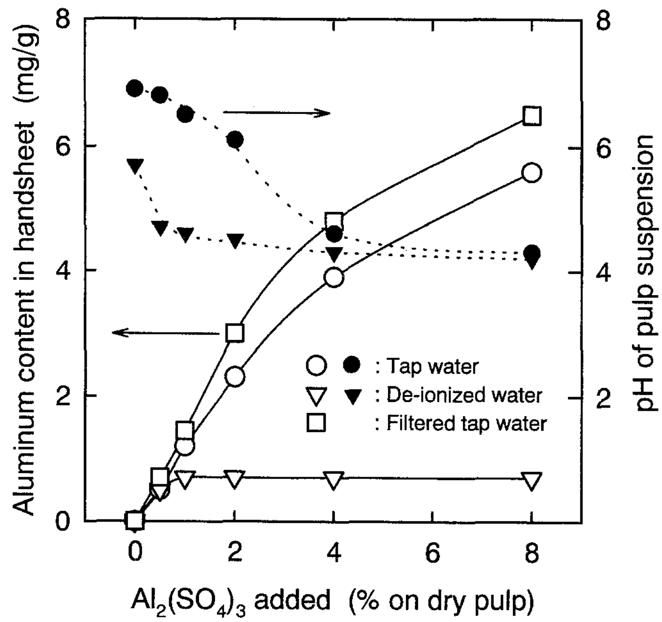

Fig. 1. Aluminum contents in handsheets prepared from pulp suspensions with aluminum sulfate using tap water, filtered tap water, and deionized water. pH values of pulp suspensions after the aluminum sulfate addition are also shown

On the other hand, when deionized water was used for handsheet making, a clearly different pattern of aluminum retention was observed. Aluminum contents had a plateau level of about 0.7 mg/g in the range of 1%–8% addition levels. Aluminum components originating from aluminum sulfate added to the pulp suspensions form cationic aluminum flocs, cationic polyaluminum compounds, or both to some extent by OH^- ions present in water, and some of these flocs are retained in the handsheets by the physical filtration effect, coordinate adsorption on pulp fibers, or both.[15] Therefore, the pH of pulp suspensions must significantly influence the aluminum contents in the handsheets. In fact, the pH of deionized water used in this study was about 5.7, possibly because of partial dissolution of atmospheric CO_2 into the deionized water. The pH of deionized water dropped to 4.7 after the 0.5% $Al_2(SO_4)_3$ addition, whereas that of tap water decreased more gradually. Substances dissolved in the tap water may have some buffering effects on the pH. Although most fundamental experiments reported so far concerning aluminum retention on paper in papermaking have been carried out using deionized water, the result obtained in Fig. 1 indicates that the deionized water systems are unsuitable for explaining retention behavior of aluminum components on paper in practical papermaking systems.

Effect of substances dissolved in papermaking water

To explain the result in Fig. 1, the factors influencing high aluminum content in the handsheets prepared using tap water are described in this section. The ionic strength of tap water may affect the aluminum contents in the handsheets prepared thereof because electrostatic properties of pulp fiber surfaces are influenced by the ionic strength of the water. Furthermore, precipitation of aluminum components on pulp fiber surfaces may proceed by the salting-out effect, when the ionic strength of the water increases. As shown in Fig. 2, however, aluminum contents in the handsheets were roughly constant with sodium sulfate concentrations in deionized water, in the range of 0–10 mEq/l. Thus, the high aluminum contents in the handsheets prepared using tap water cannot be explained in terms of the ionic strength of the papermaking water.

Figure 3 shows the effect of oxalic acid, sodium oxalate, calcium ions, and magnesium ions in deionized water on aluminum contents in the handsheets prepared using water. Oxalic acid, oxalate salts, or both are present in bleached kraft pulp to some extent as degradation products of lignin.[20] Because the tap water used in this study contained calcium and magnesium ions of 0.60 and 0.22 mEq/l, respectively, the effect of these divalent alkali metal ions on aluminum contents in the handsheets was also studied using deionized water with or without these ions. As shown in Fig. 3, the addition of oxalic acid or sodium oxalate to deionized water brought about lower aluminum contents in the handsheets prepared using water, irrespective of the presence of calcium or magnesium ions in the water. The presence of such low-molecular-weight anionic substances as oxalic acid may consume aluminum components, forming aluminum salts, to some extent by ion exchange and form small insoluble flocs, which are removable from the pulp mat by the drainage process during handsheet-making. The addition of magnesium chloride to deionized water resulted in lower aluminum contents in the handsheets. Divalent magnesium ions probably compete with trivalent aluminum to some extent for adsorption on pulp fibers in the pulp suspensions.

On the other hand, aluminum contents in the handsheets increased when the deionized water containing calcium chloride at 0.60 mEq/l was used for the handsheet-making. Irrespective of the presence of magnesium ions, oxalic acid, or sodium oxalate in the water, the addition of calcium chloride to deionized water resulted in 50%–115% higher aluminum contents in the handsheets than those prepared without calcium chloride. Figure 4 shows how aluminum contents in the handsheets increase by the pH adjustment or calcium chloride addition to deionized water (or both). A diluted NaOH solution was used to adjust the pH of the water. As shown in Fig. 4, when calcium chloride was added to deionized water and its pH was adjusted to 7, the handsheets had aluminum content almost equal to that of the handsheets prepared with tap water. Therefore, both

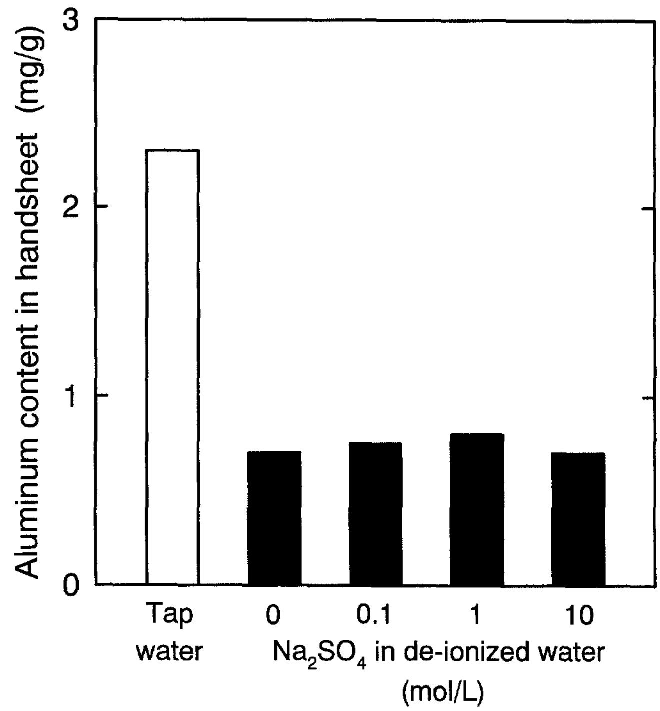

Fig. 2. Aluminum contents in handsheets prepared from pulp/deionized water suspensions containing sodium sulfate. Addition level of $Al_2(SO_4)_3$: 2% on dry weight of pulp

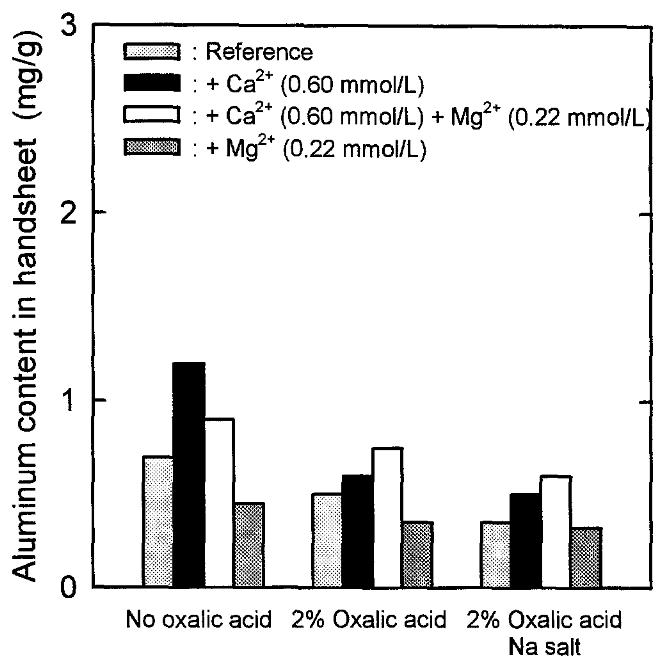

Fig. 3. Aluminum contents in handsheets prepared from pulp/deionized water suspensions containing oxalic acid, sodium oxalate, calcium ions, magnesium ions, or calcium plus magnesium ions. Addition level of $Al_2(SO_4)_3$: 2% on dry weight of pulp

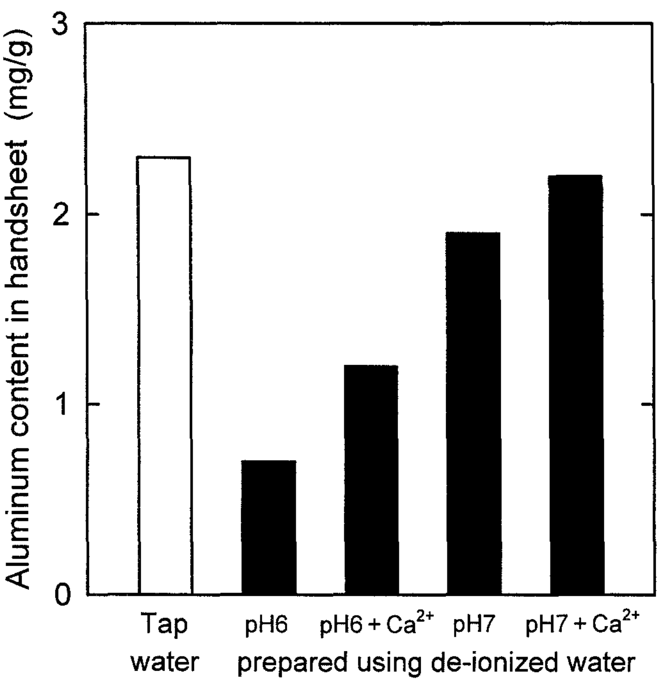

Fig. 4. Effect of pH and calcium ions in pulp/deionized water suspensions on aluminum contents in handsheets prepared using the water. Addition level of $Al_2(SO_4)_3$: 2% on dry weight of pulp

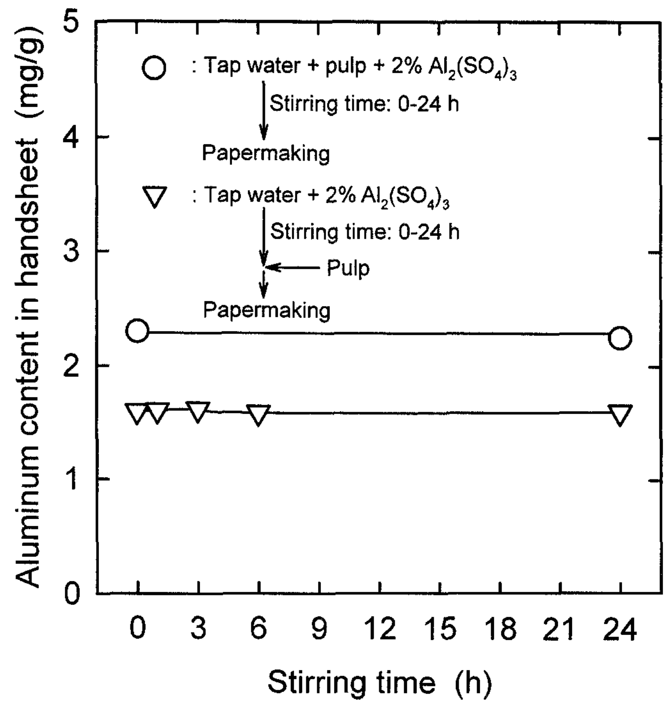

Fig. 5. Effect of sequence when preparing pulp suspensions on aluminum contents in handsheets. Addition level of $Al_2(SO_4)_3$: 2% on dry weight of pulp

pH and calcium ions in the tap water may cause the higher aluminum contents in the handsheets, compared with the case when deionized water is used.

Although both calcium and magnesium ions are divalent alkali metal ions, calcium ions can form calcium carbonate in water, where atmospheric CO_2 is partly dissolved. Probably the presence of this calcium carbonate and pH around 7 for the tap water promote the formation of cationic aluminum flocs or cationic polyaluminum compounds originating from aluminum sulfate, resulting in higher aluminum contents in the handsheets. On the other hand, single ions such as Al^{3+}, $Al(OH)^{2+}$, and $Al(OH)_2^+$ may predominantly be present in the pulp suspensions at pH 4.2–4.5 when deionized water is used, resulting in a lower, constant aluminum content in the handsheets (Fig. 1). Furthermore, the results in Fig. 1 indicate that aluminum components cannot be adsorbed on hydroxyl groups of pulp fibers at pH 4.2–4.5. As described in the latter section, these aluminum components are primarily adsorbed on carboxyl groups in the pulp fibers.

Effect of pH of aluminum sulfate/water solutions

As shown in Fig. 1, the addition of aluminum sulfate to pulp suspensions decreases their pH, depending on the addition levels of aluminum sulfate. This decrease in pH is inevitable so long as $Al_2(SO_4)_3$ is added to pulp suspensions. Thus, the structure of the cationic compounds originating from aluminum sulfate may partly or greatly change by this change in the pH of the pulp suspensions. On the other hand, this pH change can be avoided by modifying the addition sequence of aluminum sulfate, where pulps are added to $Al_2(SO_4)_3$/water solutions. Figure 5 shows the aluminum contents in handsheets prepared using tap water by the normal and modified addition sequences. In the case of the normal addition sequence, the pH of the initial pulp suspension and that after the 2% $Al_2(SO_4)_3$ addition was 6.5 and 6.1, respectively. On the other hand, when the pulp was added to the $Al_2(SO_4)_3$/water solution, the pH 6.1 was unchanged before and after the pulp addition. Aluminum contents in the handsheets prepared by the modified sequence were about one-third lower than those for the normal sequence. The formation of nonionic $Al(OH)_3$ was probably increased by the modified addition sequence, resulting in lower aluminum contents in the handsheets. Therefore, adsorption of cationic aluminum components on pulp fibers may dynamically proceed in pulp suspensions by competing with OH^- ions in water. Although the two addition sequences gave different aluminum contents in the handsheets, each value was roughly unaffected by the stirring time of the pulp/$Al_2(SO_4)_3$/water suspensions or $Al_2(SO_4)_3$/water solutions.

As reported in a previous paper, aluminum components originating from aluminum sulfate are retained in the handsheets by (1) ionic interactions between cationic aluminum species and anionic sites of pulp, (2) nonionic interactions such as the simple filtration effect during the handsheet-making process, and (3) coordinate bond formation and others. On the basis of the results in Fig. 5, the following hypotheses may be practically adaptable.

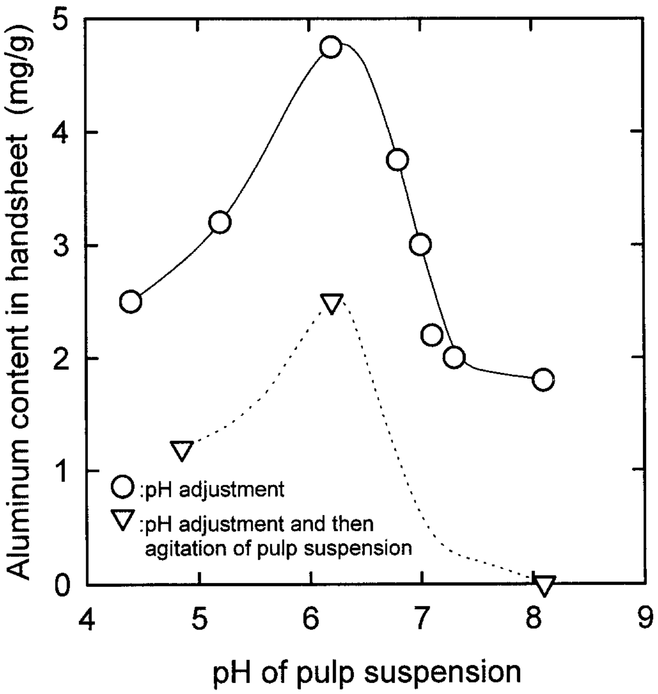

Fig. 6. Aluminum contents in handsheets prepared from pulp suspensions, which are prepared by adding the pulp to tap water containing aluminum sulfate at various pH levels. Addition level of $Al_2(SO_4)_3$: 4% on dry weight of pulp. *Dotted line*, aluminum contents in handsheets after repetition of drainage and agitation of the pulp suspensions in the cylinder of the handsheet machine

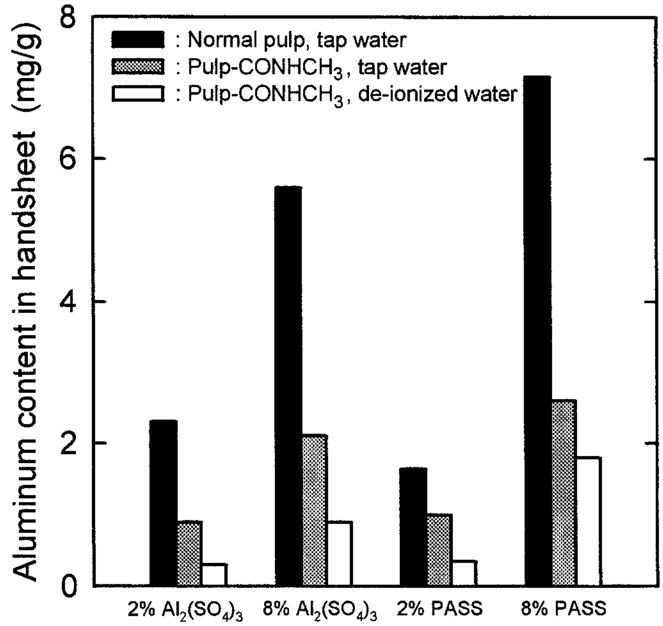

Fig. 7. Aluminum contents in handsheets prepared from normal pulp and carboxyl-group-blocked pulp suspensions with $Al_2(SO_4)_3$ or polyaluminum silicate sulfate (PASS)

1. Aluminum components once adsorbed on pulp fibers by ionic interactions and coordinate interactions are not removed even by extending the stirring time of the pulp suspensions.
2. Aluminum flocs once formed in water do not change their floc sizes or surface charges by extending the stirring time of the $Al_2(SO_4)_3$/water solutions.

Figure 6 shows aluminum contents in the handsheets prepared from fines-free pulp by adding the pulp to equilibrium $Al_2(SO_4)_3$/tap water solutions at various pH levels (*i.e.*, by the modified addition sequence in Fig. 5). The handsheets had various aluminum contents, depending on the pH of the $Al_2(SO_4)_3$/tap water solutions used for the handsheet-making. Aluminum contents gradually increased with increasing the pH from 4.3 to 6.2; it reached a maximum value at pH 6.2. The aluminum contents in the handsheets drastically decreased at a pH of more than 6.8. This pattern of retention behavior of aluminum components in the handsheets is similar to that reported by Proxmire and Stratton.[4] On the other hand, as shown in Fig. 6, the repetition of mechanical agitation of the pulp suspensions in the cylinder of the handsheet machine resulted in a clear decrease in aluminum contents in the handsheets. Therefore, considerable amounts of nonionic $Al(OH)_3$ flocs must be formed at any pH between 4.3 and 8.1 by ionic interactions between cationic aluminum species and OH^- ions in water. Some of these $Al(OH)_3$ flocs are retained in the pulp fiber mat by the filtration effect during the handsheet-making process and in turn can be removed from the pulp fibers by repeated mechanical agitation of the pulp suspensions in the cylinder of the handsheet machine.

Furthermore, the result in Fig. 6 suggests that aluminum components are adsorbed on pulp fibers at pH 6.2 by ionic interactions between pulp fibers and cationic aluminum flocs or cationic aluminum polymers, which are formed around this pH. The higher aluminum contents in the handsheets were then obtained. On the other hand, single aluminum ions such as Al^{3+}, $Al(OH)^{2+}$, and $Al(OH)_2^+$ may be predominant around pH 4.3, resulting in lower aluminum contents in the handsheets. Because nearly no aluminum components are retained in the handsheets prepared at pH 8.1 after mechanical agitation of the pulp suspension, any cationic aluminum components are not present in the water at this high pH under equilibrium conditions.

Effect of carboxyl groups in pulp

Figure 7 shows aluminum contents in the handsheets prepared from the normal and carboxyl group-blocked pulp with aluminum sulfate or polyaluminum sulfate silicate (PASS). In both aluminum compounds, the aluminum contents in the handsheets prepared from the carboxyl group-blocked pulp were clearly lower than those for the normal pulp in any of the cases examined. Thus, irrespective of the molecular weight of aluminum components, they are predominantly adsorbed on pulp fibers by ionic interactions between cationic aluminum species and anionic carboxyl groups in pulp.

On the other hand, however, certain amounts of aluminum components were still retained in the handsheets prepared even from the carboxyl group-blocked pulp using tap

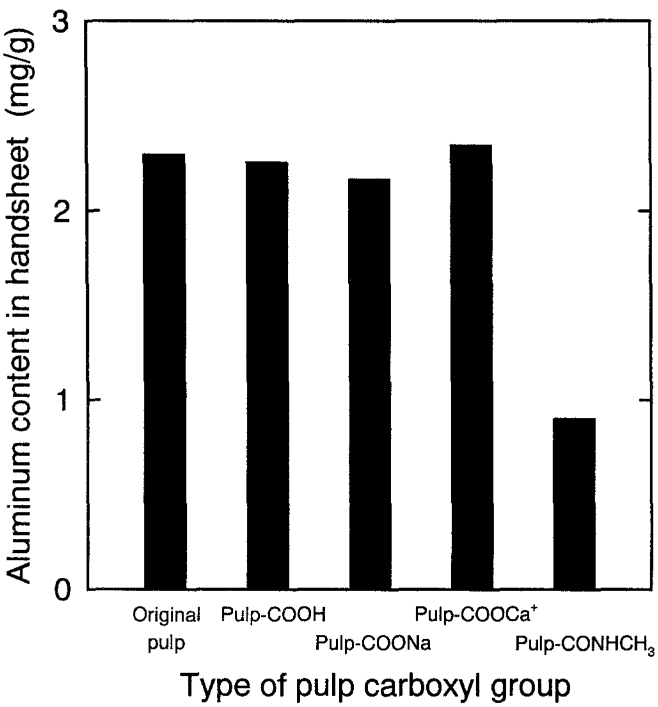

Fig. 8. Aluminum contents in handsheets prepared from pulps having various structures of carboxyl groups using tap water. Addition level of $Al_2(SO_4)_3$: 2% on dry weight of pulp

water. When deionized water was used for the handsheet-making with the carboxyl group-blocked pulp, aluminum contents in the handsheets decreased further. These aluminum components retained in the handsheets for the carboxyl group-blocked pulp may be physically trapped in the pulp fiber mats by the filtration effect during the handsheet-making process. Because the aluminum floc formation is restricted in deionized water, as described in the previous section, aluminum contents in the handsheets decreased further for the carboxyl group-blocked pulp. Similar effects of carboxyl groups in pulp on retention of wet-end additives have been observed for internal sizes and cationic starches.[17,18,21]

Figure 8 shows aluminum contents in the handsheets prepared from pulps having different counterions or structures at the carboxyl groups. Tap water was used for the handsheet making. As shown in Fig. 8, the aluminum contents were roughly equal among the handsheets prepared from the original pulp and the pulps with structures of pulp-COOH, pulp-COONa, and pulp-$COOCa^+$. Therefore, irrespective of the kinds of counterions at the carboxyl groups in the pulp at the initial state, they may have similar structures of carboxyl groups in tap water, where calcium and magnesium ions of 0.60 and 0.22 mEq/l, respectively, are present.

Conclusions

The following conclusions were reached based on the results of this study.

1. When deionized water is used in the handsheet-making process, aluminum content in the handsheets prepared with $Al_2(SO_4)_3$ levels off at about 0.7 mg/g. On the other hand, when tap water is used, aluminum content increased with increasing $Al_2(SO_4)_3$ addition levels.
2. This difference in retention behavior of aluminum components in the handsheets is explained in terms of pH and the presence of calcium ions in the papermaking water. The presence of oxalic acid or magnesium ions in water decreases the aluminum content in the handsheets. The ionic strength of papermaking water has little influence on retention behavior of aluminum components in handsheets.
3. Aluminum components originating from aluminum sulfate or PASS added to pulp suspensions primarily adsorb on pulp fibers by electrostatic interactions between carboxyl groups in the pulp and the cationic aluminum species formed. Furthermore, adsorption of cationic aluminum components on pulp fibers proceeds in pulp suspensions by competing with OH^- ions in water. On the other hand, nonionic $Al(OH)_3$ flocs are formed in some quantity, and some are retained in the handsheets by the simple filtration effect without any electrostatic interactions during the drainage process in the handsheet-making.
4. Pulps having different counterions at carboxyl groups, pulp-COOH, pulp-COONa, and pulp-$COOCa^+$ give similar aluminum contents in the handsheets prepared when tap water is used.

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