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## Adsorption behavior of aluminum compounds on pulp fibers at wet-end

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**Abstract** Various aluminum compounds were added to pulp suspensions, and the adsorption behavior of their aluminum components on pulp fibers was studied. Aluminum contents in the handsheets were determined using an energy dispersive X-ray analyzer attached to a scanning electron microscope and an X-ray fluorescence analyzer. Although aluminum contents in the handsheets increased with increasing additions of the aluminum compounds, the detailed adsorption patterns varied among the aluminum compounds used. Their chemical structures and the pH values of the pulp suspensions greatly influence the adsorption behavior. When fines are present in the pulp suspensions, the aluminum components are predominantly adsorbed on the fines, probably due to their larger surface areas or the higher carboxyl contents compared to those of coarse fibers. Not only aluminum flocs but also far smaller components such as various aluminum cations seemed to be adsorbed on pulp fibers. Most aluminum flocs, which are formed in pulp suspensions by reacting with  $\text{OH}^-$  and entrapped in a fiber matrix by filtration effects, are removable by repeated mechanical agitation of the pulp suspensions.

**Key words** Aluminum sulfate · Aluminum compounds · Adsorption · Wet-end · Pulp fiber

### Introduction

Aluminum compounds such as alum have long been widely used as wet-end additives in practical papermaking. Re-

cently, alkaline papermaking has been extended, and alum and other aluminum compounds have been used to some extent for various purposes even under alkaline conditions. It is well known that aluminum components have varied and complicated structures and ionic properties in water, depending on the pH and other conditions.<sup>1–6</sup> Essentially, the structural changes of aluminum components in water due to pH changes are initiated by reactions between cationic aluminum components and  $\text{OH}^-$  ions.<sup>3–5</sup> When pulp fibers are present in the system, not only  $\text{OH}^-$  ions but also dissociated carboxyl groups in pulp (and those of anionic trash present in the pulp suspensions) must be able to react competitively with cationic aluminum components.<sup>7–12</sup> However, some experimental results regarding the behavior of aluminum components in water systems under equilibrium conditions without pulp fibers have been introduced to explain the retention or adsorption mechanisms of aluminum compounds on pulp fibers at the wet-end.<sup>1–4</sup>

It has been reported that polynuclear aluminum cations are formed from low-molecular-weight aluminum compounds in water at room temperature by gradual neutralization with alkali.<sup>6,13–15</sup> It should be noted that during the papermaking process the lapse of time between the addition of aluminum compounds as wet-end additives to paper stock and the following drainage process on wire is in the range of minutes or even less than 1 min. Furthermore, dissociated carboxyl groups present in pulp fibers and anionic trash are always present in the paper stock together with  $\text{OH}^-$  ions. Thus, when explaining the retention or adsorption mechanisms of the aluminum components in pulp fibers at the wet-end of the papermaking process, the dissociated carboxyl groups of pulp and anionic trash can compete with  $\text{OH}^-$  ions for cationic aluminum components. This competing reaction may be more essential and significant for the papermaking process than polymerization of aluminum components in water. Ödberg et al. reported that aluminum flocs, once adsorbed on pulp fibers, were partly transferred to clay particles by mechanical agitation of the pulp suspensions.<sup>16</sup> Other possibilities, such as  $\text{Al}^{3+}$ ,  $\text{Al}(\text{OH})^{2+}$ ,  $\text{Al}(\text{OH})_2^+$ ,  $\text{Al}(\text{OH})_3$  molecules, and nonionic  $\text{Al}(\text{OH})_3$  flocs were not taken into consideration.

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Recently, some new polyaluminum compounds have been proposed for wet-end additives, and their adsorption behaviors on pulp fibers vary, depending on their chemical structures. In this paper the effects of chemical structures of the aluminum compounds, the pH values of pulp suspensions, and the fines fraction in pulp on the retention patterns of aluminum for the handsheets are discussed with the hope of elucidating the retention or adsorption mechanisms of aluminum compounds on pulp fibers at the wet-end of the papermaking process.

## Materials and methods

### Materials

Commercial bleached hardwood kraft pulp was beaten to 450 ml Canadian Standard Freeness with a PFI mill. The fines fraction in the beaten pulp was removed according to the Tappi test method.<sup>17</sup> Aluminum sulfate, aluminum chloride, aluminum sodium sulfate, and sodium aluminate were pure grades (Wako Chemicals Co., Japan) and used as low-molecular-weight aluminum compounds. Polyaluminum silicate sulfate (PASS) (Nihon Keikinzoku Co., Japan) and polyhydroxyaluminum chloride (PHAC) (Riken Green Co., Japan) were used as polyaluminum compounds. The information about PASS and PHAC reported by the manufacturers was as follows:

PASS:  $\text{Al}_2(\text{OH})_3(\text{SO}_4)_{1.5}(\text{SiO}_2)_{0.08}$ , molecular weight > 300 000, 10 weight % solution as  $\text{Al}_2\text{O}_3$ , pH 3.1, and  $d = 1.34$

PHAC:  $\text{Al}_2(\text{OH})_5\text{Cl}$ , 23.4 weight % solution as  $\text{Al}_2\text{O}_3$ , pH 3.5–4.0, 50% solid content,  $d = 1.33$

### Handsheet production

All aluminum compounds except PASS were diluted with deionized water to 1 weight % and added to 0.15% pulp suspension with continuous stirring. In the case of PASS, the original PASS solution was added to the pulp suspensions with a micro-syringe. In the typical procedure, the pH of the pulp suspensions was not controlled; the pH of pulp suspensions decreased, for example, after the aluminum sulfate addition. In some cases the pulp suspensions were adjusted to about pH 7 with 0.05N NaOH using a pH stat (an automatic pH controller), during addition of the aluminum compound dropwise to the pulp suspension. For removing fines fractions, including aluminum components physically adsorbed on pulp fibers, water-feeding, agitation, and drainage in the cylinder of the handsheet machine were repeated for some pulp suspensions.<sup>18</sup> After stirring for 30s, handsheets with a basis weight of about 60 g/m<sup>2</sup> were prepared using tap water according to the Tappi test method.<sup>19</sup> Just after making the handsheet the pH of the remaining pulp suspensions was measured. The wet-pressed handsheets were dried at 20°C and 65% relative humidity for more than 1 day. In this study, no curing treatments were applied to the handsheets.

### Analyses

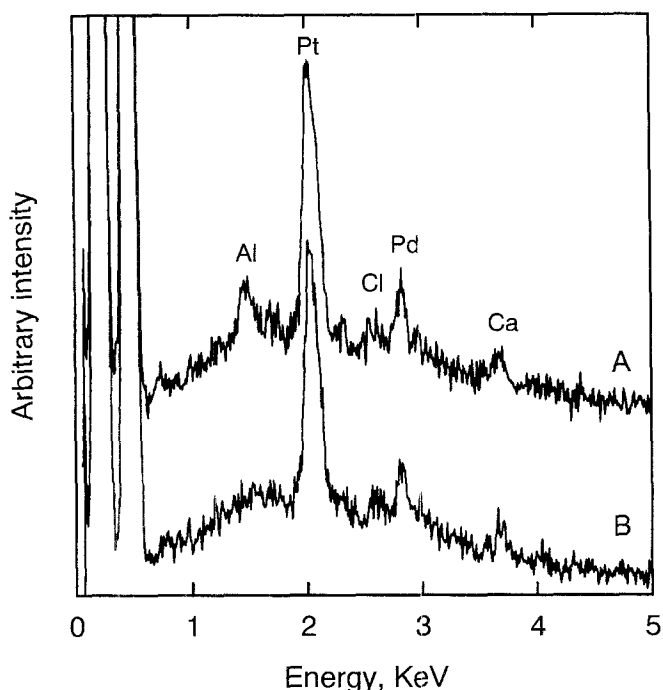
A scanning electron microscope (SEM) (S-4000; Hitachi Co., Japan) equipped with an energy dispersive X-ray analyzer (EDXA) (EMAX-5770X; Horiba Co., Japan) and an X-ray fluorescence analyzer (XFA) (MESA-500, Horiba Co., Japan) were used to determine the aluminum contents in the handsheets with 0–8 and 0–20 mg/g aluminum content, respectively. Measuring conditions for the SEM-EDXA were as follows: 20 kV acceleration voltage and  $3.0 \times 2.3$  mm determination area for SEM, and measuring time of 500s with a highly quantitative mode for EDXA. The plate sides of the handsheet samples were coated with Pt containing a small amount of Pd by means of an ion sputtering apparatus, simultaneously with a control handsheet sample, whose aluminum content was measured beforehand by XFA.<sup>10</sup> The aluminum contents in the handsheets were calculated from the peak ratios of Al/Pt in the EDXA patterns; Pt was therefore used as an internal standard for the aluminum determination. Measuring conditions for the XFA were as follows: 15 kV and 500  $\mu\text{A}$  acceleration voltage and current, respectively; about 44 mm<sup>2</sup> determination area; and measuring time of 100s. The plate sides of the handsheet samples were irradiated by X-rays in vacuum.

## Results and discussion

### Determination of aluminum contents by SEM-EDXA and XFA

The reliability of aluminum contents determined by SEM-EDXA was examined beforehand using handsheet samples, whose aluminum contents were determined by XFA<sup>10</sup> and atomic absorption spectroscopy after extraction with a concentrated HCl solution.<sup>20</sup> SEM-EDXA and XFA give information about elements present on solid surfaces up to about 10 and 100  $\mu\text{m}$  depth, respectively. In the case of handsheet samples, good agreement was obtained for aluminum contents determined by SEM-EDXA, XFA, and the atomic absorption spectroscopic method up to an aluminum content of about 8 mg/g. For the handsheets having aluminum contents of 0–8 mg/g, the values obtained by both SEM-EDXA and XFA can be regarded as those of bulk handsheets. Variations of aluminum contents obtained by SEM-EDX and XFA were within the range of  $\pm 6\%$  and  $\pm 4\%$ , respectively. In the case of handsheets having an aluminum content of more than 8 mg/g, only XFA was used to determine the aluminum content, although the values obtained even by XFA may be inaccurate when the aluminum components are unevenly distributed in the depth direction from the surface to the inside of the handsheets.

The SEM-EDXA patterns of the handsheets prepared with 1%  $\text{Al}_2(\text{SO}_4)_3$  and 16%  $\text{NaAlO}_2$  on dry weight pulp are shown in Fig. 1. A clear peak due to aluminum was observed in the EDXA pattern for the 1%  $\text{Al}_2(\text{SO}_4)_3$  addition, whereas no peak due to aluminum was detected in the EDXA pattern for the 16%  $\text{NaAlO}_2$  addition. Anionic alu-



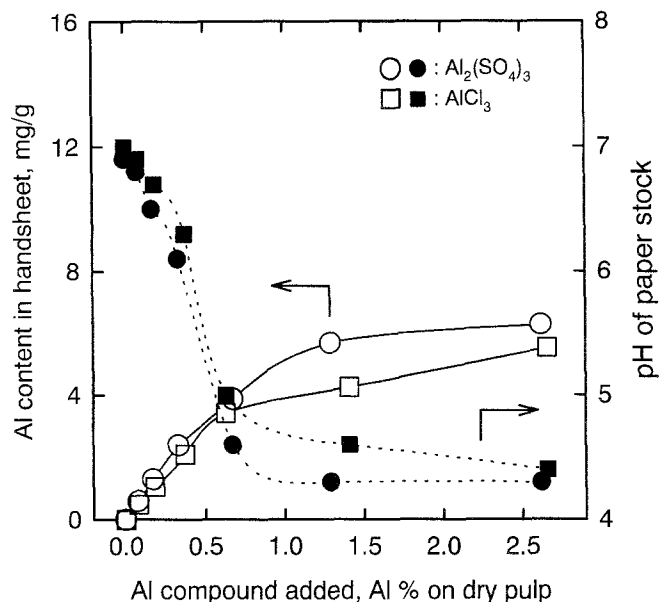
**Fig. 1.** Scanning electron microscope – energy dispersive X-ray analyzer (SEM-EDXA) patterns of handsheets prepared with 1%  $\text{Al}_2(\text{SO}_4)_3$  (A) and 16%  $\text{NaAlO}_2$  (B) on dry weight pulp. The handsheets were coated with Pt-Pd using a sputtering apparatus

minate ion ( $\text{AlO}_2^-$ ) has no chance to be adsorbed on anionic pulp fibers in the pulp suspension.

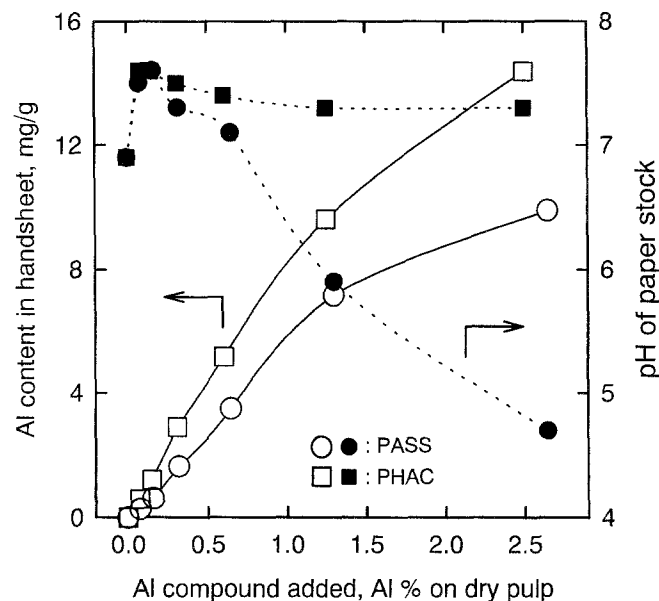
#### Retention behavior of aluminum compounds

Figure 2 shows the relations between the amount of  $\text{Al}_2(\text{SO}_4)_3$  or  $\text{AlCl}_3$  added and the aluminum content in the handsheets, where the x-axis of Fig. 2 was expressed as the amount of aluminum (% on dry weight of pulp) in  $\text{Al}_2(\text{SO}_4)_3$  or  $\text{AlCl}_3$  added to the pulp suspensions. The seven addition levels measured for  $\text{Al}_2(\text{SO}_4)_3$  in Fig. 2 correspond to those of 0, 0.5%, 1%, 2%, 4%, 8%, and 16%  $\text{Al}_2(\text{SO}_4)_3$  on dry weight of pulp. The pH values of the pulp suspensions decreased with the increasing levels of the aluminum compounds and plateaued at about 4.3–4.6. Aluminum contents in the handsheets increased linearly with the increased amount added up to about 0.7%, and then increased gradually. The drastic decrease in the pH values of the pulp suspensions at the 0.3%–0.7% addition levels must have been related to the leveling-off behavior of the aluminum retention, as described later. When  $\text{NaAl}(\text{SO}_4)_2$  was used as the additive, the retention pattern was similar to those for  $\text{Al}_2(\text{SO}_4)_3$  and  $\text{AlCl}_3$  (not shown).

Figure 3 shows the relations between addition levels of PASS or PHAC and the aluminum content in the handsheets. The x-axis in Fig. 3 is expressed as the amount of aluminum (% on dry weight of pulp) in PASS or PHAC added to the pulp suspensions. The aluminum content increased with increasing addition levels of these



**Fig. 2.** Aluminum contents in handsheets prepared from pulp suspensions with  $\text{Al}_2(\text{SO}_4)_3$  or  $\text{AlCl}_3$ . The x-axis shows the levels of aluminum (% on dry weight of pulp) in the additives



**Fig. 3.** Aluminum contents in the handsheets prepared from pulp suspensions with polyaluminum silicate sulfate (PASS) or polyhydroxyaluminum chloride (PHAC). The x-axis shows addition levels of aluminum (% on dry weight of pulp) in the additives

polyaluminum compounds, even up to the high levels, compared with the patterns for  $\text{Al}_2(\text{SO}_4)_3$  or  $\text{AlCl}_3$  in Fig. 2. Because hydroxyl ions are already present in PASS and PHAC molecules to some extent as counterions, the pH patterns of the pulp suspensions obtained by the PASS and PHAC additions were different from those for the  $\text{Al}_2(\text{SO}_4)_3$  and  $\text{AlCl}_3$  additions. Therefore, the results in Figs. 2 and 3 suggest that aluminum retention is greatly

influenced by the pH of the pulp suspensions. Strangely, the pH of the pulp suspensions increased from 6.9 to about 7.7 at 0.1%–0.3% addition levels for PASS and PHAC, which were originally acidic solutions. When PASS or PHAC was added to water without pulp, such increases in pH were not observed; some interactions between PASS or PHAC and impurities present in the bleached hardwood kraft pulp used may have brought about such phenomena as the pH increase.

Retention percentages of aluminum in the handsheets for the aluminum compounds used in this study are shown in Fig. 4, where retention values are expressed as follows: (Al retained in the handsheet/Al added to the pulp suspension)  $\times$  100 (%). PHAC had the highest retention values in the aluminum compounds at all addition levels. In the case of low-molecular-weight aluminum compounds,  $\text{Al}_2(\text{SO}_4)_3$  and  $\text{AlCl}_3$ , the retention values decreased with increasing addition levels of the aluminum compounds. On the other hand, PASS and PHAC showed a maximum peak in the range of the addition levels examined.

#### Effects of fines fraction in pulp

Figure 5 shows the aluminum content and relative basis weight of handsheets prepared from the normal and fines-free pulps with 2%  $\text{Al}_2(\text{SO}_4)_3$  on dry weight of pulp. In this experiment, the cycle of water-feeding, agitation, and drainage in the cylinder of the handsheet-machine was repeated up to five times.<sup>18</sup>

As expected,<sup>18</sup> the relative basis weight of the handsheets prepared from the normal pulp decreased through repeated

mechanical agitation of the pulp suspensions, probably due to partial removal of fines in the beaten pulp. On the other hand, when the fines-free pulp was used, nearly no decrease in basis weight was observed even after the repeated treatment. Aluminum contents were constant for the handsheets prepared from the fines-free pulp, whereas about 40% of the aluminum components were removed from the normal pulp handsheets through the five-repetition treatment, together with partial removal of fines. In this case, about 40% of the aluminum components were adsorbed on fines, which occupied about 7% in the total beaten pulp. Thus, aluminum components are predominantly adsorbed on fines, probably due to larger surface areas or higher carboxyl contents than those of coarse fibers (or both).

Figure 6 shows the results for 8%  $\text{Al}_2(\text{SO}_4)_3$  additions on the dry weight of pulp. Compared with the results in Fig. 5, the aluminum contents in the handsheets increased with increasing addition levels of  $\text{Al}_2(\text{SO}_4)_3$ , from 2% to 8%. Similar patterns were obtained in terms of the effect of fines on aluminum retention. The PASS additions also produced patterns similar to those for  $\text{Al}_2(\text{SO}_4)_3$ , indicating that both low-molecular-weight aluminum and polyaluminum compounds were preferably adsorbed on the fines fraction in pulp suspensions (Figs. 7, 8).

When the fines-free pulp was used with the same addition levels of the aluminum compounds, the amount of aluminum retained in the handsheets was lower, compared with those for the normal pulp, as shown in Figs. 5–8. This result indicates that when fines are not present in the pulp suspension part of the aluminum compounds added to the pulp suspensions are no longer adsorptive on pulp fibers.

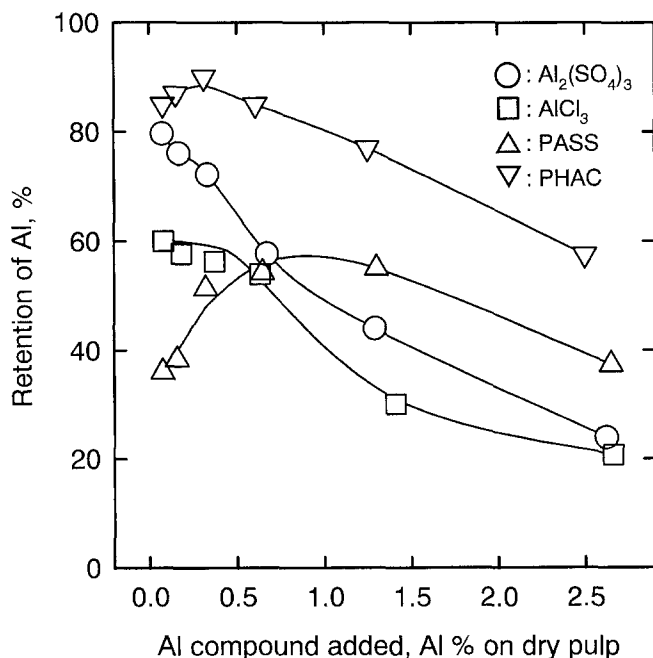


Fig. 4. Retention of aluminum in handsheets prepared from pulp suspensions with various aluminum compounds

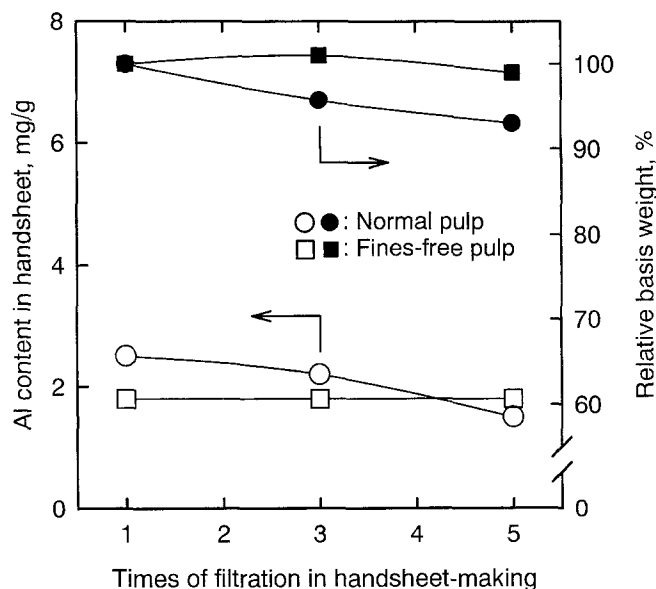
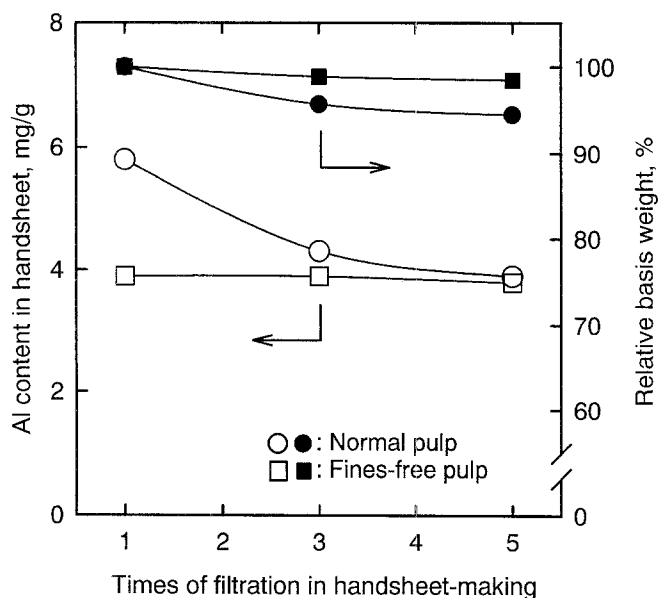
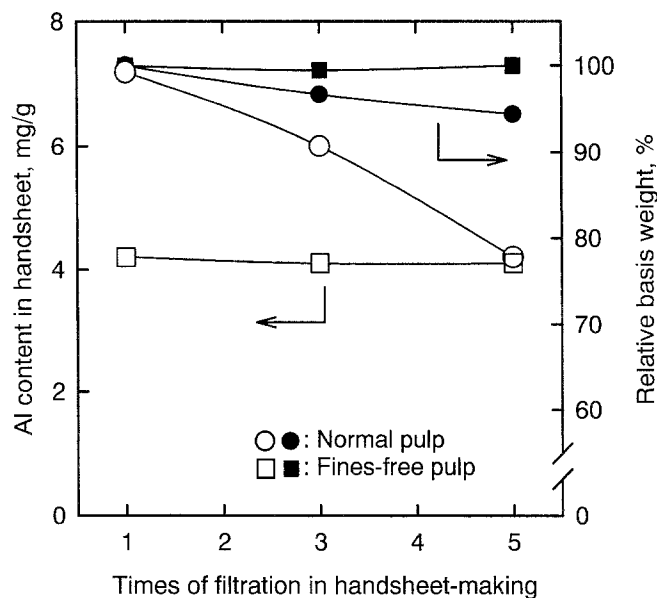


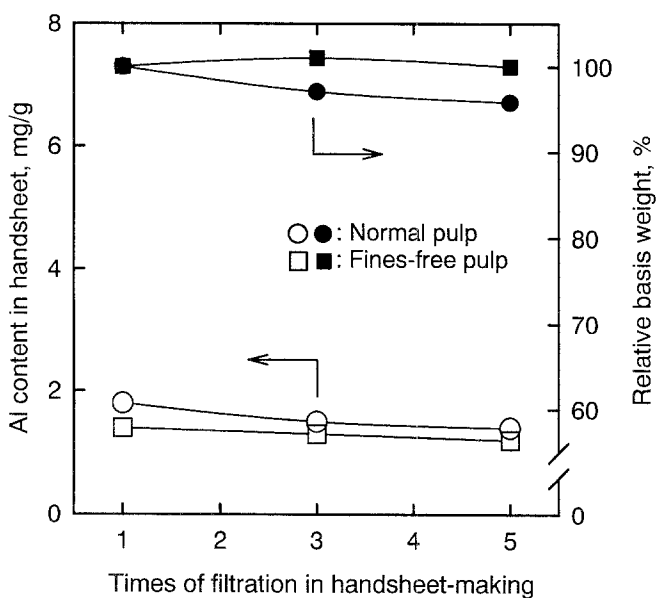
Fig. 5. Aluminum contents and relative basis weight of handsheets prepared from normal and fines-free pulps with 2%  $\text{Al}_2(\text{SO}_4)_3$  by repetition of water-feeding, agitation, and drainage in the cylinder of the handsheet machine



**Fig. 6.** Aluminum contents and relative basis weight of handsheets prepared from normal and fines-free pulps with 8%  $\text{Al}_2(\text{SO}_4)_3$  by repetition of water-feeding, agitation, and drainage in the cylinder of the handsheet machine



**Fig. 8.** Aluminum contents and relative basis weight of handsheets prepared from normal and fines-free pulps with 8% PASS by repetition of water-feeding, agitation, and drainage in the cylinder of the handsheet machine



**Fig. 7.** Aluminum contents and relative basis weight of handsheets prepared from normal and fines-free pulps with 2% PASS by repetition of water-feeding, agitation, and drainage in the cylinder of the handsheet machine

The most probable explanation of these phenomena is that, instead of being adsorbed on fines, some of the cationic aluminum components react with  $\text{OH}^-$  ions, which are present in the pulp suspensions, to form nonionic aluminum hydroxide or nonionic polyaluminum hydroxide. Thus, the formation of these nonionic aluminum compounds resulted in the decrease in retention values of aluminum for the handsheets prepared from the fines-free pulp.

Furthermore, it is notable that most aluminum components, once adsorbed on the fines-free pulp, cannot be removed from the pulp fibers during mechanical agitation of the pulp suspensions. As described later, aluminum flocs, which are formed by reacting with  $\text{OH}^-$  in the pulp suspensions and entrapped in the fiber matrix by filtration effects during the handsheet-making process, can be removed from the pulp fibers by mechanical agitation of the pulp suspensions. Therefore, there may be two types of aluminum components adsorbed on coarse fibers in Figs. 5–8; one is linked to carboxyl groups in the pulp by ionic bonds, and another is formed by precipitation of  $\text{Al}(\text{OH})_3$  molecules through coordination bonds or the van der Waals force on the aluminum components, which are linked to carboxyl groups in pulp fibers by ionic bonds.

#### Influence of the pulp suspension pH

As shown in Figs. 2 and 3, the retention patterns of aluminum in the handsheets seem to be influenced by the pH of the pulp suspensions. It is well known that aluminum components in water change their structures depending on the pH; reactions between cationic aluminum components and  $\text{OH}^-$  (i.e., ionic interactions between them) bring about the structural changes of the aluminum components in water.<sup>3–5</sup> In the case of pulp suspensions, dissociated carboxyl groups in pulp and those of anionic trash in pulp must have a chance to react with cationic aluminum components, competing with  $\text{OH}^-$ . In fact,  $\zeta$ -potentials of cellulose particles strongly depend on the lapse of time between the alum addition and the  $\zeta$ -potential measurement.<sup>8</sup> Furthermore, dilution of the cellulose particle suspensions with water after the alum addition resulted in changes in the

$\zeta$ -potentials from cationic to anionic, because cationic sites of the aluminum components on the cellulose particle surfaces react with  $\text{OH}^-$  ions during the dilution process to form nonionic sites.<sup>8</sup>

Figure 9 illustrates the aluminum contents of handsheets prepared from the fines-free pulp with  $\text{Al}_2(\text{SO}_4)_3$  or PASS, where the pulp suspensions were adjusted to about pH 7 with a diluted NaOH solution using an automatic pH controller. The aluminum contents in the handsheets, which were prepared from the above pulp suspensions at pH 7 by the three-repetition treatment of water-feeding, agitation, and drainage cycle in the cylinder of the handsheet machine, are also shown in Fig. 9. The aluminum content in the handsheets drastically increased after the pH adjustment, compared with the results in Figs. 2 and 3; and more than 80% of aluminum components added to the pulp suspensions as  $\text{Al}_2(\text{SO}_4)_3$  or PASS were retained in the handsheets. Thus, the pH of the pulp suspensions (i.e., amount of  $\text{OH}^-$  present in the pulp suspensions) greatly influenced aluminum retention. However, as shown in Fig. 9, more than 70% of the aluminum components, once retained on the fines-free pulp fiber mat, were removed by the three-repetition treatment of agitation and drainage of the pulp suspensions after pH adjustment. Therefore, removal of these aluminum components by mechanical agitation of the pulp suspensions must be due to aluminum flocs physically adsorbed on fibers or entrapped in the fiber matrix by filtration effects without ionic or coordinate interactions. Therefore, even though adjustment of the pulp suspensions to about pH 7 with the NaOH solution leads to higher retention values of

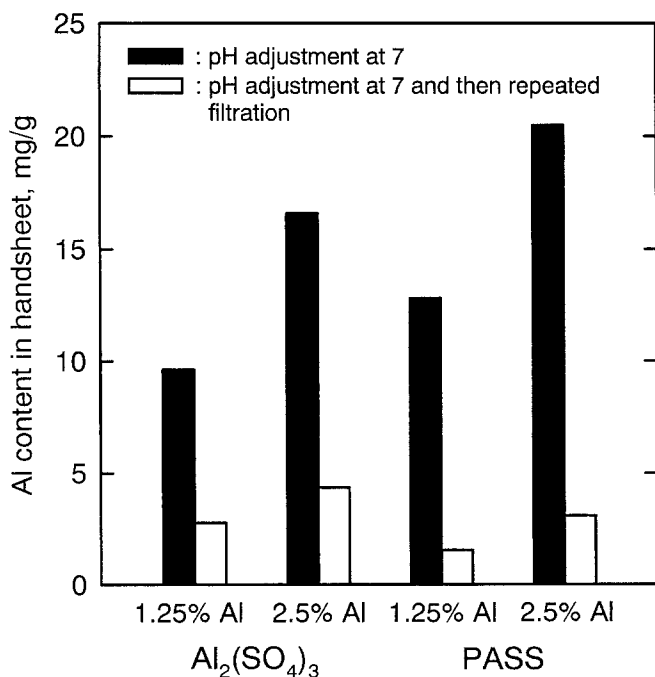


Fig. 9. Aluminum contents of handsheets prepared from fines-free pulp with  $\text{Al}_2(\text{SO}_4)_3$  or PASS at pH 7 and those treated by three-times repetition of water-feeding, agitation, and drainage in the cylinder of the handsheet machine after the pH adjustment

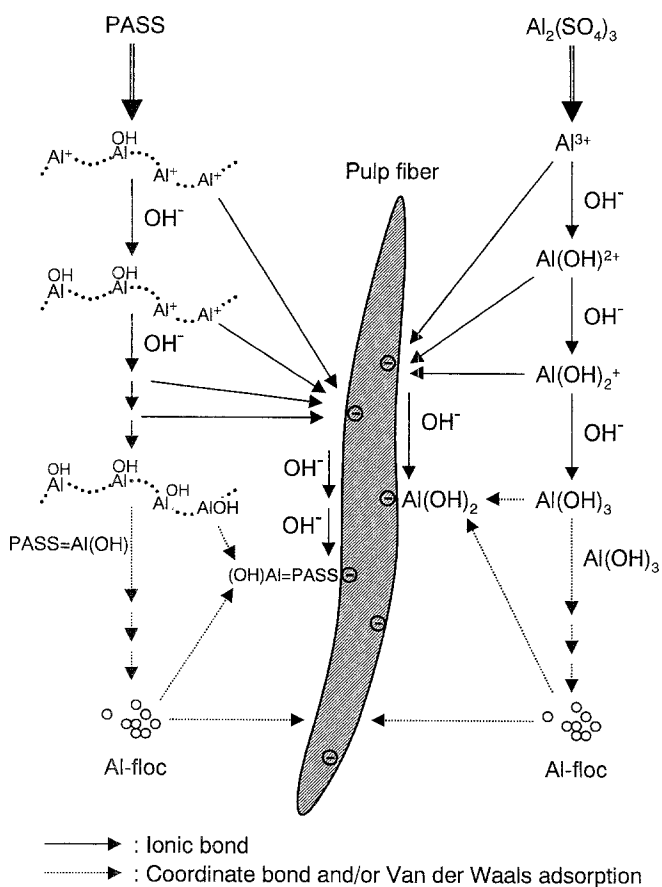
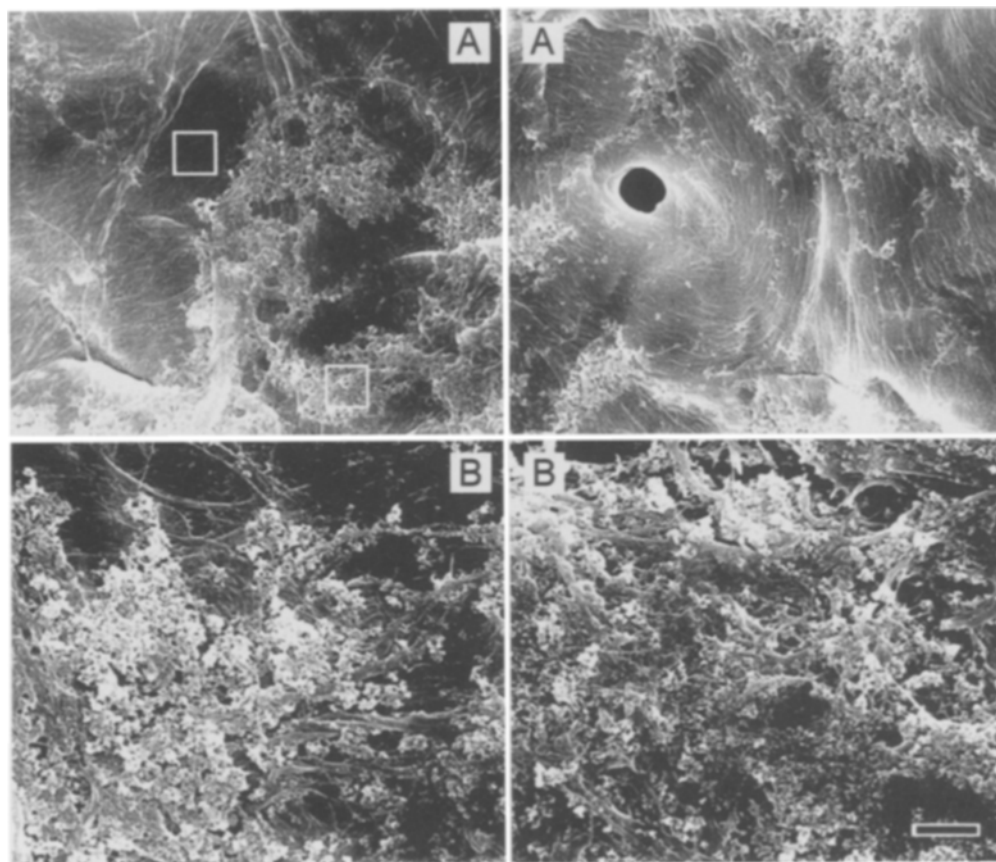
aluminum components in the handsheets, these aluminum components may not have the capability to adsorb further anionic compounds, such as internal sizes by ionic interactions.<sup>21</sup> Therefore, cationic charges must have been lost for these aluminum components on pulp fibers.<sup>21</sup>

Figure 10 shows SEM microphotographs of surfaces of the handsheets prepared from the fines-free pulp with 8%  $\text{Al}_2(\text{SO}_4)_3$ . The pH of the pulp suspension was not controlled for handsheet A in Fig. 10 and was adjusted to about pH 7 with a diluted NaOH solution using an automatic pH controller for handsheet B in Fig. 10. In the case of handsheets without pH adjustment, two clearly distinguishable regions are observed: the region of the pulp fiber surface with microfibrils and that covered with aluminum flocs less than  $0.1\ \mu\text{m}$  in diameter. Because the fines-free pulp was used for the handsheets in Fig. 10, fines were not included in the floc-like substances. These aluminum flocs seem to be formed on pulp fiber surfaces, resulting in formation of the stable precipitates on pulp fibers to the mechanical agitation of the pulp suspensions. SEM-EDXA analysis was carried out on two focused areas: the fibrils and aluminum floc areas (Fig. 10A). The aluminum content of the floc area was about twice that of the fibril area. Thus, even though aluminum flocs were not observed, aluminum components were present in the fibril area, probably forming salts of carboxyl groups in the pulp.

The 8% addition level of  $\text{Al}_2(\text{SO}_4)_3$  for the handsheets in Fig. 10 is unusually high for practical papermaking. When handsheets were prepared with  $\text{Al}_2(\text{SO}_4)_3$  at the usual addition levels (i.e., 0.5%–2.0% on dry weight of pulp), the aluminum flocs seen in Fig. 10 were not observed clearly on the pulp fiber surfaces. Therefore, the aluminum flocs observed in Fig. 10A are not necessarily the only form of aluminum components adsorbed on pulp fibers. Much smaller aluminum flocs – each  $\text{Al}(\text{OH})_3$  molecule and cationic aluminum ion species such as  $\text{Al}^{3+}$ ,  $\text{Al}(\text{OH})^{2+}$ , and  $\text{Al}(\text{OH})_2^+$  – must participate in the adsorption of aluminum components on pulp fibers in pulp suspensions through ionic interactions, coordinate bonds, or van der Waals adsorption. As described previously, the ionic bond formation of cationic aluminum compounds with either  $\text{OH}^-$  in the pulp suspensions or carboxyl groups in the pulp is a competing reaction. Because the number of carboxyl groups in pulps is limited ( $60\ \mu\text{Eq/g}$  for the bleached hardwood kraft pulp used in this study), it is natural that as the addition levels of aluminum compounds are increased more aluminum flocs are formed by reacting with  $\text{OH}^-$  in the pulp suspensions.

On the other hand, the surface of the handsheet prepared by the pH adjustment (Fig. 10B) was covered with larger aluminum flocs in a more extended area. Because these flocs could mostly be removed by mechanical agitation of the pulp suspensions, they must be formed in the pulp suspensions with  $\text{OH}^-$  and then entrapped in the fiber matrix by the filtration effect, similar to filler retention, during the handsheet production process. The adsorption mechanisms of aluminum components on pulp fibers when  $\text{Al}_2(\text{SO}_4)_3$  or PASS is added to pulp suspensions are summarized in Fig. 11.

**Fig. 10.** SEM microphotographs of surfaces of handsheets prepared from fines-free pulp with 8%  $\text{Al}_2(\text{SO}_4)_3$ . The pH of the pulp suspension was not controlled for **A** and was adjusted to pH 7 with a diluted NaOH solution for **B**. Scale bar corresponds to 1  $\mu\text{m}$ . Outlined areas were analyzed by focused EDXA for determining aluminum contents



**Fig. 11.** Retention mechanisms of aluminum compounds on pulp fibers for  $\text{Al}_2(\text{SO}_4)_3$  or PASS additions

## Conclusions

The SEM-EDXA and XFA methods were applied to the determination of aluminum contents in handsheets. The following results were obtained in terms of adsorption behavior of aluminum components on pulp fibers.

1. Retention patterns of aluminum components in handsheets varied among the aluminum compounds added to the pulp suspensions. The chemical structures of the aluminum compounds and the pH of the pulp suspensions greatly influence the retention behavior of the aluminum components.

2. When aluminum compounds were added to pulp suspensions as wet-end additives, their aluminum components were predominantly adsorbed on fines, probably due to the larger surface areas and the higher carboxyl content than those of coarse fibers.

3. The SEM observations and spot EDX analysis revealed that not only aluminum flocs but also far smaller species, such as aluminum ions, seemed to be adsorbed on pulp fibers.

4. There were two types of aluminum floc retained in the handsheets; one could not be removed from pulp fibers by mechanical agitation of the pulp suspensions, and another could be. Aluminum flocs, which are formed from cationic aluminum components in pulp suspensions by reacting with  $\text{OH}^-$  and entrapped in fiber matrix, similar to filler retention, during the handsheet-making process must be capable of being removed.

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