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# Studies on interactions between aluminum compounds and cellulosic fibers in water by means of $^{27}$Al-NMR

**Abstract** Interactions between pulp fibers and aluminum compounds in pulp suspensions were studied using fibrous cellulose (FC) and fibrous carboxymethylcellulose (FCMC) powders as models of pulp fibers by X-ray fluorescence analysis and $^{27}$Al nuclear magnetic resonance. When deionized water was used at pH 4–5, water-soluble cationic aluminum species ($Al^{3+}$, aluminum oligomer, and polyaluminum species) were adsorbed on the solid FCMC, forming carboxylic acid aluminum salts by cation exchange. The formation of these nondissociated pulp-COOAl type structures in paper sheets may contribute to some decreases in hydrophilic property. On the other hand, the water-soluble cationic aluminum species had nearly no interactions with hydroxyl groups of solid cellulose in the suspensions at pH 4–5. When tap water was used at pH 5–7, some aluminum components were retained on not only FCMC but also the FC sample. Probably, water-insoluble $Al(OH)_3$ flocs are formed in the suspensions at pH 5–7 and retained on the FC sample by simple filtration effect. Therefore, two mechanisms of the aluminum retention (i.e., electrostatic interactions and a simple filtration effect) may exist between pulp fibers and aluminum components in the practical papermaking process.

**Key words** Aluminum compound · Cellulose powder · Carboxymethylcellulose · $^{27}$Al-NMR · Water retention value

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## Introduction

Aluminum compounds such as aluminum sulfate have been widely used to enhance the retention of anionic wet-end additives and pulp fines and to improve the runnability of practical papermaking process. It is well known that aluminum components have complicated chemical structures and ionic charges in water, depending on pH values and other factors.[1-6] The structural changes of aluminum components in water are initiated by ionic interactions between cationic aluminum species and OH$^-$ ions, and in some cases cationic polyaluminum species are formed from low-molecular-weight cationic aluminum species.[4,7-9] On the basis of these experimental results, some hypotheses concerning the retention mechanisms of aluminum compounds in paper sheets have been reported.[7,9-11] In pulp suspensions, however, not only OH$^-$ ions but also dissociated carboxyl groups in pulp must be able to react competitively with the cationic aluminum species. This competing reaction may be more essential and significant for the papermaking process than polymerization of aluminum components in water. Thus, the detailed behavior and functions of aluminum compounds in papermaking have not yet been established.

In our previous studies,[12,13] the retention behavior of aluminum components was found to be sensitively influenced by their chemical structures, the pH of the pulp suspensions, and the presence of the fines fraction. 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 mechanical agitation of the pulp suspensions. On the other hand, nonionic aluminum flocs are formed to some extent between cationic aluminum species and OH$^-$ ions in pulp suspensions, and some of them are retained on handsheets by entrapping in pulp fiber mats during the filtration process. However, these aluminum flocs are mostly removable by repeated mechanical agitation of the pulp suspensions. When fines are present in

the pulp suspensions, the aluminum components are predominantly adsorbed on the fines owing to their larger surface areas or higher carboxyl contents than those of coarse fibers.[6]

In this study, fibrous cellulose (CF) powder and fibrous carboxymethylcellulose (FCMC) powder were used as models of bleached kraft pulp fibers, and the retention behavior or adsorption behavior of aluminum components on these cellulosic powders was analyzed by X-ray fluorescence analysis and solution-state $^{27}$Al nuclear magnetic resonance (NMR). Especially, the roles of carboxyl groups and hydroxyl groups in pulp fibers in the adsorption behavior of various aluminum species ($Al^{3+}$ ion, aluminum oligomers, and polyaluminum species) were discussed for elucidating the retention mechanisms of aluminum compounds on pulp fibers at the wet-end of the papermaking process.

## Materials and methods

### Materials

A fibrous microcrystalline cellulose powder (FC) (CF1; Whatman Co., UK) and a fibrous carboxymethylcellulose powder (FCMC) (CM23; Whatman Co., UK) were used as cellulosic powder samples. Carboxyl contents of FC and FCMC determined by the TAPPI test method[14] were 0 and 0.6 mEq/g, respectively; the degree of substitution of FCMC was about 0.11. Polyaluminum chloride [PAC; rational formula: $Al_2(OH)Cl_5$] (Nippon Light Metal Co., Japan) and polyhydroxyaluminum chloride [PHAC; rational formula: $Al_2(OH)_5Cl$] (Riken Green Co., Japan) were used as high-molecular-weight aluminum compounds.[12] The aluminum oligomer $Al_{13}O_4(OH)_{24}(H_2O)_{12}^{7+}$ was prepared from an aluminum chloride solution by partial neutralization with diluted NaOH.[11] Aluminum sulfate and other reagents were commercial products (Wako Chemicals, Japan). The tap water used contained $Ca^{2+}$ and $Mg^{2+}$ ions at 0.60 and 0.22 mEq/l, respectively.

### Adsorption of aluminum compounds on cellulosic fibers

A known amount of a 1% aluminum sulfate solution was added to a 0.15% FC or FCMC suspension prepared with deionized water or tap water. After stirring for 30s, the suspension was filtered using a Buchner funnel. Without washing, the powder-like wet residue was dried by two procedures: (1) drying at 20°C for 24h and (2) heating at 105°C for 2h. For $^{27}$Al-NMR analysis, a known amount of FC or FCMC was added to a 0.1% (or 0.01% in some experiments) aluminum sulfate solution, and the FC or FCMC suspension was directly subjected to the NMR analysis.

### Analyses

The aluminum content in dried-state cellulosic samples was determined using an X-ray fluorescence analyzer

(XFA) (MESA-500; Horiba Co., Japan).[12,13] A calibration curve for quantitative analysis was obtained using mixtures of FC and aluminum hydroxide with various known ratios. Brunauer-Emmett-Teller (BET) specific surface areas of cellulosic samples were measured using a nitrogen adsorption apparatus (SA 3100; Coulter Co., USA). Fouries transform infrared (FT-IR) spectra of cellulosic samples were recorded on an FT-IR 8100M (Shimadzu Co., Japan) using the KBr disk method. Solution-state $^{27}$Al-NMR spectra of cellulose suspensions containing aluminum compounds were collected at 20°C on a JEOL JNM-A500 FT-NMR system operating at 130.32MHz using 12μs for 90° pulse. A spectral width of 52000Hz with 16000 data points was selected, and data accumulation time was in the range of 1–5min, depending on the samples. The peak due to $Al(H_2O)_6^{3+}$ was used as a standard for 0ppm. When plural NMR spectra were compared in one figure, magnification of the y-axis of each spectrum was adjusted to the same value. FCMC samples treated with diluted HCl or $Al_2(SO_4)_3$ and dried at 20° or 105°C were subjected to determination of water retention values (WRV), which were calculated from the following equation.

$$WRV(\%) = \frac{W_2 - W_1}{W_1} \times 100$$

where $W_1$ is the sample weight after drying at 105°C for 2h, and $W_2$ is the sample weight after soaking in deionized water for 24h followed by dehydration using centrifugation at 2500g for 15min.

## Results and discussion

### Adsorption of aluminum components on cellulosic fibers in deionized water

Figure 1 shows the aluminum content in FC and FCMC samples prepared from their suspensions in deionized water, to which 0%–4% (based on the dry weight of the cellulosic sample) aluminum sulfate was added. Clear difference in the retention behavior of aluminum components was observed between FC and FCMC samples. No aluminum components were retained in FC, whereas the aluminum content linearly increased for FCMC with increasing aluminum sulfate addition. The pH values of the FC and FCMC suspensions decreased by the aluminum sulfate addition, although the FCMC suspension had higher pH values in the range of the aluminum sulfate addition level of 0%–2% (based on the dry weight of the cellulosic sample).

Table 1 represents carboxyl contents and specific surface areas of the FC and FCMC samples. Although the specific surface area of FC was larger than that of FCMC, aluminum components were not retained in the FC at all. Thus, the different aluminum retention behavior between FC and FCMC in Fig. 1 is ascribed to that in the carboxyl content; carboxyl groups, rather than specific surface areas of the cellulosic samples, primarily govern the aluminum retention behavior at pH 4.8–4.4 in deionized water.[6] These
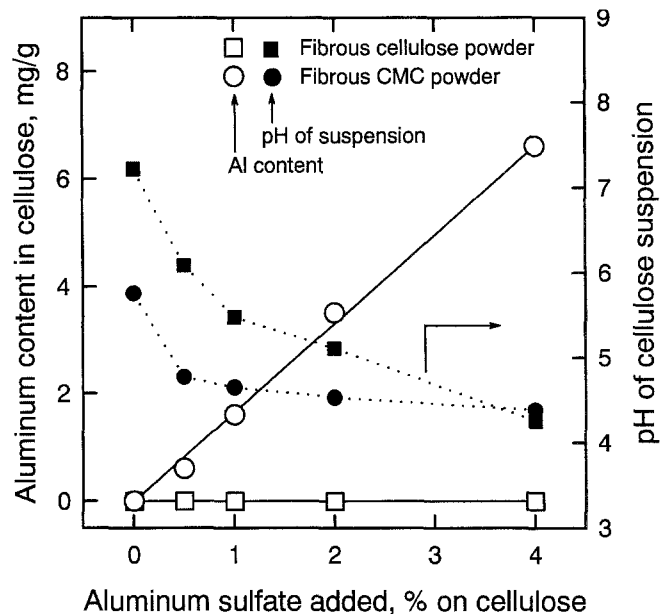
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Fig. 1. Aluminum content in fibrous cellulosic powders prepared from their suspensions in deionized water to which aluminum sulfate was added

Table 1. Carboxyl content and specific surface area of fibrous cellulosic powders used in this study

| Sample | Carboxyl content (mEq/g) | Specific surface area (m²/g) |
|---|---|---|
| Fibrous cellulose (FC) | 0.0 | 0.621 |
| Fibrous carboxymethylcellulose (FCMC) | 0.6 | 0.330 |



Fig. 2. $^{27}$Al-NMR (nuclear magnetic resonance) spectra of aluminum sulfate solutions, to which fibrous cellulosic powders were added. $A$, 0.1% Solution of aluminum sulfate; $B$, $A$ + fibrous cellulose powder; $C$, $A$ + fibrous carboxymethylcellulose powder

results indicate that aluminum components originating from aluminum sulfate are adsorbed on cellulosic fibers through electrostatic interactions between cationic aluminum components and anionic carboxyl groups of cellulosic fibers in the suspensions. Furthermore, nearly no interactions between hydroxyl groups of cellulose and aluminum components exist in the suspensions at pH 4.8–4.4.

Figure 2 shows $^{27}$Al-NMR spectra of 0.1% aluminum sulfate solutions before and after the FC or FCMC addition. The original aluminum sulfate solution has large and small resonance peaks at 0 and −3.3 ppm due to $Al(H_2O)_6^{3+}$ and $Al(H_2O)_5(SO_4)^+$, respectively.[15] Whereas the FC addition had no influence on the $^{27}$Al-NMR pattern, both peaks disappeared after the FCMC addition, resulting from adsorption of these water-soluble aluminum components on the solid FCMC. This result also supports that nearly no interactions are present between cellulose hydroxyl groups and aluminum components in deionized water, but electrostatic interactions take place between carboxyl groups of FCMC and aluminum components.

When the aluminum sulfate concentration in the solutions was decreased to 0.01%, which was close to the practical papermaking level, the resonance peak at −3.3 ppm
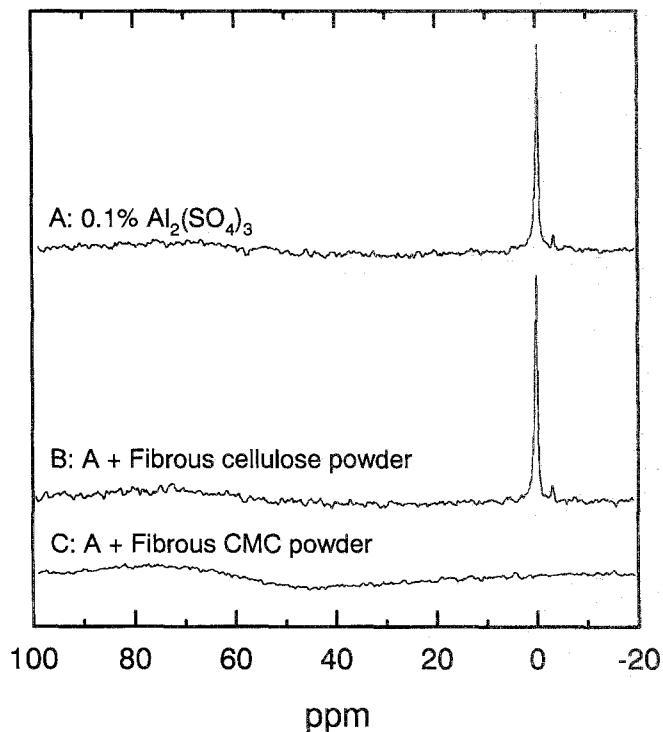


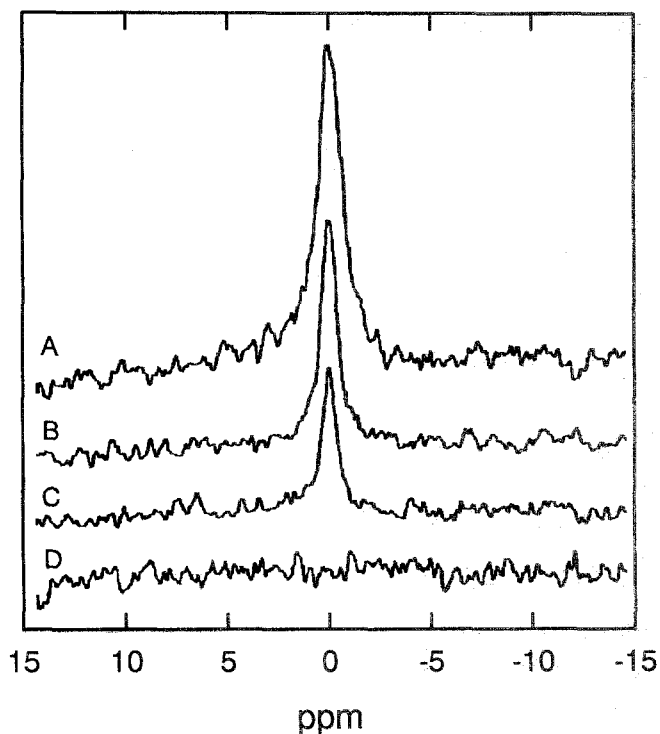Fig. 3. $^{27}$Al-NMR spectra of 0.01% aluminum sulfate solutions to which fibrous carboxymethylcellulose (FCMC) powder was added. Molar ratios of Al/sodium carboxylate in FMC in the suspensions are 1:0 ($A$), 1:1 ($B$), 1:2 ($C$), and 1:4 ($D$)
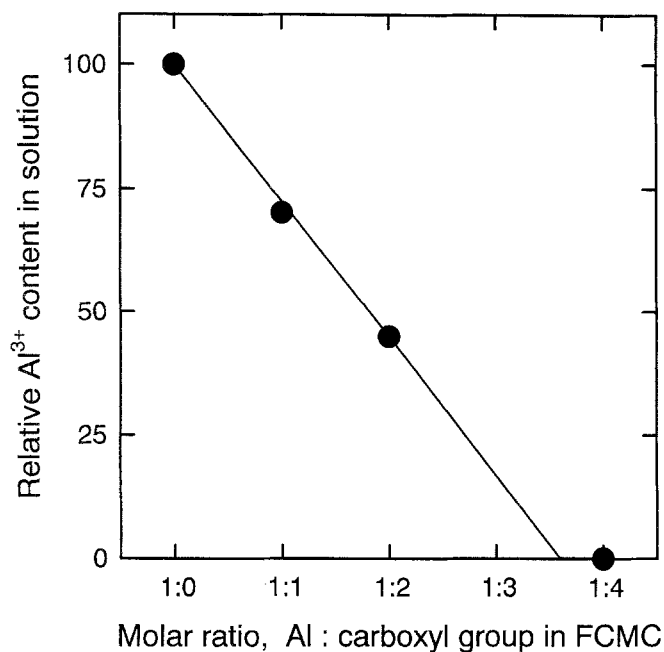
**Fig. 4.** Relative $Al^{3+}$ content in 0.01% aluminum sulfate solutions to which fibrous carboxymethylcellulose powder was added

could not be detected, probably because of low signal/noise ratios (Fig. 3A). The peak at 0 ppm due to $Al(H_2O)_6^{3+}$ decreased with increasing FCMC addition to the aluminum sulfate solution (Fig. 3B–D). Relations between the molar aluminum carboxyl group ratio of FCMC and the relative $Al(H_2O)_6^{3+}$ content in the suspension obtained in Fig. 3 were plotted in Fig. 4. The $Al^{3+}$ content in the suspension linearly decreased with increasing molar ratio of the carboxyl group in FCMC, resulting from adsorption of water-soluble $Al^{3+}$ on the solid FCMC. Furthermore, the pattern in Fig. 4 indicates that 1 mol of $Al^{3+}$ consumes approximately 3 mol of carboxyl group in the FCMC in the suspension, forming tricarboxylic acid aluminum salt, $(FCMC-COO)_3Al$.

Figure 5 shows the $^{27}Al$-NMR spectra of polyaluminum chloride (PAC), polyhydroxyaluminum chloride (PHAC), and aluminum oligomer solutions before and after the FCMC addition, where the amount of FCMC added was arbitrary. PAC has a large resonance peak at 0 ppm due to $Al(H_2O)_6^{3+}$ and a broad peak in the range from 0 to 14 ppm due to polyaluminum compounds, which have maximum peaks at 5 and 10 ppm (Fig. 5A). The $^{27}Al$-NMR spectrum of PHAC has a large, broad resonance peak in the range from −10 to 40 ppm due to polyaluminum compounds, which have a maximum peak at 11 ppm. Probably the chemical structures and their cationic charges are different between the polyaluminum species in PAC and PHAC (Fig. 5A,B). Small resonance peaks at 0 and 63 ppm due to $Al(H_2O)_6^{3+}$ and $Al_{13}O_4(OH)_{24}(H_2O)_{12}^{7+}$, respectively, were detected in the PHAC spectrum. When an aluminum chloride solution was partly neutralized with NaOH, the resonance peak due to $Al_{13}O_4(OH)_{24}(H_2O)_{12}^{7+}$ appeared at 63 ppm together with that due to $Al(H_2O)_6^{3+}$ at 0 ppm (Fig. 5C). Although these $^{27}Al$-NMR patterns were unchanged by the addition of FC
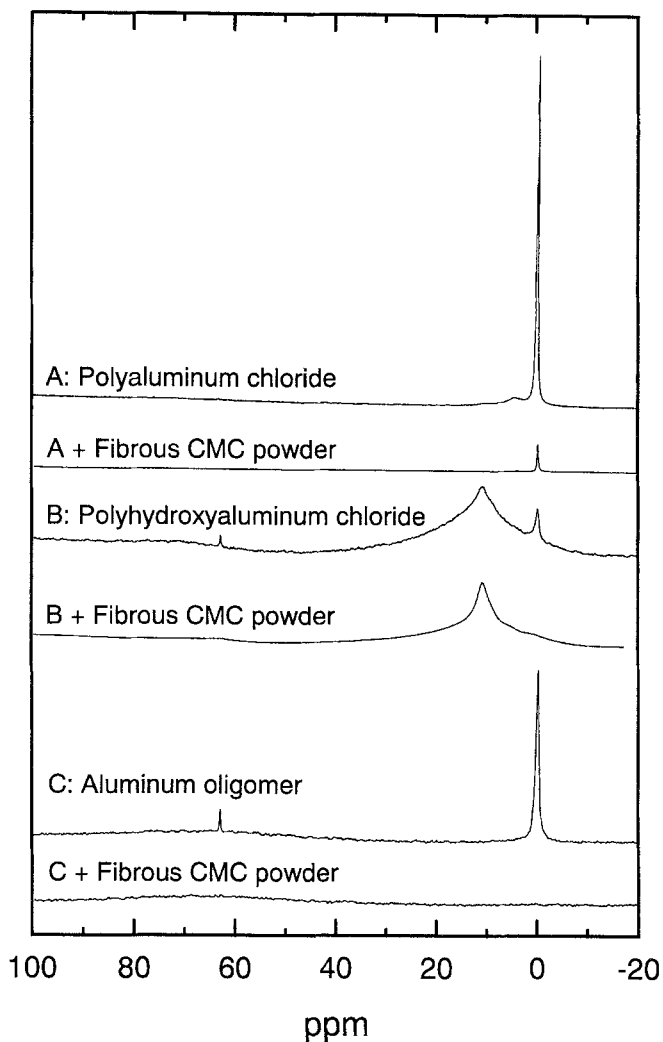


**Fig. 5.** $^{27}Al$-NMR spectra of polyaluminum chloride (*A*), polyhydroxyaluminum chloride (*B*), and aluminum oligomer (*C*) solutions to which an arbitrary amount of fibrous carboxymethylcellulose powder was added. Aluminum contents in solutions A, B, and C were adjusted to be the same as that of a 1% aluminum sulfate solution

to the solutions, the resonance peaks disappeared or clearly decreased after the FCMC addition. These results indicate that cellulose hydroxyl groups have nearly no interactions with low-molecular-weight aluminum components, aluminum oligomer, or high-molecular-weight polyaluminum components in the suspensions. On the other hand, all these water-soluble aluminum species are adsorbed on the solid FCMC through electrostatic interactions.

Figure 6 shows infrared (IR) spectra of FCMC samples treated with aluminum sulfate in the suspensions. All samples had an absorption band at 1680 cm$^{-1}$ due to deformation vibration of water molecules present in the samples. Because the original FCMC has the structure of FCMC-COONa, the band at about 1600 cm$^{-1}$ is due to dissociated carboxyl groups (Fig. 6A). When FCMC was soaked in acidic water at pH 4 and filtered, the band due to isolated free carboxyl groups appeared on the sample at about 1740 cm$^{-1}$ in the IR spectrum (Fig. 6B). The aluminum sulfate-treated FCMC had shoulder bands at about 1600
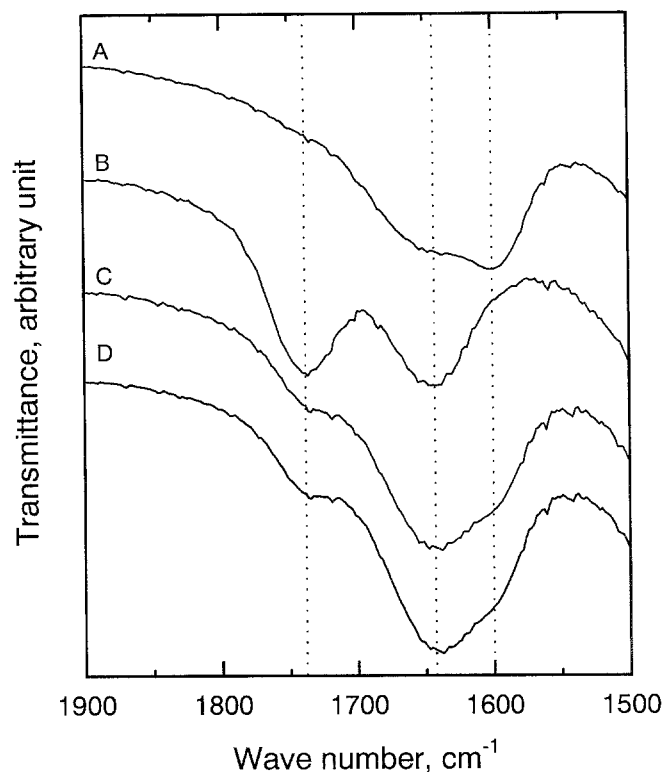
**Fig. 6.** Infrared (IR) spectra of fibrous carboxymethylcellulose (FCMC) powders prepared from their suspensions in water to which aluminum sulfate was added. A, Original FCMC; B, FCMC treated with diluted HCl at pH 4; C, FCMC treated with $Al_2(SO_4)_3$ and dried at 20°C; D, FCMC treated with $Al_2(SO_4)_3$ and dried at 105°C



**Fig. 7.** Aluminum content in fibrous cellulosic powders prepared from their suspensions in tap water to which aluminum sulfate was added

and $1740 \, cm^{-1}$ due to carboxylic acid salts and free carboxyl groups, respectively. No clear difference in the IR patterns was observed between the FCMC samples dried at 20° and 105°C; the heat treatment has nearly no influence on the structure of carboxyl groups in the aluminum sulfate-treated FCMC. Because XFA analysis showed that the aluminum sulfate-treated FCMC samples contained no sodium, but aluminum was present, the shoulder peaks at $1600 \, cm^{-1}$ were assigned to carboxylic acid aluminum salts, FCMC-COOAl. Thus, cationic aluminum species are adsorbed on FCMC, forming carboxylic acid aluminum salts in the suspensions by cation exchange from FCMC-COONa to FCMC-COOAl. Although the results in Figs. 3 and 4 suggest the formation of tricarboxylic acid aluminum salts, $(FCMC-COO)_3Al$, in the suspension, the IR spectra of Fig. 6C,D show that not only the aluminum salt structures but also the free acid structures are formed from the FCMC-COONa to some extent in the aluminum sulfate-treated FCMC at pH 4.4–4.8. The different addition sequence between the two experiments may have resulted in a somewhat different result between Figs. 3 and 6.

### Adsorption of aluminum compounds on cellulosic fibers in tap water

Figure 7 shows the aluminum content in the FC and FCMC samples prepared from their suspensions in tap water, to
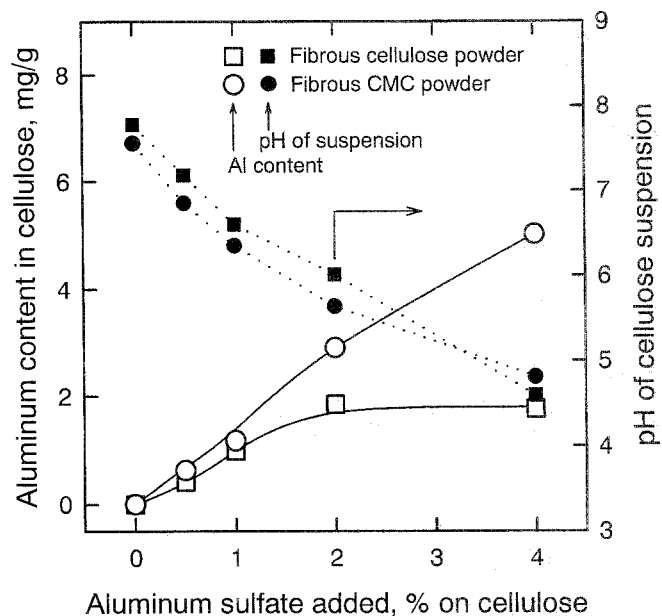
which 0%–4% (based on the dry weight of the cellulosic sample) aluminum sulfate was added. When tap water was used, the pH values of the suspensions after the aluminum sulfate addition were clearly higher than those for deionized water due to the buffering effect of the calcium ion present in the tap water.[13] However, the pH value of the FC suspension and FCMC suspensions decreased in a manner similar to that seen with the aluminum sulfate addition. The aluminum content in the FCMC samples prepared using tap water was almost equal to or slightly lower than that for deionized water. On the other hand, the aluminum content in the FC samples clearly increased when tap water was used. It is well known that water-insoluble nonionic $Al(OH)_3$ flocs and water-soluble cationic $Al^{3+}$, $Al(OH)^{2+}$, $Al(OH)_2^+$, and $Al_{13}O_4(OH)_{24}(H_2O)_{12}^{7+}$ species are present with various ratios in water at pH 5–7 under equilibrium conditions.[16] Because cationic aluminum species and cellulose hydroxyl groups have no interactions in the suspensions (Figs. 2, 5), most aluminum components retained in the FC sample in Fig. 7 may consist of the $Al(OH)_3$ flocs, which are physically entrapped in the FC residue during the filtration process. Electrostatic interactions between carboxyl groups of FCMC and cationic aluminum species must be present to some extent even at pH 5–7, resulting in higher aluminum contents in the FCMC samples than for the FC samples (Fig. 7).

Figure 8 shows ^{27}Al-NMR spectra of 0.01% aluminum sulfate solutions prepared using deionized water and tap water. Because the broad peak-like waves around 60 ppm were observed in any ^{27}Al-NMR spectra at such high magnifications for solutions even containing no aluminum compounds, these waves of baselines are due to some factor other than the aluminum species. Thus, only the resonance peak due to $Al(H_2O)_6^{3+}$ was present in both spectra, and neither aluminum oligomers nor polyaluminum species

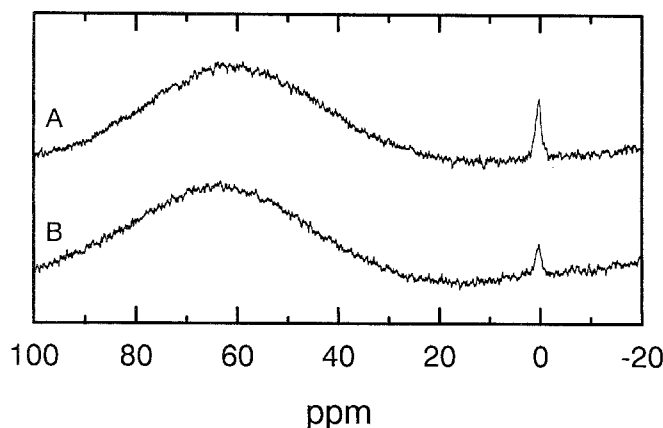Fig. 8. $^{27}$Al-NMR spectra of 0.01% aluminum sulfate solutions prepared using deionized water ($A$) and tap water ($B$)



Structure of carboxyl groups in the FCMC powder

Fig. 9. Water retention value of fibrous carboxymethylcellulose powders having carboxyl groups of different types

were present. The peak area due to $Al(H_2O)_6^{3-}$ in tap water is smaller than that for deionized water probably because water-insoluble $Al(OH)_3$ flocs are formed from $Al(H_2O)_6^{3+}$ to some extent by $OH^-$ ions in tap water at pH 5–7. This result supports the previously described hypothesis of aluminum retention on the FC samples when tap water is used.

Hence, there are two mechanisms for adsorption of aluminum components on cellulosic fibers in the papermaking process. One is the electrostatic interaction between anionic carboxyl groups of cellulosic fibers and cationic aluminum species, which occurs in pulp suspensions at a pH lower than 5. Another is the physical retention of water-insoluble nonionic aluminum flocs, which are formed at pH 5–7 on wet webs by the simple filtration effect during the drainage process of papermaking.

Effect of carboxyl group structures in cellulose on hydrophilic property

As described previously, cationic aluminum species are adsorbed on FCMC, forming carboxylic acid aluminum salts in the FCMC suspension. The hydrophilic property of FCMC samples having different structures of carboxyl groups was then evaluated from their water retention values (Fig. 9). The FCMC sample having free carboxylic acids was prepared by the same method as for sample B in Fig. 6, and that having carboxylic acid aluminum salts and free carboxyl groups was prepared by the same method as for sample C in Fig. 6. When these FCMC samples were dried at 20°C, their water retention values were in the order FCMC-COONa > FCMC-COOH > (FCMC-COOAl + FCMC-COOH). This result agrees with the degree of dissociation of these carboxyl groups. Thus, conversion of hydrophilic dissociated carboxyl groups in FCMC to nondissociated carboxylic acid aluminum salts brings about a decrease in hydrophilic property of the FCMC samples.[17,18] Not only the hydrophobicity of the FCMC-COOAl type structure but also formation of cross-linkages between cellulose chains through the FCMC-COO-Al-OOC-FCMC type structure may have resulted in the lower
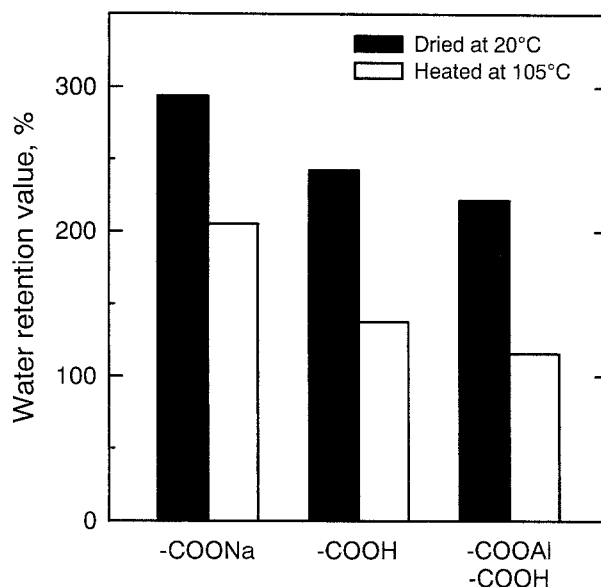
water retention value or the lower swelling degree in water for the aluminum sulfate-treated FCMC.

When the FCMC samples were dried at 105°C for 2h, their water retention values decreased further. However, the order was the same as for the FCMC samples dried at 20°C. Because the structure of carboxyl groups is not changed by the heat treatment for the aluminum sulfate-treated FCMC sample (Fig. 6), the decrease in water retention values after heat treatment may be due to formation of irreversible hydrogen bonds in the FCMC samples.[19]

## Conclusions

Interactions between fibrous cellulosic powders and aluminum compounds in water were studied using X-ray fluorescence analysis, solution-state $^{27}$Al-NMR spectroscopy, and other techniques. The following conclusions were obtained.

1. When deionized water is used at pH 4–5, water-soluble cationic aluminum species ($Al^{3+}$, aluminum oligomer, and polyaluminum compounds) originating from aluminum compounds added to FCMC suspensions are adsorbed on the solid FCMC, forming carboxylic acid aluminum salts by electrostatic interactions.

2. Water-soluble cationic aluminum species have almost no interactions with hydroxyl groups of solid cellulose in the suspensions prepared using deionized water at pH 4–5.

3. Not only carboxylic aluminum salts but also free carboxyl groups are formed from FCMC sodium salt by the addition of aluminum sulfate.

4. When tap water is used at pH 5–7, on the other hand, some aluminum components are retained on the FC sample. Water-insoluble $Al(OH)_3$ flocs are formed in the

suspensions at pH 5–7 and are probably retained on the FC sample by simple filtration effect.

5. Therefore, there are two mechanisms to explain the aluminum retention on paper sheets during the papermaking process: electrostatic interactions and a simple filtration mechanism.

6. The formation of carboxylic acid aluminum salts in paper sheets may contribute to some decreases in hydrophilic properties.

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