THE CHEMISTRY OF ALUMINUM SALTS IN PAPERMAKING: II INFLUENCE ON THE ADSORPTION OF A CATIONIC POLYELECTROLYTE

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ABSTRACT

The adsorption of a cationic polyelectrolyte onto cellulose fibers in the presence of aluminum species was investigated. Solutions of either aluminum chloride or aluminum sulfate (alum) were used in the pH range 4.1-5.5. An apparatus was designed to simulate the mixing and turbulent conditions and to permit the short polyelectrolyte adsorption times found on typical paper machines. The effect of the aluminum species on the polymer adsorption depended on their concentration, counter-ion, pH, and time. From a knowledge of the equilibria of the aqueous aluminum species, it was possible to identify two distinct pH regions for aluminum and polyelectrolyte adsorption. At low pH, only soluble aluminum species were present and both aluminum salts reduced the rate and amount of polymer adsorption. At high pH the two aluminum salts formed distinctly different precipitates having very different effects upon polymer adsorption. The adsorption characteristics of each region are discussed and related to papermaking.

INTRODUCTION

The study of the interactions of aluminum species in paper-making systems has generally been inhibited by the complicated aqueous solution chemistry of the aluminum ion. Recent work on the hydrolysis and precipitation of aluminum by Hayden and Rubin (1) and on the adsorption of aluminum by Arnson (2,3) has provided a better understanding of aqueous aluminum chemistry and the interactions of aluminum with cellulosic fibers. Using

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their work as a basis for understanding the interactions of aluminum, the present study was undertaken to improve the understanding of the interactions between aluminum and the adsorption of cationic polyelectrolyte on cellulosic fibers.

In the first part of this series (4) the adsorption of aluminum was reexamined in greater depth than in Arnson's study. There, aluminum adsorption was shown to occur in a systematic and predictable manner directly related to the aqueous chemistry of the aluminum ion. Using the aqueous equilibria of aluminum, we separated the adsorption of aluminum from dilute solutions of either aluminum chloride or aluminum sulfate into two distinct pH regions. The dividing point was the pH at which aluminum starts to precipitate (pHp). As in Hayden and Rubin's study, the pHp was a function of the aluminum concentration and the aluminum salt anion. The work in part I (4) also showed that the pHp can be affected by the presence of cellulosic fibers.

Below the pHp, where only soluble aluminum species exist, the trivalent aluminum ion was concluded to be the major species to adsorb for both salts. In this region aluminum adsorption was low and the fibers remained negatively charged. Above the pHp, where the aluminum precipitated, both salts adsorbed strongly. With either salt the fiber surface became positively charged due to a layer of adsorbed aluminum precipitate. The precipitate in the aluminum sulfate system differed from the aluminum chloride system in that it contained sulfate ions and produced a lesser cationic charge on the fibers. As a result, more of the aluminum sulfate precipitate adsorbed. In both regions, the adsorption of aluminum was dependent upon the concentration of aluminum.

The aluminum adsorption results provided a basis for studying the interactions between aluminum and the adsorption of cationic polyelectrolyte by cellulosic fibers. Details of the aluminum adsorption study and the following study are available in Crow's thesis (5).

RESULTS AND DISCUSSION

pH and Aluminum Concentration

The adsorption of polymer as a function of pH and counterion at 5.0×10^{-4}M aluminum is shown in Fig. 1. Unless indicated
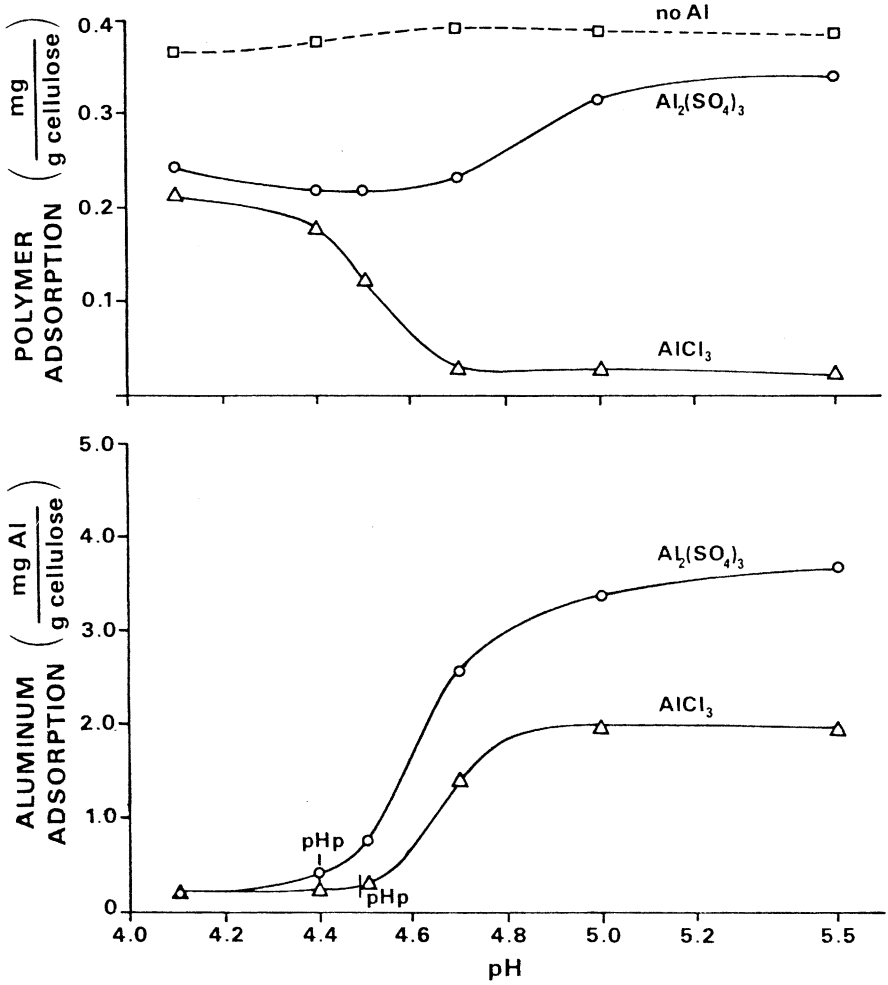
Fig 1—Top: Polymer adsorption as a function of pH and aluminum salt.

Bottom: Aluminum adsorption as a function of pH and aluminum salt (5.0 x $10^{-4}\underline{M}$ A1; 1.5 ppm polymer addition).

otherwise the polymer adsorption time in these studies was 15 seconds, comparable to that existing in many mills. For comparison, the polymer adsorption in the absence of aluminum and the aluminum adsorption are included. In results not presented here, the polymer was found to have no effect on aluminum adsorption. However, as seen in Fig. 1, aluminum can have large effect on polymer adsorption.

Using the pHp's, it is possible to separate the polymer adsorption trends into two distinct pH regions. Below the pHp, where only soluble aluminum species exist, both salts significantly reduce polymer adsorption. Above the pHp the two salts differ greatly. The precipitate in the aluminum chloride system reduces polymer adsorption to an extremely low level. This is not surprising, since the precipitate forms a highly cationic layer on the fiber surface (zeta potential is $>$ +16 mV at pH $>$ 4.7), which can repel the cationic polyelectrolyte. In contrast, the aluminum sulfate precipitate has much less effect on polymer adsorption even though it adsorbs more strongly than the aluminum chloride. A slight reduction (i.e., minimum) in polymer adsorption does occur near the pHp before much precipitate has formed. However, once sufficient precipitation occurs (higher pH's), aluminum sulfate has little effect on polymer adsorption. The aluminum sulfate precipitate produces a lesser cationic charge on the fiber (zeta potential is +11 mV) than the aluminum chloride precipitate but should still be expected to strongly reduce the adsorption of polyelectrolyte. Apparently, some other mechanism is in effect in the presence of the aluminum sulfate precipitate.

The effect of aluminum concentration on polymer adsorption is shown in Fig. 2 and 3. Below the pHp for both salts the polymer adsorption is dependent upon the aluminum concentration and consequently the aluminum adsorption. In this region an increase in aluminum concentration reduces polymer adsorption. The polymer adsorption above the pHp differs greatly. In the presence of aluminum sulfate, an increase in aluminum concentration above $2.5 \times 10^{-4}\underline{M}$ aluminum can significantly increase polymer adsorption once sufficient precipitate has formed (although not reaching the level found in the absence of aluminum). In contrast, no concentration effect is seen with aluminum chloride after sufficient precipitate has formed.

After accounting for the effects of aluminum concentration in each pH region (i.e., above and below the pHp), one can see

a good correlation between pHp's and the polymer adsorption trends. As the pHp is lowered, three shifts in the polymer adsorption data are seen. (1) The concentration dependent region which occurs with both salts in the presence of soluble aluminum species shifts to a lower pH. (2) The concentration independent region which occurs in the presence of aluminum chloride precipitate shifts to a lower pH. (3) The minimum in polymer adsorption which occurs near the pHp in the presence of aluminum sulfate shifts to a lower pH.
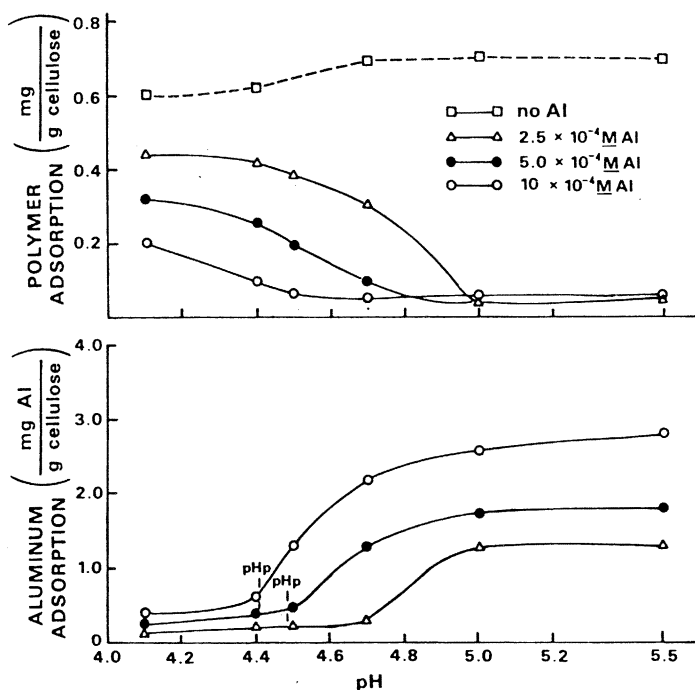
Fig 2—Top: Polymer adsorption as a function of pH and A1 concentration for AlXl$_3$ (3.0 ppm polymer addition);

Bottom: Aluminum adsorption as a function of pH and Al concentration for AlCl$_3$
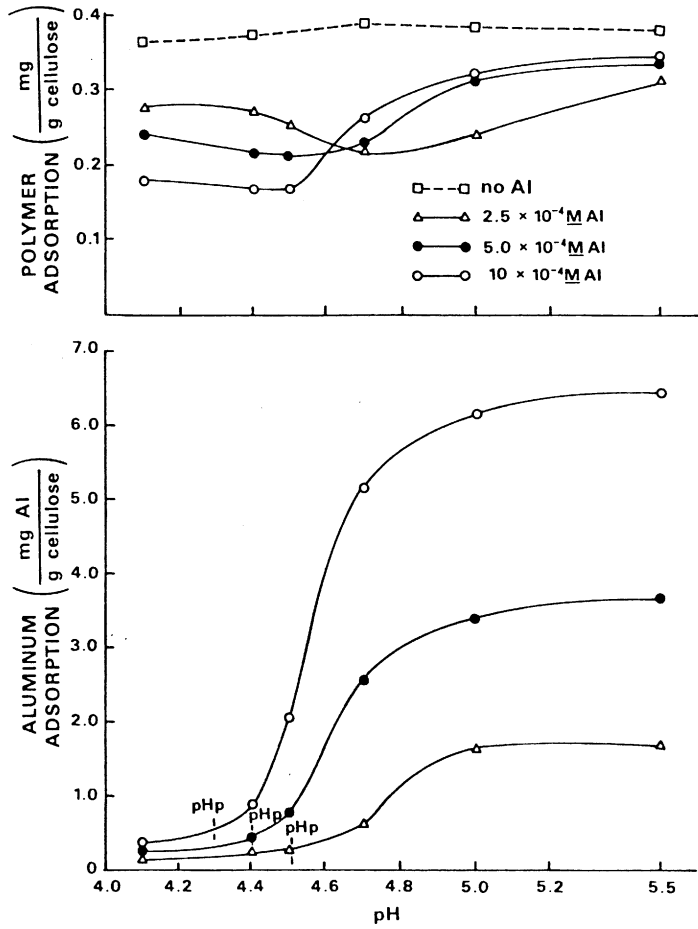
Fig 3—Top: Polymer adsorption as a function of pH and Al concentration for $Al_2(SO_4)_3$ (1.5 ppm polymer addition).

Bottom: Aluminum adsorption as a function of pH and Al concentration for $Al_2(SO_4)_3$

Polymer Concentration

The adsorption of polymer as a function of polymer concentration is shown in Fig. 4 and 5. With either salt an increase in polymer concentration increases the polymer adsorption throughout the pH range. However, the fraction of polymer adsorbed decreases everywhere except in the aluminum chloride precipitate region (Fig. 6 and 7). The fraction of polymer adsorbed also decreases in the absence of aluminum salts (Fig. 8). It is therefore likely that the same mechanism is functioning with and without aluminum, except in the case of the aluminum chloride precipitate. In the absence of aluminum salts the cationic polymer reduces the negative charge on the fibers (Fig. 9). The lower fiber charge with increasing polymer adsorption would reduce the electrostatic attraction between the polymer and the fiber surface and likely explain the decrease in fraction of polymer adsorbed. In the presence of aluminum the fiber surface is only moderately charged, except in the aluminum chloride precipitate region. The moderately charged fibers probably become more cationic as the polymer adsorbs thereby reducing the electrostatic attraction between the polymer in solution and the fiber surface, and decreasing the fraction of polymer adsorbed. In the presence of the aluminum chloride precipitate the fiber surface has such a strong cationic charge that its charge will be little affected by polymer adsorption. If the electrostatic interaction between the polymer and the fiber surface remains constant, then polymer adsorption should only be a function of polymer concentration. This would explain the increase in polymer adsorption with polymer concentration (Fig. 5).

Time Effects

At 15 seconds adsorption time equilibrium polymer adsorption probably does not occur. This is especially likely in the presence of aluminum because of the possible competition between aluminum and polymer for adsorption sites on the cellulose surface. The adsorption of polymer as a function of pH and polymer adsorption time is shown in Fig. 10 and 11. At a polymer adsorption time of 15 seconds the aluminum reduces the polymer adsorption throughout the pH range. However, after 10 minutes aluminum has only a minor effect on polymer adsorption, except for the aluminum chloride precipitate region. Even here aluminum has a decreased effect on polymer adsorption after 10 minutes, as seen by the doubling of the adsorption level. This

indicates that the polymer adsorption rate is reduced throughout the pH range in the presence of aluminum.
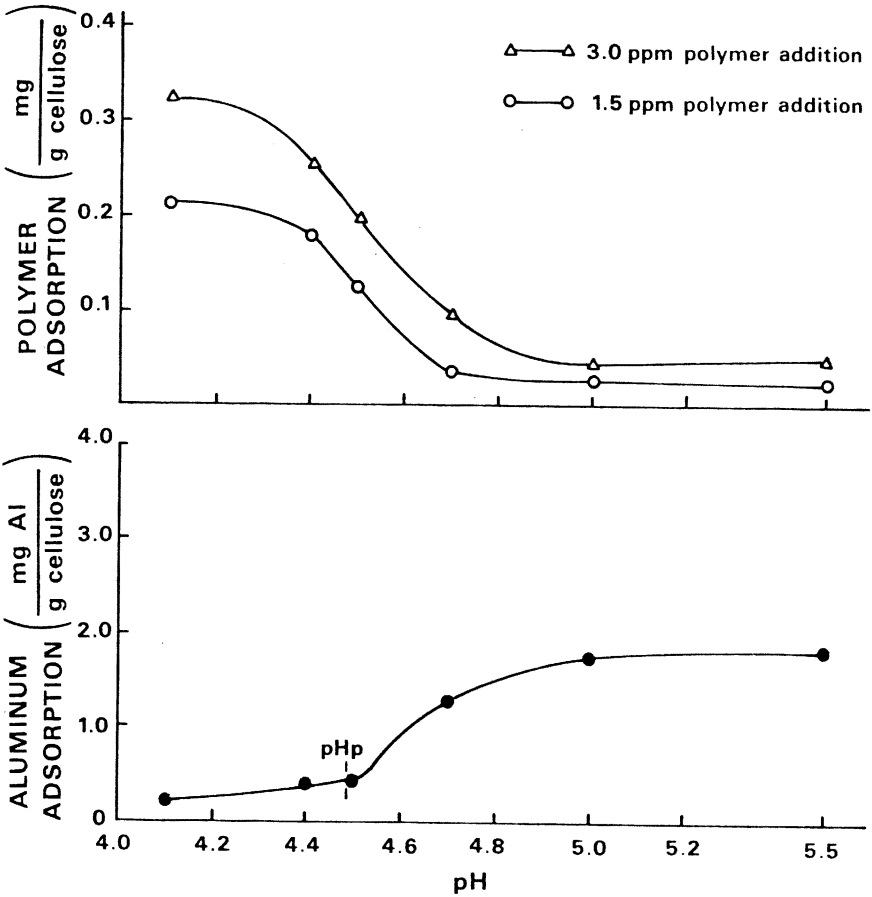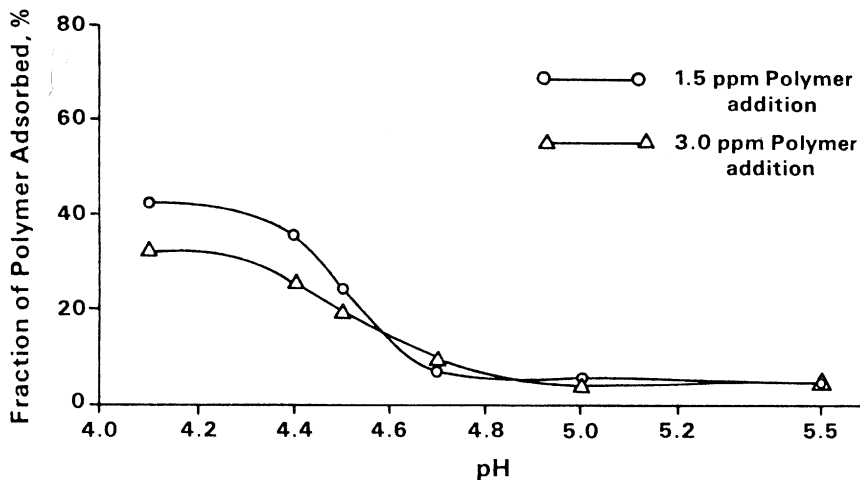

Fig 4—Top: Polymer adsorption as a function of pH and polymer addition in the presence of $AlCl_3$

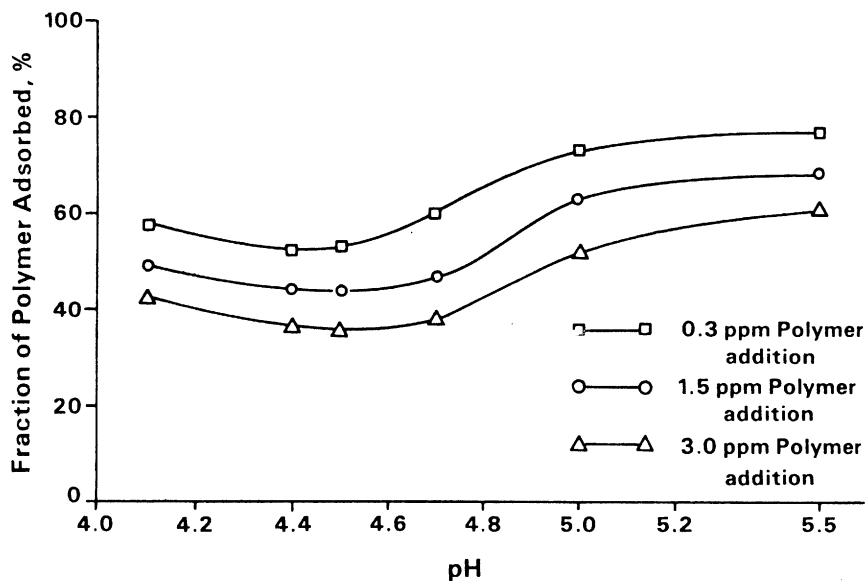Bottom: Aluminum adsorption as a function of pH for $AlCl_3$ ($5.0 \times 10^{-4}\underline{M}$ Al).
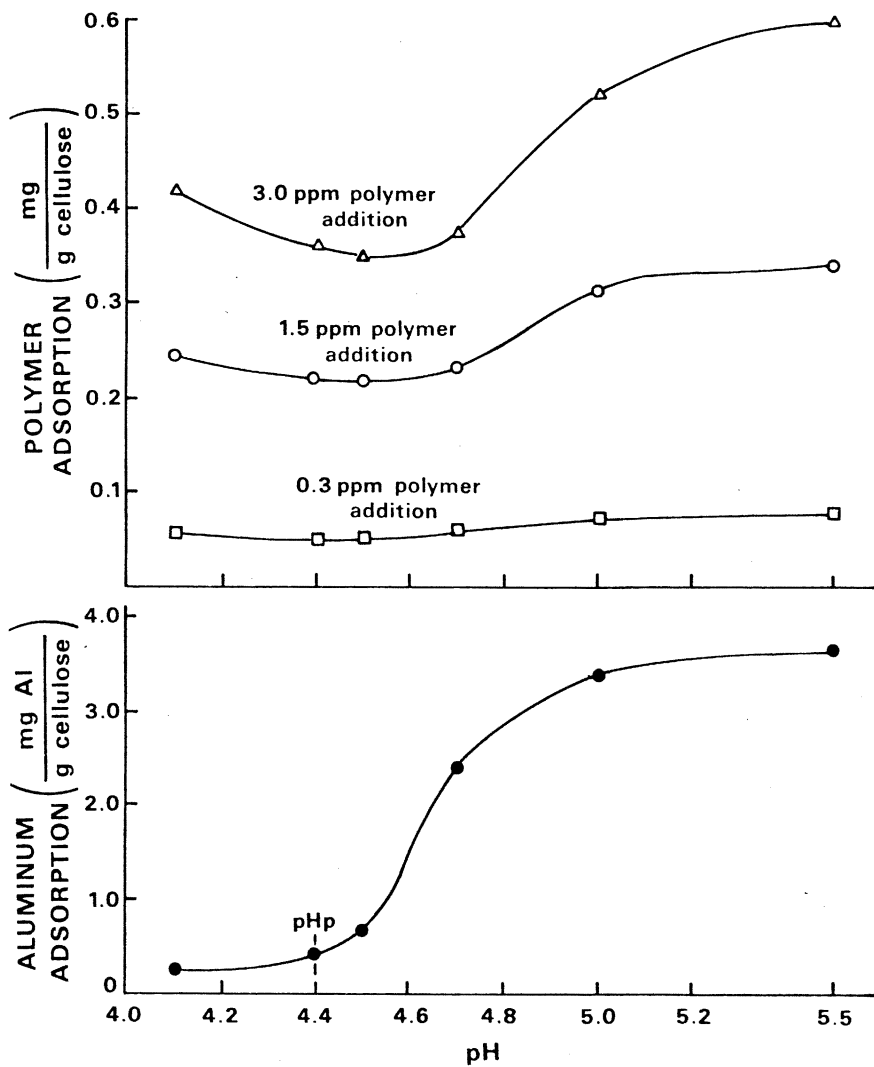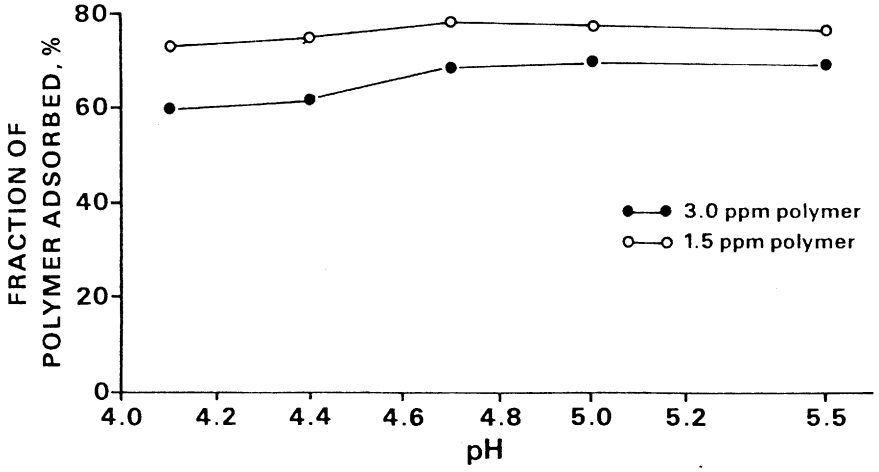
Fig 5—Top: Polymer adsorption as a function of pH and polymer addition in the presence of $Al_2(SO_4)_3$

Bottom: Aluminum adsorption as a function of pH for $Al_2(SO_4)_3$ ($5.0 \times 10^{-4}\underline{M}$ Al)

Fig 6—Fraction of polymer adsorbed as a function of pH and polymer addition in the presence of $AlCl_3$ ($5.0 \times 10^{-4}\underline{M}$ Al)
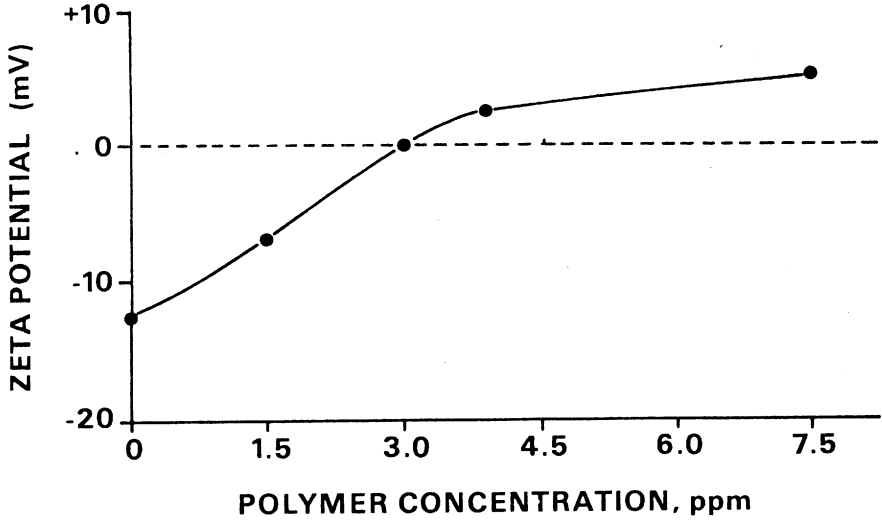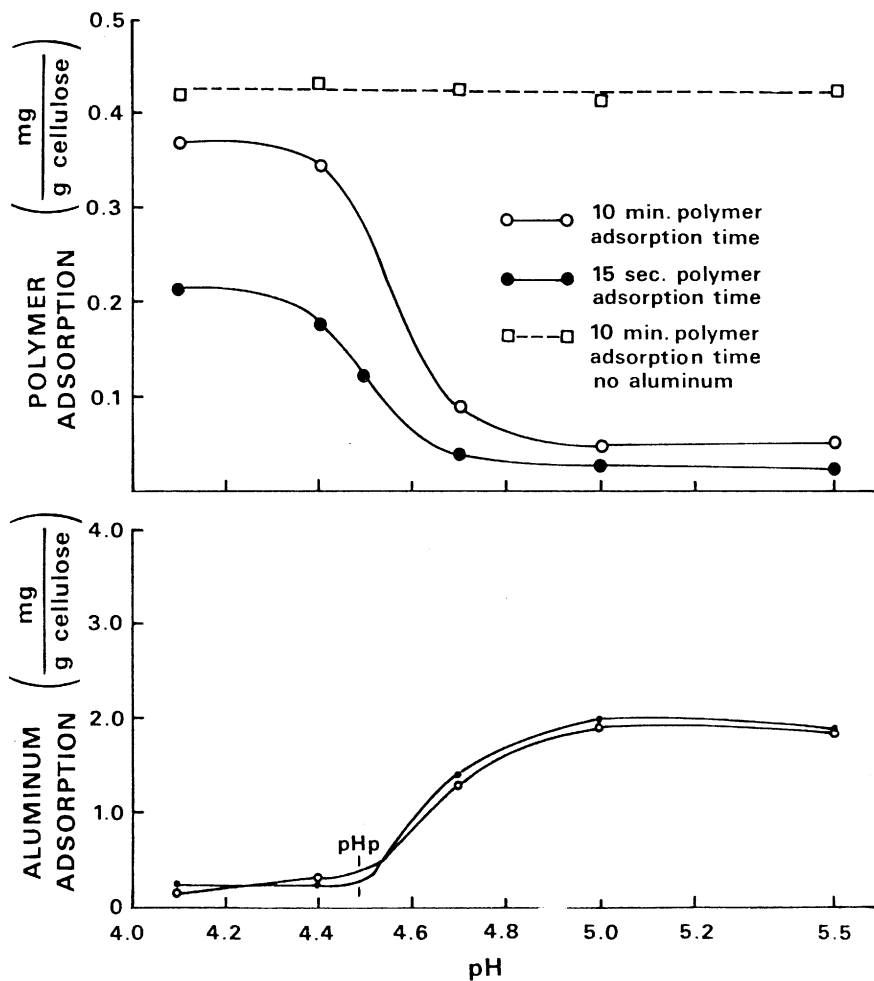

Fig 7—Fraction of polymer adsorbed as a function of pH and polymer addition in the presence of $Al_2(SO_4)_3$ ($5.0 \times 10^{-4}\underline{M}$ Al)

Fig 8—Fraction of polymer adsorbed as a function of pH and polymer concentration. (No aluminum present.)

Fig 9—Zeta potential of the fibers as a function of polymer addition in the absence of aluminum

Fig 10 — Top: Polymer adsorption as a function of pH and polymer adsorption time in the presence of $AlCl_3$

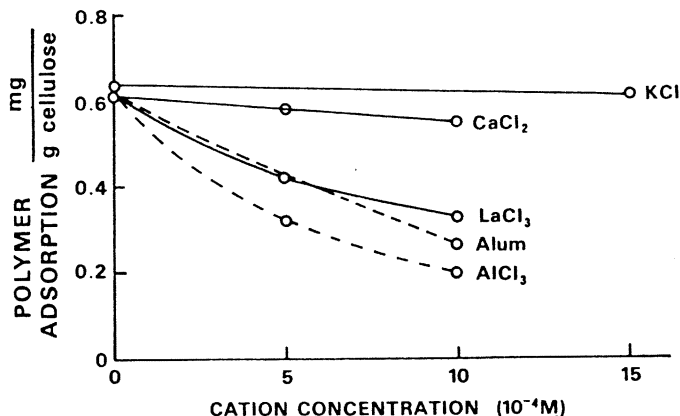Bottom: Aluminum adsorption as a function of pH for $AlCl_3$ ($5.0 \times 10^{-4}\underline{M}$ Al; 1,5 ppm polymer addition)
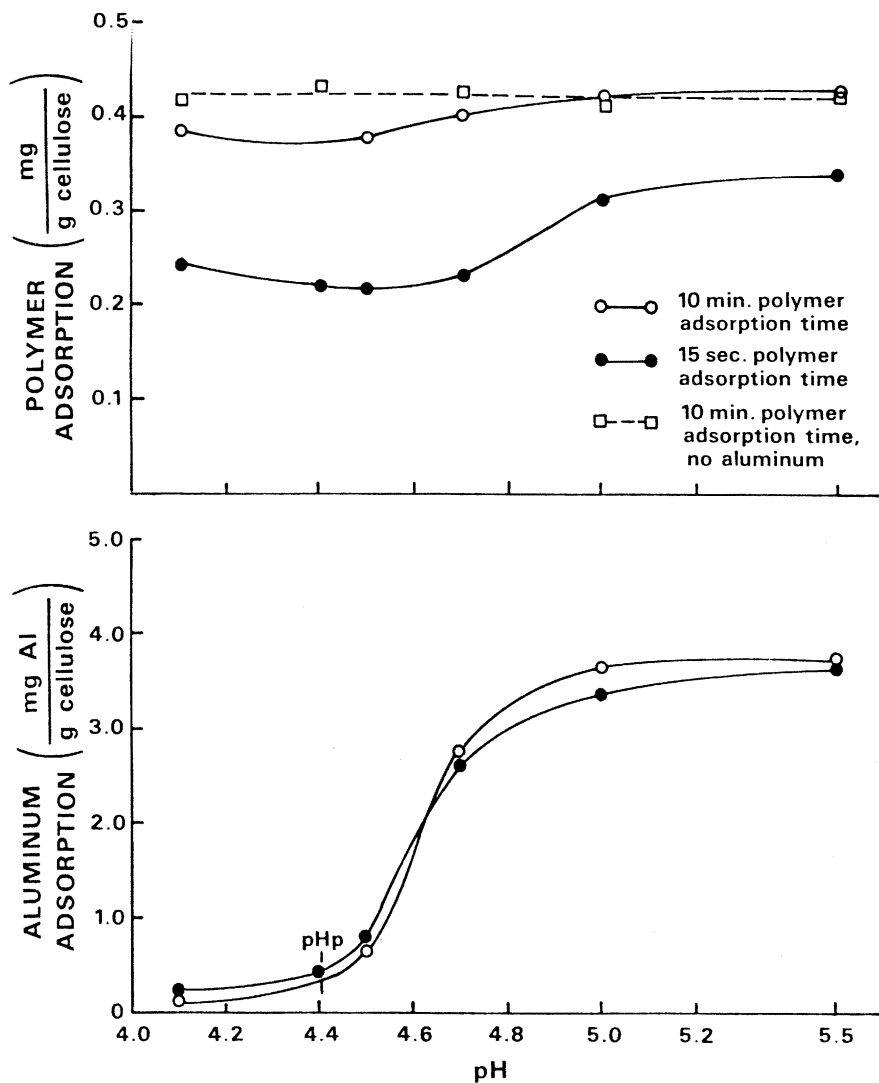
Fig 11—Top: Polymere adsorption as a function of pH and polymer adsorption time in the presence of $Al_2(SO_4)_3$

Bottom: Aluminum adsorption as a function of pH for $Al_2(SO_4)_3$ (5.0×10^{-4}M Al; 1.5 ppm polymer addition)

Cation Valence

The effects of cations of various valences and concentrations are presented in Fig. 12. Lanthanum was chosen as the trivalent ion, since it remains unhydrolyzed up to a pH of 8. This excludes any possibility of trace amounts of precipitate. For reference the effects of aluminum chloride and aluminum sulfate are represented as dashed lines. A pH of 4.1 was chosen for all tests.

The higher valence cations have a larger detrimental effect on polymer adsorption. The effect of cations on polymer adsorption appears to be a function of cation valence and concentration. The effects of aluminum chloride and aluminum sulfate at pH 4.1 closely parallel that of lanthanum chloride. This suggests that the aluminum salts at low pH are detrimental to polymer adsorption due to the adsorption of the trivalent aluminum species. Aluminum chloride, however, has a slightly greater effect than lanthanum chloride. This is possibly due to the smaller ionic radius of the trivalent aluminum ion which increases its charge density and probably its adsorption. On the other hand, aluminum sulfate has a slightly smaller effect than aluminum chloride, which may be due to the screening of the cationic charge by sulfate ions.

Fig 12—Polymer adsorption as a function of cation concentration and valence (3.0 ppm polymer addition; pH = 4.1; 0.01$\underline{N}$ KC1 background)
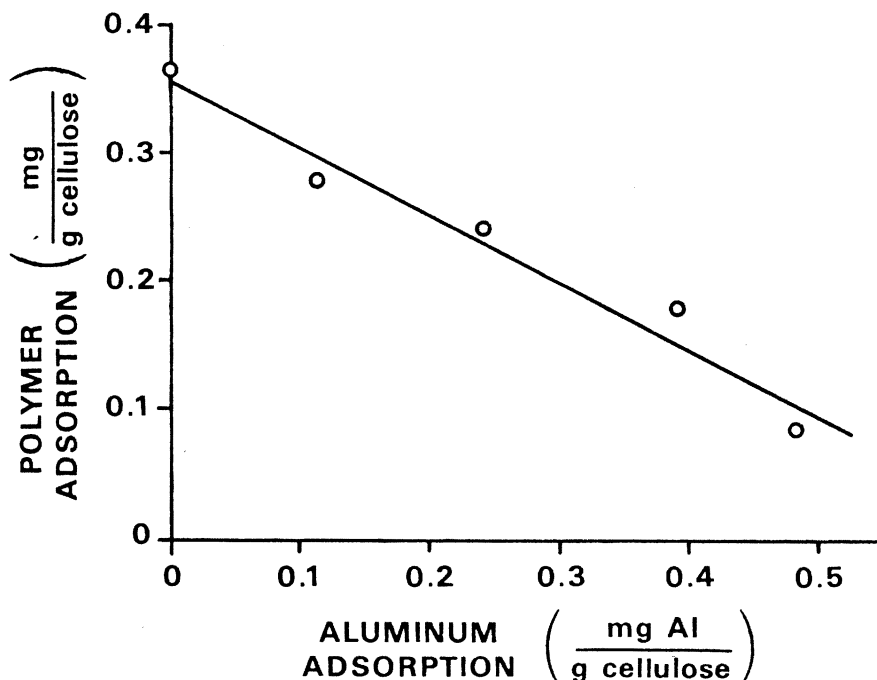
Fig 13—Polymer adsorption as a function of aluminum adsorption with aluminum sulfate at 4.1 (1.5 ppm polymer addition)

The detrimental effects of aluminum concentration at pH 4.1 can also be represented in terms of aluminum adsorption. A good correlation exists between the degree of aluminum adsorption in the case of aluminum sulfate and the degree of polymer adsorption (Fig. 13). As aluminum adsorption increases, polymer adsorption decreases. A similar trend is displayed in the case of aluminum chloride.

Proposed Mechanisms

Aluminum sulfate desorption experiments were conducted to understand how the polymer adsorbs. Polymer was added to stock containing aluminum sulfate at various pH's. After polymer adsorption, the aluminum was desorbed by acidification to pH

3.5. Any polymer which was adsorbed onto the previously adsorbed aluminum should also desorb. A cationic surfactant, trimethyldodecylammonium chloride (TDA), was added immediately before acidification to prevent the readsorption of desorbed polymer onto freshly exposed cellulose surface.

Figure 14 presents the results of the aluminum sulfate desorption study. For reference, a typical aluminum sulfate adsorption curve at $5.0 \times 10^{-4}\underline{M}$ aluminum is included. To determine the effect of TDA on polymer adsorption without acidification, a curve was generated with TDA alone. The presence of TDA alone, without acidification, produces a typical polymer adsorption curve, thus indicating that TDA has no significant effect on previously adsorbed polymer. The difference between the two curves, with and without acidification, represents the amount of indirectly absorbed polymer, that is, the amount of polymer which adsorbed onto the previously adsorbed aluminum.

The results indicate a large degree of indirectly adsorbed polymer in the aluminum sulfate precipitate region (i.e., above the pHp). However, below the pHp, where the soluble aluminum species exist, the polymer adsorbs directly onto the cellulose surface.

The presence of sulfate ions improves polymer adsorption throughout the pH range. However, screening of cationic charges on the fiber surface by sulfate ions cannot fully account for the large polymer adsorption in the presence of the aluminum sulfate precipitate. Otherwise the region below the pHp, where the fiber charge is negative, would experience higher polymer adsorption. The high polymer adsorption in the aluminum sulfate precipitate region must be due to the incorporation of the negative sulfate ions into or onto the precipitate, which serve as adsorption sites for the indirectly adsorbed polymer. Experiments showed (5) that the ratio of aluminum ions to sulfate ions for the precipitate was 4.2. Evidently, there is an appreciable sulfate ion concentration associated with the precipitate.

The minimum in polymer adsorption near the pHp in the aluminum sulfate system is difficult to interpret, due to the presence of both soluble and precipitated aluminum species. The fiber surface possesses a relatively high charge (ζ = +13 mV), which indicates that the fiber surface is essentially
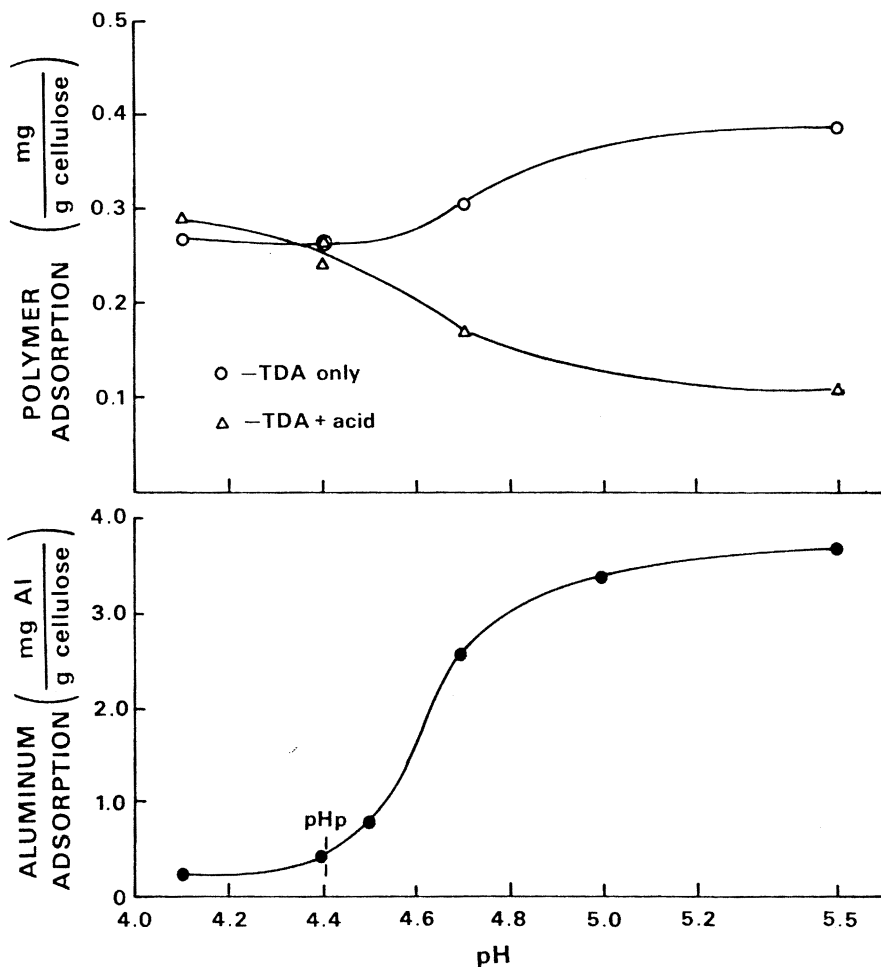
Fig 14—Top: Effect of TDA, acidification and pH on polymer adsorption in the presence of $Al_2(SO_4)_3$ at 1.5ppm polymer addition and $5.0 \times 10^{-4}\underline{M}$ Al (aluminum desorption experiments)

Bottom: Aluminum adsorption as a function of pH for $Al_2(SO_4)_3$ ($5.0 \times 10^{-4}\underline{M}$ Al; no TDA or acid).

covered by the aluminum precipitate. However, a significant portion of the aluminum is still in the form of the soluble aluminum species. The adsorbed aluminum precipitate would be expected to reduce the direct adsorption of the polymer, while the soluble aluminum species would be expected to screen and adsorb to the negative sites on the fiber (i.e., carboxyl groups and sulfate groups). Possibly the precipitate reduces the direct adsorption of the polymer, and the soluble species reduce the indirect adsorption of the polymer onto the sulfate groups of the precipitate. This explanation is consistent with the results in the other pH regions.

Impact of Adsorption Results on Papermaking

The effect of aluminum adsorption and subsequent polymer adsorption on retention of fine solids has yet to be studied. However, several possible effects on retention may be expected.

First, the adsorption of aluminum is known to alter the charge of the fiber surface. One may predict that the less negative charge on the fibers due to aluminum adsorption would decrease the polymer-fiber attraction, thereby changing the adsorbed configuration of the polymer to that consisting of longer loops and tails. This could improve the bridging characteristics of the polymer and improve retention.

Second, aluminum is known to decrease polymer adsorption. To function adequately as a retention aid, polymer must adsorb to a sufficient degree. For convenience, each pH region will be considered separately.

Above the pHp with aluminum chloride the polymer adsorption is at such an extremely low level that retention would be expected to suffer. The use of sodium aluminate as a partial replacement for alum in the papermaking system may also be detrimental to retention. Sodium aluminate when acidified has a distribution of species identical to that of aluminum chloride and therefore produces the same detrimental precipitate in the absence of sulfate ions.

Aluminum sulfate, on the other hand, has only a small effect on polymer adsorption above the pHp. However, without knowing the configuration of the polymer within and on the surface of the adsorbed precipitate layer one cannot speculate on aluminum sulfate's effects on retention.

Below the pHp for both salts polymer adsorption is inversely related to aluminum concentration and aluminum adsorption. In results not shown here an increase in aluminum concentration to 20.0 x 10^{-4}M decreased polymer adsorption to a very low level of 17% (5). Since only a small fraction of the aluminum adsorbs, white water recirculation can drastically increase the aluminum concentration. Therefore, this region can potentially be very harmful to polymer adsorption.

Third, an increase in soluble aluminum species during the recycling of the white water can alter the aqueous equilibria of the aluminum. The pH at which aluminum starts to precipitate is a function of pH and aluminum concentration. Since the soluble aluminum species are only slightly adsorbed, their concentration will build up, the pHp will be lowered to that of the operating pH, and the precipitation of the aluminum onto the fibers will result. This may change the functioning of retention aids and other additives in the wet end.

CONCLUSIONS

From a knowledge of the equilibria of the aqueous aluminum species the major conclusions can be separated into two pH regions. At low pH, where only soluble aluminum species exist, the trivalent ion was concluded to be the major adsorbing species for both salts. In this region the polyelectrolyte adsorption was inversely dependent upon the adsorption of aluminum and consequently the concentration of aluminum. The adsorbed trivalent aluminum ion was found to reduce the adsorption rate of the polyelectrolyte, but not the ultimate degree of adsorption.

At higher pH, where the aluminum precipitate exists, the effect of the two salts differed greatly. In the aluminum chloride case the fiber surface became strongly positively charged due to a layer of adsorbed aluminum precipitate. The electrostatic repulsion between this layer and the cationic polyelectrolyte reduced the polyelectrolyte adsorption to a very low level, which was independent of aluminum concentration. In the aluminum sulfate case the precipitate contained sulfate groups and did not produce as high a cationic charge on the fibers. In this system, the cationic polyelectrolyte adsorbed strongly onto the previously adsorbed precipitate and therefore was only slightly affected by the presence of aluminum at short times.

The results of the study show that aluminum salts used in papermaking systems function in a systematic and predictable manner related to and governed by the aqueous solution chemistry of the aluminum ion. With proper understanding of the aluminum aqueous equilibria and their effects on aluminum and polymer adsorption, we can begin to predict and control the interactions of aluminum species with other materials in the papermaking system.

APPENDIX. MATERIALS, EQUIPMENT, AND PROCEDURES

A refined, fines-free, oxidized cotton linters pulp was used as the cellulosic fiber adsorbent to minimize any conflicting adsorption competition from soluble hemicelluloses and lignin or from the fines. Filtered stock solutions of 0.3M aluminum chloride and aluminum sulfate were prepared and gravimetrically analyzed for use as the source of aluminum. A carbon 14-labelled, low charged, high molecular weight polyacrylamide was synthesized as the cationic polyelectrolyte.

An apparatus was designed to simulate the mixing and turbulent conditions and to permit the short polyelectrolyte adsorption times found on typical paper machines (Fig. 15). The major components of the experimental apparatus were (1) a holding tank for the stock containing the appropriate aluminum salt, (2) a long delivery tube of sufficient length and diameter to provide turbulent flow conditions, (3) a polymer injection tee with timing features to permit both uniform injection of the polymer throughout the pulp and short polymer adsorption times, (4) a dynamic drainage jar containing a 120 mesh screen, (5) a 47-mm filter holder for filtering samples through 10-μm pore size filters, and (6) a sampling and cleaning section which permits rapid and facile sampling of the filtrate without spillage for analysis of unadsorbed additives and convenient drainage and cleaning of the apparatus.

The adsorption and filtering apparatus was made of polypropylene, Teflon, polyvinyl chloride, and polymer-treated glassware to minimize the adsorption of unadsorbed additives. All adsorption runs were done at 0.3% pulp consistency under moderate agitation. The unadsorbed aluminum was determined by spectrophotometry at 450 nm after chelation with 8-hydroxyquinoline and extraction into methyl isobutyl ketone. The unadsorbed polymer was determined by liquid scintillation counting.
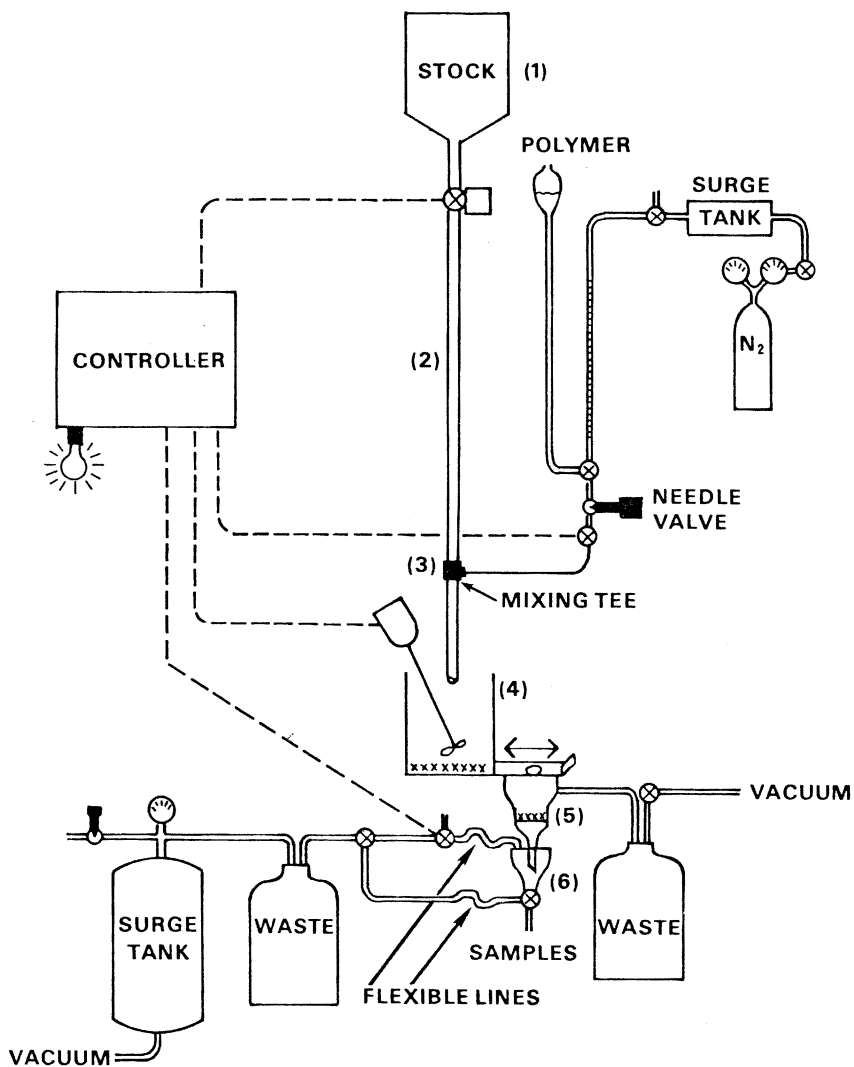
Fig 15—Experimental apparatus for polymer adsorption and separation of unadsorbed additives (schematic)

The pH and aluminum concentration were controlled independently. The pH during aluminum adsorption was always approached from the acid side so as to form the soluble species in the absence of any aluminum hydroxide precipitate. For each adsorption run, materials were added to the pulp in the following order: (a) KCl to adjust the ionic strength to approximately 0.01$\underline{N}$, (b) HCl (0.1$\underline{N}$) to adjust the stock pH to 4.0, (c) aluminum salt, (d) dilute NaOH (0.05$\underline{N}$) for adjustment and maintenance of the desired pH, and (e) polyelectrolyte solution (0.2% solids).

Zeta potential was used as a measure of fiber charge. Measurements were conducted on filtrate samples from the adsorption runs. The 120-mesh screen used for filtration removed the fibers while leaving a few fines for charge measurements.

ACKNOWLEDGMENT

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Transcription of Discussion

The Chemistry of Aluminium Salts in Papermaking: Influence on Adsorbtion of a Cationic Polyelectrolyte
by R.D. Crow and R.A. Stratton

Dr. R.W. Davison Hercules Research, Wilmington, U.S.A.

We have studied the retention of pulp fines and mineral filler using polyelectrolyte retention aids – 10 million to 15 million molecular weight – over the last three years. We found that if you have 1 to 2% of hydroxy aluminium material adsorbed onto the fibre surfaces, the cationic retention aid will still perform an effective job of flocculating by bridging and helping to retain the fine particle material.

However, by the addition of 5 – 10% or even 15% alum, based on fibre weight, which is what some mills are unknowingly doing particularly at start up in an alkaline environment, we obtained masses of hydroxy aluminium material smeared on the cellulose surfaces and our cationic retention aids could not function at all. I presume that they could not get a grip on the slimy hydroxylated aluminium surfaces. At the same time, in an alum system at below pH 5.5 or pH 6, anionic retention aids generally do not work as well as cationic retention aids for another reason.

This is because the aluminium ion species in the water, which presumably intercept these anionic retention aids before they reach the fine particle surfaces, kill the whole flocculation effect.

I think that explanation seems to agree fairly well with what you and Dr. Crow have found.

Stratton Yes, it does.

Lindström Have you investigated polyaluminium compounds?

Stratton No. These are not as popular in the U.S.A. as they are in Scandinavia.