

# The Institute of Paper Chemistry

Appleton, Wisconsin

## Doctor's Dissertation

**The Influence of Aluminum Salts on the Retention of  
Titanium Dioxide When Using Cationic Polyelectrolyte  
as a Retention Aid**

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**January, 1988**

THE INFLUENCE OF ALUMINUM SALTS ON THE RETENTION OF TITANIUM DIOXIDE  
WHEN USING CATIONIC POLYELECTROLYTE AS A RETENTION AID

A thesis submitted by

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in partial fulfillment of the requirements  
of The Institute of Paper Chemistry  
for the degree of Doctor of Philosophy  
from Lawrence University  
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## ABSTRACT

Papermaker's alum (aluminum sulfate) is a common wet-end additive that is known to affect retention when using polymeric retention aids, but reports in the literature have shown contradictory results. Recent work by Hayden and Rubin has produced a better understanding of aqueous aluminum chemistry and provided a basis for this investigation of the influence of aluminum salts on polymer adsorption and filler retention.

Retention experiments were performed in the presence of various types and amounts of aluminum species. Aluminum adsorption, polymer adsorption, and filler retention were determined. Aluminum adsorption curves were obtained which displayed low adsorption at low pH values, a sharp increase between pH 4 and 5, and high adsorption above pH 5. The sharp increases in the aluminum adsorption curves correlated with the pH values at which the aluminum starts to precipitate (pHp) as reported by Crow.

Below the pHp, the soluble aluminum species were found to be competing with the polymer for adsorption sites, thereby reducing polymer adsorption. However, the polymer was found to be directly adsorbed to the furnish surface, which resulted in a shear stable, direct bridging mechanism and good filler retention.

Above the pHp in the presence of aluminum chloride, the adsorption of large amounts of cationic aluminum precipitate greatly increased the furnish surface charge which repelled the cationic polymer and resulted in poor filler retention. Above the pHp in the presence of aluminum sulfate, the furnish surface was also positively charged because of the adsorption of large amounts of cationic aluminum precipitate. However, the surface charge was less than that in the case of aluminum chloride due to the incorporation of sulfate ions into

the aluminum precipitate. These sulfate ions were found to serve as indirect polymer adsorption sites. This indirect polymer adsorption produced a shear sensitive, indirect bridging mechanism and only fair filler retention.



## INTRODUCTION

With the increasing cost of papermaking fibers, the trend has been toward the use of more filler in paper production. In the production of fine papers, the fine solids fraction can represent 40-50% of the total furnish solids.<sup>1-2</sup> Maximum retention of fines and fillers is important for both economical and environmental reasons. In recent years, the use of synthetic polyelectrolytes has been found to be one of the best methods for improving retention.

A number of studies<sup>3-11</sup> have been performed in an attempt to define how these polymers work and under what conditions they work best. Because these studies have been on simplified systems, their results are difficult to use directly in the paper mill. These simplified studies are necessary to understand how these polyelectrolytes function, but additional studies must be performed to determine how other wet-end materials affect polyelectrolyte retention.

Alum (aluminum sulfate) is a common wet-end additive that is known to affect retention when cationic polyelectrolytes are used. Retention studies on alum-cationic polyelectrolyte systems<sup>12-20</sup> have shown alum to have differing effects on retention. These effects vary from increased retention, to decreased retention, to little effect at all.

To gain insight into how alum actually affects retention when using cationic polyelectrolytes, Arnson<sup>21</sup> studied the adsorption properties of aluminum species by cellulosic fibers and Crow<sup>22</sup> studied the influence of aluminum salts on adsorption of cationic polyelectrolyte by cellulosic fibers. The purpose of this study was to use the results obtained by Arnson and Crow and build

on them to understand how aluminum salts affect retention when using cationic polyelectrolyte as a retention aid.

## LITERATURE REVIEW

This literature review first discusses the results of previous studies on retention in alum-cationic polyelectrolyte systems. This will be followed by a review of retention mechanisms. The review will then present a brief summary of aluminum chemistry and discuss adsorption of aluminum by cellulosic fibers, adsorption of cationic polyelectrolyte, and the influence of aluminum salts on adsorption of cationic polyelectrolytes.

### RETENTION IN ALUM-CATIONIC POLYELECTROLYTE SYSTEMS

Previous studies which have investigated the effects of alum on retention when using cationic polyelectrolyte as a retention aid have shown contradictory results. It is difficult to draw overall conclusions on the basis of these studies because of differences in pH, furnish, and retention conditions used. In some instances, this information was not provided.

Pelton and Allen<sup>12</sup> studied the effect of alum on retention of a fine paper furnish (85% 1:1 bleached hardwood kraft:bleached softwood kraft, 15% TiO<sub>2</sub>) using a dynamic drainage jar. At a cationic polyacrylamide addition of 1 lb/t, the addition of alum had no effect up to 26 lb/t addition. Further additions of alum, up to 800 lb/t, decreased the retention.

Avery<sup>13</sup> studied the effect of alum on filler retention of a fine paper furnish (83% 1:1 bleached hardwood kraft:bleached softwood kraft, 17% 1:1 filler clay:TiO<sub>2</sub>, and 0.4% rosin) using a dynamic drainage jar and machine trials. At either a cationic polyacrylamide addition of 0.5 lb/t or a cationic starch addition of 10 lb/t, the addition of alum from 25 to 200 lb/t caused a reduction in filler retention.

Moore<sup>14</sup> studied the effect of alum on filler retention of a fine paper furnish (95% bleached softwood kraft, 5% TiO<sub>2</sub>) using a modified Buchner funnel apparatus. At a cationic polyacrylamide addition of 2 lb/t, the addition of alum from 0 to 200 lb/t caused the retention to initially decrease slightly and then increase rapidly to its greatest value at 200 lb/t alum addition.

Tay<sup>15</sup> studied the effect of alum on retention of newsprint stock using a dynamic drainage jar. At a cationic polyacrylamide addition level of 2 lb/t, the addition of alum from 0 to 200 lb/t caused the retention to steadily increase up to 160 lb/t alum addition.

Frankle, Sheridan, et al.<sup>16,17</sup> studied the effects of alum on filler retention of a fine paper furnish (70% bleached softwood kraft, 27% filler clay, and 3% TiO<sub>2</sub>) using a dynamic drainage jar. At cationic polymer additions of 1 and 2 lb/t, the addition of alum from 10 to 100 lb/t caused the retention to slightly increase up to the 20 lb/t level and then remain constant with further additions.

Nicke and Hartmann<sup>18</sup> found similar results when they studied the effect of alum on retention of a fine paper furnish (70% bleached aspen sulfate, 30% filler clay) using a vertical glass drainage tube. When using cationic polyacrylamide, the addition of alum from 0 to 160 lb/t caused the retention to increase up to the 40 lb/t level and then remain constant with further addition.

Guender and Auhorn<sup>19</sup> studied the effects of alum on filler retention of an unbleached paper furnish (70% 2:3 softwood kraft:mechanical pulp, 30% china clay) using a funnel filtering device. At a cationic polyacrylamide addition level of 0.6% lb/t, the addition of alum from 0 to 40 lb/t caused the retention to increase.

In another unbleached system, Arnson<sup>20</sup> studied the effects of alum on the retention of fines using a dynamic drainage jar. At a cationic polyacrylamide addition level of 2 lb/t, the addition of alum from 0 to 160 lb/t reduced the retention by more than 50%.

From these studies, it can be concluded that the effect of alum on retention when using cationic polyelectrolytes can be quite varied and is not well understood.

#### RETENTION MECHANISMS

In 1936, Haslam and Steele<sup>23</sup> proposed three mechanisms for particle retention in the papermaking process. These mechanisms are the following: (1) filtration, the physical trapping of particles in pore openings smaller than the particles, (2) entrapment, the physical collection of particles in the lumens and fibrillar structure of the fibers, and (3) coflocculation, the retention of particles onto the fibers by colloidal forces. From further studies,<sup>23-26</sup> it was concluded that fine particle retention is predominantly a coflocculation process.

Coflocculation has been considered to occur by two mechanisms, namely coagulation and flocculation.<sup>27</sup> Coagulation is the reduction of surface charges on particles with simple electrolytes such that the particles can aggregate together. Flocculation is the use of long chain polymers (usually polyelectrolytes) to agglomerate fine particles. Britt, et al.<sup>28-30</sup> studied these two mechanisms under the hydrodynamic shear conditions which occur in papermaking systems. They found that coagulation with simple electrolytes produced "soft flocs", which were easily disrupted by shear forces and resulted in poor retention. However, they found that flocculation with high molecular weight cationic

polyelectrolytes produced "hard flocs" that resisted high shear forces and resulted in high retention. Therefore, flocculation with polyelectrolytes appears to be a better means of improving retention.

Three mechanisms have been proposed for flocculation: (1) charge neutralization, (2) electrostatic patch model, and (3) polymer bridging. These mechanisms will only be briefly reviewed here, but more detailed reviews can be found elsewhere.<sup>5,7,27,31,32,33</sup>

Charge neutralization is thought to occur by a process similar to coagulation except that polyelectrolytes are used to reduce the surface charges of particles instead of simple electrolytes.<sup>34-37</sup> Flocculation caused by low molecular weight polyelectrolytes has been attributed to charge neutralization.<sup>38-39</sup> Charge neutralization is characterized as having maximum flocculation at or near a system zeta potential of zero.<sup>34-37</sup>

In the electrostatic patch mechanisms, flocculation occurs by an electrostatic interaction between anionic particles and adsorbed cationic polyelectrolytes. This mechanism was first proposed by Kasper<sup>7</sup> and has been called the charge mosaic theory by Gregory.<sup>8</sup> This is the mechanism by which high charge density polymers are believed to function. The cationic polymer adsorbs onto the surface of an anionic particle creating a patch of net positive charge. This positive patch electrostatically attracts a negative region of another particle causing flocculation.

Polymer bridging occurs when the polyelectrolyte adsorbs onto the particle surface with a configuration such that the polyelectrolyte extends out from the surface. The extending polyelectrolyte can adsorb onto other particles

creating a bridge and causing flocculation. Polymer bridging has been shown to occur in systems where the zeta potential was both very positive<sup>3,4,16-19</sup> and very negative.<sup>10</sup> A bridging mechanism is favored by low charge density, high molecular weight polymers. When the polymer is adsorbed directly onto a particle surface, the bridging which occurs will be referred to as "direct bridging". In a related mechanism, the polyelectrolyte attaches to an anion in the hydroxyaluminum complex which is on the particle surface instead of attaching directly to the particle itself.<sup>14</sup> The bridging which occurs by this mechanism will be referred to as "indirect bridging".

#### AQUEOUS ALUMINUM CHEMISTRY

In order to understand how alum affects retention when using cationic polyelectrolytes, it is necessary to first review some aqueous aluminum chemistry. A detailed review of the literature on this topic has been compiled by Arnson.<sup>21</sup>

The high charge, 3+, and small ionic radius of the aluminum ion results in its unusual chemical activity. In order to reduce its high charge density, the aluminum ion readily complexes with neutral and anionic molecules called ligands. The aluminum ion complexes with six ligands to form an octahedral structure as shown in Fig. 1. In dilute aqueous solutions, the aluminum ion will complex with  $\text{H}_2\text{O}$ ,  $\text{OH}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{H}_2\text{PO}_4^-$ , and  $\text{R-COO}^-$ , but not with  $\text{Cl}^-$ ,  $\text{NO}_3^-$ , or  $\text{ClO}_4^-$ . When aluminum salts are dissolved in an aqueous medium in the absence of complexing anions, the hydrated trivalent cation is the only species at a pH less than 3. As the pH is increased, the water ligand molecules are replaced by hydroxyl anions. This is referred to as hydrolysis. The simple hydrolysis reactions of aluminum may be written as follows:

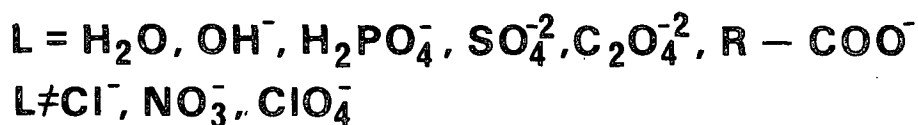
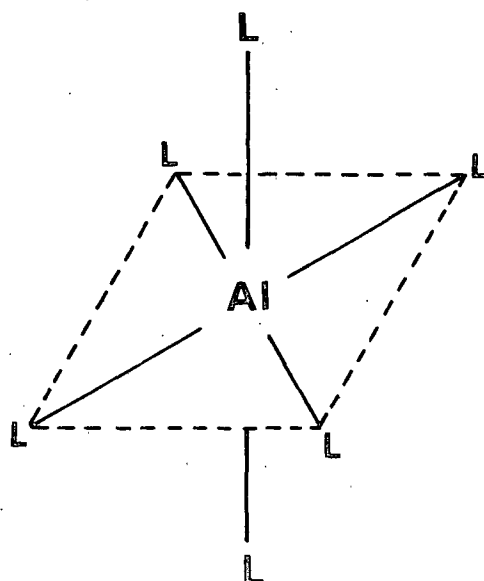
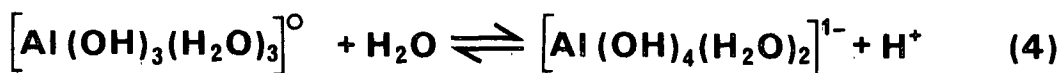
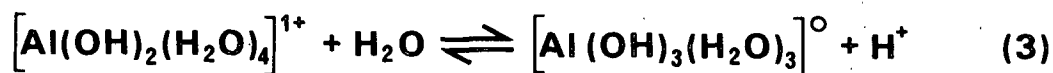
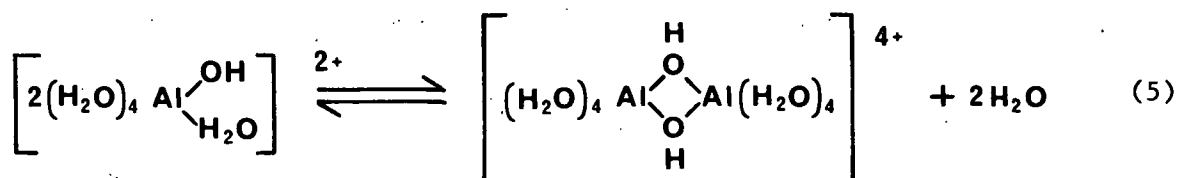


Figure 1. The octahedral structure and general complexing behavior of the aluminum ion.

In addition to simple hydrolysis, hydroxyl bridging can occur resulting in polynuclear species. This hydroxyl bridging is called olation and is shown as follows:





An extension of the olation process can lead to the formation of higher order polynuclear species. Hayden and Rubin<sup>40</sup> have performed a very complete study of the hydrolysis and precipitation of aluminum. Using potentiometric analysis techniques, they concluded that their data could explain the presence of five aluminum species when in the absence of complexing anions:  $\text{Al}^{3+}$ ,  $\text{AlOH}^{2+}$ ,  $\text{Al}_3(\text{OH})_2^{4+}$ ,  $\text{Al}(\text{OH})_3$  and  $\text{Al}(\text{OH})_4^-$ . The distribution of these aluminum species is shown in Fig. 2 for a  $5 \times 10^{-4}\text{M}$  aluminum nitrate solution.

The aluminum species present in the usual papermaking pH range of 4.0 to 5.5 are shown in Fig. 3. The species present are not only a function of pH but also a function of aluminum concentration as shown in Fig. 4.

In the presence of complexing ions, the chemistry of aluminum ions is less clear. Since alum,  $\text{Al}_2(\text{SO}_4)_3$ , is the primary source of aluminum in the paper industry, the complexing behavior of aluminum with sulfate ion is important.

Table 1 shows that the addition of sulfate ions decreases the pH of precipitation of aluminum hydroxide. This is evidence that the sulfate ions are incorporated into the precipitate. If the sulfate ions which have complexed with the aluminum are displaced by hydroxyl ions when forming aluminum hydroxide, a higher concentration of hydroxide would be required to displace the sulfate ions from the soluble complex. This would shift the pH of precipitation to a higher pH. In actuality, the pH is shifted to a lower value. Therefore,

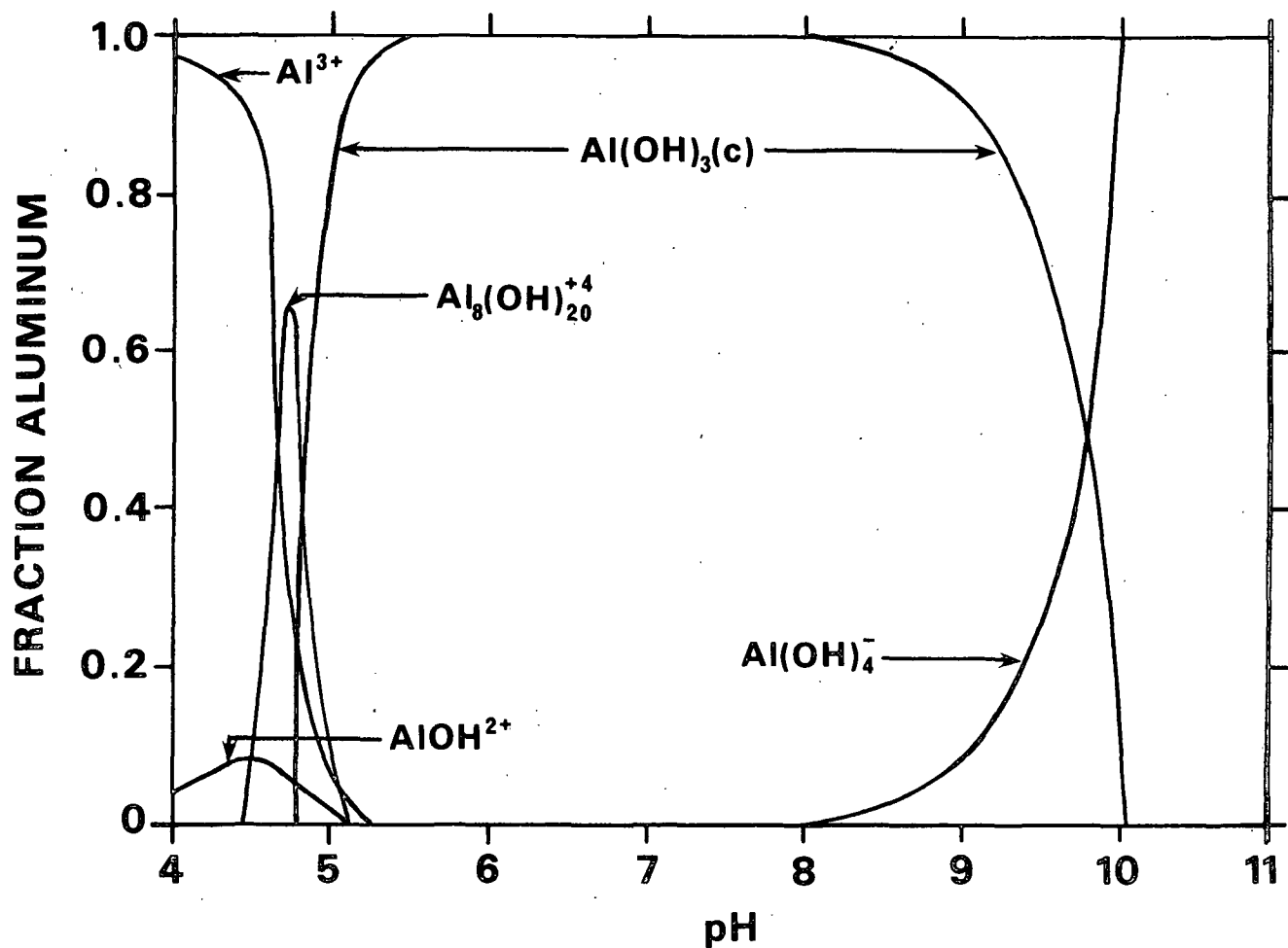


Figure 2. Distribution of aluminum species as a function of pH from pH 4 to 11 ( $5.0 \times 10^{-4} \text{ M}$  Al from aluminum nitrate).<sup>21</sup>

Table 1. Effect of sulfate ion on the pH of precipitation (pHp after 1 hour, Hayden and Rubin<sup>40</sup>).

Aluminum Concentration, <u>M</u>	pH of Precipitation	
	<u><math>\text{Al}(\text{NO}_3)_3</math></u>	<u><math>\text{Al}_2(\text{SO}_4)_3</math></u>
$1.0 \times 10^{-4}$	4.88	4.67
$2.5 \times 10^{-4}$	4.76	4.52
$5.0 \times 10^{-4}$	4.66	4.41
$10.0 \times 10^{-4}$	4.57	4.30

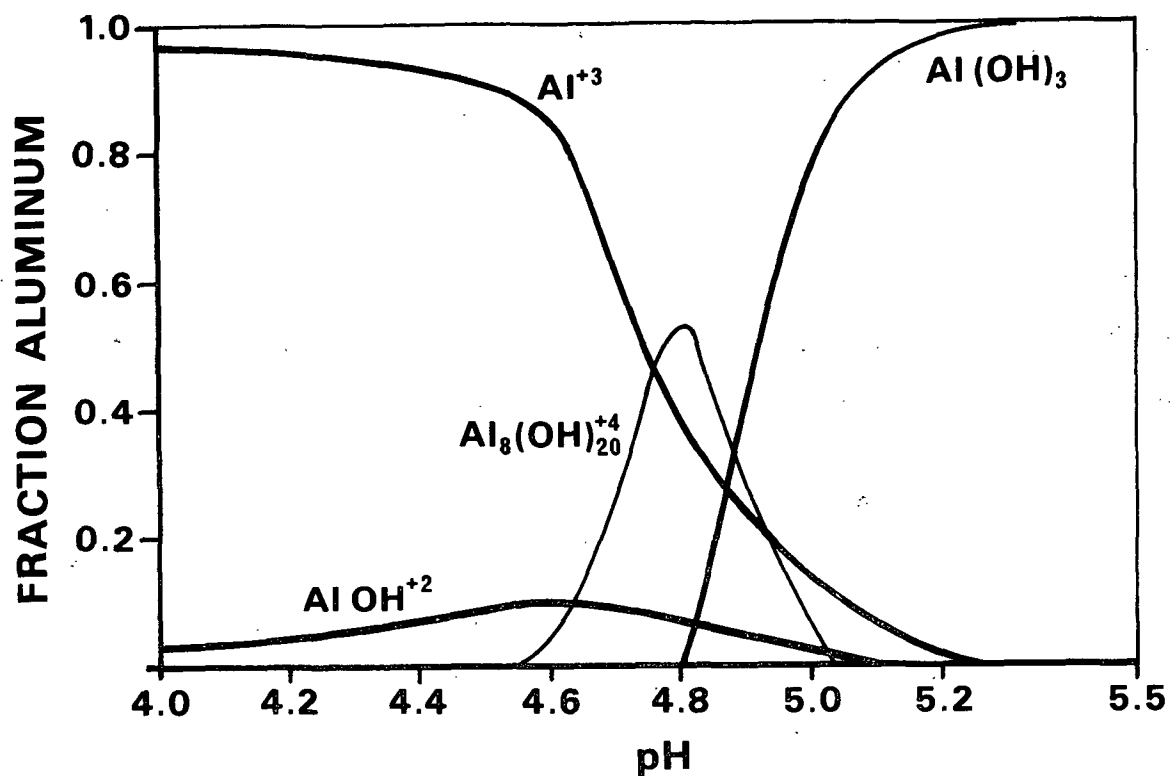


Figure 3. Distribution of aluminum species as a function of pH from pH 4.0 to 5.5 ( $2.5 \times 10^{-4} \text{ M}$  Al from aluminum nitrate).<sup>21</sup>

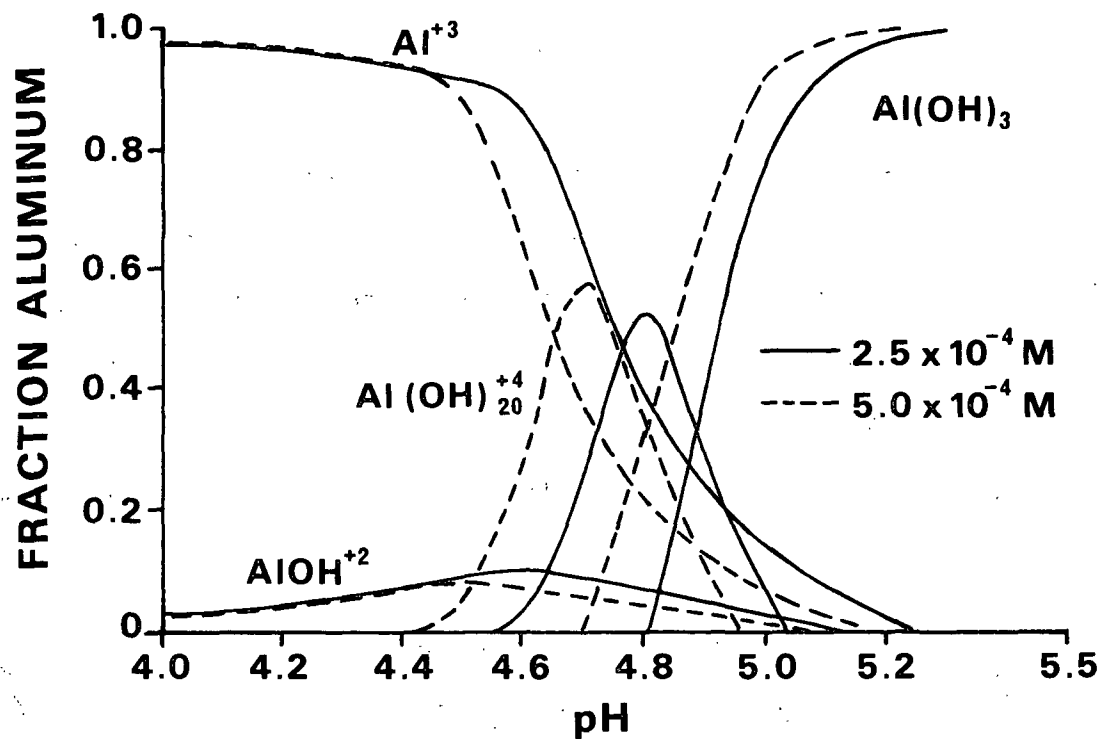


Figure 4. Distribution of aluminum species as a function of pH and aluminum concentration at pH 4.0 to 5.5.<sup>21</sup>

the sulfate must be incorporated into the precipitate, which requires a lower concentration of hydroxide for precipitation.

At a pH less than 4, it has been shown by Ow<sup>41</sup> and Stryker and Matijevic<sup>42</sup> that portions of the  $Al^{3+}$  complex with sulfate ions to form the  $AlSO_4^+$  complex. Above pH 4, Stryker and Matijevic<sup>42</sup> proposed the active complex of  $Al_8(OH)_{10}(SO_4)_5^{4+}$ , but they could not exclude the formation of other complexes.

Two important facts should be noted from this brief review of aqueous aluminum chemistry. First, the presence of complexing anions must be accounted for when using aluminum salts; and second, pH and aluminum concentrations must both be controlled in order to know which aluminum species are present.

#### ALUMINUM ADSORPTION

Now that the aqueous chemistry of aluminum has been reviewed, it is necessary to look at the adsorption properties of aluminum by cellulosic fibers. In 1952, Ninck Blok<sup>43</sup> showed that aluminum adsorption by pulp increases as the concentration of aluminum increases and that the aluminum adsorption was directly related to the carboxyl content of the pulp. Other researchers<sup>44,45</sup> have also noted a correlation between aluminum adsorption and carboxyl content. This behavior would be expected if aluminum ions use carboxyl groups as ion exchange sites. Researchers<sup>26,45-47</sup> have also shown an important relationship between pH and aluminum adsorption in the pH region between 4 and 5. Aluminum adsorption has been shown to increase linearly over this range.

Arnson<sup>21</sup> recently performed an in-depth study on the adsorption of aluminum by cellulosic fibers. Applying Hayden and Rubin's work<sup>40</sup> on aluminum hydrolysis and precipitation, he studied aluminum adsorption from both aluminum chloride

( $\text{AlCl}_3$ ) and aluminum sulfate [ $\text{Al}_2(\text{SO}_4)_3$ ]. Inclusion of aluminum chloride is beneficial to understanding alum adsorption for the following two reasons. (1) the aqueous chemistry of aluminum chloride is better defined than for alum, and (2) aluminum chloride does not have a complexing anion whereas alum does.

Figure 5 is an example of Arnson's results.

Arnson divided the adsorption of aluminum into three pH regions. One region was the lower pH region (4.0-4.5) where there was no polynuclear species and low aluminum adsorption. The second region was the middle pH region (4.4-4.8) where polynuclear species started to form and aluminum adsorption increased. The third pH region was the higher pH region (4.7-5.5) where the aluminum precipitate formed and aluminum adsorption was greatest.

Arnson also showed that aluminum adsorption from aluminum sulfate was predictable and similar to the adsorption pattern for aluminum chloride. The only differences were that the adsorption curve broke upward at a lower pH and the amount of adsorbed aluminum was greater. This is shown in Fig. 6.

In Crow's study<sup>22</sup> on the influence of aluminum salts on the adsorption of cationic polyelectrolytes by cellulosic fibers, Crow repeated Arnson's aluminum adsorption studies. He found that the break in the aluminum adsorption curves correlated with the pH at which the aluminum starts to precipitate and not with the pH at which polynuclear species start to form. He showed that the pH's of precipitation for aluminum chloride in the presence of fibers were approximately 1.6 pH units lower than the values cited by Hayden and Rubin. Therefore, Crow broke the adsorption curves into two pH regions. The first region was below the pH of precipitation where only soluble aluminum species exist and there is low aluminum adsorption. The second region was above the pH precipitation where the

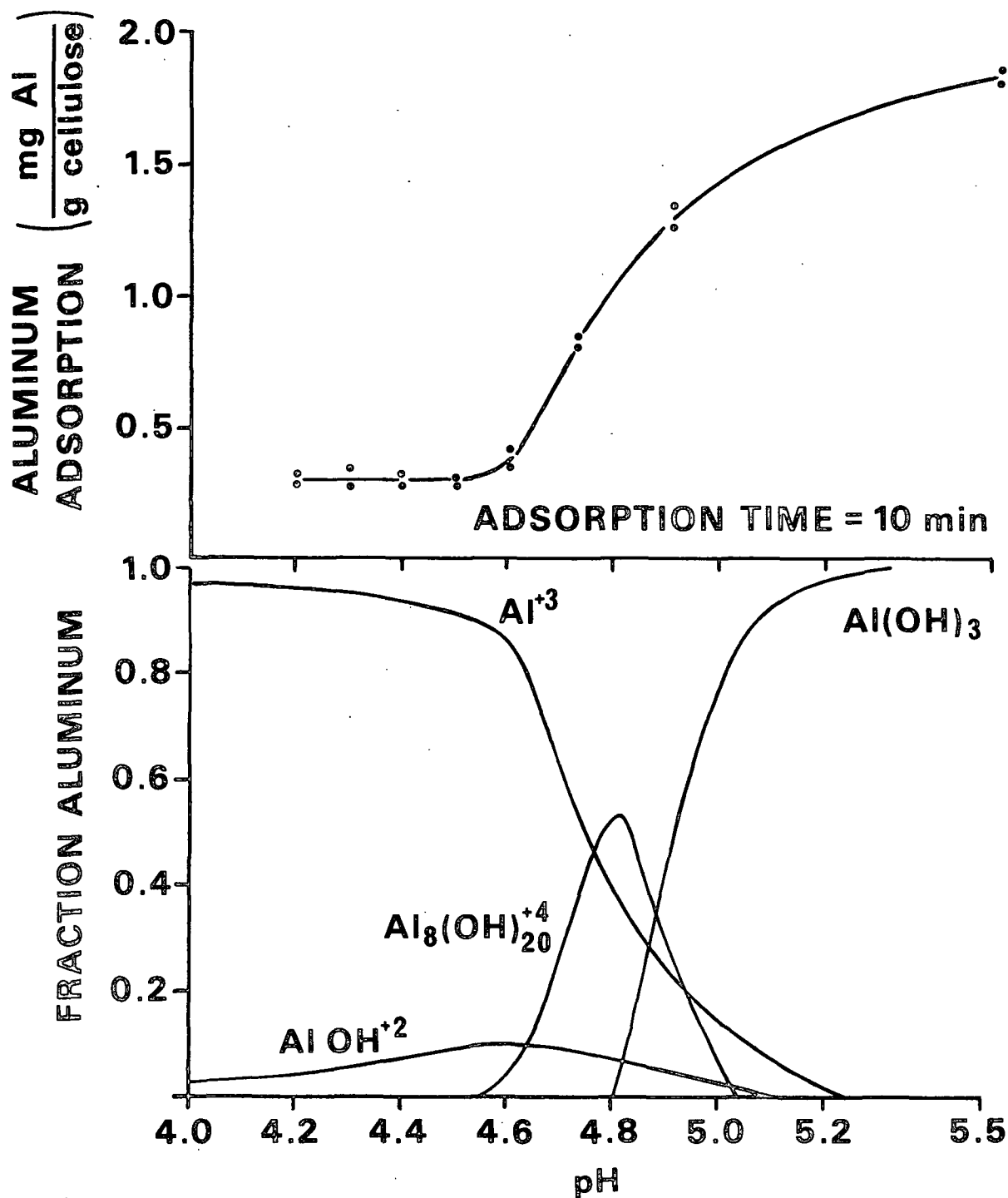


Figure 5. Top: Arnson's aluminum adsorption as a function of pH for aluminum chloride. Bottom: Distribution of aluminum species as a function of pH for aluminum chloride ( $2.5 \times 10^{-4} \text{M Al}$ ).<sup>21</sup>

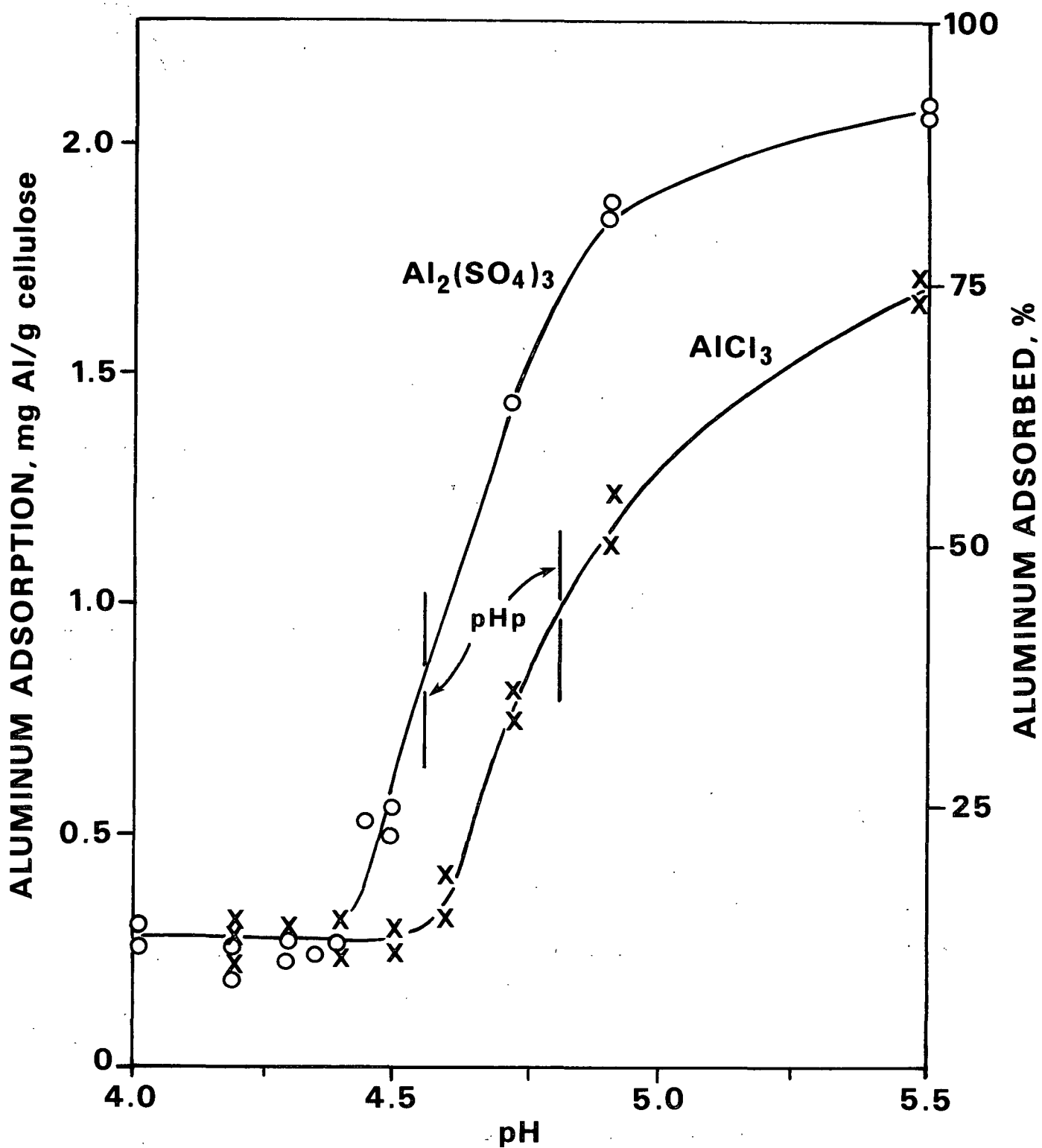


Figure 6. Arnson's comparison of aluminum adsorption for aluminum chloride and aluminum sulfate. Solid vertical lines denote the pH of precipitation formation ( $\text{pH}_p$ ) for each aluminum salt ( $2.5 \times 10^{-4} \text{M Al}$ ).<sup>21</sup>

aluminum precipitate was predominant and aluminum adsorption increased. This is shown in Fig. 7.

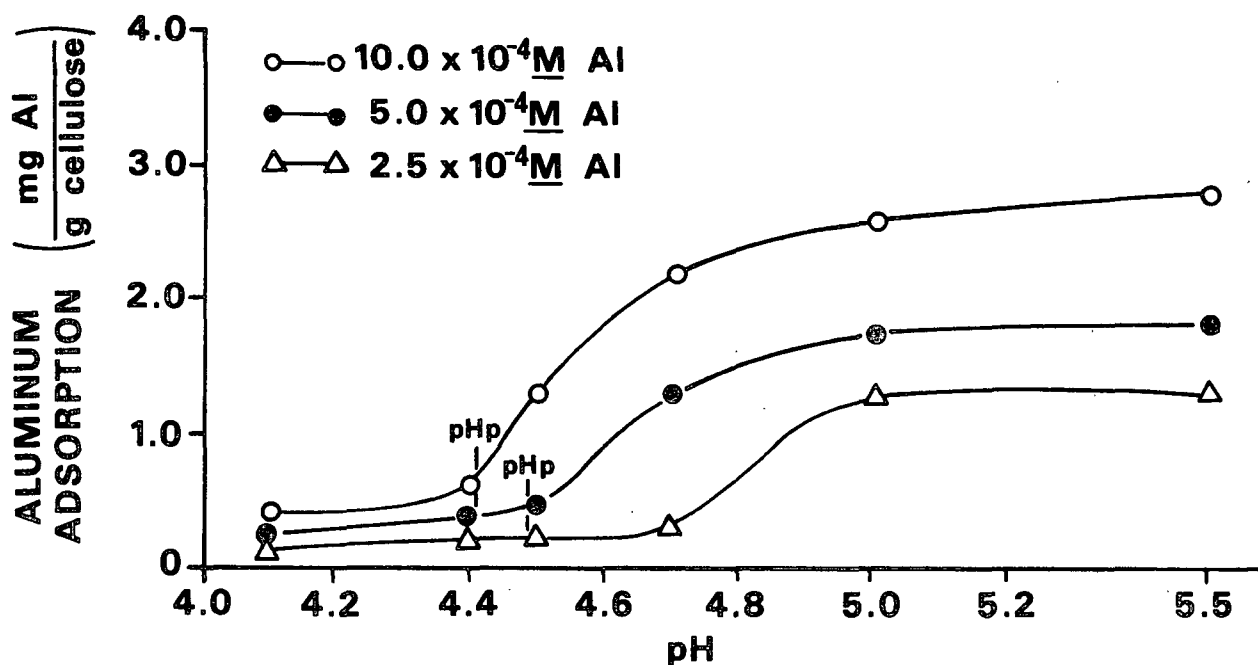


Figure 7. Crow's aluminum adsorption as a function of pH and aluminum concentration for aluminum chloride.<sup>22</sup>

From this literature review on aluminum adsorption, it can be concluded that aluminum adsorption will depend on pH, aluminum concentration, and whether or not complexing anions are present.

#### CATIONIC POLYELECTROLYTE ADSORPTION

Like aluminum, cationic polyelectrolytes adsorb onto cellulosic fibers. Equilibrium adsorption of cationic polyelectrolytes on cellulosic materials<sup>48,49</sup> and other anionic particles<sup>5,6,50-53</sup> is rapid and complete up to a constant



"monolayer saturation level." In a papermaking system, polyelectrolytes are typically added to the stock just after the fan pump. This results in a short polymer contact time, typically much less than one minute.<sup>3</sup> Therefore, polymer adsorption may not be at equilibrium in a papermaking situation. However, studies<sup>3,4</sup> suggest that initial polyelectrolyte adsorption is very rapid and that high retention levels may be reached even with short contact times. It has also been suggested that with short contact times, the polyelectrolyte enters into the flocculation process before it reaches its final equilibrium configuration. From these studies, it can be concluded that polymer contact time can be an important parameter in retention studies.

Initially, it was proposed that cationic polyelectrolytes adsorb onto cellulose by an ion-exchange mechanism.<sup>54,55</sup> In this mechanism, simple electrolytes were displaced from the carboxyl groups on the fiber surface by polyelectrolyte, which in turn formed an ionic bond with the carboxyl groups. More recent studies<sup>35,36</sup> have also suggested a secondary adsorption mechanism taking place by hydrogen bonding or Van der Waal's forces.

#### THE INFLUENCE OF ALUMINUM SALTS ON POLYELECTROLYTE ADSORPTION

Crow<sup>22</sup> recently completed a study to investigate the influence of aluminum salts on polyelectrolyte adsorption. In his study, Crow adsorbed either aluminum chloride or aluminum sulfate onto a refined, fines free, oxidized cotton linters pulp. Next, a cationic polyelectrolyte was added to the slurry and mixed in a dynamic drainage jar. Drainage samples were collected and analyzed for aluminum and polyelectrolyte content. From these measurements, the amount of aluminum and polymer adsorbed was determined for various conditions of pH, aluminum concentration, polyelectrolyte concentration, and reaction times.

A typical result of Crow's adsorption studies is shown in Fig. 8.<sup>22</sup> By applying Hayden and Rubin's<sup>40</sup> aqueous aluminum chemistry and Arnson's<sup>21</sup> and Crow's<sup>22</sup> aluminum adsorption results, the various polymer adsorption trends in the presence of aluminum could be explained. Crow concluded that below the pH<sub>p</sub> (pH of precipitation), where only soluble aluminum species exist, both aluminum chloride and aluminum sulfate salts reduced the polymer adsorption. The reduction in polymer adsorption was attributed to a reduction in adsorption rate. Above the pH<sub>p</sub> for aluminum chloride, polymer adsorption was reduced to extremely low levels. This was attributed to an unfavorable adsorbing surface of a highly charged layer of adsorbed aluminum precipitate. Above the pH<sub>p</sub> for aluminum sulfate, the polymer adsorption was greater than the level observed below the pH<sub>p</sub>. However, the polymer adsorption was still lower than the level observed without aluminum present. The reduction in polymer adsorption due to the presence of aluminum was attributed to a reduction in adsorption rate. The polymer was found to be both directly and indirectly adsorbed onto the fiber surface. The negative sulfate ions were incorporated into the aluminum precipitate and were believed to serve as additional adsorption sites for the polymer which led to increased polymer adsorption. Therefore, the polymer was indirectly adsorbed by adsorbing onto the aluminum precipitate.

Crow's work<sup>22</sup> shows the importance of comparing aluminum chloride and aluminum sulfate to demonstrate the significant effect of a complexing anion.

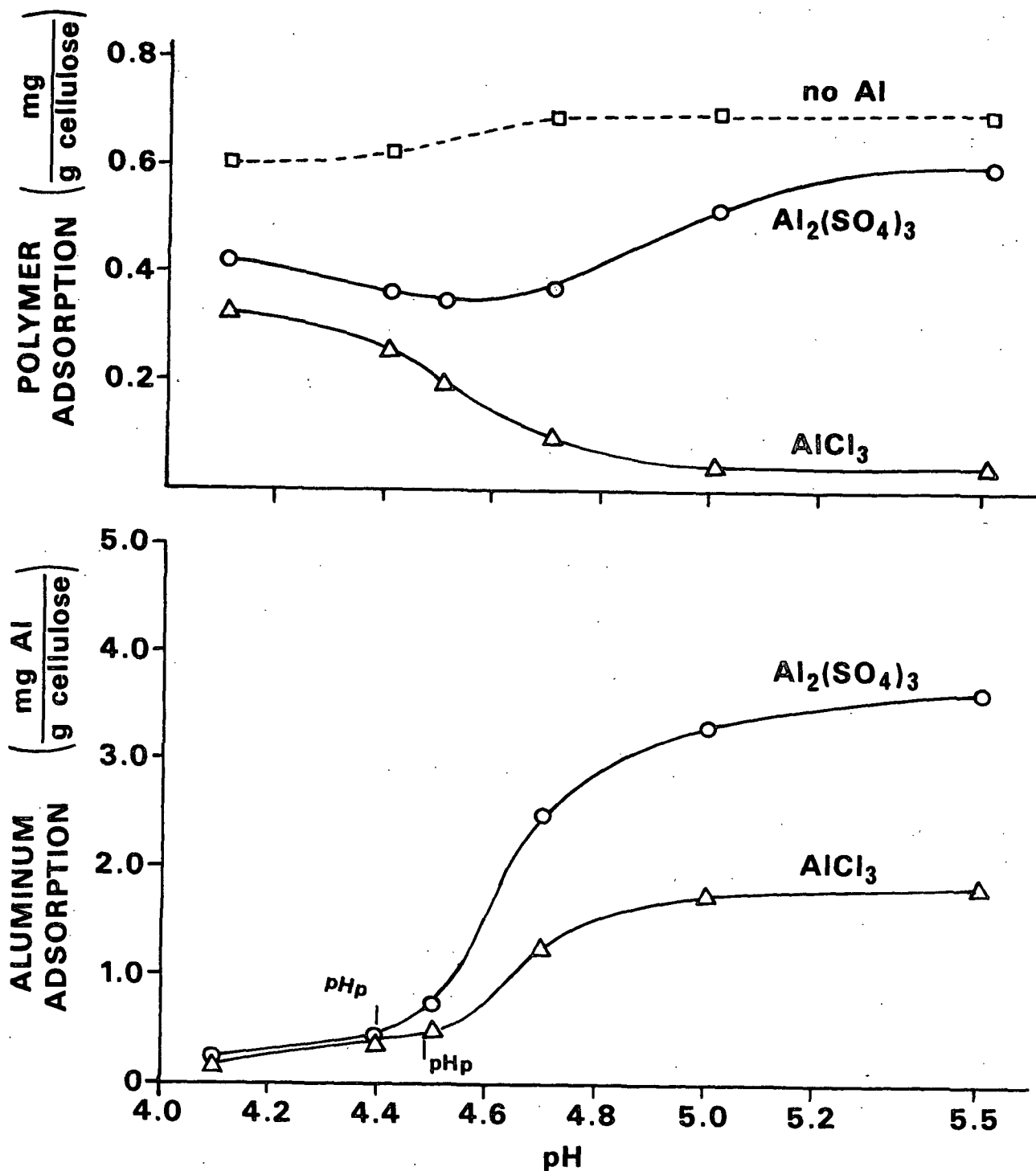


Figure 8. Top: Crow's polymer adsorption as a function of pH and aluminum salt. Bottom: Crow's aluminum adsorption as a function of pH and aluminum salt ( $5.0 \times 10^{-4} \text{M}$  Al, 3.0 ppm polymer addition).<sup>22</sup>

## PRESENTATION OF PROBLEM AND THESIS OBJECTIVES

Polyelectrolytes (polymers) are widely used in the paper industry as wet-end additives to improve fines retention and increase drainage rates. Papermaker's alum (aluminum sulfate) is another common wet-end additive which is known to affect retention when using cationic polyelectrolytes as retention aids. However, reports in the literature have shown differing effects on retention. They vary from increased retention, to decreased retention, to little effect at all. The reasons for these differences are not fully understood but the complex aqueous chemistry of the aluminum ion may account for some of the differences.

Recent work by Hayden and Rubin<sup>40</sup> has produced a better understanding of the aqueous chemistry of the aluminum ion. Their work provided a basis for Arnson's study<sup>21</sup> of aluminum adsorption by cellulosic fibers and Crow's investigation<sup>22</sup> of the influence of aluminum adsorption on polymer adsorption. All of these studies have provided a foundation on which to build a better understanding of how aluminum salts affect the retention of fine solids when using cationic polyelectrolyte as a retention aid.

Specifically, the objective of this thesis was to perform retention experiments using a system similar to that used by Crow where the effects of various aluminum species on aluminum adsorption, polymer adsorption, and filler retention could all be measured and thereby achieve the following:

1. Determine whether aluminum salts can influence retention when using cationic polyelectrolyte.
2. Determine the effects of pH, aluminum counterion, aluminum concentration, and polymer contact time on retention.
3. Determine the mechanism(s) by which aluminum salts can influence retention.

## GENERAL APPROACH

In order to accomplish the objectives of this thesis, retention experiments were performed using an apparatus designed to simulate the retention conditions found on a typical paper machine. The types of aluminum salt, pH, and aluminum concentration were varied in order to adsorb different types and amounts of aluminum species onto a furnish of cotton linters and titanium dioxide. A cationic polyacrylamide retention aid was added as the furnish was run through the retention apparatus. The drainage samples from the retention apparatus were analyzed for aluminum adsorption, zeta potential, polymer adsorption, and titanium dioxide retention in order to observe the effects of the different aluminum species.

From the work of Hayden and Rubin<sup>40</sup> and others,<sup>21,22</sup> it is evident that the pH and aluminum concentration must be systematically and independently controlled to accurately apply the principles of aluminum chemistry. This has been lacking in many of the past studies in this area but is emphasized throughout this investigation.

## EXPERIMENTAL

### MATERIALS

#### Water

The water used throughout this investigation was deionized and distilled.

#### Fibers

Cotton linters were used as the pulp in this investigation for several reasons. First, cotton linters are similar to wood pulp in that they both basically consist of cellulosic fibers which develop a similar surface upon refining. Second, unlike wood fibers, cotton linters are almost free of hemicelluloses and lignin which could interfere with aluminum and polymer adsorption.<sup>57,58</sup> A drawback is that the carboxyl content of the cotton linters is significantly lower than that of wood fibers. Since carboxyl groups are believed to serve as the primary adsorption sites for the aluminum and polymer,<sup>43-45,54-55</sup> a carboxyl content similar to that of wood fibers is desirable. It is possible to create additional carboxyl groups on cotton linters by oxidation of the fibers. Therefore, a refined, oxidized cotton linters pulp should serve as a good model for wood pulp without any adverse effects from soluble hemicelluloses or lignin.

The cotton linters used in this study were originally prepared by Arnson.<sup>21</sup> Arnson treated a commercial grade of papermaking cotton linters in the following manner: (1) refined to 250 mL CSF, (2) classified with two passes over The Institute of Paper Chemistry's web former to remove fines, (3) extracted with ethanol:benzene (1:1), (4) oxidized with potassium dichromate and acidified sodium chlorite, and (5) washed, air dried, and stored in polyethylene bags

without a preservative. Before the cotton linters were used in this study, additional washing was performed.

Some properties of the cotton linters pulp are shown in Table 2.

Table 2. Characteristic properties of the cotton linters pulp.

Fiber length

Arithmetic average	1.2 mm
Weighted average	1.5 mm
Hydrodynamic specific surface area	10,400 cm <sup>2</sup> /g $\pm$ 2%
Hydrodynamic specific volume	1.99 cm <sup>3</sup> /g $\pm$ 4%
Carboxyl content	3.03 meg/100 g $\pm$ 2%

The fiber length measurements were determined by the Wood and Fiber Science Group of The Institute of Paper Chemistry using an optical projection technique developed by Ilvessalo-Pfaffli and Alfthan.<sup>59</sup> The fiber length of the cotton linters is similar to that of most hardwood species.<sup>60,61</sup> The hydrodynamic specific surface area and volume were determined by the Papermaking Group of The Institute of Paper Chemistry using a filtration resistance technique developed by Ingmanson.<sup>62</sup> The hydrodynamic specific surface area of the cotton linters is similar to that of a moderately beaten, classified wood pulp.<sup>48</sup> The carboxyl content of the cotton linters was determined by two methods, namely, TAPPI Standard Method T 237 os-77<sup>63</sup> and Davidson's<sup>44</sup> methylene blue dye adsorption method. The carboxyl content is similar to that of a bleached kraft softwood pulp.<sup>10,64</sup> Therefore, the cotton linters used in this study appear to be a good model of the long fiber fraction of a papermaking furnish. Details of the cotton linters washing and carboxyl content determinations are provided in Appendix I. Further

information concerning the preparation and characterization of the original cotton linters is presented in Arnson's thesis.<sup>21</sup>

### Filler

In this investigation, the titanium dioxide used had a larger average particle size than the filler used typically in papermaking systems. The large particle size was necessary in order to separate the unretained filler from the unadsorbed aluminum and polymer. Appendix II shows the effects of various pore size polycarbonate filters on aluminum and polymer removal and the reason for using the large particle size titanium dioxide.

A sample of large particle size anatase titanium dioxide was separated by a sedimentation technique into a fraction having an average particle size of 4.2 microns and a fairly narrow particle size distribution. A Coulter Counter Model TAI was used for the particle size and distribution measurements. After obtaining the desired size titanium dioxide, tetrasodium pyrophosphate dispersant was added to produce a surface charge similar to that of a conventionally used particle size titanium dioxide; namely, a zeta potential of -13 mV at pH 4.0. For comparison purposes in the retention experiments, a more typical particle size anatase titanium dioxide was also prepared. Details on the preparation, separation, and size measurement of the titanium dioxide samples are provided in Appendix III.

### Aluminum Salts

Both aluminum chloride ( $\text{AlCl}_3 \times 6\text{H}_2\text{O}$ ) and aluminum sulfate [ $\text{Al}_2(\text{SO}_4)_3 \times 18\text{H}_2\text{O}$ ] were used in this investigation. These two aluminum salts were used so that the differences between the noncomplexing chloride ion and the complexing



sulfate ion could be observed. Stock solutions of approximately 0.3M in aluminum were prepared from analytical reagent grade chemicals. These solutions were filtered twice through 0.22 micron Millipore filters to remove any colloidal precipitate which may have formed during preparation. The aluminum content of the stock solutions was determined gravimetrically by reacting the aluminum with 8-hydroxyquinoline to form an insoluble precipitate, aluminum oxinate.<sup>65</sup> This concentrated aluminum analysis procedure is outlined in Appendix IV.

Dilute aluminum solutions were freshly prepared from the stock solutions just before use in the retention experiments.

#### Cationic Polyelectrolyte

The cationic polyelectrolyte (Q5) used in this investigation was a commercial, high molecular weight, low-charge density polyacrylamide. This type of polymer is similar to the majority of cationic retention aids commonly used in the paper industry.<sup>66</sup> It is a copolymer with approximately 5 mole percent of methacryloxyethyl trimethyl-ammonium methosulfate monomer and 95 mole percent of acrylamide monomer. The molecular weight of this polymer has been determined by two methods. A molecular weight of  $2.72 \times 10^6$  was determined from a sedimentation equilibrium technique.<sup>67</sup> Using the intrinsic viscosity and a relationship developed by Francois, et al.,<sup>68</sup> a molecular weight of  $3.23 \times 10^6$  was obtained.<sup>3</sup> Therefore, the molecular weight of this polymer is approximately three million.

The net charge on the polyelectrolyte was determined using a modification of a colloid titration technique.<sup>69</sup> This technique has also been used by Crow<sup>22</sup> and Brigham<sup>70</sup> for this purpose. The basic principle behind this technique is that a cationic polymer can displace a cationic dye from an anionic polymer. If

known amounts of cationic polymer are added to a standard amount of cationic dye-anionic polymer complex, then the amount of dye released will correspond to the amount of cationic charge on the polymer. By spectrophotometrically measuring the amount of dye released, the charge on the polymer is indirectly measured. Using this method, a net cationic charge of 4.2 mole percent was obtained for the polymer.

The amount of anionic charge associated with the cationic polymer was measured by potentiometric titrations. Anionic groups on the polymer would most likely be a result of polymer hydrolysis. Hydrolysis results in the formation of carboxylic acid groups in the form of acrylic acid. The  $pK_a$  of acrylic acid is 4.25; therefore, solutions of hydrolyzed polymer should show a buffering capacity at low pH's. Thus, the degree of hydrolysis can be determined by comparing the extent of buffering of a polymer solution to that of distilled water. Potentiometric titrations of polymer solutions showed no buffering capacity, thus, no hydrolysis or anionic charge. Details of the molecular weight, net cationic charge, and anionic charge determinations are provided in Appendix V.

Concentrated stock solutions were prepared at 1000 mg/L by slowly adding the dry polymer to distilled water under moderate agitation. The solution was then allowed to slowly mix for 24 hours before being used. Dilute solutions were prepared fresh from the concentrated stock solution just prior to use in the retention experiments.

#### APPARATUS

The experimental apparatus used in this investigation is shown in Fig. 9 and 10. Parts of the apparatus and labware exposed to the aluminum and polymer

solutions were made of low-surface energy materials (polypropylene, Teflon, and polyvinyl chloride) and polymer-treated glassware in order to reduce the loss of aluminum and polymer.

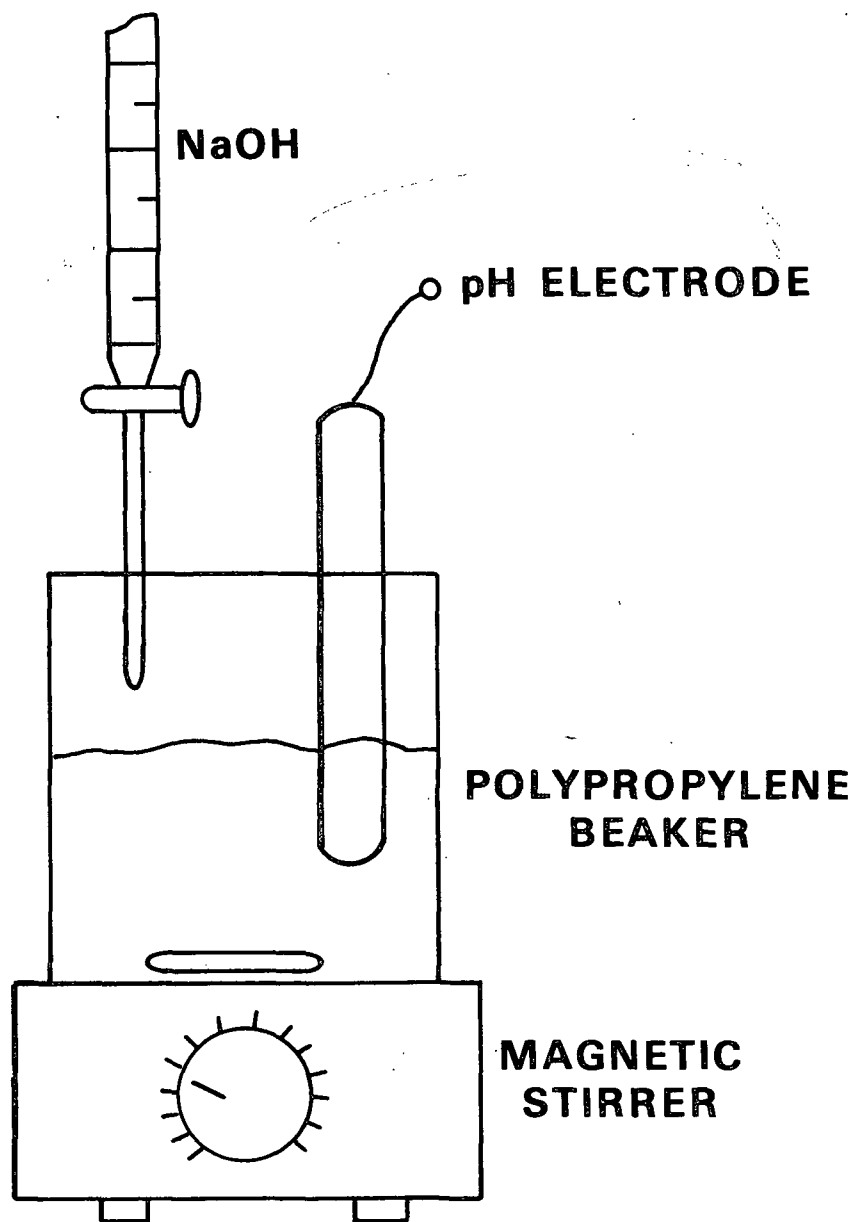


Figure 9. Aluminum adsorption apparatus.

Figure 9 shows the apparatus used for the aluminum adsorption. It consists of a polypropylene beaker, a magnetic stirrer, a buret, and a pH meter.

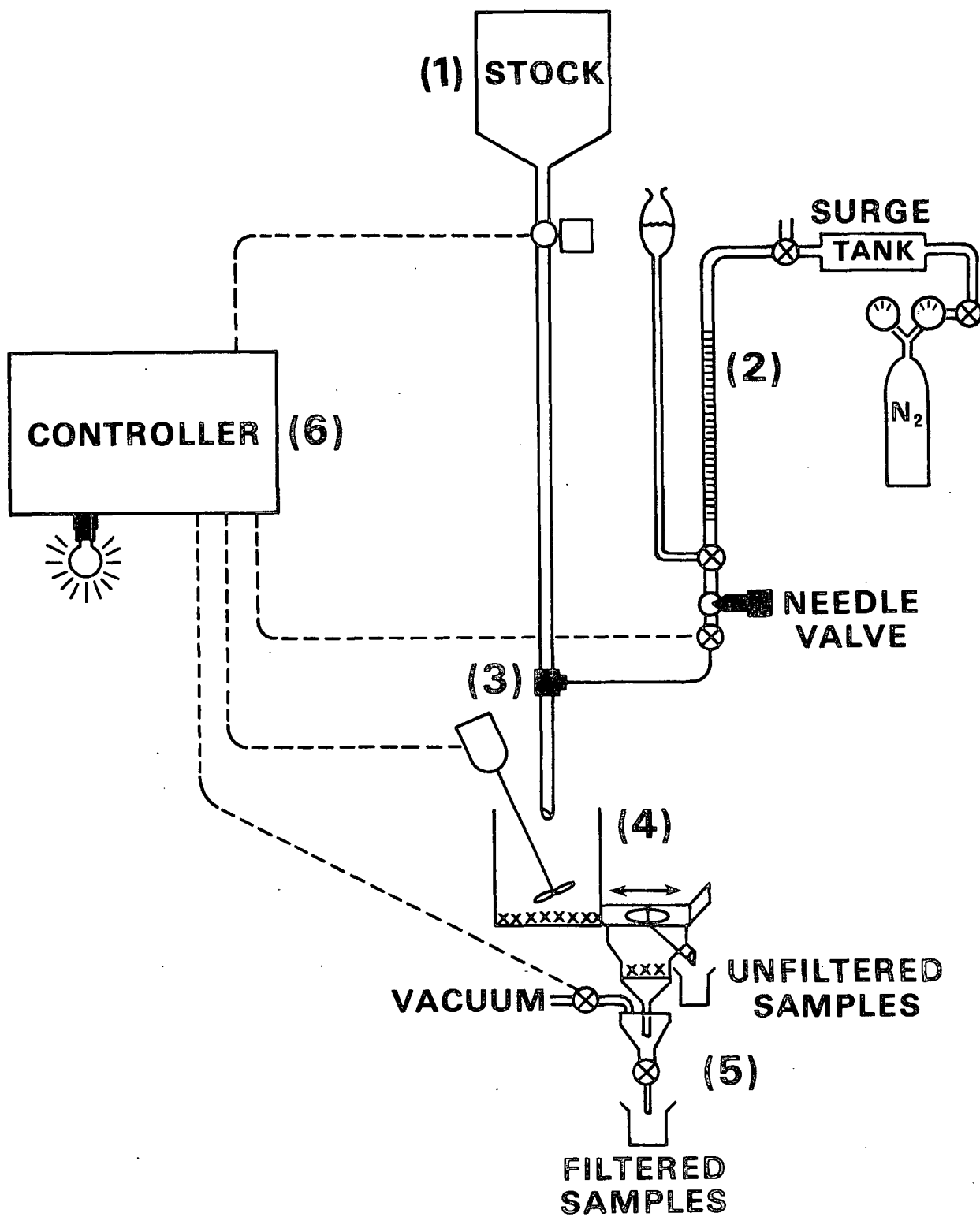


Figure 10. Schematic of experimental apparatus.

The magnetic stirrer was used to agitate the stock in the polypropylene beaker at a rate sufficient to prevent settling of fibers or titanium dioxide. Dilute NaOH was added to the stock from the buret to obtain the desired pH's. A Corning Model 12 Research pH meter, readable to 0.001 pH unit, was used to monitor the pH.

Figure 10 shows the apparatus used to simulate retention on a paper machine. It consists of (1) a furnish delivery section, (2) a polymer delivery system, (3) a mixing tee, (4) a dynamic drainage jar, (5) a sampling section, and (6) a controller.

The furnish delivery system was designed to deliver a pulp slurry to the mixing tee in a well dispersed state. It consists of a polyvinyl chloride (PVC) holding tank, a controlled pneumatic valve, and a PVC delivery tube. The delivery tube is 45 inches long and 1/2 inch in diameter to ensure turbulence in the gravity fed, 0.3% consistency fiber suspension.

The polymer delivery section was designed to deliver a specified amount of polymer throughout the furnish as it passes the mixing tee. It consists of a polymer reservoir, a buret, a needle valve, a controlled solenoid valve, and a constant nitrogen pressure head. The polymer reservoir served as storage for a 200 mg/L polymer solution and was used to refill the buret between retention experiments. The buret measured the amount of polymer being added. The nitrogen pressure head supplied a constant driving force for the polymer addition. The solenoid valve was controlled by timers in the controller so that polymer addition would start as the leading edge of the furnish plug passed the mixing tee and stop as the trailing edge of the furnish plug approached the mixing tee. In order to eliminate loss of the polymer, the polymer delivery section

was pretreated with a high charge density, high molecular weight, cationic polyelectrolyte.

The mixing tee was designed for rapid and uniform mixing of the polymer throughout the furnish. As shown in Fig. 11, it consists of a polymer addition line and a series of mixing rods. The polymer addition line traverses the furnish delivery tube and injects the polymer solution upstream against the furnish flow from a series of small holes. Immediately above and below the polymer addition line, three polypropylene coated rods traverse the furnish delivery tube in different directions. These rods help ensure rapid and uniform mixing of the polymer and furnish.

The dynamic drainage jar was designed to simulate the turbulent mixing and retention conditions found on a paper machine. It consists of a cylindrical vessel, a screen, a sliding gate, and a mixer. The cylindrical vessel contains one baffle and is constructed of polyvinyl chloride. At the bottom of the vessel is a plastic, 90 x 95 mesh screen. Beneath the screen is a sliding gate with a Teflon surface. This prevented the drainage sample from passing through the screen until a sample was desired. A variable speed mixer with a polypropylene coated propeller and shaft was used to agitate the furnish in the vessel. Unless otherwise specified, a mixer speed of 1000 rpm was used.

The sampling section was designed to separate the drainage sample into two parts. As the sliding gate was opened and the drainage sample passed through the screen of the dynamic drainage jar, part of the drainage sample would fall into a polypropylene beaker and the other portion would fall into a filtering apparatus. The drainage sample in the beaker was later used to analyze for titanium dioxide retention and zeta potentials. The drainage sample in the

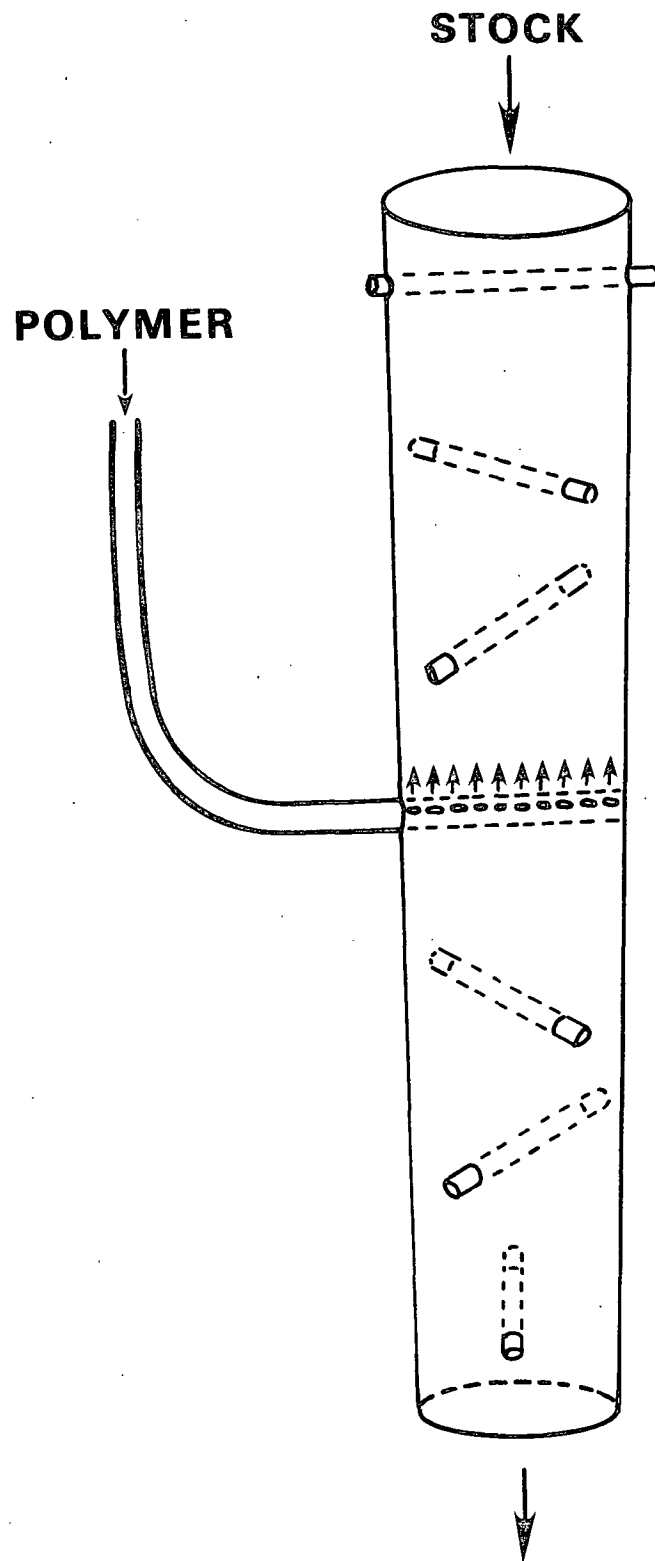


Figure 11. Schematic of mixing tee.

filtering apparatus was immediately filtered through a 2.0 micron pore size, polymer treated, polycarbonate filter (Nuclepore No. 111111) to separate the unretained filler and fines from the unadsorbed aluminum and polymer. This sample was used for the aluminum and polymer analysis. A 28 inch vacuum was used for fast reproducible filtration through the polycarbonate filter. A controlled solenoid valve applied the vacuum immediately upon taking a drainage sample. The filter holder was constructed from polyvinyl chloride, the support screen for the polycarbonate filter was Teflon coated stainless steel, and the receiving vessel for the filtered drainage sample was polypropylene. The polycarbonate filters were pretreated with the polymer in order to reduce adsorption losses. This was performed by soaking the filters in 200 ppm polymer solution and then thoroughly washing with distilled water.

The controller was designed to coordinate the various sections of the apparatus. It consisted of five timers. The first timer opened the furnish delivery line. The second and third timers started the polymer addition at the leading edge of the furnish plug and stopped the polymer addition at the trailing edge of the furnish plug. The fourth timer started the mixer in the dynamic drainage jar as soon as the furnish started entering. The fifth timer activated a light indicating when to manually open the gate and take a drainage sample; at the same time, it also applied vacuum to the filter holder in order to filter part of the drainage sample through the polycarbonate filter.

## PROCEDURES

### Basic Retention Run

In order to properly interpret which aluminum species are present and to prevent the premature formation of aluminum hydroxide precipitate, all of the



retention runs were performed in a systematic manner. The same addition order of materials was used in every retention run and the desired pH was always approached from the acid side. The retention runs were performed in the following manner.

Approximately 450 mL of dispersed cotton linters containing 1.5 g of dry fibers was placed into a 1000 mL polypropylene beaker. Five mL of 3% solids titanium dioxide was added. Next, 25 mL of 0.20N KCl was added to provide an ionic strength background. When investigating the effects of aluminum concentration at constant pH, there is an effect on the ionization of carboxyl groups from variations in ionic strength.<sup>71,72</sup> However, an ionic strength background of 0.01N KCl is sufficient to eliminate this influence without dominating the adsorption behavior of the system.<sup>72</sup> The pH of the furnish was then adjusted to 3.9 with 0.1N HCl and the desired amount of the aluminum salt was added from a dilute aluminum stock solution. Next, the pH was increased with 0.05N NaOH to the desired value and the aluminum adsorption time (10 minutes) was started. Additional NaOH was added throughout the adsorption time, if necessary, in order to maintain the desired pH within 0.025 pH units. Distilled water was added to reach a total volume of 500 mL. The pulp, KCl, and aluminum were present at the desired concentration at this volume.

After the 10 minute aluminum adsorption time, the furnish was placed in the stock holding tank of the retention apparatus and the controller was immediately activated. The pneumatic valve in the furnish section opened allowing the furnish to flow down to the mixing tee where polymer was added. In approximately 5 seconds, all of the furnish had dropped into the dynamic drainage jar where the polymer was usually allowed to adsorb for 15 seconds while being agitated at

1000 rpm. The sliding gate in the sampling section was then partially opened to take a drainage sample. The drainage sample was split into two parts. Approximately 50 mL of the drainage sample fell into the filtering apparatus and was immediately filtered through a 2.0 micron pore size polymer treated, polycarbonate filter. The unretained fines were collected on the filter paper and separated from the unadsorbed aluminum and polymer. The drainage and filtering process was completed within approximately 10 seconds. The filtered drainage sample was used for the aluminum and polymer measurements. Approximately 75 mL of the drainage sample fell into a polypropylene beaker and was later used for titanium dioxide retention and zeta potential measurements. The zeta potential was measured within 5 minutes following the retention run. This time is not critical, since the aluminum adsorption has already reached equilibrium and is the predominant factor influencing zeta potential.

The retention apparatus was then cleaned by first draining the remaining liquid from the dynamic drainage jar. Next, the bottom of the jar was opened in order to remove the fiber pad from the screen. The jar was then closed and approximately 600 mL of distilled water was run through the apparatus with the polymer delivery line closed. After draining the water from the jar, the screen and sampling section were further washed with distilled water. The apparatus was then reassembled and ready for the next run.

#### Aluminum Analysis

The aluminum concentration in the filtered drainage samples were measured using a modification of a procedure published by Fishman.<sup>73</sup> In his procedure, the aluminum in a dilute aqueous solution is chelated with 8-hydroxyquinoline in an ammonium acetate buffer. The aluminum chelate is then extracted into methyl

isobutyl ketone and measured by atomic absorption spectroscopy. The extraction of the aluminum into a small amount of ketone concentrates the aluminum and results in more accurate aluminum determinations.

Crow<sup>22</sup> modified this procedure by measuring the amount of aluminum in the ketone spectrophotometrically instead of by atomic absorption. The chelated aluminum in the ketone produces a yellow color proportional to the concentration of aluminum. By measuring the absorbance at 450 nm in a 1-cm cell, a linear relationship between absorbance and aluminum concentration is obtained. The unknown aluminum concentrations are determined by comparison to standard samples. This method was reproducible with 1% variability. A complete description of the aluminum analysis procedure is provided in Appendix VI.

#### Polymer Analysis

The polymer concentration in the filtered drainage samples was determined by a modification of the colloid titration technique.<sup>69</sup> The basic principle behind the colloid titration technique is that a cationic polymer can displace a cationic dye from an anionic polymer. If an unknown concentration of cationic polymer is added to a standard amount of cationic dye-anionic polymer complex, the amount of dye released from the complex will correspond to the amount of polymer in the unknown sample. By comparing unknown samples to known samples, the polymer concentration in the unknown samples can be determined. In order for this procedure to work, the amount of dye released from the complex must be measured. By choosing a dye with an absorbance that changes when released from the anionic polymer, it is possible to measure the dye concentration spectrophotometrically.

The cationic dye, o-Toluidine Blue (OTB), and the anionic polymer, potassium polyvinyl sulfate (PVSK), were used in this procedure. In order for this procedure to be used in the retention experiments, the aluminum in the drainage samples had to be tied up or removed so it would not interfere with the colloid titration. Maltol (3-hydroxy-2-methyl-4-pyrone) has been reported by Finnegan *et al.*<sup>74</sup> to form a water soluble aluminum complex. It was found that the addition of maltol would tie up the aluminum so that acceptable polymer measurements could be obtained. As shown in Fig. 12, variability was still observed depending upon the initial aluminum concentration; but since the aluminum concentrations were also measured in the retention experiments, it was easy to correct for this variance.

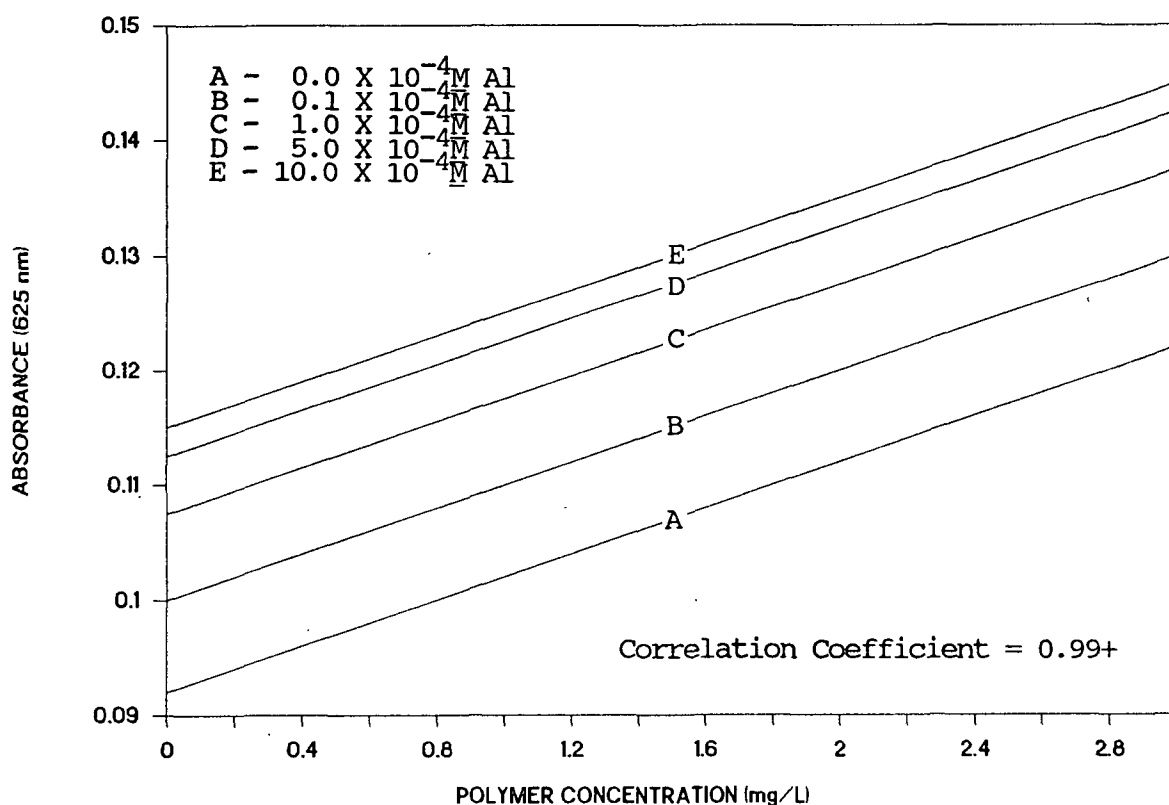


Figure 12. Polymer concentration measurement using a modified colloid titration technique.

### Aluminum and Polymer Adsorption

After the aluminum and polymer concentrations in the drainage samples were determined, the amount of adsorbed aluminum and polymer could be calculated from Eq. (6). The amount adsorbed was expressed on a weight/weight basis of weight of the adsorbed additive to weight of the fibers.

$$A = \frac{(C_I - C_F) V}{M} \quad (6)$$

where A = Amount of adsorbed additive, mg/g fiber

$C_I$  = Initial concentration of additive, mg/L

$C_F$  = Final concentration of additive in drainage sample, mg/L

V = Total volume of solution, 0.5 L

M = Mass of cotton linter fibers, 1.5 g

### Titanium Dioxide Retention

The amount of titanium dioxide filler in the unfiltered drainage samples was determined gravimetrically. 50.0 mL of a drainage sample was slowly filtered through a No. 42 Whatman, ashless filter paper. The unretained titanium dioxide and cotton linter fines were filtered out onto the filter paper. This was washed two times with 5 mL of 0.1N HCl to dissolve and remove any aluminum precipitate that may have been present. This was followed by several distilled water washes. The sample was then ashed at 925°C for ten minutes in a tared crucible to remove the filter paper and cotton linters fines. Like the filter paper, the cotton linters were also ashless. After cooling, the crucible was reweighed to determine the amount of titanium dioxide in the 50 mL drainage sample. The titanium dioxide retention was then calculated from the following equation:

$$R = \frac{W_a}{V_a} \times \frac{V_T}{W_T} \quad (7)$$

where R = Titanium dioxide retention, %

$V_a$  = Volume of drainage sample ashed, 0.050 L

$V_T$  = Total volume, 0.500 L

$W_a$  = Weight of drainage sample ashed, g

$W_T$  = Total weight of titanium dioxide. 0.15 g

### Zeta Potential Analysis

At the end of each retention run, the electrophoretic mobility of the unfiltered drainage sample was measured using a Zeta Meter Model B. The electrophoretic mobilities were converted directly to zeta potentials by using the Helmholtz-Smoluchowski equation.<sup>75</sup>

$$(ZP) = 113,000 \frac{V_t}{D_t} \times (EM) \quad (8)$$

where ZP = Zeta potential, millivolts

$V_t$  = Viscosity of suspending liquid, poise

$D_t$  = Dielectric constant of suspending liquid

EM = Electrophoretic mobility, microns/sec per volt/cm

The zeta potential was used as a measure of surface charge of the furnish in the retention runs.

### Reproducibility

One of the best measures of experimental error for a procedure is the reproducibility. The various experiments in this study were typically duplicated and the results are compiled in Appendices VIII through XIV. However, the

retention experiments at  $10.0 \times 10^{-4}\text{M}$  aluminum from aluminum sulfate and 3.0 mg/L polymer were performed five different times (Appendix VIII). The 95% confidence intervals for these experimental results were less than  $\pm 0.087$  mg aluminum/g cellulose for the aluminum adsorption,  $\pm 0.016$  mg Q5/g cellulose for the polymer adsorption,  $\pm 1.5\%$  for the titanium dioxide retention, and  $\pm 3.0$  mV for the zeta potentials.

#### Basic Polymer Adsorption Experiments

In order to help characterize the polymer used in this study, some basic polymer adsorption experiments were performed. The effects of polymer adsorption time and polymer concentration were studied independently.

Polymer adsorption times were studied by varying the contact time from 15 seconds to 120 minutes for the adsorption of the polymer onto the cotton linters plus titanium dioxide. The adsorption runs were performed in 50 mL polycarbonate centrifuge tubes at the same concentrations which were used in the retention experiments. The cotton linters were at 0.3% consistency. The titanium dioxide was 10% of the dry cotton linters weight.

A 0.01N KCl background and 3.0 mg/L polymer concentration were used. These concentrations were attained and the adsorption time was started when the polymer solution was added to the other components and a total volume of 50 mL was obtained. The slurries were mixed by continually inverting the tubes. After the desired polymer adsorption times, a portion of the slurry was immediately filtered through a 2.0 micron pore size, polymer treated, polycarbonate filter. The filtrate was then analyzed for polymer concentration.

Similar experiments were also performed in the presence of aluminum sulfate at  $1.0 \times 10^{-3}\text{M}$  Al and pH's of 4.0 and 5.5.

The effect of polymer concentration was studied in an equilibrium adsorption isotherm experiment. Again, the experiments were performed in 50 mL polycarbonate centrifuge tubes at the same cotton linters, titanium dioxide, and potassium chloride concentrations. The polymer concentration was varied from 1.5 mg/L to 240 mg/L. An equilibrium adsorption time of 120 minutes was used. The samples were mixed on a rotating wheel unit at 30 rpm in a 25.0°C water bath. This unit has been used in numerous adsorption studies<sup>5,6,70,76,77</sup> and was designed to produce a rocking agitation within the sample. After the 120 minute adsorption time, the samples were centrifuged at 10,000 rpm for 15 minutes. The supernatant was then analyzed for polymer concentration.

#### Aluminum Precipitate Desorption Experiments

Aluminum precipitate desorption experiments were performed to determine where the polymer was adsorbing. Since the polymer was added after the aluminum was already adsorbed, it was possible that the polymer was adsorbing onto the aluminum instead of directly to the furnish surface. By desorbing the aluminum, any polymer adsorbed onto the aluminum should also be released and when measured would indicate the amount of indirectly adsorbed polymer.

Retention experiments were performed in the usual procedure except after the polymer was adsorbed for one minute, the aluminum precipitate was desorbed by acidification with HCl to a pH of 3.5. Before the aluminum desorption, 25 mL of  $1 \times 10^{-2}M$  cetyltrimethyl ammonium bromide, a cationic surfactant, was added to the furnish in the dynamic drainage jar. The cationic surfactant was added to prevent readsorption of the polymer onto any surfaces freshly exposed by the aluminum desorption. After acidification, a 40 mL filtered drainage sample was obtained and placed in an ultrafiltration apparatus.



Ultrafiltration was necessary to separate the cationic surfactant from the polymer so that the polymer concentration could be measured. The ultrafiltration also removed the aluminum, which complicates the polymer analysis. A YM-10 membrane (Amicon) was used in the ultrafiltration cell. This membrane had a 10,000 nominal molecular weight cut-off and low adsorption characteristics. It was still necessary to pretreat the membrane with polymer to reduce polymer losses. This was accomplished by soaking the membrane in 200 mg/L Q5 polymer for at least 24 hours and then thoroughly washing with distilled water. The drainage sample was ultrafiltered under 50 psi pressure until 300 mL of distilled water had been filtered through. The sample was then concentrated to approximately 20 mL and then transferred to a 60 mL polypropylene bottle. The ultrafiltration cell was then washed two times with 10 mL of distilled water. The washes were also added to the polypropylene bottle and the polymer concentration was determined.

The aluminum precipitate desorption experiments were performed at  $1 \times 10^{-3} \text{M}$  Al from aluminum sulfate with 3.0 mg/L polymer. As in the usual retention experiments, the pH of the aluminum adsorption step was varied from 4.0 to 5.5. Experiments were also performed by the above procedure without acidification to determine the effect of the cationic surfactant alone on the polymer adsorption.

## RESULTS AND DISCUSSION

### ALUMINUM ADSORPTION

#### Initial Considerations

The principle variables which affect aluminum adsorption during retention experiments were the type of aluminum salt, the aluminum concentration, and the system pH. The aluminum salts used were aluminum chloride and aluminum sulfate. The aluminum concentrations used were 0,  $2.5 \times 10^{-4}\text{M}$ ,  $5.0 \times 10^{-4}\text{M}$ , and  $10.0 \times 10^{-4}\text{M}$ ; at the 0.3% pulp consistency used in the retention experiments, this corresponds to alum additions of 0, 50, 100, and 200 lb/ton, respectively. The pH was varied from 4.0 to 5.5, and the aluminum adsorption time was held constant at 10 minutes.

The amount of aluminum adsorbed during the retention experiments is expressed on a weight/weight basis as mg aluminum per g cellulose. Complete removal of the aluminum from solution or 100% aluminum adsorption corresponds to 2.27 mg aluminum/g cellulose at  $2.5 \times 10^{-4}\text{M}$ , 4.54 mg aluminum/g cellulose at  $5.0 \times 10^{-4}\text{M}$ , and 9.08 mg aluminum/g cellulose at  $10.0 \times 10^{-4}\text{M}$ .

#### Effects of pH and Aluminum Concentration

The influence of pH and aluminum concentration on aluminum adsorption during the retention experiments is presented in Fig. 13 and 14 for aluminum chloride and aluminum sulfate, respectively. The aluminum adsorption data for the basic retention experiments is compiled in Appendix VIII. These results are from retention experiments where 3.0 mg/L of polymer was added. Similar aluminum adsorption results were obtained when no polymer was added, indicating that the polymer had no effect on the amount of aluminum adsorbed. This would be

expected since the aluminum was added and allowed to adsorb to equilibrium before the polymer was added.

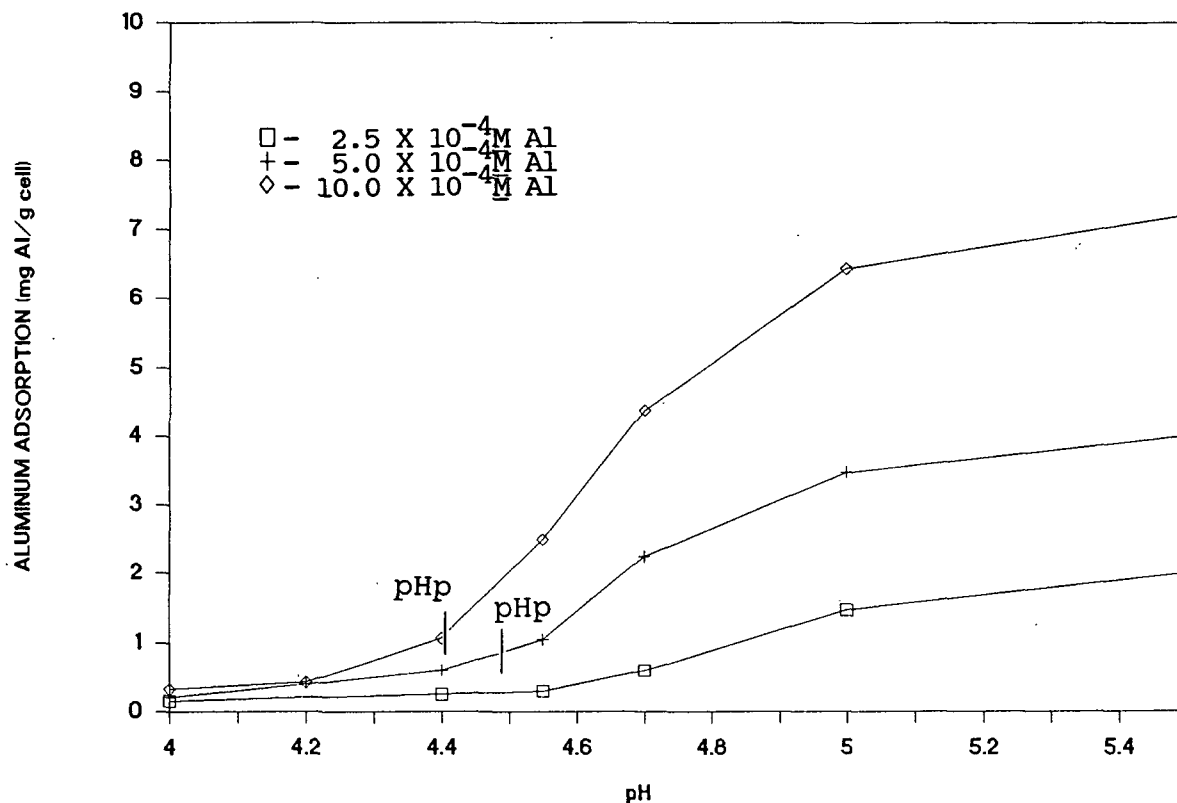


Figure 13. The influence of pH and aluminum concentration on aluminum adsorption for aluminum chloride.

The shape of the aluminum adsorption curves is typical of that observed by other researchers<sup>21,22,43,45-47</sup> with low aluminum adsorption at low pH values, a sharp increase in aluminum adsorption between pH 4 and 5, and high aluminum adsorption above pH 5. For reference, Crow's pH of precipitation values (pHp) for the aluminum salts are included. The sharp increases in the aluminum adsorption curves correspond fairly well with these pHp values. With both aluminum salts, increasing the aluminum concentration caused (1) the aluminum

adsorption to increase and (2) the break in the aluminum adsorption curves to occur at a lower pH.

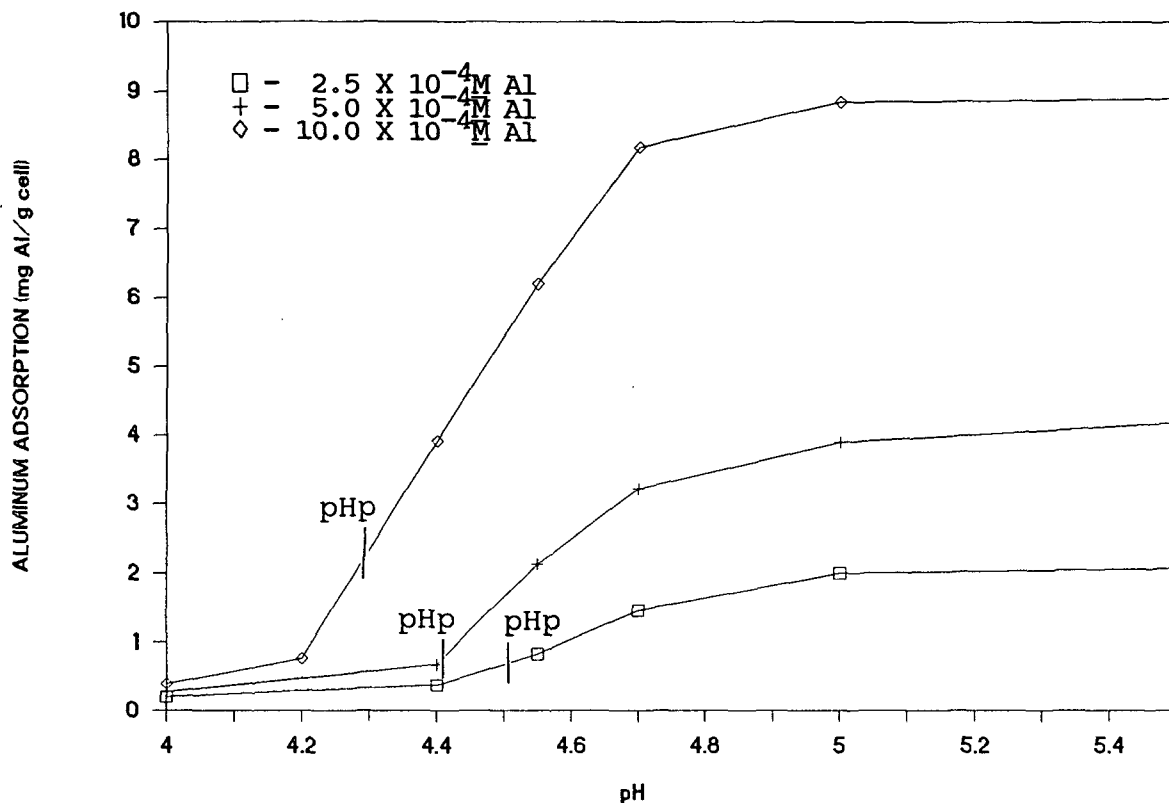


Figure 14. The influence of pH and aluminum concentration on aluminum adsorption for aluminum sulfate.

#### Comparison of Aluminum Chloride and Aluminum Sulfate

Figures 15, 16, and 17 compare the aluminum adsorption for aluminum chloride to aluminum sulfate at  $2.5 \times 10^{-4}$ ,  $5.0 \times 10^{-4}$ , and  $10.0 \times 10^{-4}$  M aluminum, respectively. Once again, the breaks in the aluminum adsorption curves correspond fairly well with pHp values reported by Crow. These figures also show that (1) the aluminum adsorption is greater for aluminum sulfate than for aluminum chloride and (2) the break in the aluminum adsorption curve occurs at a lower pH for aluminum sulfate than for aluminum chloride. These aluminum

adsorption trends agree with the results obtained by Crow; however, the aluminum adsorption is generally greater than the values reported by Crow. This is most likely caused by differences in the adsorbate surfaces. In Crow's work, only cotton linters were used, but in this study a combination of cotton linters and titanium dioxide provide the surfaces for adsorption.

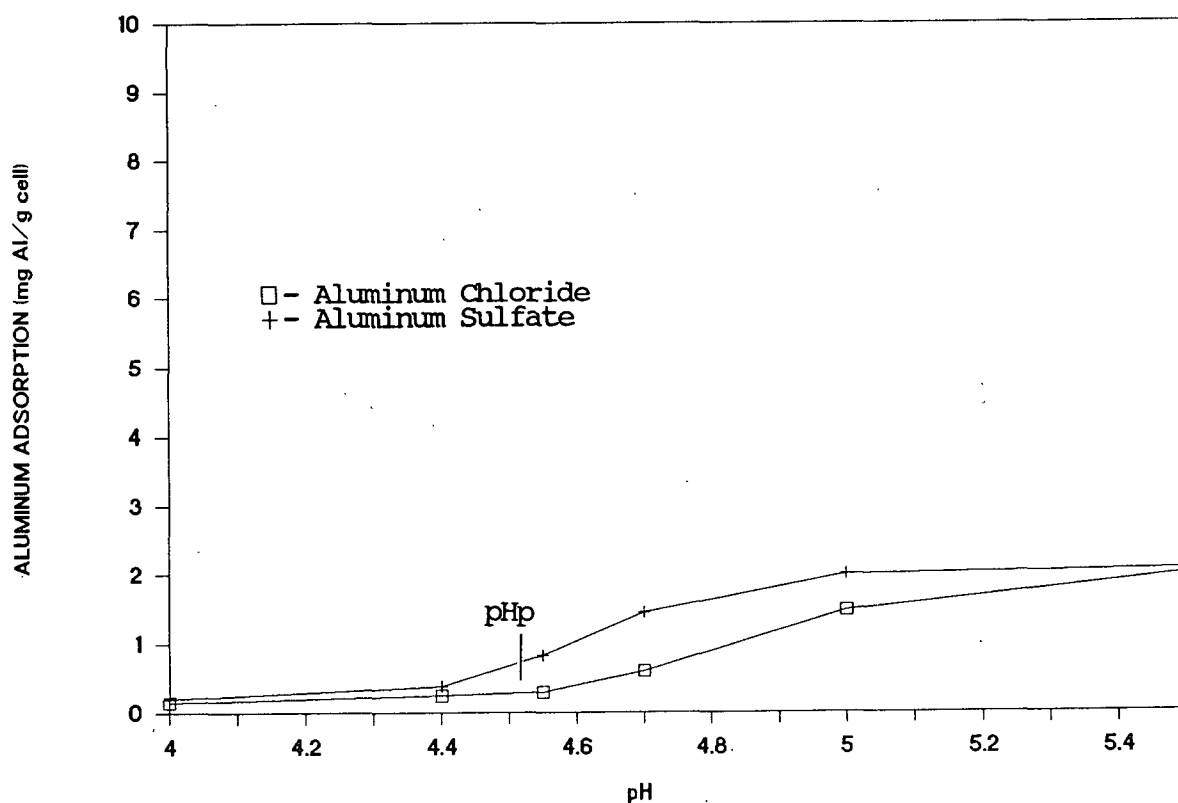


Figure 15. Comparison of aluminum adsorption for aluminum chloride and aluminum sulfate ( $2.5 \times 10^{-4}M$  Al).

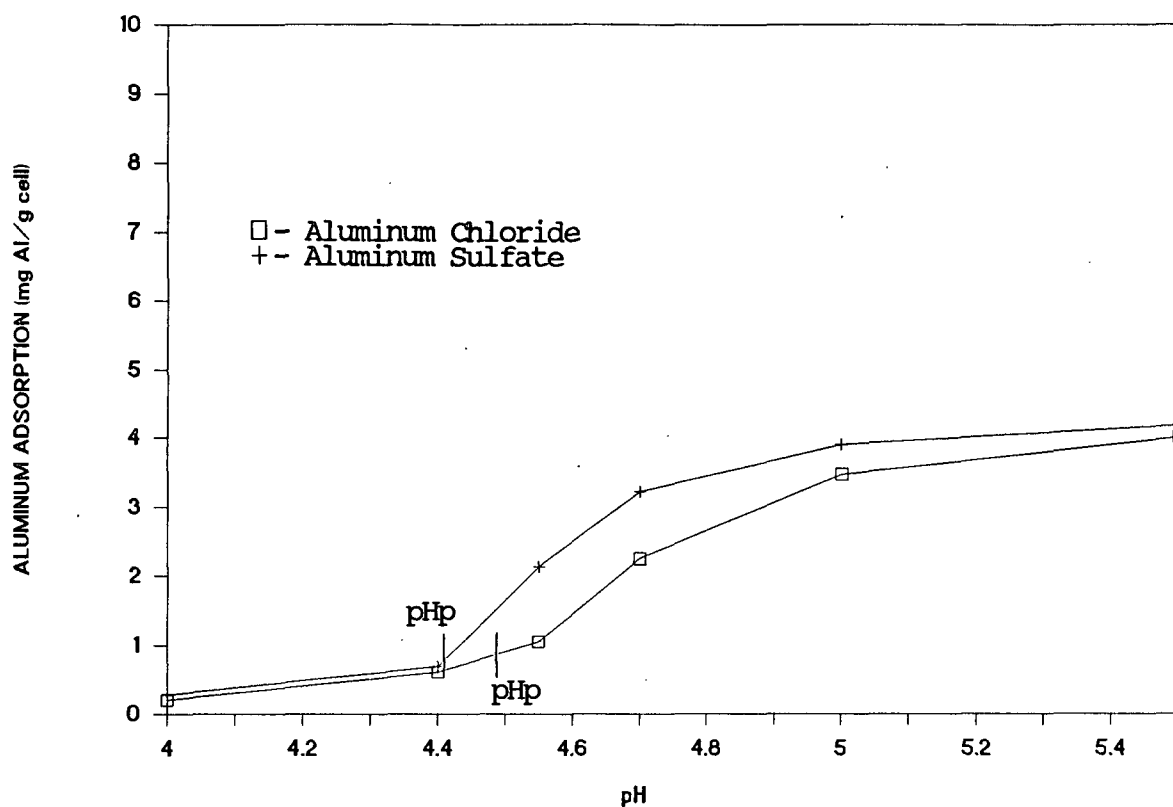


Figure 16. Comparison of aluminum adsorption for aluminum chloride and aluminum sulfate ( $5.0 \times 10^{-4} \text{ M Al}$ ).

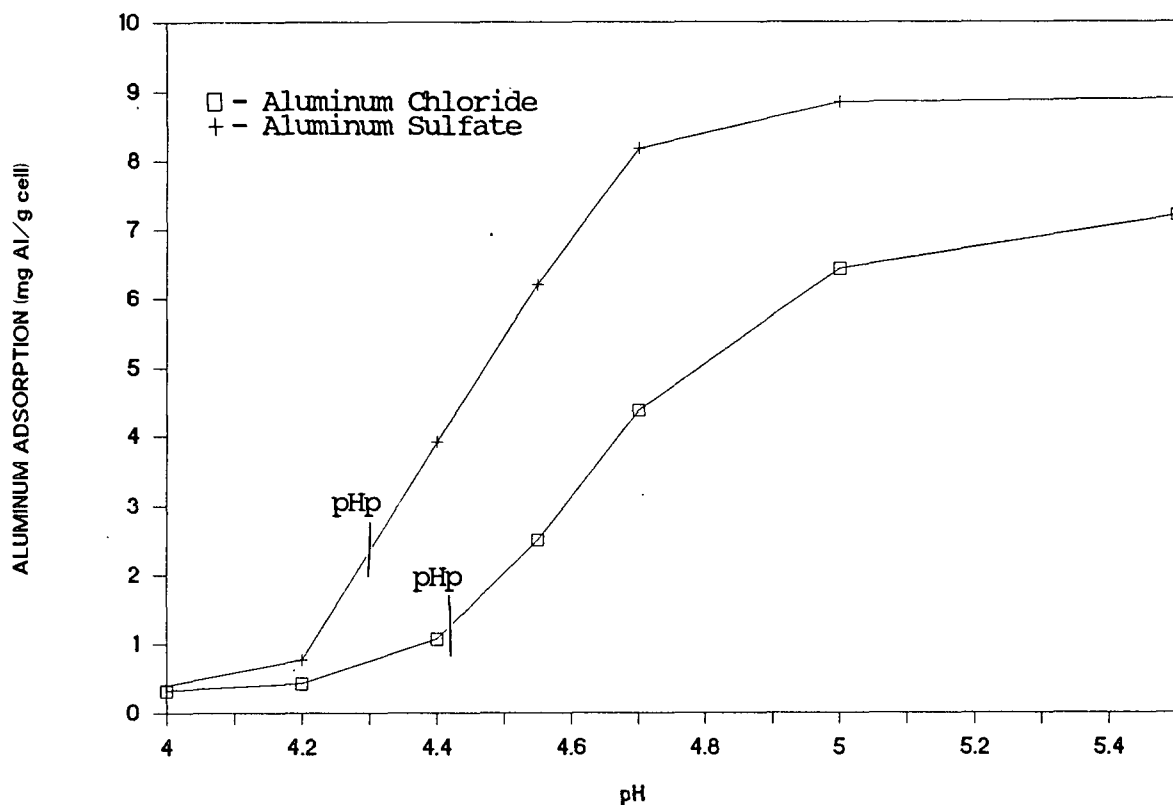


Figure 17. Comparison of aluminum adsorption for aluminum chloride and aluminum sulfate ( $10.0 \times 10^{-4} \text{ M Al}$ ).

# ZETA POTENTIALS

The influence of pH, aluminum concentration, and aluminum salt on zeta potential for the drainage samples is presented in Fig. 18. The zeta potential data for the basic retention experiments is compiled in Appendix VIII. The aluminum salts produced zeta potential curves with similar shapes. The zeta potentials for aluminum chloride, which adsorbed to a lesser degree, were significantly higher than the zeta potentials of aluminum sulfate. With both aluminum salts, the zeta potential started at its lowest value at pH 4 and then steadily increased as the pH was raised to 5, after which there was a slight decrease as the pH was raised further to 5.5. This figure also shows that there was usually only a slight increase in zeta potential as the aluminum concentration was increased even though the aluminum adsorption increases substantially.

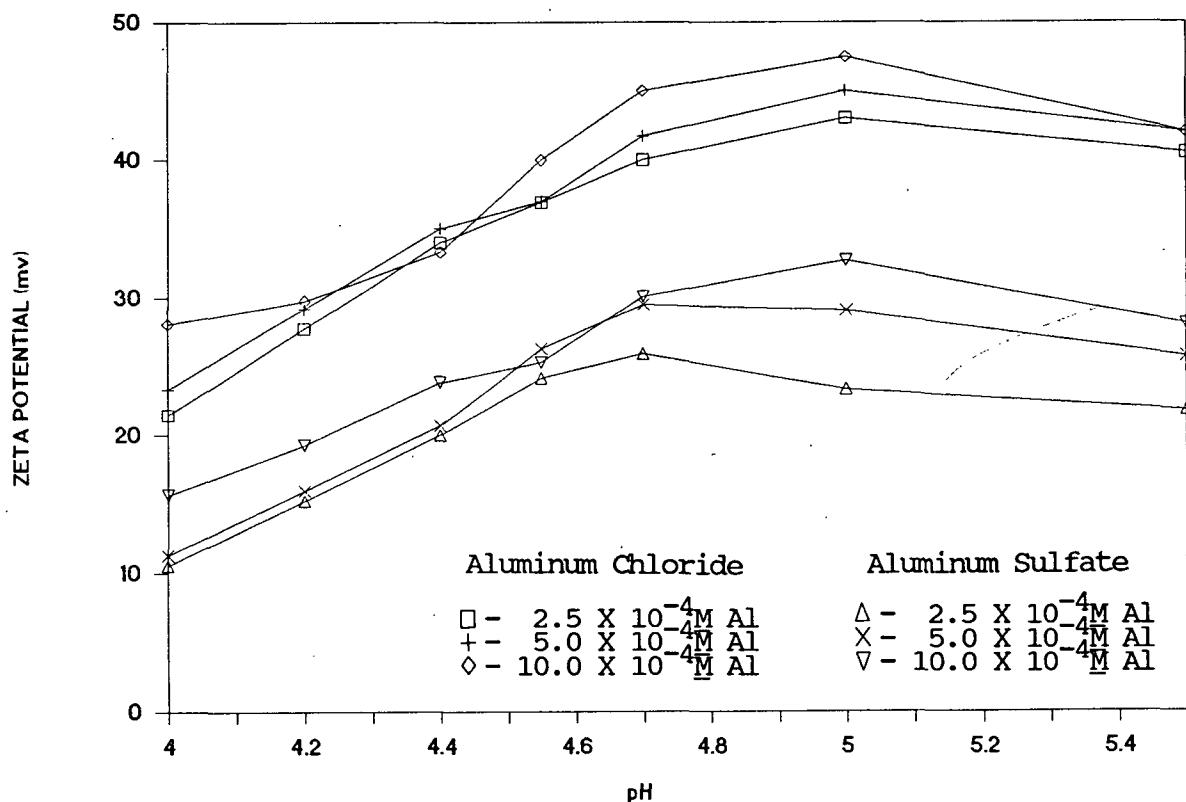


Figure 18. The influence of pH, aluminum salt, and aluminum concentration on zeta potential.

The zeta potential of the drainage sample in the absence of aluminum salts and polymer was approximately -9mV. The zeta potential in the presence of 3.0 mg/L of polymer was approximately -1mV. As shown in Fig. 18, the zeta potentials for the drainage samples where both aluminum and polymer are present range from + 10 mV to + 48 mV. Therefore, both aluminum salts impart a significant cationic charge to the furnish surfaces.

#### INTERPRETATION OF THE ALUMINUM ADSORPTION AND ZETA POTENTIAL RESULTS

The aluminum adsorption trends observed in this study are similar to those seen by other researchers<sup>21,22,43,45-47</sup> with low aluminum adsorption at low pH values, a sharp increase in aluminum adsorption between pH 4.0 and 5.0, and high aluminum adsorption above pH 5. Arnson<sup>21</sup> showed that the sharp increase in aluminum adsorption was not due to an increase in the number of adsorption sites caused by the ionization of carboxyl groups when the pH was increased but from the changes in the aqueous chemistry of the aluminum ion. He found that this sharp increase corresponded with the formation of the polynuclear aluminum species,  $Al_8(OH)_{20}^{4+}$ . However, Crow<sup>22</sup> found that the sharp increase in aluminum adsorption corresponded with the formation of the aluminum precipitate and not to the formation of the polynuclear species. He showed that aluminum chloride precipitates at a lower pH when it is in the presence of cotton linter fibers. According to Hayden and Rubin<sup>40</sup>, aluminum chloride solutions near the pH<sub>p</sub> are initially highly oversaturated. The cotton linter fibers most likely act as a destabilizing agent causing the aluminum chloride to precipitate without becoming oversaturated, thus lowering the pH<sub>p</sub>.<sup>22</sup>



### Above the pHp

The sharp increases in the aluminum adsorption curves obtained in this study correspond fairly well with the values reported by Crow<sup>22</sup> (Fig. 13 and 14). Therefore, the sharp increase in aluminum adsorption is believed to be caused by the adsorption of aluminum hydroxide precipitate. When the aluminum precipitate is formed, it has a strong positive charge and can be thought of as a cationically charged colloidal particle.<sup>78-80</sup> This is supported by the increasing zeta potentials for the drainage samples after the pHp (Fig. 18). Since the aluminum precipitate is cationically charged, it would be expected that electrostatic forces are partially involved in aluminum precipitate adsorption. Arnson<sup>21</sup> showed that electrostatic forces did play a part in aluminum precipitate adsorption. He varied the carboxyl content of the adsorbing fibers and found that higher carboxyl content fibers produced higher aluminum adsorption.

Since the drainage samples were cationically charged below the pHp at all aluminum concentrations, it is likely that only a small portion of the aluminum adsorption is due to an electrostatic attraction between the aluminum precipitate and the furnish surface. The majority of the aluminum adsorption is most likely occurring by a mechanism proposed elsewhere.<sup>46,78,81</sup> In this mechanism as the colloidal precipitate comes out of solution, it accumulates at the liquid-solid interface on the surface of the furnish and is bound through short range molecular forces.

The precipitate formed from aluminum sulfate is less cationic than that formed from aluminum chloride due to the incorporation of sulfate ions into the precipitate.<sup>22,40</sup> The zeta potential results (Fig. 18) support this conclusion. The zeta potentials of the aluminum sulfate drainage samples are less than that

of the aluminum chloride drainage samples even though more aluminum is adsorbing. The lower cationic charge of the aluminum sulfate precipitate is the reason for the increased aluminum adsorption. The lower charge reduced the lateral repulsive interaction between precipitate particles, allowing increased adsorption.

#### Below the pH<sub>p</sub>

Below the pH<sub>p</sub> where only soluble aluminum species exist, the aluminum adsorption is extremely low for both aluminum salts. Low aluminum adsorption would be expected if the soluble aluminum species were adsorbing by a simple ion exchange mechanism. An ion exchange mechanism would be supported by the concentration dependent aluminum adsorption observed in this study and by Crow.<sup>22</sup> It is also supported by the dependence of aluminum adsorption in this region on the carboxyl content of pulp as seen by Arnson<sup>21</sup> and others.<sup>43-45</sup>

The trivalent aluminum ion,  $\text{Al}^{3+}$ , is most likely the adsorbing species in this region due to its high charge density and concentration over the other soluble species  $\text{AlOH}^{2+}$  and  $\text{AlSO}_4^+$ . The aluminum adsorption does not increase greatly between the low pH values and the pH<sub>p</sub>. Therefore, it does not appear that the polynuclear species are preferentially adsorbed over the  $\text{Al}^{3+}$  ion. If this were the case, substantial increases would be observed before the pH<sub>p</sub>. The polynuclear species may possess a higher charge than  $\text{Al}^{3+}$ , but due to its large size, it would have a low charge density. Thus,  $\text{Al}^{3+}$  would be expected to be preferentially adsorbed because of its high charge density.

## POLYMER ADSORPTION

### Initial Considerations

In order to further characterize the components used in the retention experiments, some basic polymer adsorption experiments were performed. These included equilibrium adsorption isotherms and the effect of polymer adsorption time on polymer adsorption. In the retention experiments, the principal variables affecting polymer adsorption studied were the pH, polymer concentration, polymer adsorption time, aluminum salt, and aluminum concentration. The pH was varied from 4.0 to 5.5. The polymer concentration was set at 3.0 mg/L (0.10% polymer addition) and 1.5 mg/L (0.05% polymer addition), and the polymer adsorption time was set at 15 seconds and 1 minute. The aluminum salts and concentrations have been described earlier.

Like the aluminum adsorption, the polymer adsorption is also typically expressed on a weight/weight basis as mg Q5 polymer/g cellulose. Complete removal of the polymer from solution or 100% polymer adsorption corresponds to 1.0 mg Q5 polymer/g cellulose at 3.0 mg/L polymer addition and 0.5 mg Q5 polymer/g cellulose at 1.5 mg/L polymer addition.

### Equilibrium Adsorption Isotherm

Equilibrium adsorption isotherms were performed to determine how well the Q5 polymer adsorbs and how much polymer the furnish surface can adsorb. Cotton linter fibers and cotton linter fibers plus titanium dioxide filler were treated with increasing concentrations of polymer in the presence of 0.01N potassium chloride background. Furnish concentrations were the same as used in the retention experiments. After 120 minutes polymer adsorption time, the polymer

adsorption was determined. The equilibrium adsorption results are compiled in Appendix IX.

Figure 19 presents the polymer adsorption as a function of polymer addition. The adsorption isotherms are of the high affinity type with near 100% adsorption at lower polymer concentrations and a leveling off at higher polymer concentrations. The leveling off is considered to be the maximum or saturation adsorption value of the absorbent under a particular set of conditions. The Langmuir adsorption equation<sup>82</sup> was employed to determine the saturation adsorption values.

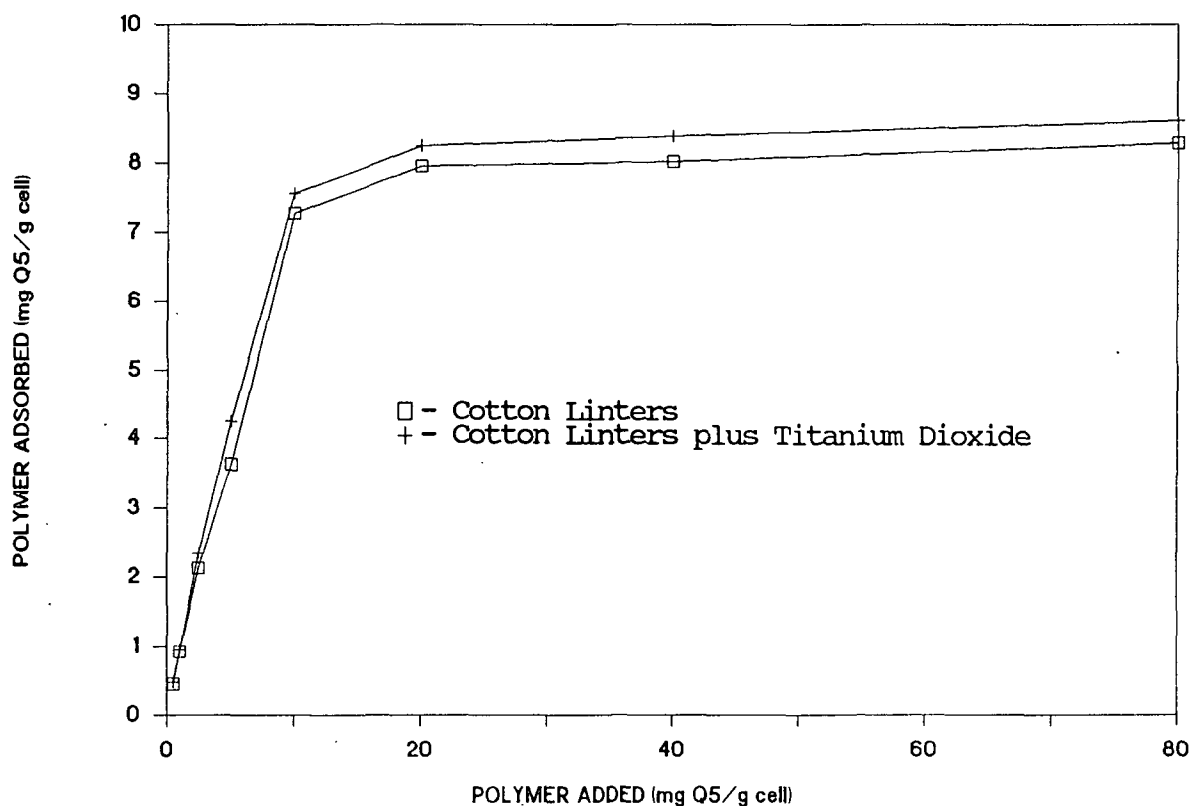


Figure 19. Equilibrium adsorption isotherms (0.01N KCl, 120 minutes polymer adsorption time).

$$C_{*} = K C_M C_E / (1 + K C_E) \quad (9)$$

where  $C_E$  = Equilibrium concentration, mg/L

$C_{*}$  = Specific adsorption at  $C_E$ , mg/L

$K$  = Langmuir constant

$C_M$  = Maximum amount adsorbed, mg/L

The Langmuir equation can be rearranged in the following manner so that a plot of  $C_E/C_{*}$  versus  $C_E$  has a slope of  $1/C_M$  and an intercept of  $1/KC_M$ :

$$C_E/C_{*} = 1/K C_M + C_M + C_E/C_M \quad (10)$$

Figure 20 shows the Langmuir plots obtained from the adsorption isotherms. Using linear regression, a maximum adsorption value of 24.98 mg/L was obtained for the cotton linters and 25.93 mg/L for the cotton linters plus titanium dioxide. Thus, the addition of titanium dioxide only increased the polymer adsorption by approximately 3.7%.

Assuming the titanium dioxide is comprised of spherical particles with an average particle diameter of 4.2 microns, the increase in total surface area when added at 10% weight basis to the cotton linters fibers is 3.5%. This increase corresponds quite well with the observed increase in the saturation adsorption value.

#### Polymer Adsorption Time

The polymer adsorption time was varied from 15 seconds to 120 minutes to observe the effect on polymer adsorption of 3.0 mg/L of polymer. A furnish of cotton linters plus titanium dioxide was used at the same concentrations which were used in the retention experiments with a 0.01N potassium chloride

background. The effect of having  $10.0 \times 10^{-4} \text{M}$  aluminum sulfate present at pH 4.0 and 5.5 was also investigated. The results of these experiments are compiled in Appendix IX.

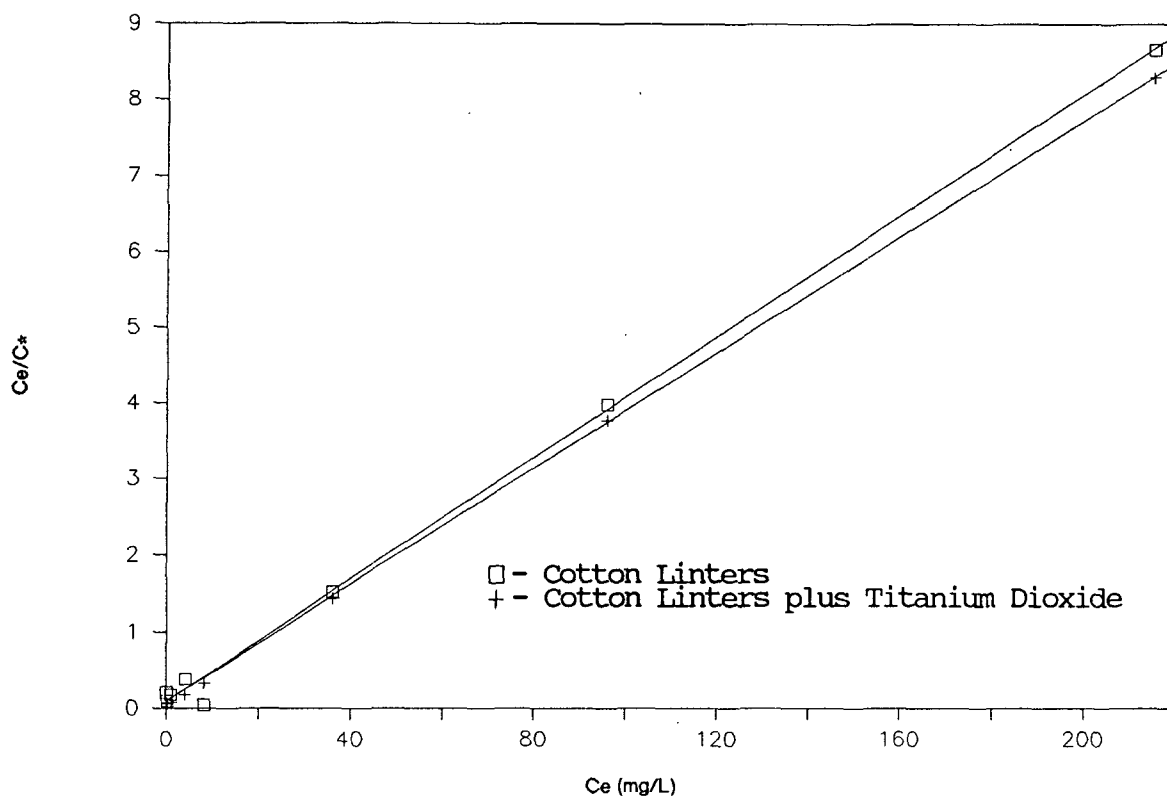


Figure 20. Langmuir plots of equilibrium adsorption isotherms.

Figure 21 presents the influence of polymer adsorption time on polymer adsorption. Initially, there is a rapid increase in the polymer adsorbed as the adsorption time is increased followed by a leveling off or reaching of equilibrium. As shown in Fig. 22, on a percentage basis, the polymer adsorption rapidly increases to approximately 90% in 10 minutes and then to approximately 95% in 120 minutes. Since the polymer contact times in the paper industry and in these studies are typically less than one minute,<sup>3</sup> the nonequilibrium situation less than 10 minutes is important.

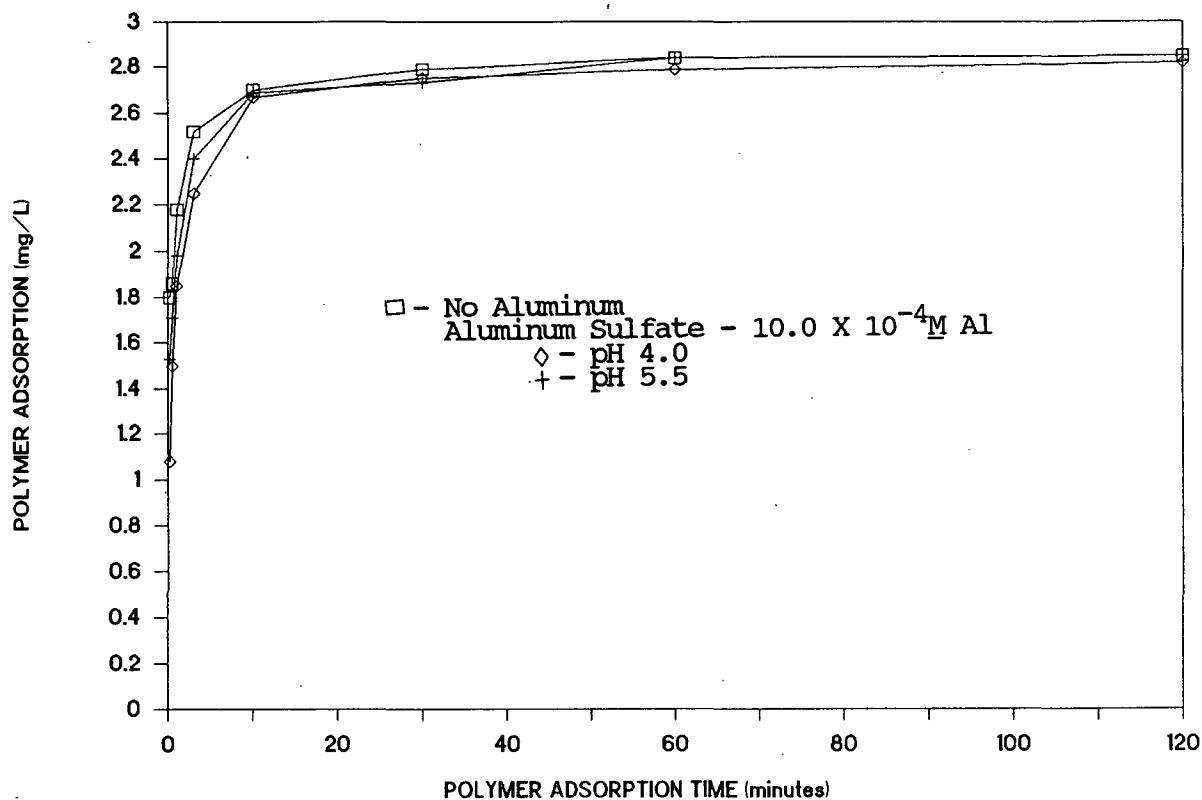


Figure 21. The influence of adsorption time on polymer adsorption (0.01N KCl, 3.0 mg/L polymer addition).

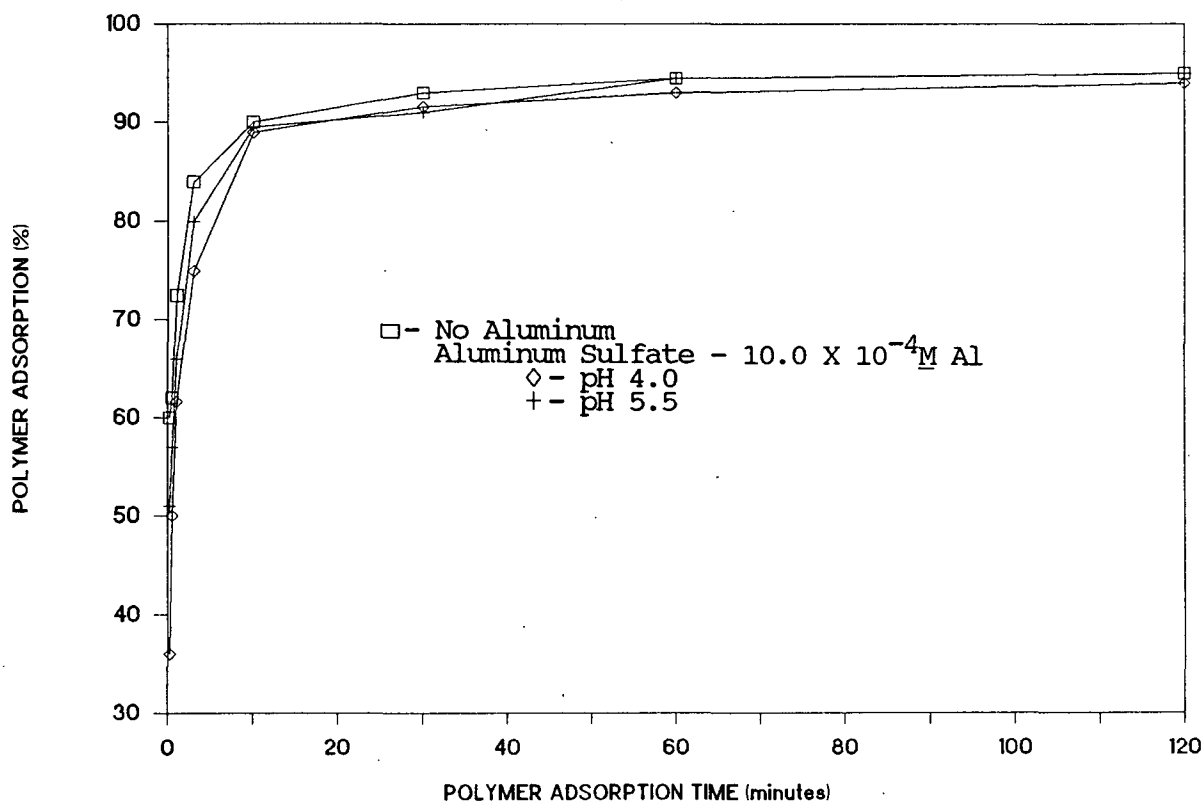


Figure 22. The influence of adsorption time on relative polymer adsorption (0.01N KCl, 3.0 mg/L polymer addition).

Figures 23 and 24 show an expansion of the first 10 minutes of the polymer adsorption curves. It is obvious that a nonequilibrium situation exists at less than 10 minutes polymer adsorption time. This emphasizes the importance of consistent and rapid polymer separation from the furnish during the retention experiments. This figure also shows that aluminum sulfate reduces the polymer adsorption at short polymer contact times but reaches the same adsorption levels at longer polymer contact times. This is evidence that aluminum sulfate decreases the polymer adsorption rate and that the adsorption rate is slower at pH 4.0 than at pH 5.5.

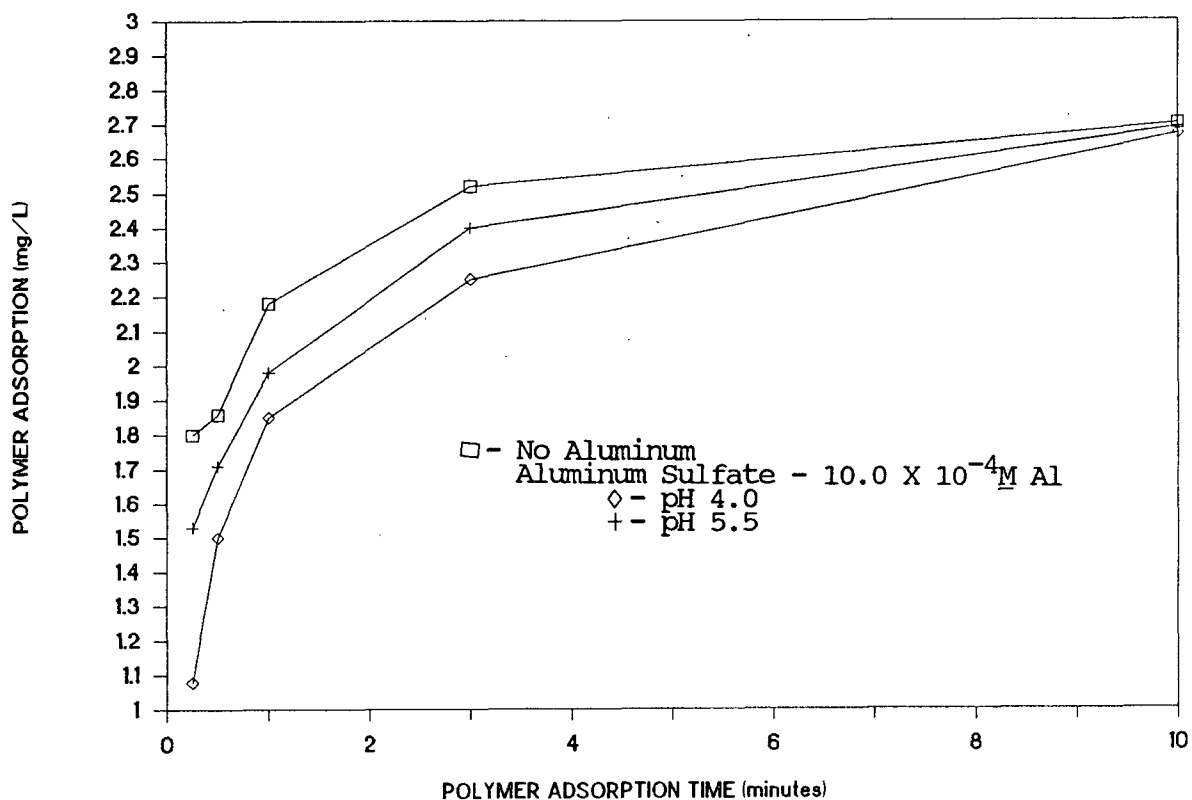


Figure 23. The initial influence of adsorption time on polymer adsorption (0.01N KCl, 3.0 mg/L polymer addition).



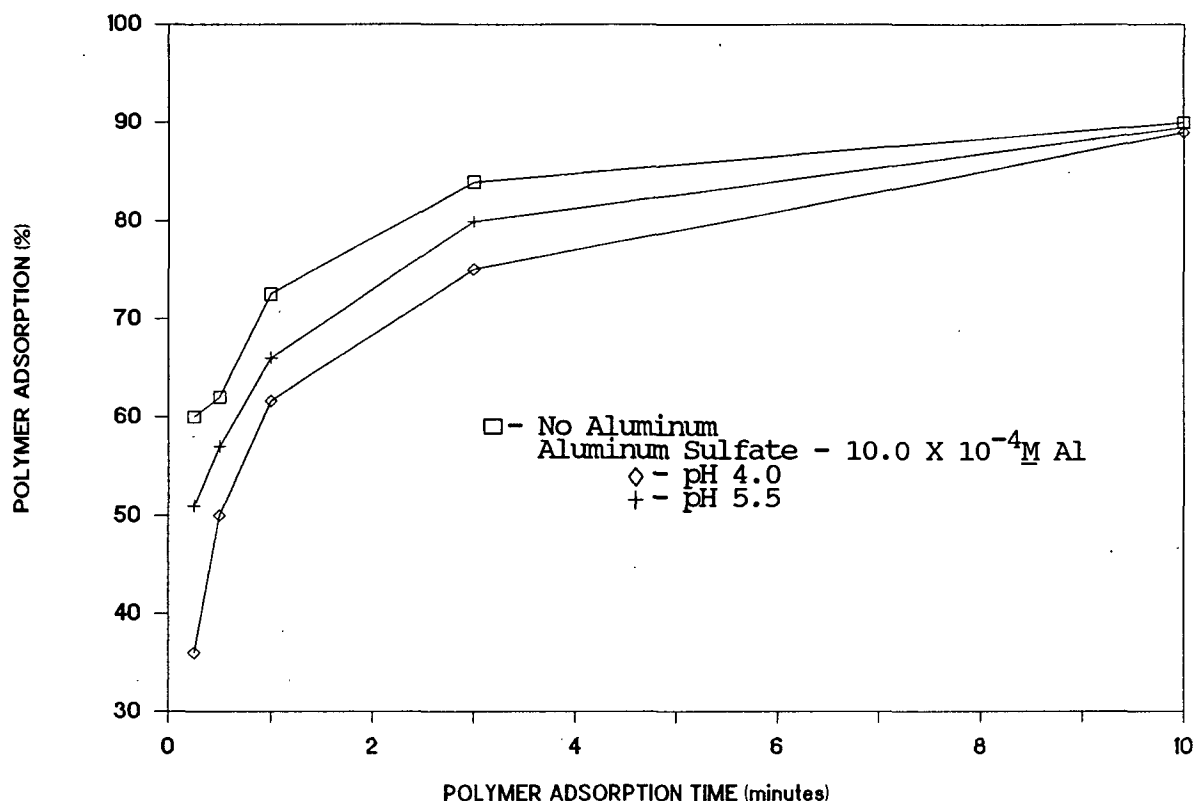


Figure 24. The initial influence of adsorption time on relative polymer adsorption (0.01N KCl, 3.0 mg/L polymer addition).

#### Effect of pH and Polymer Concentration

##### Without Aluminum Sulfate

The influence of pH at 3.0 mg/L and 1.5 mg/L polymer additions on polymer adsorption is presented in Fig. 25. The results of these retention experiments are compiled in Appendix X. A slight increase in polymer adsorption is observed as the pH is increased. This is most likely due to the change in ionization of the furnish surface groups and was not believed to be significant enough to warrant further investigation.

The effect of polymer concentration on polymer adsorption is also shown in Fig. 25. Increasing the polymer concentration from 1.5 mg/L to 3.0 mg/L

substantially increased the polymer adsorption; however, as shown in Fig. 26, the relative polymer adsorption is slightly decreased. Since these retention experiments were performed with 15 seconds of polymer adsorption time, a non-equilibrium condition exists. As the polymer concentration is increased, there is more competition for adsorption sites; and in the nonequilibrium condition, all of the polymer may not have a chance to adsorb.

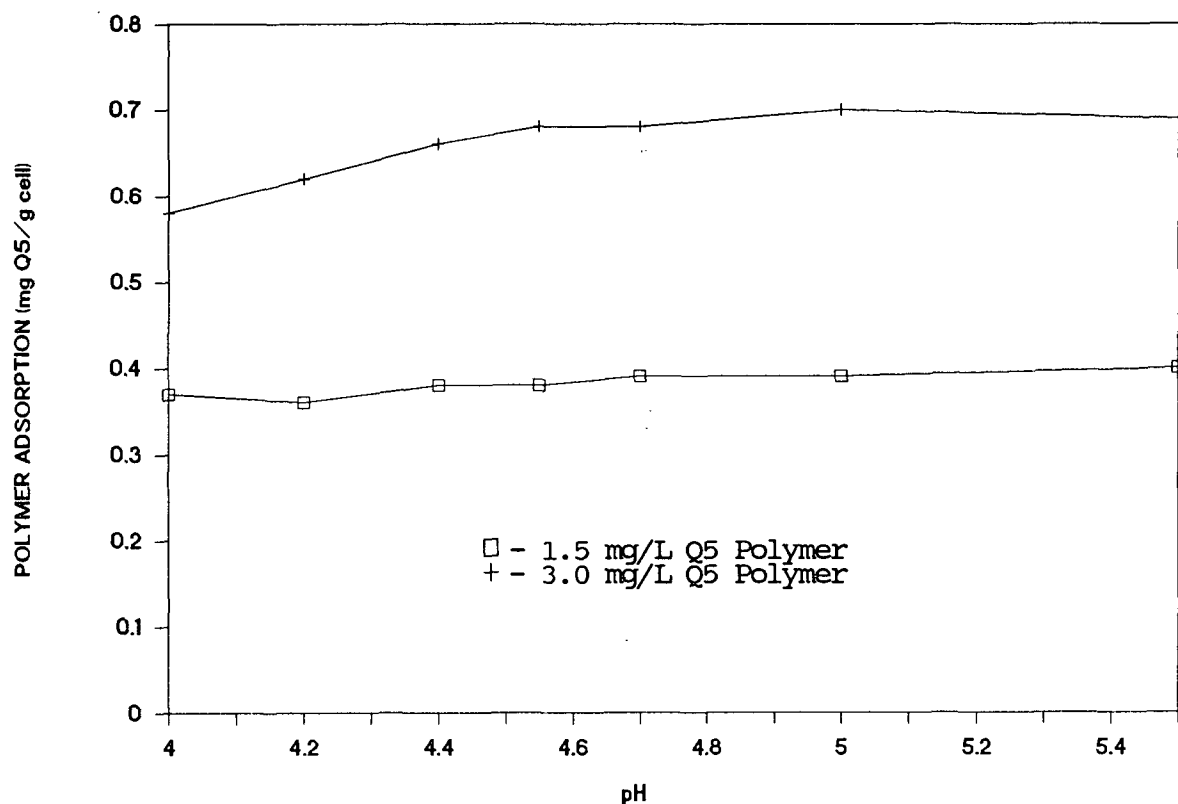


Figure 25. The influence of pH and polymer concentration on polymer adsorption (no aluminum salt present).

#### With Aluminum Sulfate

The influence of pH and polymer concentration on polymer adsorption in the presence of  $10.0 \times 10^{-4}M$  aluminum from aluminum sulfate is presented in Fig.

27. The results of these experiments are compiled in Appendix VIII. The effect

of pH on polymer adsorption in the presence of aluminum salts will be discussed later. Increasing the polymer concentration in the presence of aluminum sulfate also increases the polymer adsorption. Again, the relative polymer adsorption decreases as the polymer concentration is increased, which is a result of the nonequilibrium adsorption conditions (Fig. 28).

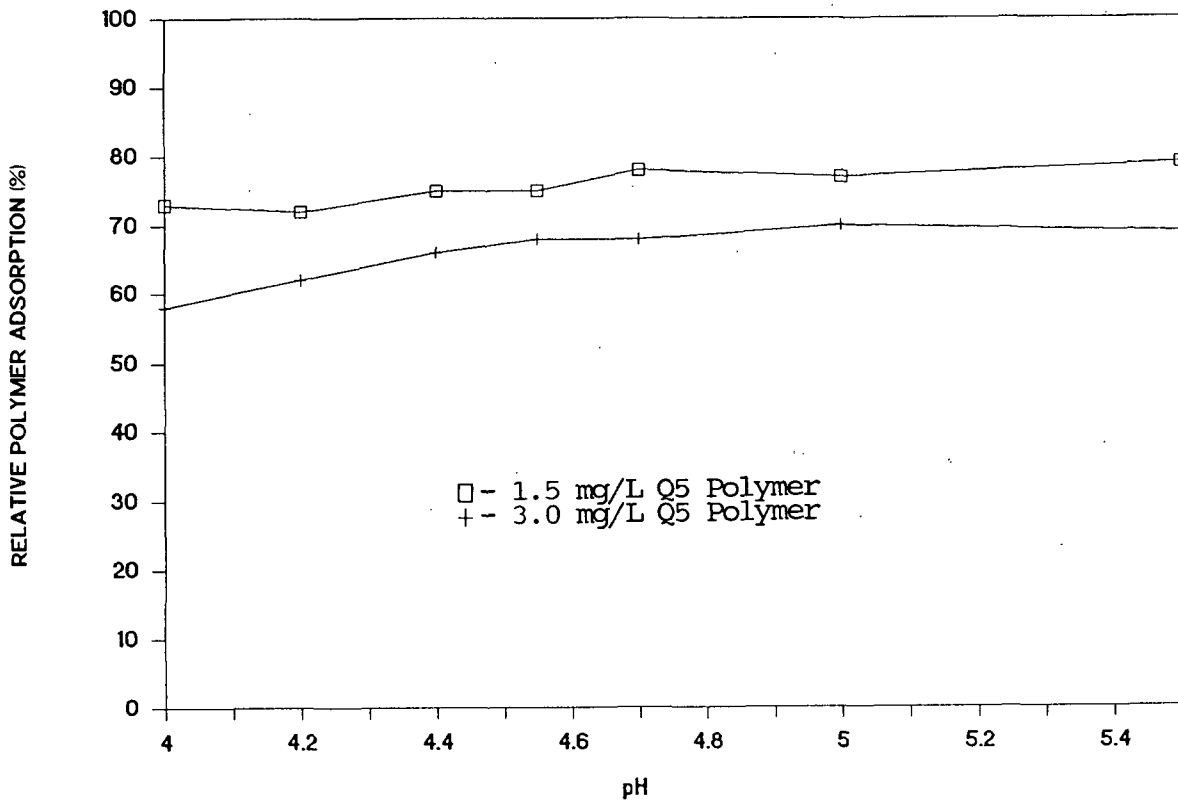


Figure 26. The influence of pH and polymer concentration on relative polymer adsorption (no aluminum salt present).

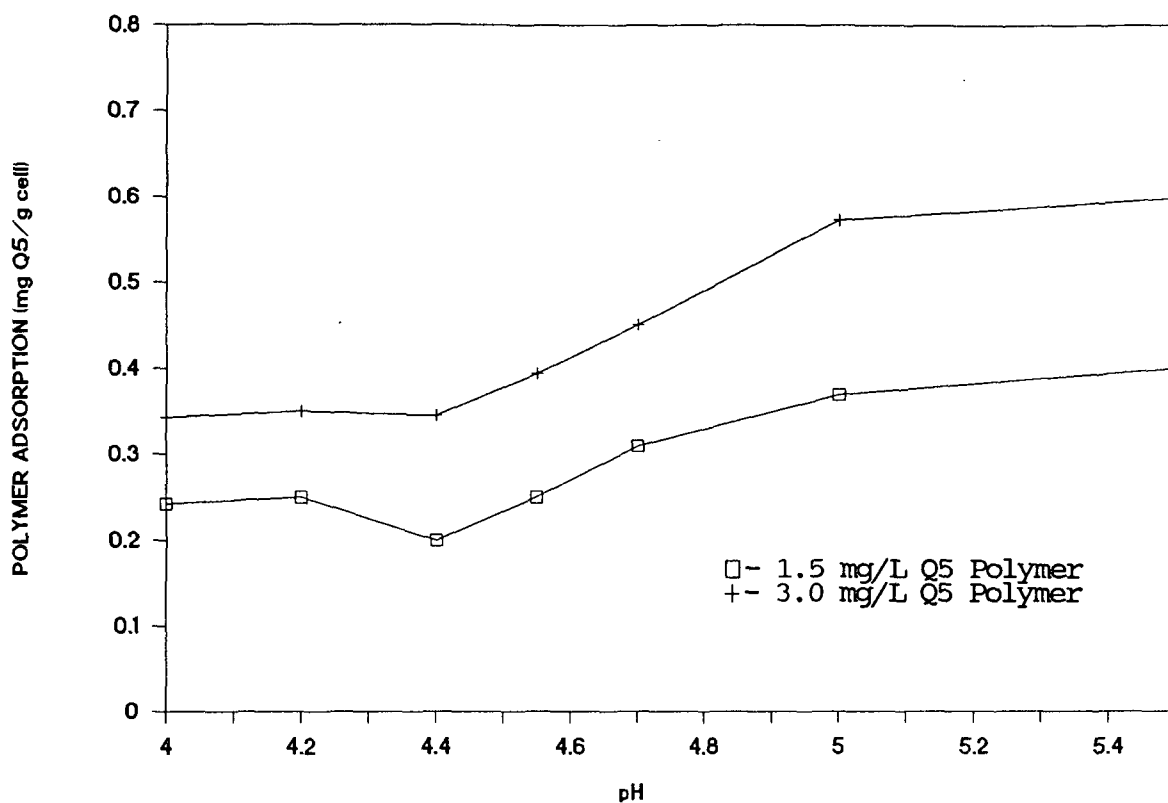


Figure 27. The influence of pH and polymer concentration on polymer adsorption ( $10.0 \times 10^{-4}M$  Al from aluminum sulfate).

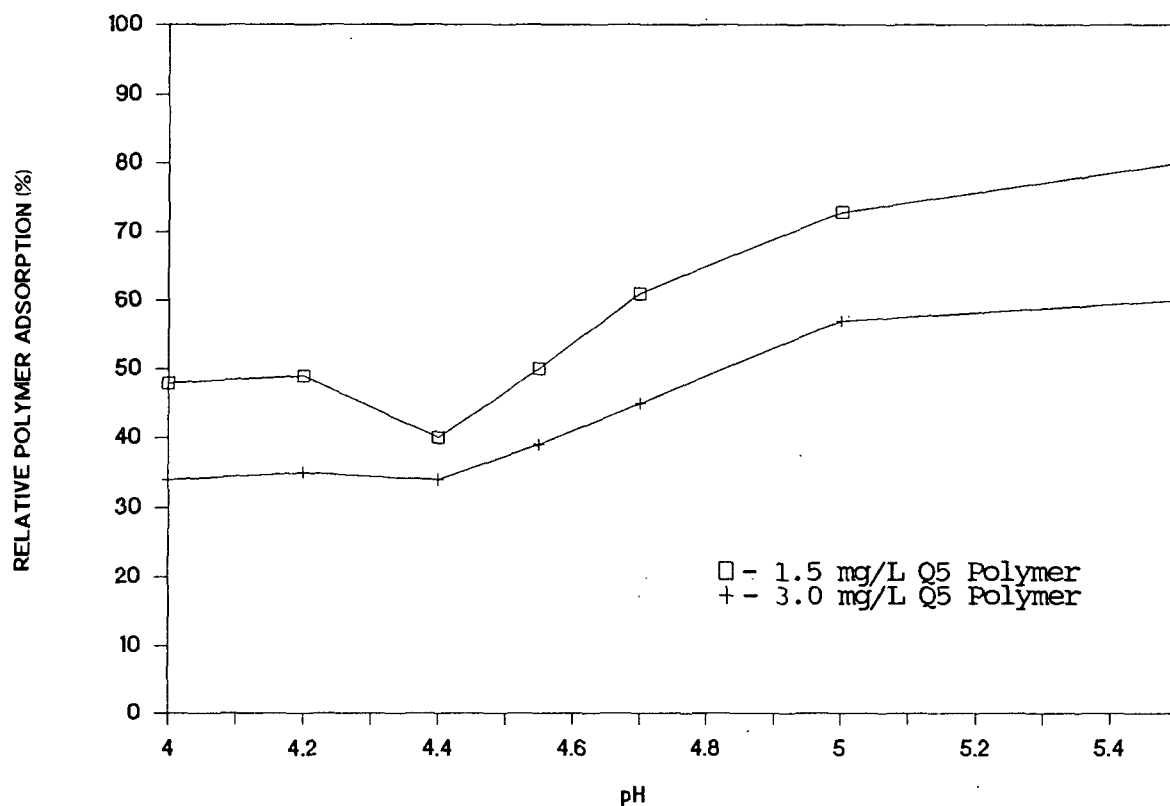


Figure 28. The influence of pH and polymer concentration on relative polymer adsorption ( $10.0 \times 10^{-4}M$  Al from aluminum sulfate).

### Effect of Polymer Adsorption Time

The effect of adsorption time on polymer adsorption of 3.0 mg/L of polymer during the retention experiments is presented in Fig. 29 for  $10.0 \times 10^{-4} \text{M}$  aluminum from aluminum sulfate. Experimental data for these experiments is compiled in Appendices VIII and XI. Increasing the polymer adsorption time from 15 seconds to one minute resulted in a steady increase in the polymer adsorption curve. This indicates that nonequilibrium conditions are present as would be expected from the data in Fig. 23 and 24.

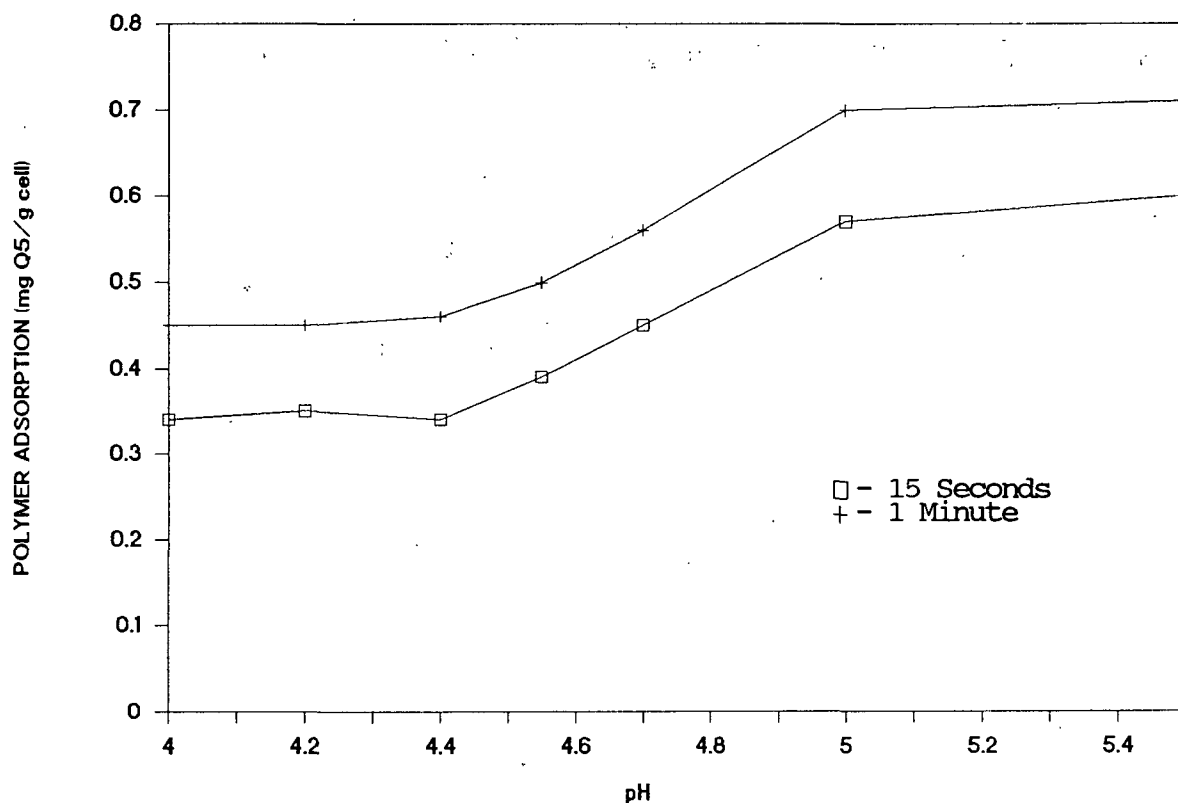


Figure 29. The influence of pH and adsorption time on polymer adsorption ( $10.0 \times 10^{-4} \text{M}$  Al from aluminum sulfate, 3.0 mg/L polymer addition).

### Effect of pH and Aluminum Concentration

#### Aluminum Chloride

The effect of pH and aluminum chloride concentration on polymer adsorption at  $2.5 \times 10^{-4}$ ,  $5.0 \times 10^{-4}$ , and  $10.0 \times 10^{-4}$  M aluminum and 3.0 mg/L polymer addition is presented in Fig. 30 (Appendix VIII). For comparison, the polymer adsorption curve in the absence of aluminum salts is included. As seen in this figure, the polymer adsorption is strongly influenced by both pH and aluminum concentration when aluminum chloride is present.

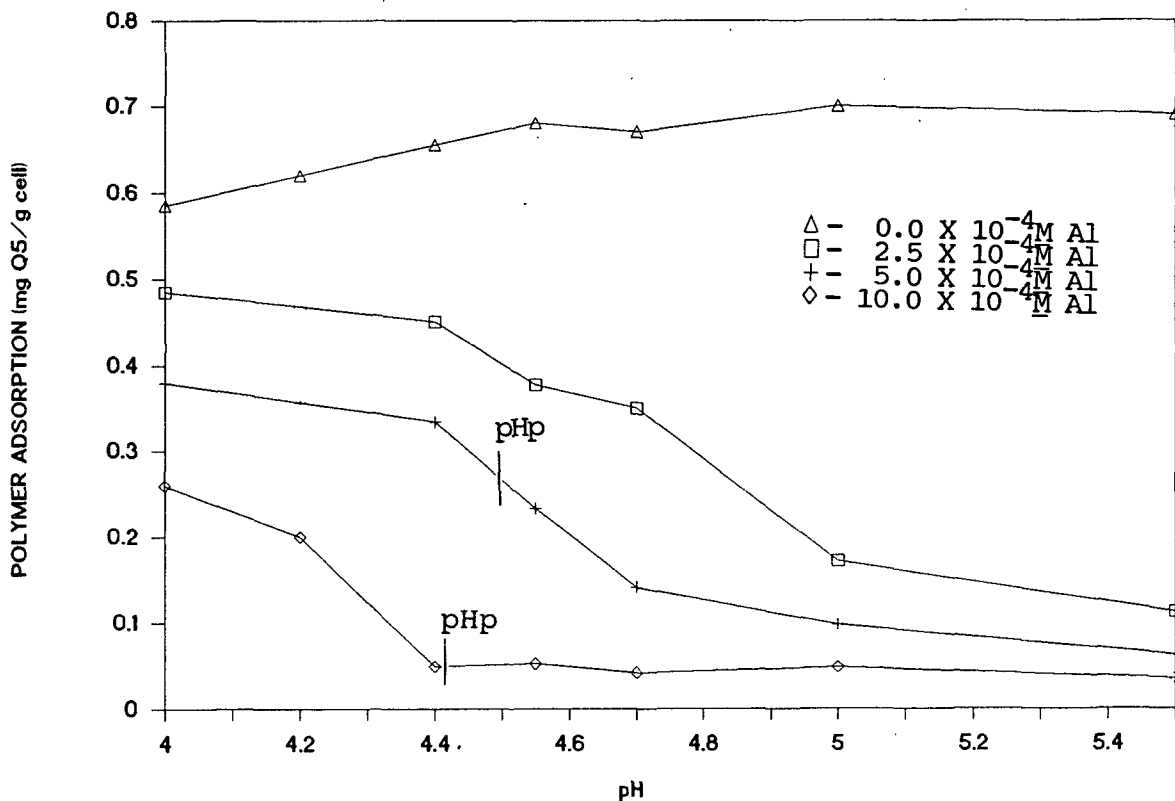


Figure 30. The influence of pH and aluminum concentration on polymer adsorption for aluminum chloride (3.0 mg/L polymer addition).

As with the aluminum adsorption results, the polymer adsorption results can be best interpreted by dividing the curves into two pH regions, one below the

pHp where only soluble aluminum species exist, and one above the pHp where the aluminum precipitate is formed. At all pH values, aluminum chloride reduces the polymer adsorption. Below the pHp where soluble aluminum species exist, polymer adsorption is at its highest level. As the pH is increased and the aluminum precipitates, the polymer adsorption decreases and reaches very low levels.

#### Aluminum Sulfate

The effect of pH and aluminum sulfate concentration on polymer adsorption at  $2.5 \times 10^{-4}$ ,  $5.0 \times 10^{-4}$ , and  $10.0 \times 10^{-4}$  M aluminum and 3.0 mg/L polymer addition is presented in Fig. 31 (Appendix VIII). For comparison, the polymer adsorption curve in the absence of aluminum salts is also included. Again, the polymer adsorption is influenced by both the pH and aluminum concentration when aluminum sulfate is present.

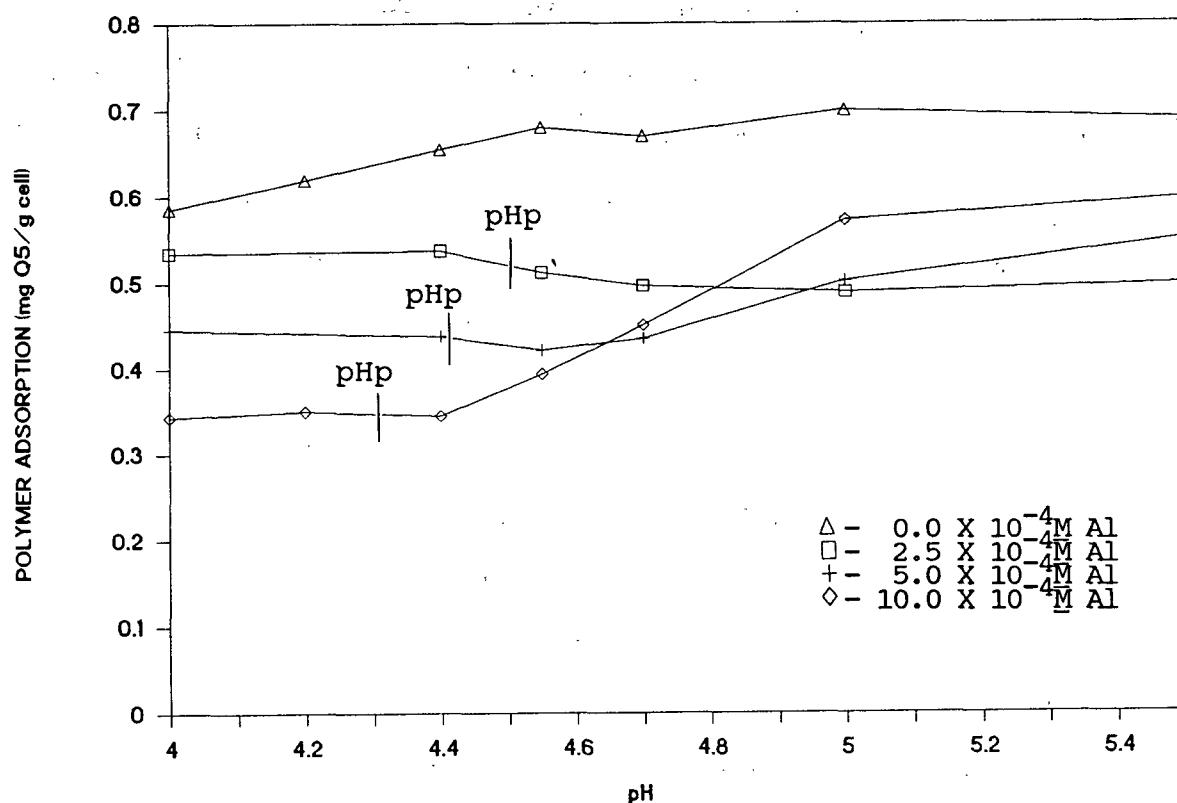


Figure 31. The influence of pH and aluminum concentration on polymer adsorption for aluminum sulfate (3.0 mg/L polymer addition).

At all pH values, aluminum sulfate reduces polymer adsorption. As with aluminum chloride, below the pH<sub>p</sub> where soluble aluminum species are present, increasing the aluminum concentration decreases the polymer adsorption. However, unlike aluminum chloride above the pH<sub>p</sub> where the aluminum precipitate is formed, increasing the aluminum concentration increases the polymer adsorption.

#### Comparison of Aluminum Chloride and Aluminum Sulfate

Figures 32, 33, and 34 show comparisons of the influence of pH on polymer adsorption for aluminum chloride and aluminum sulfate at  $2.5 \times 10^{-4}$ ,  $5.0 \times 10^{-4}$  and  $10.0 \times 10^{-4}$  M aluminum, respectively. Below the pH<sub>p</sub> where soluble aluminum species exist, both aluminum salts produce similar effects on polymer adsorption, but aluminum chloride produces a slightly greater reduction in polymer adsorption than does aluminum sulfate. A similar mechanism would be occurring in this region for both aluminum salts. Above the pH<sub>p</sub> where the aluminum precipitate is formed, the two aluminum salts produce quite different results. The aluminum chloride precipitate reduces the polymer adsorption to low levels, and increasing the aluminum concentration decreases the polymer adsorption. But with the aluminum sulfate precipitate, the polymer adsorption does not decrease, and increasing the aluminum concentration increases the polymer adsorption. Different mechanisms appear to be functioning in this pH region. These mechanisms will be discussed in the "Mechanisms" and "Interpretation of Polymer Adsorption and Titanium Dioxide Retention" sections. It should be noted that as the aluminum concentration is increased, the separation between the two polymer adsorption curves increases and the break between the two curves occur at a lower pH which corresponds to a decrease in the pH<sub>p</sub> values.



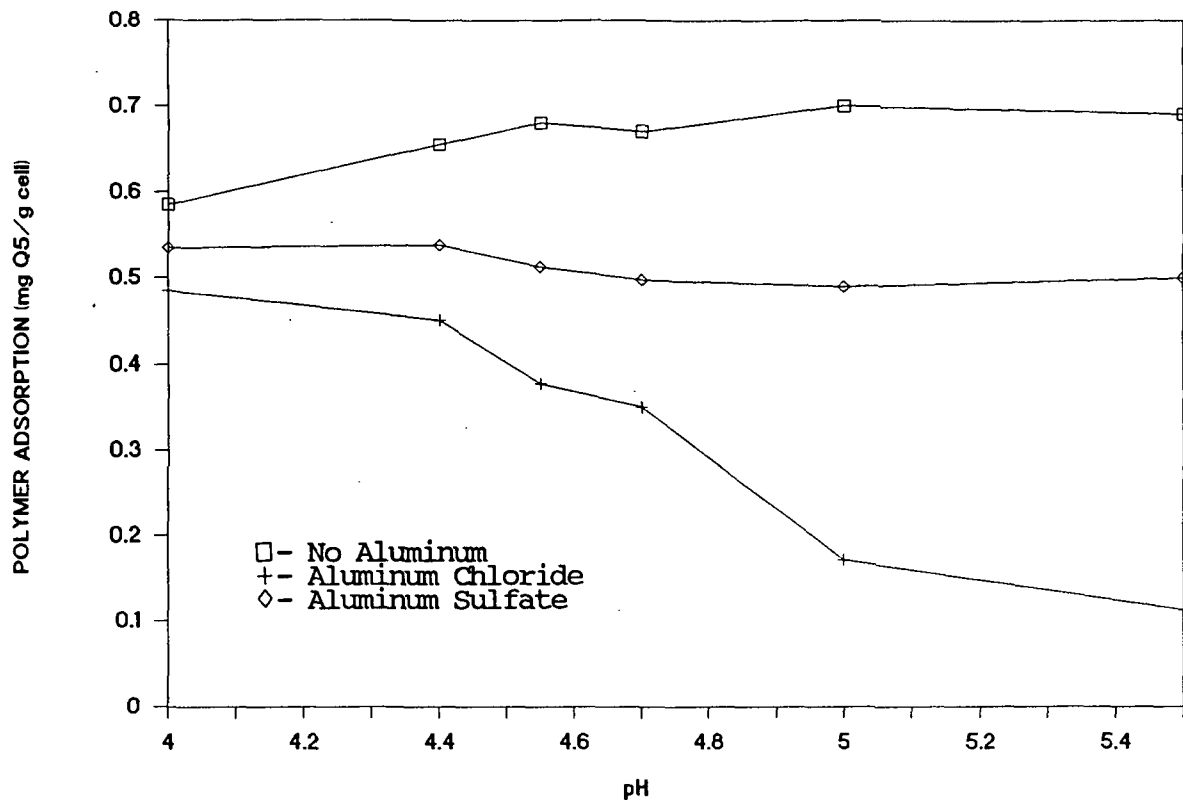


Figure 32. Comparison of polymer adsorption for aluminum chloride and aluminum sulfate ( $2.5 \times 10^{-4}M$  Al, 3.0 mg/L polymer addition).

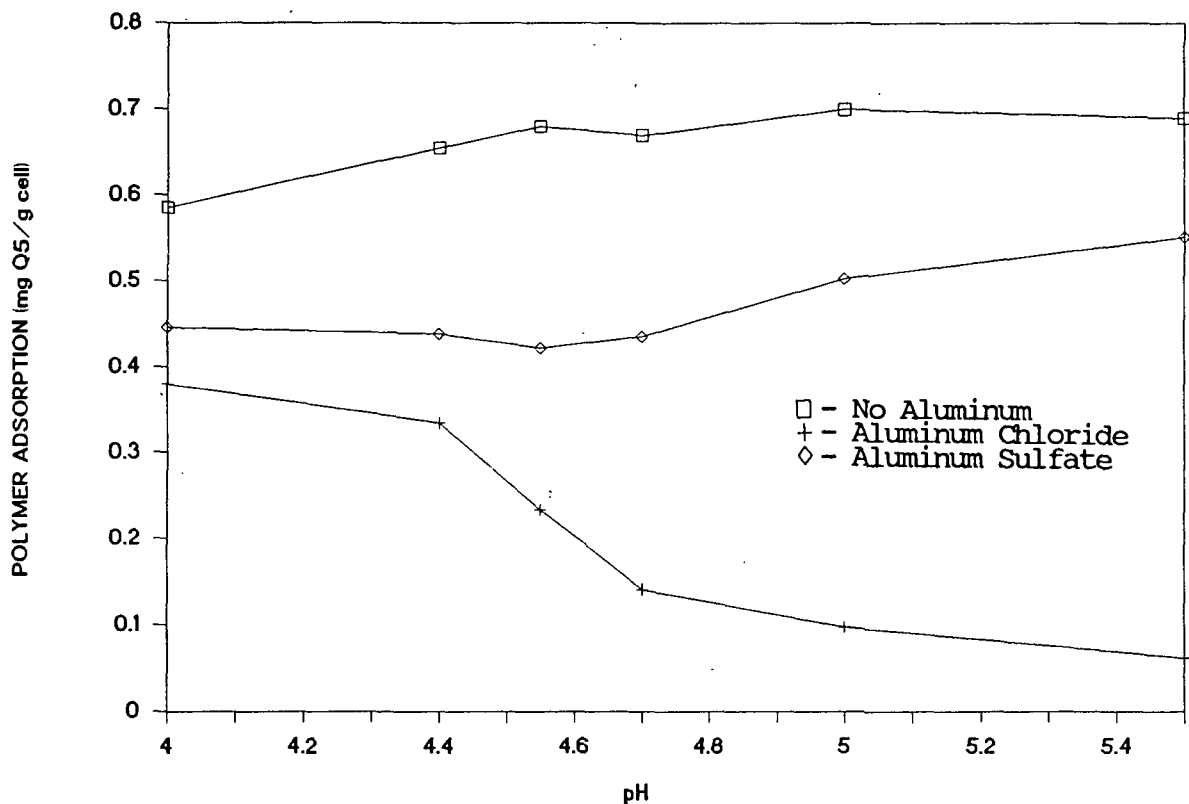


Figure 33. Comparison of polymer adsorption for aluminum chloride and aluminum sulfate ( $5.0 \times 10^{-4}M$  Al, 3.0 mg/L polymer addition).

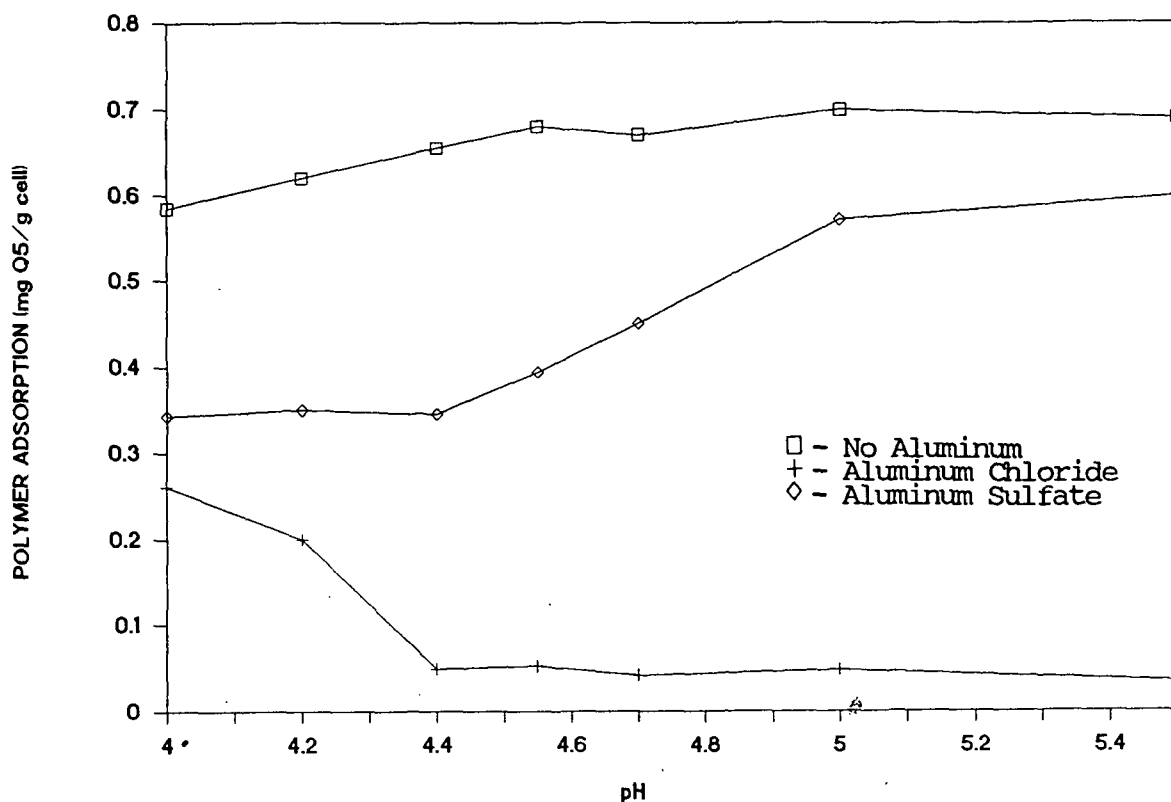


Figure 34. Comparison of polymer adsorption for aluminum chloride and aluminum sulfate ( $10.0 \times 10^{-4}M$  Al, 3.0 mg/L polymer addition).

## TITANIUM DIOXIDE RETENTION

### Effect of pH and Polymer Concentration

#### Without Aluminum Sulfate

Figure 35 presents the influences of pH and polymer concentration on titanium dioxide retention without aluminum salts present. The titanium dioxide retention results without aluminum salts present are compiled in Appendix X. Similar to the polymer adsorption, the titanium dioxide retention with no aluminum salts present remains fairly constant at both polymer concentrations as pH is increased.

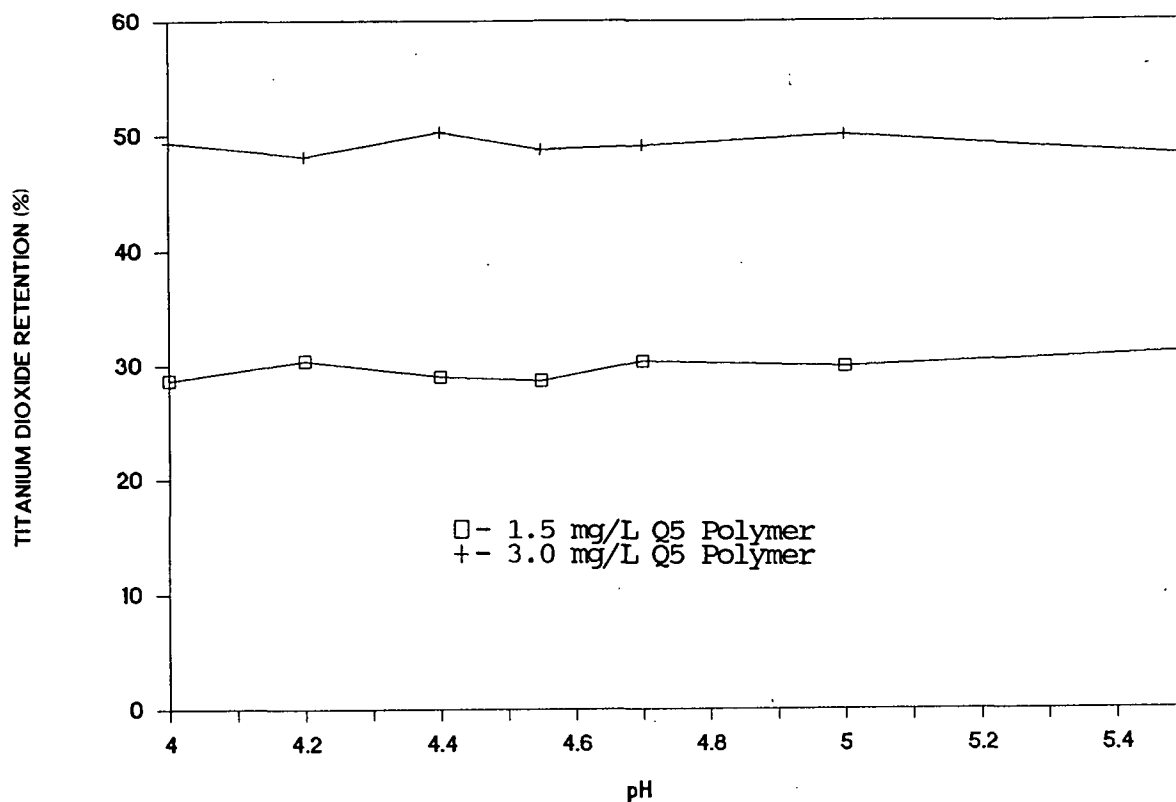


Figure 35. The influence of pH and polymer concentration on titanium dioxide retention (no aluminum salt present).

Doubling the polymer concentration from 1.5 mg/L to 3.0 mg/L substantially increased the titanium dioxide retention but did not double it. This is expected since the doubling of polymer concentration does not double the polymer adsorption.

#### With Aluminum Sulfate

The influence of pH and polymer concentration on titanium dioxide retention in the presence of  $10 \times 10^{-4}M$  aluminum from aluminum sulfate is presented in Fig. 36. These titanium dioxide retention results are compiled in Appendix VIII. The influence of pH on titanium dioxide retention in the presence of aluminum sulfate will be discussed later. Increasing the polymer concentration in

the presence of aluminum sulfate caused a significant increase in the titanium dioxide retention which paralleled the increase in polymer adsorption.

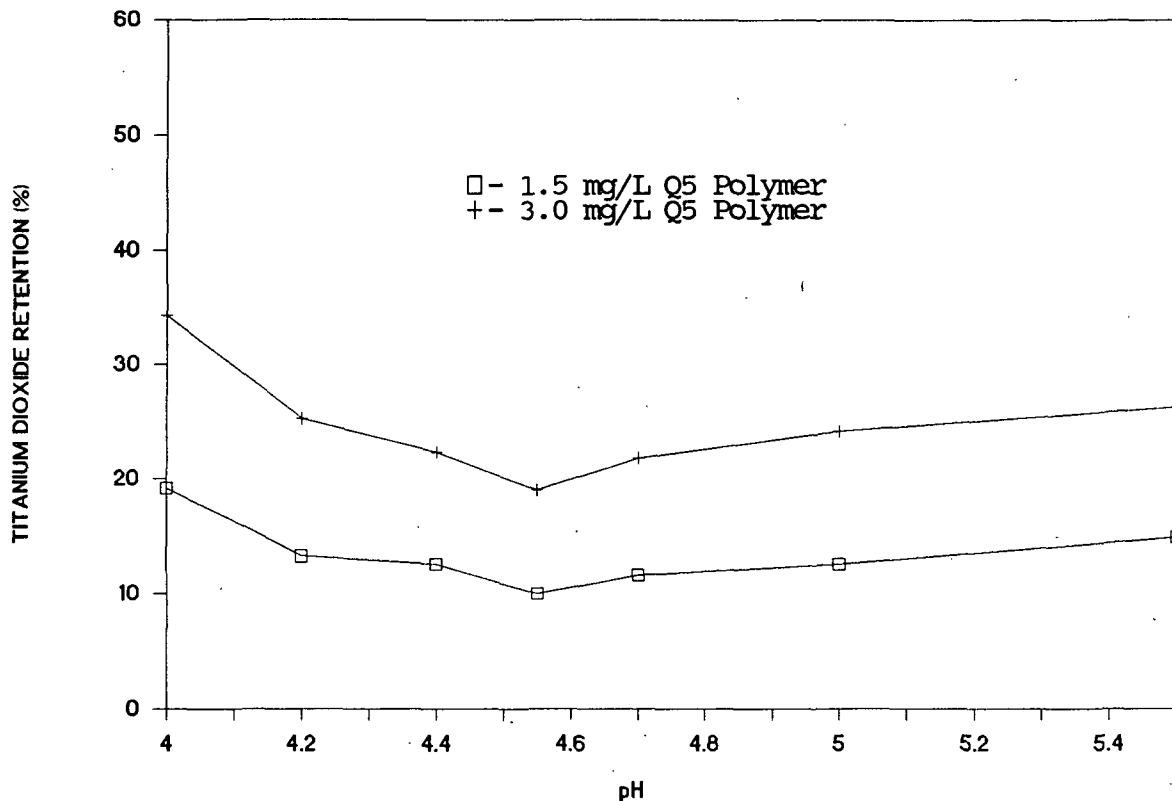


Figure 36. The influence of pH and polymer concentration on titanium dioxide retention ( $10.0 \times 10^{-4}M$  Al from aluminum sulfate).

#### Effect of Polymer Adsorption Time

The influence of polymer adsorption time on titanium dioxide retention for  $10.0 \times 10^{-4}M$  aluminum from aluminum sulfate and 3.0 mg/L polymer is presented in Fig. 37. Experimental data on titanium dioxide retention is compiled in Appendix XI for 1 minute polymer adsorption time and Appendix VIII for 15 seconds polymer adsorption time. Increasing the polymer adsorption time resulted in an increase in the titanium dioxide retention. This is expected since the retention experiments are performed at nonequilibrium conditions with respect

to polymer adsorption. Increasing the polymer adsorption time increases the polymer adsorption which in turn increases the titanium dioxide retention.

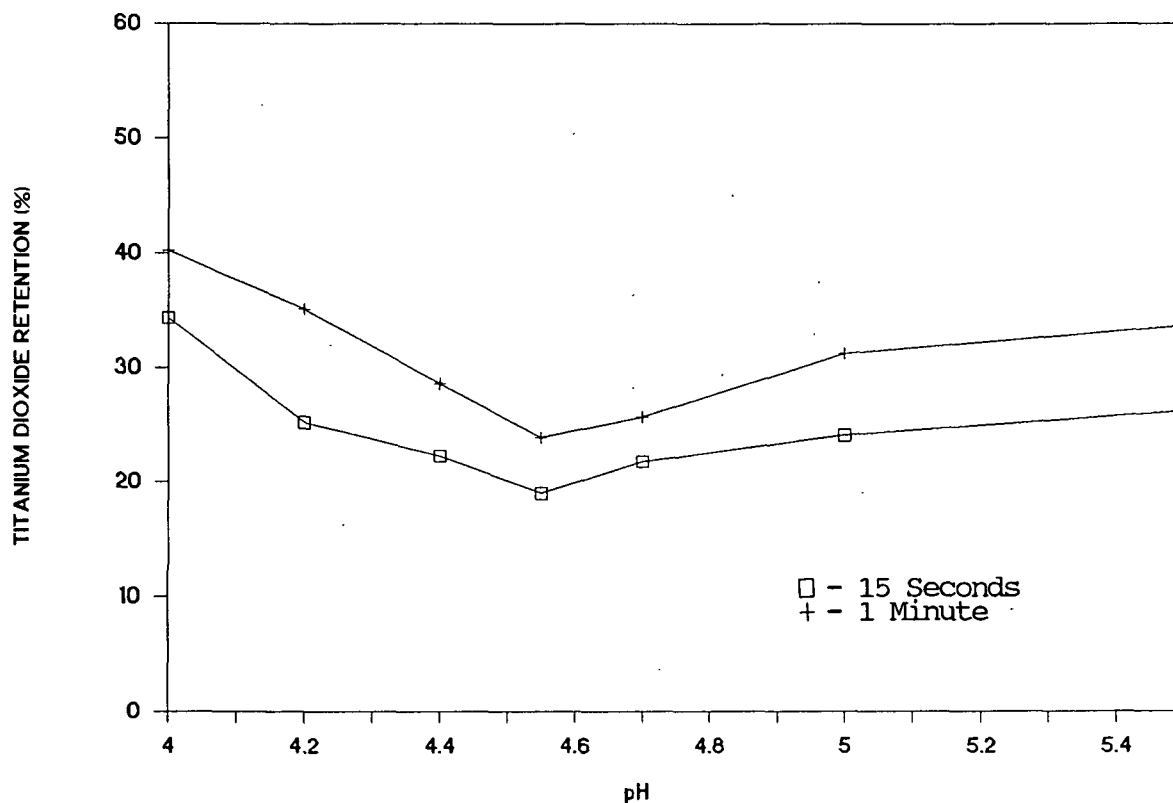


Figure 37. The influence of pH and polymer adsorption time on titanium dioxide retention ( $10.0 \times 10^{-4}M$  Al from aluminum sulfate, 3.0 mg/L polymer addition).

#### Effect of pH and Aluminum Concentration

##### Aluminum Chloride

The influence of pH and aluminum chloride concentration on titanium dioxide retention at  $2.5 \times 10^{-4}$ ,  $5.0 \times 10^{-4}$ , and  $10.0 \times 10^{-4}M$  aluminum and 3.0 mg/L polymer addition is presented in Fig. 38 (Appendix VIII). For comparison, the titanium dioxide retention curve in the absence of aluminum salts is included. The titanium dioxide retention is significantly reduced by the presence of aluminum chloride and appears to be influenced by pH and aluminum concentration.

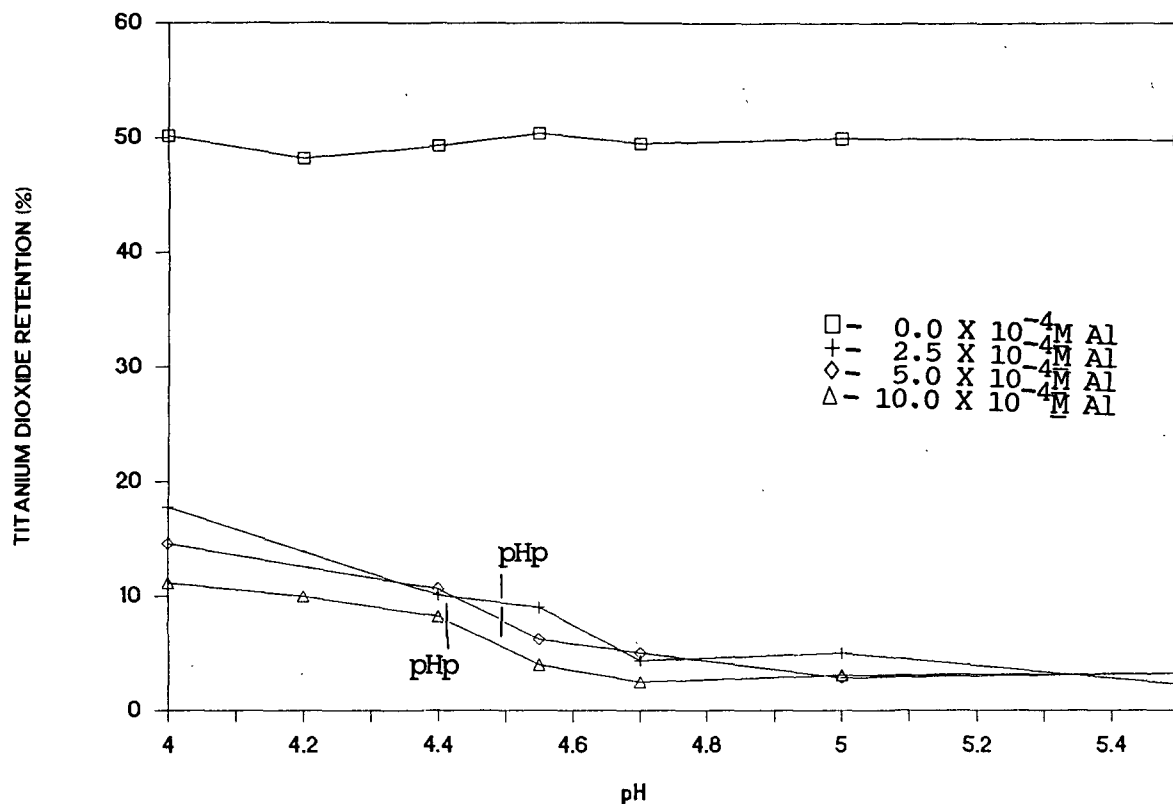


Figure 38. The influence of pH and aluminum concentration on titanium dioxide retention for aluminum chloride (3.0 mg/L polymer addition).

At low pH values below the  $pH_p$ , the titanium dioxide retention is at its highest level. Increasing the aluminum concentration in this lower pH region generally decreases the titanium dioxide retention. As the pH is increased, the titanium dioxide retention decreases to a very low level that is not significantly affected by aluminum concentration.

#### Aluminum Sulfate

The influence of pH and aluminum sulfate concentration on titanium dioxide retention at  $2.5 \times 10^{-4}$ ,  $5.0 \times 10^{-4}$ , and  $10.0 \times 10^{-4} M$  aluminum and 3.0 mg/L polymer addition is presented in Fig. 39 (Appendix VIII). For comparison, the titanium dioxide retention curve in the absence of aluminum salts is included.

Like aluminum chloride, aluminum sulfate also reduces titanium dioxide retention and is influenced by both pH and aluminum concentration.

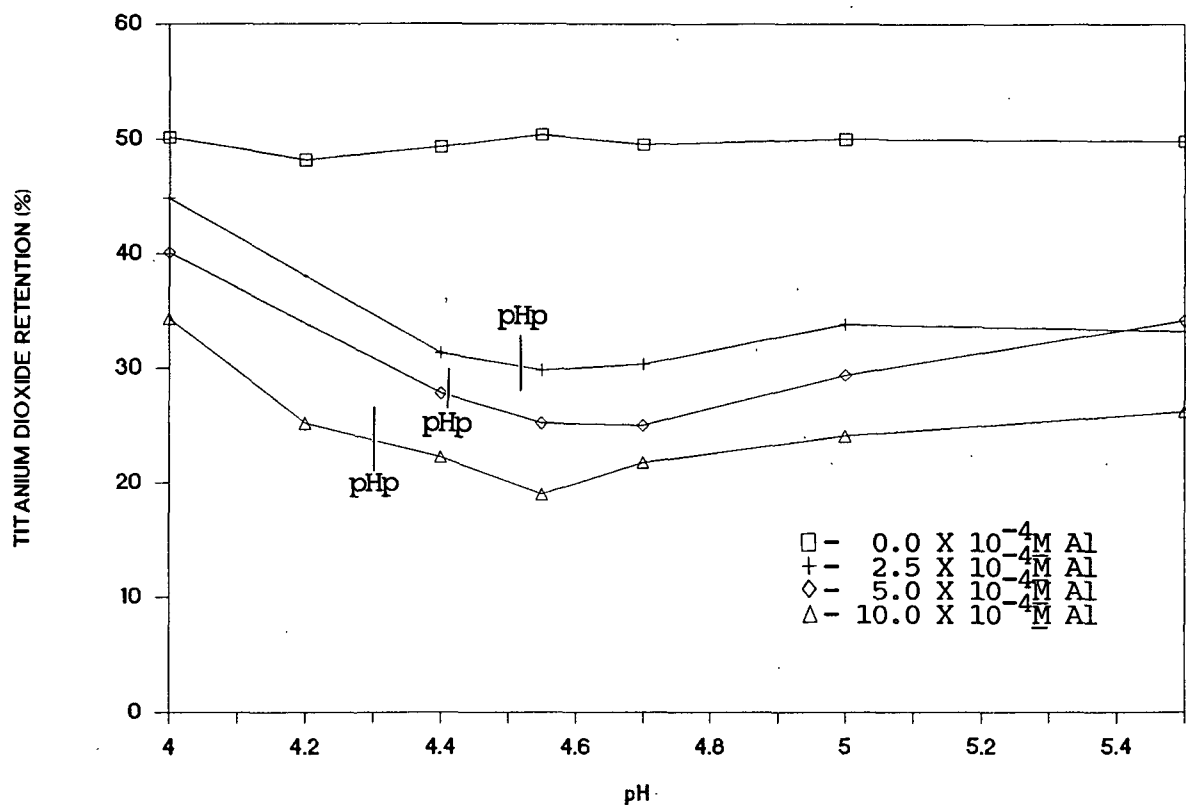


Figure 39. The influence of pH and aluminum concentration on titanium dioxide retention for aluminum sulfate (3.0 mg/L polymer addition).

At low pH values, the titanium dioxide retention is at its highest level. As pH is increased, the titanium dioxide retention decreases and reaches its lowest level shortly after the pHp where both the aluminum precipitate and soluble aluminum species are present. As the pH is increased further, the titanium dioxide retention increases slightly but does not attain the level of retention achieved at the lowest pH value.

#### Comparison of Aluminum Chloride and Aluminum Sulfate

Figures 40, 41, and 42 show comparisons of the influence of pH on titanium dioxide retention for aluminum chloride and aluminum sulfate at  $2.5 \times 10^{-4}$ ,  $5.0$

$\times 10^{-4}$ , and  $10.0 \times 10^{-4} \text{ M}$  aluminum, respectively, at 3.0 mg/L polymer addition. For comparison, the titanium dioxide retention curve in the absence of aluminum salts is included. In all cases, the presence of aluminum salts reduced the titanium dioxide retention, and as the aluminum concentration is increased, the titanium dioxide retention is reduced.

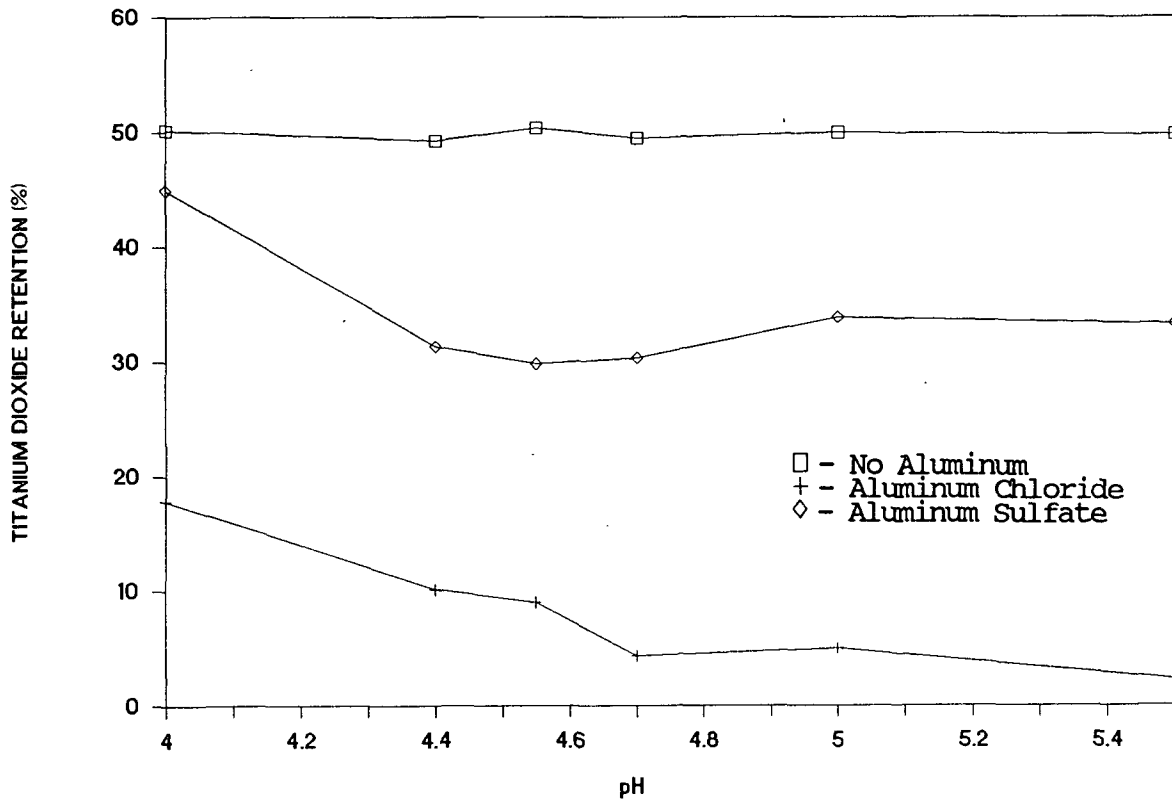


Figure 40. Comparison of titanium dioxide retention for aluminum chloride and aluminum sulfate ( $2.5 \times 10^{-4} \text{ M Al}$ , 3.0 mg/L polymer addition).



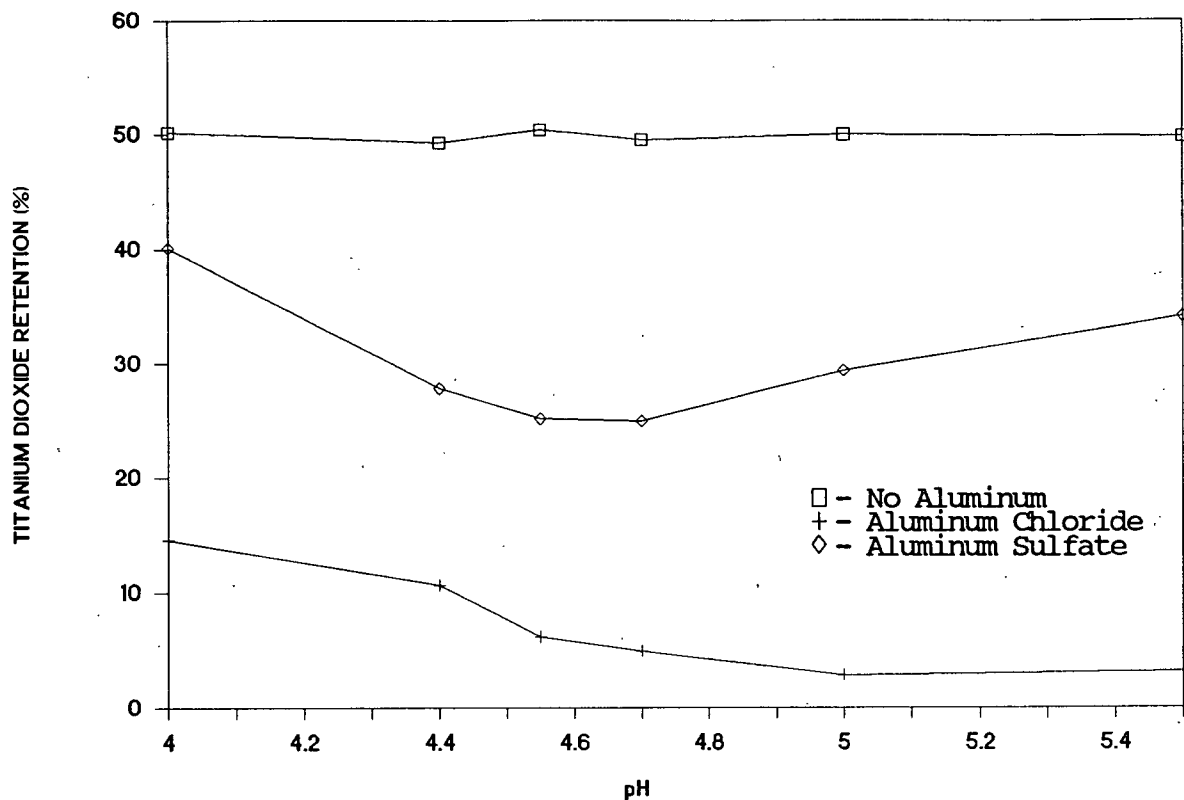


Figure 41. Comparison of titanium dioxide retention for aluminum chloride and aluminum sulfate ( $5.0 \times 10^{-4} \text{ M Al}$ , 3.0 mg/L polymer addition).

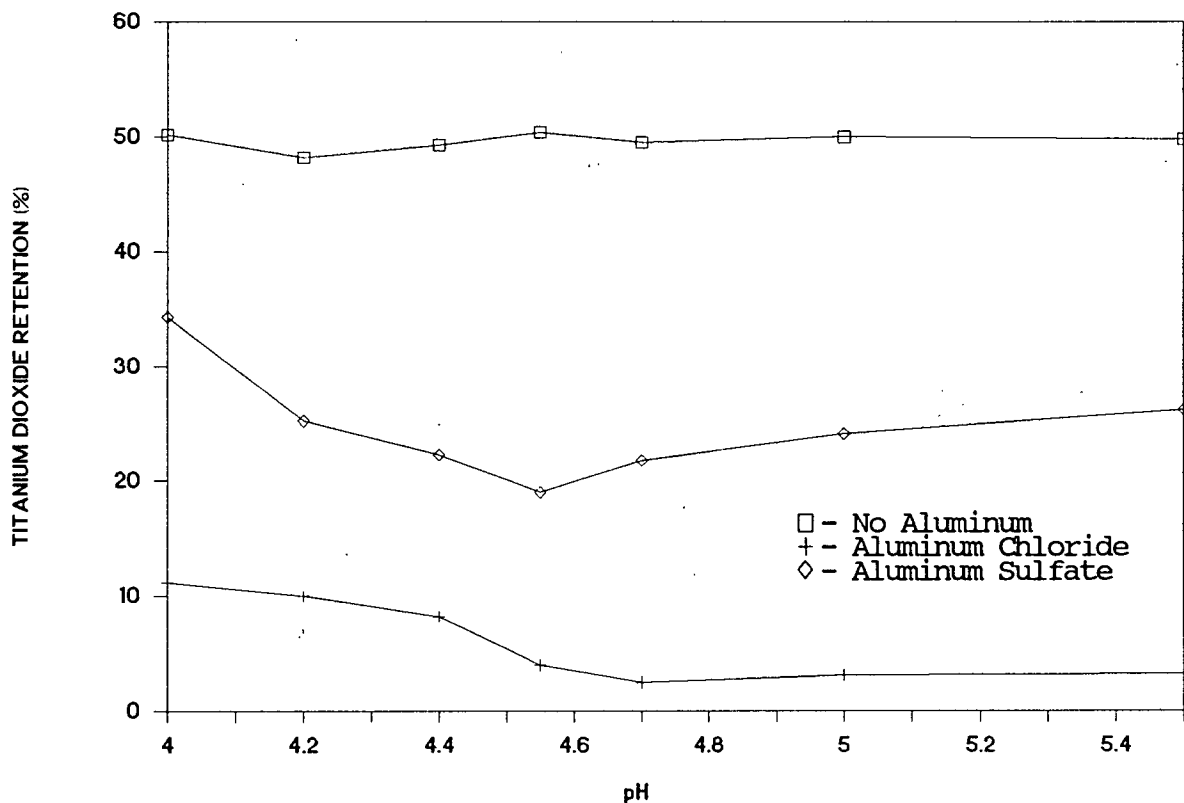


Figure 42. Comparison of titanium dioxide retention for aluminum chloride and aluminum sulfate ( $10.0 \times 10^{-4} \text{ M Al}$ , 3.0 mg/L polymer addition).

At the same aluminum concentrations, the titanium dioxide retention in the presence of aluminum chloride is significantly lower than that of aluminum sulfate. With both aluminum salts, the best titanium dioxide retention occurs at the lowest pH value, and as the pH is initially increased, the titanium dioxide retention decreases. However, as the pH is increased further, the titanium dioxide retention in the presence of aluminum chloride continues to decrease, whereas the titanium dioxide retention in the presence of aluminum sulfate increases. At the higher pH values, a different retention mechanism appears to be functioning with the different aluminum salts. These mechanisms will be discussed in the "Mechanisms" and "Interpretation of Polymer Adsorption and Titanium Dioxide Retention" sections.

#### Retention Without Polymer

The titanium dioxide retention from  $10.0 \times 10^{-4}\text{M}$  aluminum from aluminum sulfate at various pH levels is presented in Fig. 43. Experimental data on titanium dioxide retention without polymer present are compiled in Appendix XIII. For comparison, the titanium dioxide retention at  $10.0 \times 10^{-4}\text{M}$  aluminum from aluminum sulfate with 3.0 mg/L of polymer added is included.

The titanium dioxide retention is substantially lower when polymer is not used, which is evidence that the polymer is functioning as a retention aid. Without polymer present, the titanium dioxide retention is at its highest level at the lowest pH. As the pH is increased, the retention rapidly decreases to very low levels. Since aluminum sulfate affects retention by a coagulation type mechanism, these observations would be expected because the zeta potentials are at their lowest levels at low pH values and then increase as the pH is increased.

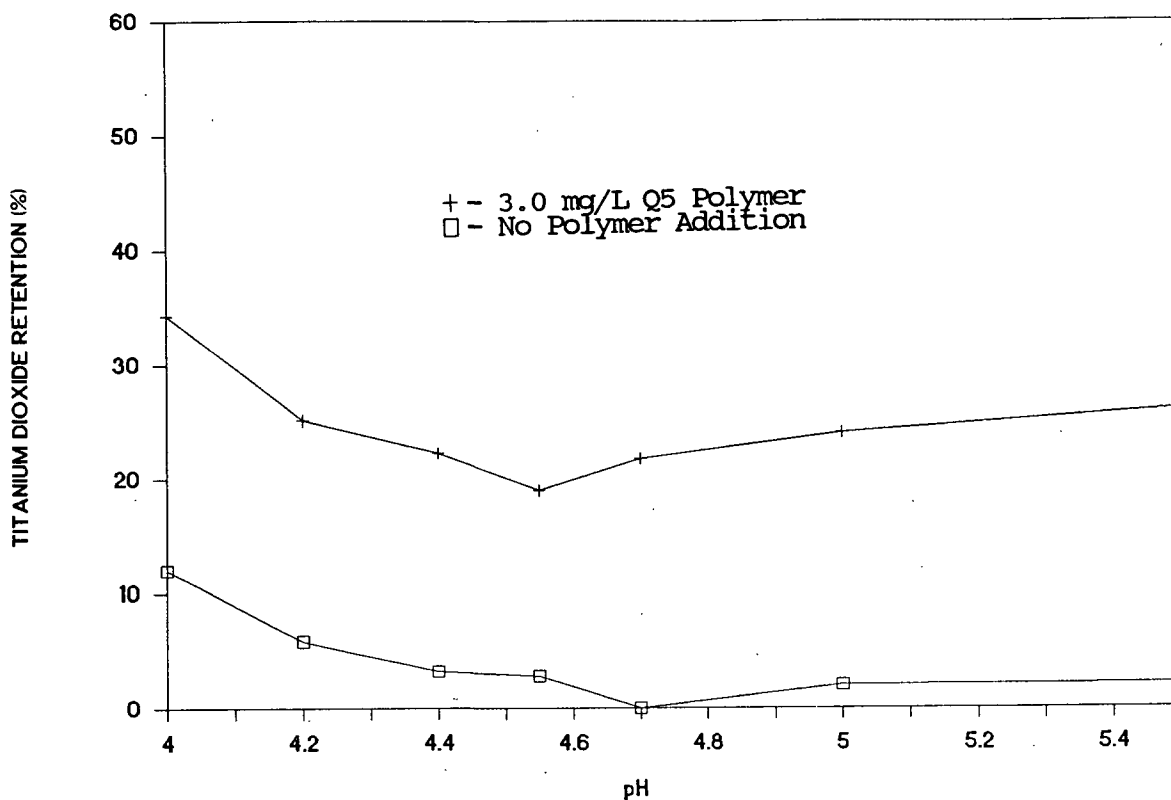


Figure 43. The influence of polymer addition on titanium dioxide retention ( $10.0 \times 10^{-4}M$  Al from aluminum sulfate).

#### Small Size Titanium Dioxide

In order to measure aluminum and polymer adsorption, a titanium dioxide with an average particle size larger than that typically used in the paper industry had to be used in the retention experiments. To determine whether this large particle size titanium dioxide was possibly influencing the results of this investigation, retention experiments were also performed with titanium dioxide typically used in the paper industry. The weight average diameter of this titanium dioxide was approximately 0.15 micron. With this smaller average particle size titanium dioxide, the aluminum and polymer adsorptions could not be measured. Titanium dioxide retention experiments were conducted and the results are compiled in Appendix XII.

Figure 44 presents a comparison of the influence of pH on the retention of large and small average particle size titanium dioxide for  $10.0 \times 10^{-4}M$  aluminum from aluminum sulfate and 3.0 mg/L polymer addition. Similarly shaped curves were obtained from both particle size titanium dioxides indicating that the particle size does not appear to affect the retention trends or mechanisms.

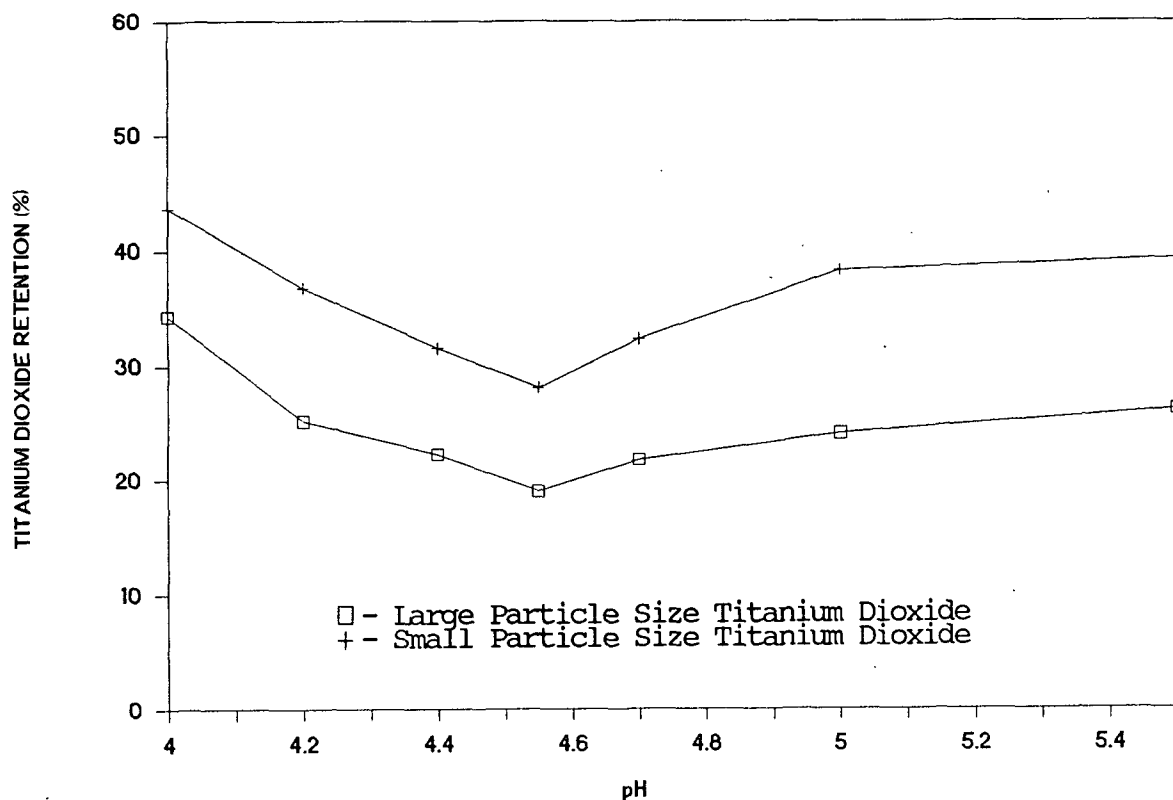


Figure 44. The influence of particle size on titanium dioxide retention ( $10.0 \times 10^{-4}M$  Al from aluminum sulfate, 3.0 mg/L polymer addition).

There are several possible explanations for the higher retention for the small particle size titanium dioxide. With the small size titanium dioxide, there is an increase in particle surface area, an increase in the number of particles, and a decrease in the particle size. Increasing the particle surface

area may increase the number of polymer adsorption sites. Increasing the number of particles may result in more polymer and filler particle collisions, and decreasing the particle size can reduce the drag forces on the particles. All of these factors can contribute to the increase in retention observed using the smaller size titanium dioxide.

#### MECHANISMS

Both alum and polymers are commonly used in the papermaking industry as retention aids. Alum is known to improve retention through a coagulation type mechanism where the aluminum ion is used to reduce surface charges so that particles can aggregate together.<sup>29</sup> In this study, the contribution from alum alone to the total retention via a coagulation mechanism was rather small (Fig. 43).

The primary objective of this study was to determine how aluminum salts affect retention when using cationic polyelectrolyte retention aid. Retention of fine particles with polymers is a flocculation process<sup>27</sup> for which three mechanisms have been proposed: (1) charge neutralization, (2) electrostatic patch model, and (3) polymer bridging. Charge neutralization, like coagulation, is characterized as having maximum retention at or near a system zeta potential of zero.<sup>34-37</sup> Because the retention trends in this study did not always correlate with zeta potentials, charge neutralization is most likely not an important mechanism. Electrostatic patch mechanisms are favored by high charge density polymers. Since a low charge density polymer was used in this study, an electrostatic patch mechanism is very unlikely. The low charge density, high molecular weight polymer used in this study favors a bridging mechanism. A bridging mechanism is also supported by the fact that good retention can be obtained when the zeta potential is very positive<sup>3,4,16-19</sup> as was observed in

this investigation. However, two mechanisms have been proposed for bridging<sup>14</sup>: (1) direct polymer bridging where the polymer adsorbs directly on the furnish surface and (2) hydroxyaluminum-sulfate anion-polymer bridging where the polymer adsorbs onto the anion in the hydroxyaluminum complex which is on the furnish surface. It was desired to establish whether this second type of bridging was occurring and under what conditions it was favored.

#### Scanning Electron Micrographs

In order to understand how the polymer adsorbs, scanning electron micrographs were taken to determine how the aluminum precipitate was adsorbing. Figure 45 shows a scanning electron micrograph of a clean fiber surface and Fig. 46 shows a fiber with precipitated aluminum on its surface. The precipitated aluminum fiber was obtained from a 0.3% cotton linters slurry with  $10.0 \times 10^{-4}M$  aluminum from aluminum sulfate at pH 5.5. At this aluminum concentration, the aluminum precipitate covers a large portion of the fiber surface. Therefore, it is likely that the polymer is adsorbing to the aluminum precipitate instead of directly onto the fiber surface. The fact that the polymer adsorption increases in this pH region as the aluminum concentration for aluminum sulfate is increased also supports this conclusion.

#### Agitation Effects

Retention experiments were performed at varying degrees of agitation to determine how effectively the polymer was performing in the different pH regions. Retention experiments were performed at 500, 1000, and 1500 rpm in the dynamic drainage jar with an aluminum sulfate concentration of  $10.0 \times 10^{-4}M$  aluminum and a polymer concentration of 3.0 mg/L. The aluminum and polymer adsorptions were not affected by changes in the agitation rate, but substantial

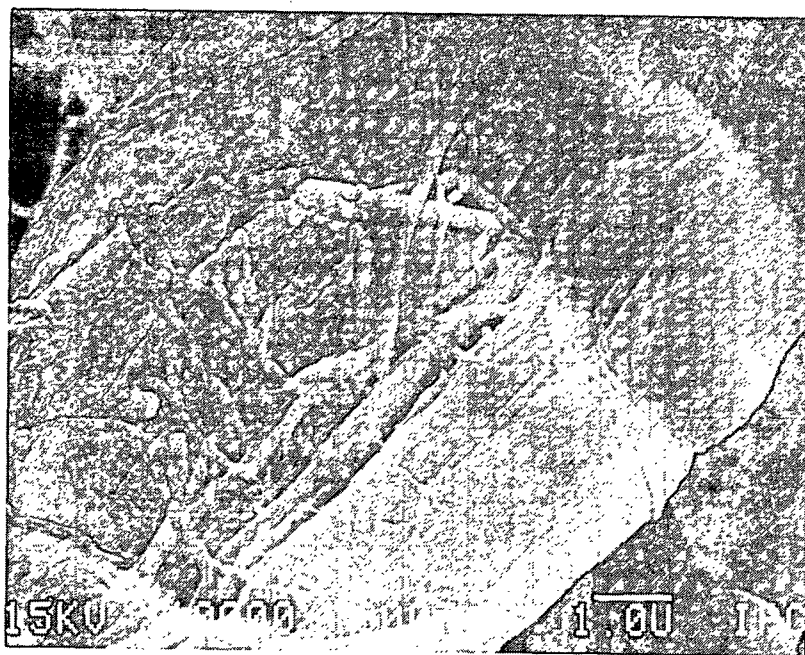


Figure 45. Scanning electron micrograph of clean fiber surface.

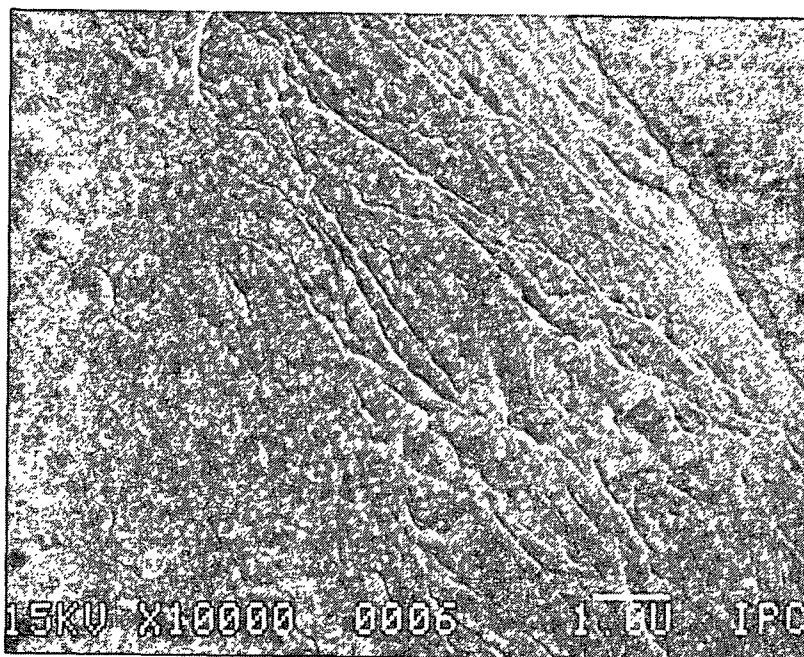


Figure 46. Scanning electron micrograph of fiber surface covered with aluminum precipitate from aluminum sulfate ( $10.0 \times 10^{-4}$  M Al, pH 5.5).

effects were observed in the titanium dioxide retention. The titanium dioxide retention results at 500 and 1500 rpm are compiled in Appendix XIII.

As shown in Fig. 47, the titanium dioxide retention trends varied between the low and high pH regions at the various agitation levels. In the low pH region, the titanium dioxide retention curves showed similar trends with better retention as the degree of agitation decreased. However, in the upper pH region, various retention trends were observed. At the low agitation level, there was a large increase in retention with higher pH. At the medium agitation level, there was a moderate increase in retention; and at the high agitation level, there was a decrease in retention. This indicates that the polymer bonding in the upper pH region is rather weak as would be expected if the polymer were adsorbing onto the aluminum precipitate instead of directly to the fiber surface.

#### Aluminum Sulfate Desorption Experiments

Aluminum sulfate desorption experiments were performed in order to determine where the polymer was adsorbing. Retention experiments were performed in the usual manner, except that after the polymer was adsorbed for one minute, the aluminum sulfate precipitate was desorbed by acidification. Polymer which had been adsorbed onto the aluminum sulfate precipitate would also desorb. A cationic surfactant, cetyltrimethyl ammonium bromide, was added immediately before acidification to prevent readsorption of any desorbed polymer onto the newly exposed surfaces and any additional time dependent polymer adsorption. The results of these desorption experiments at  $10.0 \times 10^{-4}M$  aluminum from aluminum sulfate and 3.0 mg/L polymer addition are compiled in Appendix XIV.



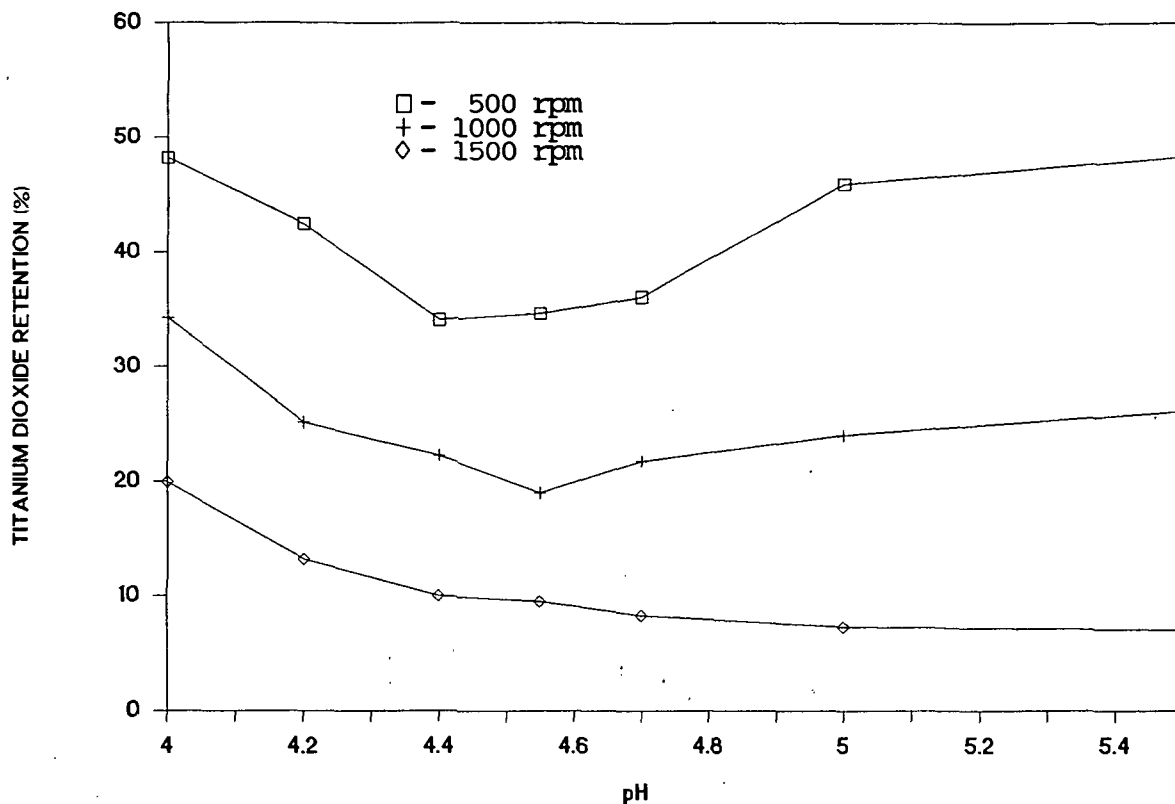


Figure 47. The influences of pH and agitation rate on titanium dioxide retention for aluminum sulfate ( $10.0 \times 10^{-4} \text{M}$  Al, 3.0 mg/L polymer addition).

The polymer adsorption results in the presence of the surfactant alone and surfactant plus acid are shown in Fig. 48. When the surfactant was added without acidification, a typical polymer adsorption curve was obtained indicating that the surfactant has no significant effect on the adsorbed polymer. However, when the surfactant was added and the system was acidified, similar polymer adsorption values were obtained in the low pH region; but the polymer adsorption substantially decreased in the high pH region. The difference between the two curves indicates the amount of polymer adsorbed onto the aluminum sulfate precipitate. Therefore, in the low pH region, the polymer adsorbed

directly onto the furnish surfaces; but in the high pH region, a large portion of the polymer was indirectly adsorbed by adsorbing onto the aluminum sulfate precipitate.

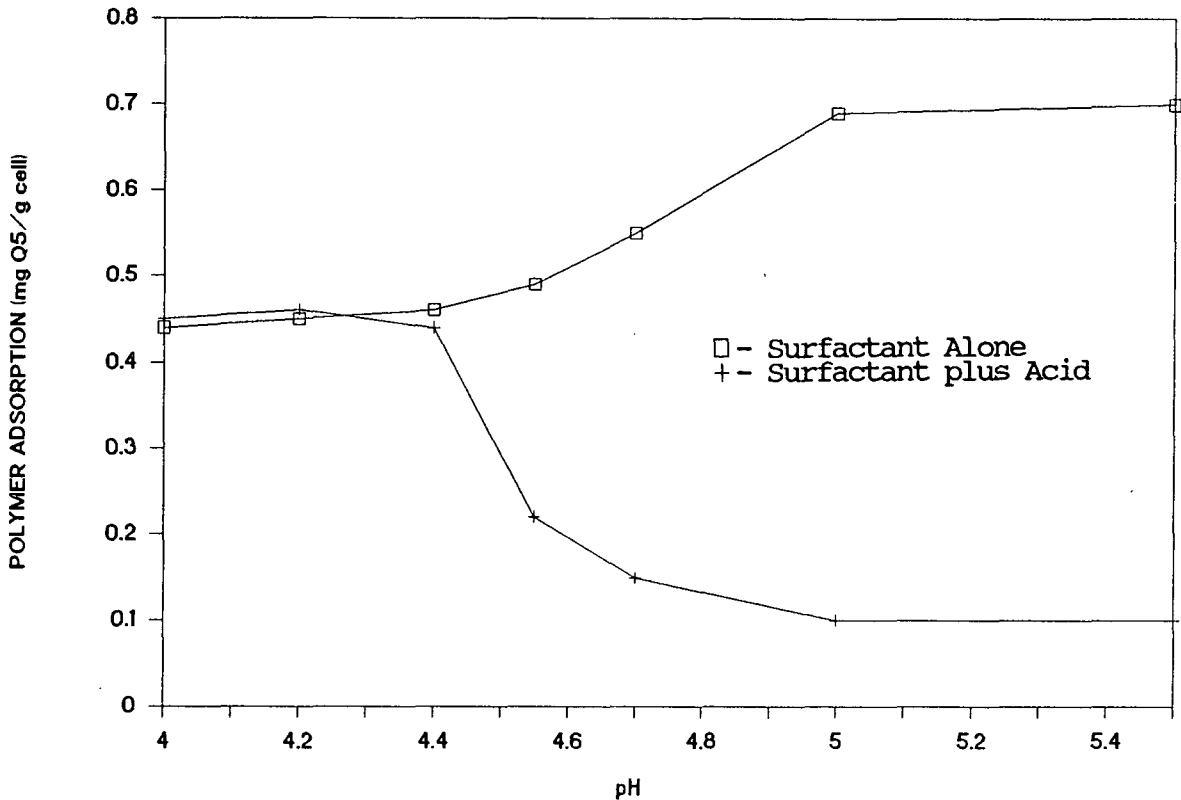


Figure 48. The influence of aluminum precipitate desorption on polymer adsorption for aluminum sulfate ( $10.0 \times 10^{-4}M$  Al, 3.0 mg/L polymer addition, 1 minute polymer adsorption time).

Table 3 presents the aluminum desorption results at pH 5.5 for  $2.5 \times 10^{-4}$ ,  $5.0 \times 10^{-4}$ , and  $10.0 \times 10^{-4}M$  aluminum from aluminum sulfate with 3.0 mg/L polymer addition. When surfactant was added without acidification, the polymer adsorption increased as the aluminum concentration was increased. This would be expected from the previous polymer adsorption results at pH 5.5 (see Polymer Adsorption - Aluminum Sulfate). However, when surfactant was added and the

system was acidified, the polymer adsorption decreased as the aluminum concentration was increased. Therefore, as the aluminum concentration was increased, the total polymer adsorption increased; the direct polymer adsorption decreased; and the indirect polymer adsorption increased. The greater amount of directly adsorbed polymer at lower aluminum concentrations is most likely the reason that the titanium dioxide retention at higher aluminum concentration does not increase above that at lower aluminum concentrations (Fig. 39) even though there is a larger total amount of polymer adsorbed (Fig. 31).

Table 3. Aluminum desorption results for various aluminum concentrations (pH 5.5, 3.0 mg/L Q5, 1 minute polymer adsorption time).

Aluminum Concentration (M Aluminum)	Polymer Adsorption (mg/g cellulose)	
	Surfactant Alone	Surfactant + Acid
$2.5 \times 10^{-4}$	0.61	0.19
$5.0 \times 10^{-4}$	0.65	0.16
$10.0 \times 10^{-4}$	0.70	0.10

#### INTERPRETATION OF POLYMER ADSORPTION AND TITANIUM DIOXIDE RETENTION

The cationic polyacrylamide polymer used in this study exhibited a typical, high affinity, Langmuir adsorption isotherm with nearly 100% adsorption at low polymer concentrations. As shown in Fig. 22, close to 100% of the 3.0 mg/L polymer added in this study adsorbed at equilibrium. However, the retention experiments were carried out at short polymer contact times where nonequilibrium conditions exist and polymer adsorption is less than optimum. As shown in Fig. 23 and 24, the presence of aluminum sulfate at short adsorption times reduces polymer adsorption even further. However, this reduction in polymer adsorption was not observed at longer polymer adsorption times ( $> 10$  minutes). This

indicates that aluminum sulfate reduces the polymer adsorption rate. If these retention experiments were performed at longer adsorption times, it is possible that the presence of aluminum sulfate would have had no effect on polymer adsorption and retention. The nonequilibrium condition in the retention experiments is shown in Fig. 29 and 37. Increasing polymer adsorption time increases polymer adsorption which in turn increases titanium dioxide retention.

Polymer adsorption was also increased by increasing the polymer concentration. Increasing polymer adsorption as polymer concentration is increased is observed both without alum (Fig. 25) and with alum present (Fig. 27). However, the relative polymer adsorption in both cases is greater at low polymer concentration (Fig. 26 and 28). This indicates that polymer molecules are competing for adsorption sites. In the nonequilibrium, short adsorption times used in retention experiments, some of the additional polymer from the increase in polymer concentration is unable to find adsorption sites. As would be expected, the titanium dioxide retention increases from the increase in polymer adsorption when the polymer concentration is increased. This effect was observed for systems both with alum present (Fig. 36) and without alum present (Fig. 35).

#### Below the pH<sub>p</sub> - Both Aluminum Salts

The presence of aluminum was found to decrease polymer adsorption and titanium dioxide retention at all pH values and aluminum concentrations used in this investigation. At low pH values where only soluble aluminum species exist and aluminum adsorption is low, increasing the aluminum concentration for either aluminum chloride or aluminum sulfate results in decreasing polymer adsorption (Fig. 30 and 31). This is due to a reduction in polymer adsorption rate in the presence of aluminum. The reduced adsorption rate indicates that there is

competition between the soluble aluminum species and the polymer for adsorption sites as would be expected in an ion exchange adsorption mechanism.

At all aluminum concentrations, the polymer adsorption was greater for aluminum sulfate than for aluminum chloride (Fig. 32, 33, and 34). The sulfate ions from aluminum sulfate are able to screen cationic charges, which reduces the zeta potential (Fig. 18). This results in less electrostatic repulsion between the cationic polymer and cationic furnish surface, thereby increasing polymer adsorption.

In this pH region, the polymer was found to be directly adsorbed to the furnish surface (Fig. 48); therefore, titanium dioxide retention occurs by a direct polymer bridging mechanism which was shown to be shear stable (Fig. 47). The titanium dioxide retention follows the polymer adsorption trends with decreasing retention from increasing aluminum concentrations (Fig. 38 and 40). Also, the titanium dioxide retention was greater for aluminum sulfate than for aluminum chloride (Fig. 40, 41, and 42) because of the increased polymer adsorption and lower zeta potentials created by the sulfate ion.

#### Above the pHp - Aluminum Chloride

At high pH values in the presence of aluminum chloride, the furnish adsorbs large amounts of cationic aluminum precipitate. This makes the furnish surface very positively charged (Fig. 18) which repels the cationic polymer and results in low polymer adsorption (Fig. 30). When the aluminum concentration is increased, more cationic aluminum precipitate adsorbs onto the furnish surface and the polymer adsorption is reduced further. The low polymer adsorption and high zeta potentials result in very low titanium dioxide retention.

#### Above the pH<sub>p</sub> - Aluminum Sulfate

At high pH values in the presence of aluminum sulfate, the furnish also adsorbs large amounts of cationic aluminum precipitate. The cationic charge on the furnish is less than that created by aluminum chloride even though more precipitate is adsorbing. This is because aluminum sulfate incorporates negative sulfate ions into its precipitate which reduces its cationic charge. The cationic furnish surface would be expected to repel the cationic polymer; but at the low aluminum concentrations, the polymer adsorption is approximately constant and increasing the aluminum concentration increases the amount of polymer adsorbed (Fig. 31).

In agreement with Crow's work,<sup>22</sup> the polymer in this region was found to be both directly and indirectly adsorbed to the furnish surface (Fig. 48). Indirect polymer adsorption was a result of the polymer adsorbing onto the aluminum precipitate on the furnish surface instead of directly to the furnish surface itself. The negative sulfate ions in the aluminum precipitate were believed to serve as the polymer adsorption sites. As the aluminum concentration and thus aluminum adsorption was increased, the indirect polymer adsorption rapidly increased due to an increase in the number of adsorption sites provided by the adsorbed aluminum. However, the direct polymer adsorption slowly decreased since more of the furnish surface was covered by the aluminum precipitate. The large increase in indirect polymer adsorption coupled with the slight decrease in direct polymer adsorption resulted in an overall increase in polymer adsorption.

Consequently, in this pH region, the titanium dioxide retention was a result of both a direct polymer bridging mechanism and an indirect hydroxyaluminum-sulfate anion-polymer bridging mechanism. Even though the polymer adsorption in

the high pH region was the same as, or greater than, that in the low pH region, the titanium dioxide retention was lower. This was due to higher zeta potentials and the shear sensitive nature of the indirect bonding present in the high pH region. When the aluminum concentration was increased in the high pH region, the titanium dioxide retention decreased even though more polymer was adsorbed. This is because at higher aluminum concentration there was more indirect polymer adsorption which is shear sensitive and less direct adsorption which is shear stable.

#### Near the pH<sub>p</sub> - Aluminum Sulfate

In the middle pH region, the titanium dioxide retention reaches a minimum level. This is difficult to interpret because both the aluminum precipitate and soluble aluminum species are present. The aluminum precipitate is adsorbed onto the furnish which increases its surface charge. The higher zeta potentials and screening effects of the soluble aluminum species may interfere with the bridging mechanism and reduce filler retention.

## CONCLUSIONS

The presence of aluminum salts has a significant effect on polymer adsorption and titanium dioxide retention. Both aluminum chloride and aluminum sulfate were found to reduce polymer adsorption and titanium dioxide retention at all pH values and aluminum concentrations studied in this investigation. The reduction in polymer adsorption was a result of a decrease in polymer adsorption rate.

Below the pHp for both aluminum salts, the trivalent aluminum ion appeared to be the primary adsorbing species and adsorbed by an ion exchange mechanism. As the aluminum concentration was increased, aluminum adsorption increased, which in turn resulted in decreasing polymer adsorption. This indicates that there is competition between the soluble aluminum species and polymer for adsorption sites. In this pH region, the polymer was found to be directly adsorbed to the furnish surface. Good titanium dioxide retention was obtained from low zeta potentials and a shear stable, direct bridging mechanism.

At high pH values, the aluminum salts precipitated and produced high aluminum adsorption. With aluminum chloride, the furnish became coated with the highly cationic aluminum precipitate, which repelled the cationic polymer and resulted in low filler retention. With aluminum sulfate, the furnish also became coated with a cationic aluminum precipitate but had a lower charge due to the incorporation of sulfate ions. The polymer was found to be both directly and indirectly adsorbed to the furnish surface. The sulfate ions in the aluminum precipitate were believed to serve as adsorption sites for the indirect polymer adsorption. When the aluminum concentration was increased and more aluminum was adsorbed, the polymer adsorption increased. The bridging which forms



as a result of indirectly adsorbed polymer was found to be shear sensitive. This along with higher zeta potentials resulted in moderate titanium dioxide retention.

## APPLICATION OF RESULTS

The results of this study clearly show the varying effects that aluminum salts can have on polymer adsorption and filler retention. These effects can be directly related to the aqueous chemistry of the aluminum ion. This study shows the importance of controlling pH and aluminum concentration independently in order to influence which aluminum species are present. Typically, the pH in a papermaking system is regulated by alum addition alone, and this does not allow efficient control of the aluminum chemistry. By controlling the aluminum chemistry in a papermaking system, it should be possible to influence the zeta potential, polymer adsorption, and fine particle retention.

This study indicates that the negative zeta potentials typically found in a papermaking system could be reduced or even be made positive by increasing the pH so that cationic aluminum precipitate is formed and adsorbed onto the furnish. The aluminum precipitate could also provide additional polymer adsorption sites and increase retention through an indirect bridging mechanism. However, an increase in retention might only be observed in slower speed papermaking systems where there are lower levels of turbulence. In systems with higher levels of turbulence, a lower system pH may be desired so that a shear stable, direct bridging mechanism would be favored.

There are many factors in a real papermaking system that could alter the results of this study so that they would not be directly applicable. Aluminum salts are added to papermaking systems not only to control pH but also to react with other wet-end additives and "anionic trash". The reaction of aluminum salts with these materials should reduce the anionic charge in the system, allowing the polymeric retention aid to be more effective. If the aluminum

salts react with other materials, an indirect bridging mechanism may be less favored. Also in a real papermaking system, there is typically more fine particle material with a smaller average particle size. This results in a greater overall surface area which may result in more direct polymer adsorption and bridging. However, the smaller particles should also be less influenced by drag, which could allow greater retention with an indirect bridging mechanism. By controlling the pH and aluminum concentration independently, the aqueous aluminum chemistry can be controlled so that the most favorable retention conditions are obtained.

This investigation also indicates some possible reasons for the variability reported in the literature for the effects of alum on fine particle retention when using a cationic polyelectrolyte retention aid. Because of inadequate information about these studies, it is not possible to directly apply the results of this study to the interpretation of their results.

## SUGGESTIONS FOR FUTURE RESEARCH

This study has attempted to simulate some aspects of a real papermaking system, such as short polymer contact times and turbulent retention conditions. However, additional studies could be performed to more closely simulate a real papermaking system. These studies could possibly investigate the influences of the following on aluminum adsorption, zeta potential, polymer adsorption, and fine particle retention:

1. The influence of wet-end additives, such as rosin sizes and wet strength additives.
2. The influence of "anionic trash" materials, such as soluble wood polymers, pulping residues, and recycled additives.
3. The influence of various fine particle types, sizes, and surface areas.
4. The influence of various polymer types, molecular weights, and charge densities.

#### ACKNOWLEDGMENTS

The author wishes to express his sincere gratitude to his Thesis Advisory Committee. Dr. Robert Stratton, who served as Chairman of the Advisory Committee, is thanked for his guidance, knowledge, understanding, and friendship throughout this study. I also wish to thank the other members of the Advisory Committee, Dr. Dwight Easty, Dr. Hardev "Doug" Dugal, and Mr. John Waterhouse for contributing their time and knowledge leading to the completion of this thesis.

I would like to recognize the Board of Trustees and member companies for their support to The Institute of Paper Chemistry and its unique graduate studies program.

A special thanks is extended to Dr. Thomas Arnson and Dr. Roger Crow for their work in this area which provided the foundation for this research study.

Appreciation is also extended to the staff, faculty, and students of the Institute for their help and friendship. Everyone has made my stay at the Institute very enjoyable and full of memories that will last my lifetime.

Finally, a loving thank you is given to my wife, Deb, for her love, support, help, and sacrifices during the past years of this study.

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APPENDIX I  
COTTON LINTERS

WASHING

Before being used in this study, the cotton linters were rewashed to ensure clean fibers and free carboxyl groups. This involved two 12-hour soakings of the cotton linters in distilled water at 0.25% consistency with the pH adjusted to approximately 2.5 using nitric acid. This was followed by three 24-hour soakings in distilled water at 0.25% consistency without any pH adjustment. Between each washing, the pulp was centrifuged to approximately 33% solids to remove the wash water. After the last washing, the centrifuged pulp was run several times through a lump-breaker in order to produce small pieces of pulp which would dry quickly and redisperse easily. The cotton linters pulp was then air dried and stored in polyethylene bags.

CARBOXYL CONTENT

TAPPI Standard Method T237 os-77(63)

The TAPPI Standard method for determination of carboxyl content is based on the work of Wilson<sup>83</sup> and has been outlined by Wilson and Mandel.<sup>84</sup> In this procedure, the deashed pulp is reacted with a solution of sodium chloride and sodium bicarbonate. This is then titrated to a methyl red endpoint with hydrochloric acid and compared to a blank sample.

Specifically, pulp samples of known oven dry weight (approximately 2.5 g each) were slurried with 250 mL of 0.1M HCl. After 2 hours, the samples were collected on fritted glass funnels and washed with distilled water saturated with carbon dioxide. The washing was continued until the filtrate, after

boiling, did not require more than one or two drops of 0.01M NaOH to change the color of a methyl red indicator. The wet pulp pads were then weighed and placed in 250-mL Erlenmeyer flasks. Next, a 50 mL solution of 0.1M sodium chloride and 0.01M sodium bicarbonate was added to each sample. The flasks were shaken to disperse the pulp. After one hour, each sample was filtered through a clean, dry fritted glass funnel and 25.0 mL of the filtrate was titrated with 0.01M HCl to a methyl red endpoint. When the first color change appeared in each sample, it was boiled to expel the carbon dioxide. The titration was then continued to a sharp color change. A blank of 25 mL of sodium chloride-sodium bicarbonate solution was also measured. The carboxyl content was then determined using Eq. (11).

$$X, \text{ meq./100 g} = (b-a-(a)(v)/50) 2/G \quad (11)$$

where,

G = Oven dry weight of pulp, g

v = Weight of water in wet pulp pad, g

a = Volume of 0.01M HCl to titrate 25 mL of the sample solution, mL

b = Volume of 0.01M HCl to titrate blank, mL

Using this method, a carboxyl content of 3.02 meq./100 g + 2% was obtained.

#### Methylene Blue Dye Method

The carboxyl content of the cotton linters was also determined by the methylene blue dye method. This method was developed by Davidson<sup>44</sup> and has also been outlined by Wilson and Mandel.<sup>84</sup> In this procedure, an ion exchange occurs between the carboxyl groups of the pulp and a methylene blue dye solution. The carboxyl content is determined from the amount of pulp necessary for 50% consumption of the methylene blue dye.

Two stock solutions were prepared: (1) 2.0 millimolar methylene blue chloride solution and (2) 6.25 millimolar diethyl barbituric acid plus 4.0 millimolar sodium hydroxide buffer solution.

In determining the carboxyl content of the pulp, 100 mL of the dye plus 100 mL of the buffer were mixed and diluted to 1 liter. 25 mL of this solution was added to a series of pulp samples ranging from 0.0675 to 0.1290 gram. After agitating on a rotating wheel overnight, the samples were centrifuged and 5.0 mL of the supernatant was pipetted off, added to 5.0 mL of 0.01M HCl, and diluted to 50 mL in a volumetric flask. The absorbance of this solution was then measured at 620 nm.

A calibration curve was obtained by preparing a series of standard solutions ranging from 0.0 to 20.0 x 10<sup>-6</sup>M methylene blue with a constant buffer concentration of one-tenth that of the buffer stock solution. 5.0 mL of each of these solutions was added to 5.0 mL of 0.10M HCl and diluted to 50 mL. The absorbance was then measured at 620 nm. Figure 49 shows the calibration curve obtained. From the calibration curve, the amount of dye consumed for the various pulp samples was calculated. As shown in Fig. 50, a plot of the dye consumed versus the weight of fibers resulted in a straight line. Using Eq. (12) the carboxyl content was determined from the amount of pulp necessary for 50% dye consumption, namely 0.822 g.

$$X, \text{ meq./100 g} = \frac{0.0025 \text{ meq.} \times 100}{\text{grams of pulp for 50\% dye consumption}} \quad (12)$$

Using this method, a carboxyl content of 3.04 meq./100 g was determined.

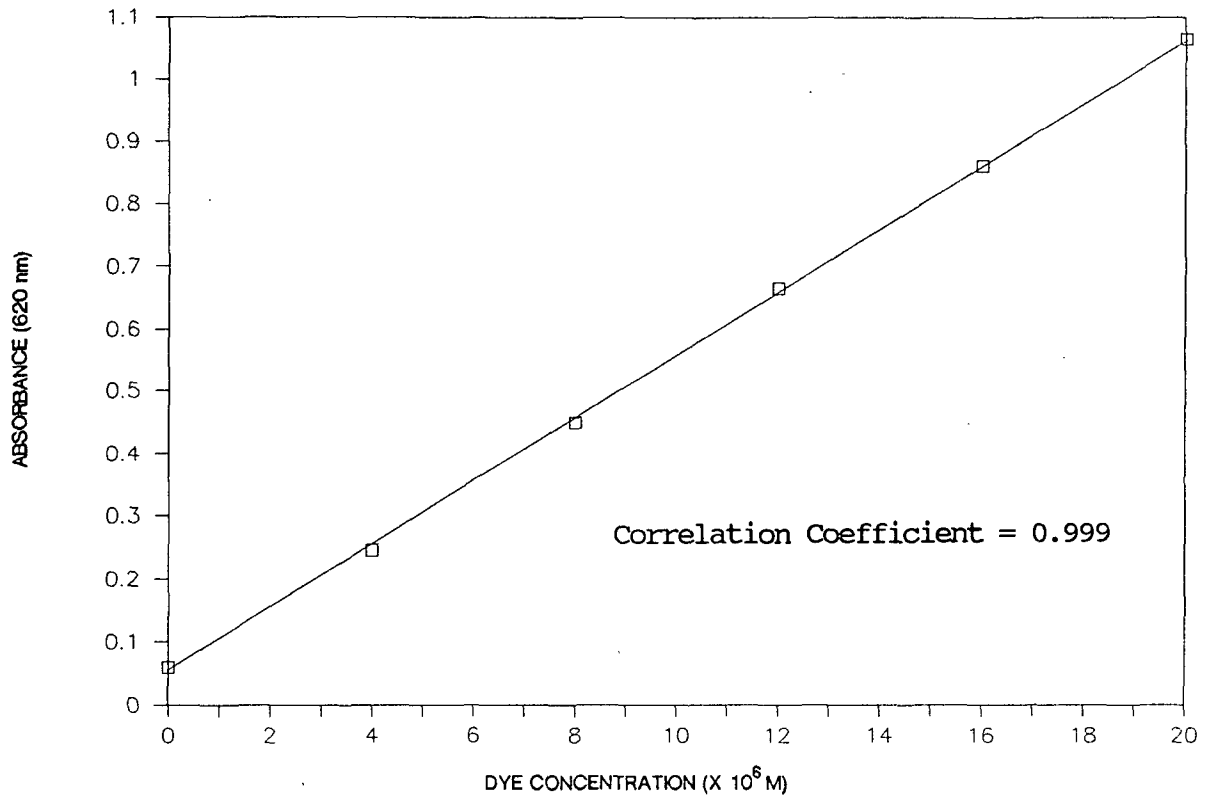


Figure 49. Calibration curve for methylene blue dye carboxyl content determination.

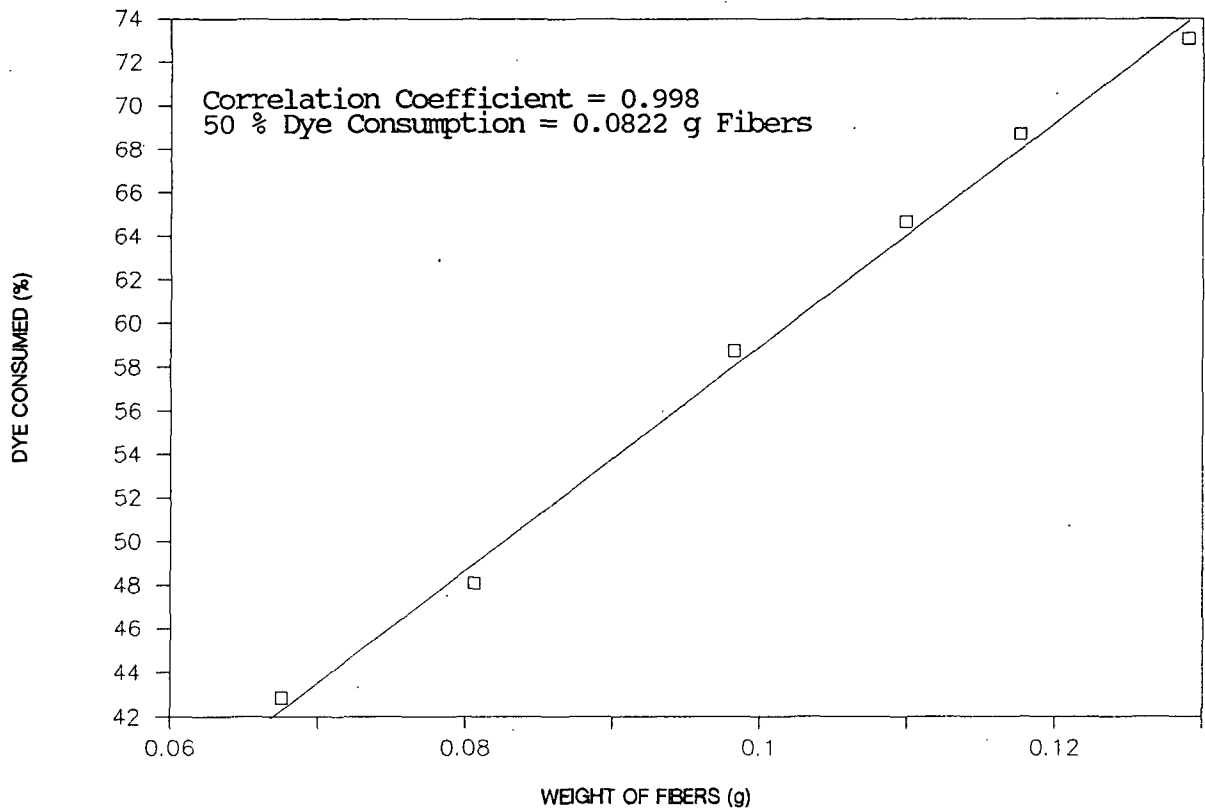


Figure 50. Methylene blue dye consumption by cotton linter fibers.

## APPENDIX II

### EFFECT OF POLYCARBONATE FILTERS ON ALUMINUM AND POLYMER REMOVAL

Various pore size polycarbonate filters were evaluated for their effect on removing aluminum and polymer from solution during filtration. Initially, cellulose ester, Teflon, and polycarbonate filters were compared. The cellulose ester filters produced undesirable aluminum and polymer losses. The Teflon filters showed fairly low losses, but they were more difficult to work with, produced slow filtration rates, and were more costly than the polycarbonate filters. Therefore, polycarbonate filters were used in this investigation.

In order to reduce polymer losses, it was necessary to pretreat the filters with polymer. This was accomplished by soaking the filters 24 hours in a 200 mg/L polymer solution. This was followed by a thorough distilled water wash. The effects of various pore size, polymer treated polycarbonate filters on aluminum and polymer removal are shown in Table 4. The filters were tested at  $10.0 \times 10^{-4} \text{M}$  Al from aluminum sulfate at pH of 4.0 and 5.5 and 3.0 mg/L polymer.

In order to obtain negligible aluminum and polymer losses, it was felt that a 2.0 micron pore size filter was the smallest filter that could be used. With this requirement, it was necessary that a larger than usual particle size (>2.0 micron) titanium dioxide be used as the filler in the retention experiments. The large particle titanium dioxide would be filtered out by the 2.0 micron polycarbonate filter while the unadsorbed aluminum and polymer would pass through the filter without significant losses.

Table 4. Effect of polycarbonate filters on aluminum and polymer removal  
( $10.0 \times 10^{-4}$  M Al from aluminum sulfate; 3.0 mg/L polymer).

Pore Size (microns)	Aluminum Removed (%)		Polymer Removed (%)
	pH 4.0	pH 5.5	
10	0.0	1.7	0.0
5	0.0	2.1	0.0
2	0.0	3.3	0.0
1	0.0	27.2	0.0
0.8	0.0	59.3	1.7
0.6	0.0	87.2	1.7
0.4	0.0	93.1	3.3
0.2	0.0	94.2	13.3
0.1	0.0	94.2	23.3



### APPENDIX III

#### TITANIUM DIOXIDE

#### LARGE PARTICLE SIZE

##### Preparation

In order to separate the unretained fillers from the unadsorbed aluminum and polymer, a larger than normal particle size titanium dioxide had to be used. A sample of large particle size anatase titanium dioxide was obtained from SCM Pigments, Incorporated. The sample reportedly consisted of particles ranging from 1.0 to 20.0 microns. An average particle size greater than 2.0 microns with a fairly narrow particle size distribution was desired. Therefore, the sample of large particle size titanium dioxide had to be fractionated to remove some of the smaller and larger size particles.

The particle size fractionation was accomplished by first dispersing the titanium dioxide in distilled water at 60% solids. The slurry was mixed for three minutes in a water cooled Waring Blendor and then diluted to approximately 5% solids. Since the larger titanium dioxide particles would settle out of solution faster than the smaller particles, the slurry could be fractionated by sedimentation. If a larger average particle size was desired, the settled fraction was used and the supernatant fraction was discarded. If a smaller average particle size was desired, the settled fraction was discarded and the fraction in suspension was used. A number of these settling separations were performed at 5% solids until a titanium dioxide sample of the desired average particle size and distribution was obtained. Between each of the separations, particle size measurements were performed to determine the average particle size and direction for the next separation.

### Particle Size

A Coulter Counter (model TA II Coulter Electronics) was used to measure the average particle size and distribution of the titanium dioxide samples. A Coulter Counter measures the number and size of particles passing through an aperture. Two electrodes on opposite sides of the aperture monitor the current of a conductive fluid. As a particle in the conductive fluid passes through the aperture, the resistance between the electrodes is momentarily altered which produces a current pulse proportional to the particle volume. The size of the particle is classified into one of 16 channels. Each channel has a lower boundary that corresponds to a particle volume that is twice the particle volume of the lower boundary of the preceding channel. A cumulative volume distribution was obtained from the Coulter Counter which could be converted into equivalent spherical diameters.

During the particle size determinations of the titanium dioxide, a 100 micron diameter aperture and a 1% sodium chloride conductive fluid were used. The salt solution was initially filtered twice, once through a 0.22 micron Millipore filter and once through a 0.10 micron Millipore filter. This was necessary to remove dust and reduce background interference. The channel boundaries were calibrated with monodisperse polystyrene latex particles having a 10.07 micron diameter. Figure 51 shows the cumulative volume distribution eventually obtained for the titanium dioxide particles used in the retention experiments. At 50% cumulative volume, an average equivalent spherical diameter of 4.2 microns was obtained. This figure also shows that the titanium dioxide has a fairly narrow particle size distribution.

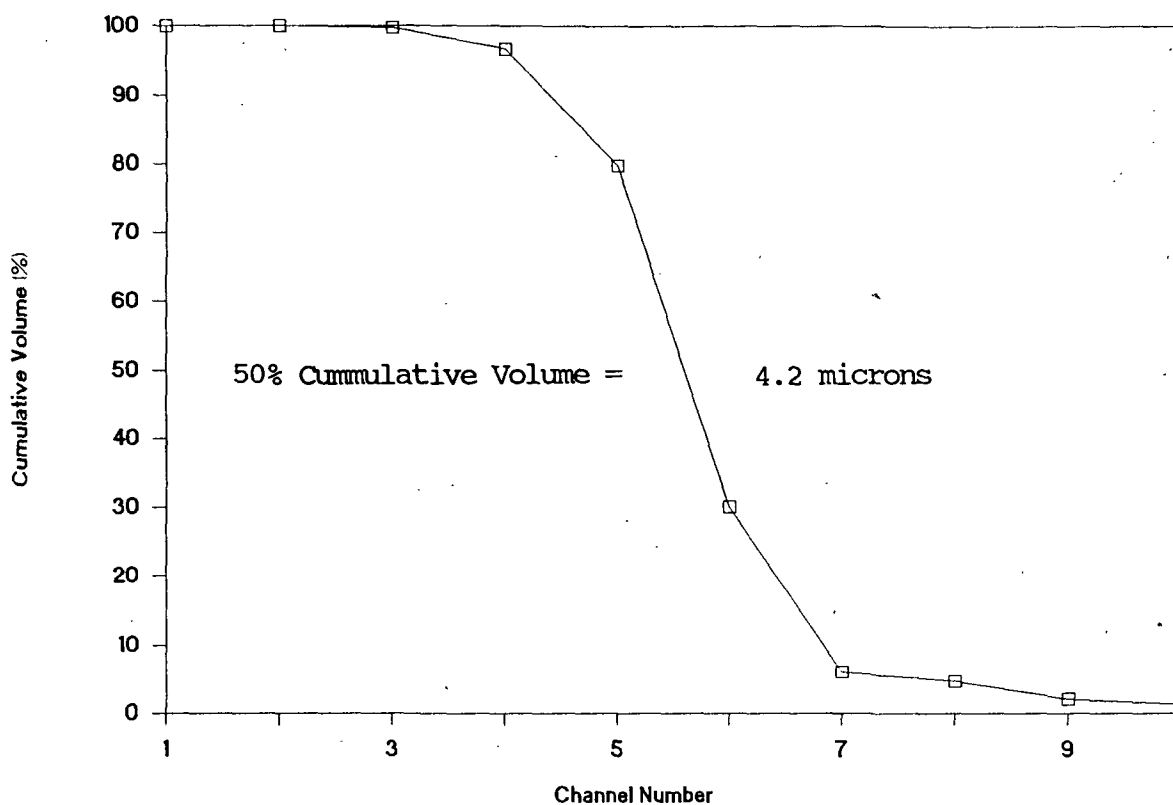


Figure 51. Particle size determination by a Coulter Counter (average equivalent spherical diameter per channel in microns: 1-1.44, 2-1.82, 3-2.29, 4-2.88, 5-3.63, 6-4.58, 7-5.77, 8-7.27, 9-9.15, 10-11.54).

#### Particle Charge

The particle size separation by sedimentation technique caused the titanium dioxide surface to change. The numerous settling separations apparently washed away much of the dispersant, resulting in positively charged particles. Therefore, sufficient tetrasodium pyrophosphate dispersant, TSPP, was added to the titanium dioxide to obtain a zeta potential of approximately -13.0 mV at pH 4.0. This was similar to the zeta potential of the smaller sized titanium dioxide typically used in the paper industry.

### Storage

The titanium dioxide was stored in polypropylene bottles at 3% solids on a rotor. The samples were continuously rotated at approximately 6 rpm when not being used to prevent settling and aggregation.

### PARTICLE SIZE TYPICALLY USED IN PAPERMAKING

### Preparation

For comparison purposes in the retention experiments, a normal particle size titanium dioxide was also prepared. RG-grade, anatase titanium dioxide (The Glidden Company) was dispersed in distilled water at 73% solids. Three minutes of mixing in a water cooled Waring Blendor produced a thick paste. This was diluted to 8.0% solids and vigorously stirred for three hours with a Lightnin' mixer. A vacuum was then applied to remove any entrained air. In order to remove any large undispersed particles, the titanium dioxide slurry was allowed to settle for 24 hours. Then, the upper three-fourths of the slurry, containing the smaller particles, was siphoned off. This was stored in polypropylene bottles on a rotor to prevent settling and aggregation.

### Particle Size

According to previous work,<sup>85</sup> this grade of titanium dioxide prepared in this manner should have a weight average diameter of 0.15 micron and a fairly narrow size distribution with approximately 90% of the particles between 0.10 and 0.20 micron.

## APPENDIX IV

### CONCENTRATED ALUMINUM ANALYSIS

#### DESCRIPTION

The aluminum content of the stock solutions was determined gravimetrically by reacting the aluminum with 8-hydroxyquinoline to form an insoluble precipitate, aluminum oxinate.<sup>65</sup>

#### REAGENTS

1. 5% 8-hydroxyquinoline in 2 N acetic acid:

5.7 mL of glacial acetic acid was warmed to 75°C in a small beaker.

When at temperature, 2.5 g 8-hydroxyquinoline was added and stirred until dissolved. Then 40 mL of distilled water was immediately added. The solution was diluted to 50 mL in a volumetric flask.

2. 2 N ammonium acetate:

77.10 g of ammonium acetate was dissolved in distilled water and diluted to 500 mL.

#### PROCEDURE

In a 250 mL beaker, 2 mL of the aluminum stock solution was added to 50 mL of distilled water and warmed to 75°C. Next, 6 mL of the 5% 8-hydroxyquinoline solution was added. Then the 2N ammonium acetate was added until a precipitate started to form. Then an additional 20 mL of the 2N ammonium acetate was added to ensure precipitation. The solution was allowed to sit for one hour without heating. The precipitate was filtered on a medium porosity, tared fritted glass

filter crucible, washed with cold water, and then dried at 130°C. The precipitate formed was aluminum oxinate,  $\text{Al}(\text{C}_9\text{H}_6\text{ON})_3$ . A relative error of  $\pm 0.6\%$  was observed with this procedure.

## APPENDIX V

### CATIONIC POLYELECTROLYTE CHARACTERIZATION

#### MOLECULAR WEIGHT

The molecular weight of the cationic polyelectrolyte used in this study has been determined by sedimentation equilibrium and viscosity techniques. The sedimentation equilibrium technique uses ultracentrifugation. In this technique, a series of polymer solutions was prepared at various concentrations in 0.1N NaCl. The salt solution was used to screen the long range effects of the charged groups. Sedimentation equilibrium values, a measure of the apparent molecular weight, were then obtained for these solutions over a range of rotational speeds. These values were then extrapolated back to zero rotational speed and zero concentration to provide a measure of the molecular weight. A molecular weight of  $2.72 \times 10^6$  was obtained using this technique.<sup>67</sup>

In the viscosity technique, the reduced viscosity of a series of polymer solutions at various concentrations in 0.1N NaCl was determined using a Ubbelohde viscometer. Again, the salt solution was used to screen the long range effects caused by the charged groups. The reduced viscosities were extrapolated to zero concentration to yield the intrinsic viscosity. Using a relationship developed by Francois, *et al.*<sup>68</sup> for polyacrylamide in 0.1N NaCl, it was possible to relate the intrinsic viscosity to the molecular weight. This relationship is shown in Eq. (13).

$$[\eta] = 9.33 \times 10^{-3} M_w^{0.75}, \text{ mL/g} \quad (13)$$

An intrinsic viscosity of 710 cm<sup>3</sup>/g was determined for this polymer. This yields a calculated molecular weight of  $3.2 \times 10^6$ .<sup>3</sup>

Thus, the molecular weight of the cationic polyacrylamide used in this study was approximately three million.

#### NET CATIONIC CHARGE

The net cationic charge of the polyelectrolyte was determined using a colloid titration technique<sup>69</sup> as modified by Crow<sup>22</sup> and Brigham<sup>70</sup> for charge determination. The basic procedure and the principles involved are outlined in the experimental section "Cationic Polyelectrolyte".

The anionic polymer, potassium polyvinyl sulfate (PVSK), and the cationic dye, o-toluidine blue (OTB), were used as the reactants in this procedure. Specifically, 2.5 mL of OTB dye solution (12.7 mg/L) and 4.0 mL of PVSK solution (1.8 mg/L) were added to varying amounts (0-20 mL) of the polymer solution (3.0 mg/L). This was diluted to a total volume of 50 mL in a 60 mL polypropylene bottle. The absorbance of this solution was then measured at 625 nm in a 10.0 cm path length cylindrical cell using a Perkin-Elmer 320 spectrophotometer. A plot of absorbance versus the amount of polymer added results in a straight line. A calibration curve was obtained for OTB with various amounts of PVSK added. A plot of the absorbance versus the moles of PVSK equivalents also yields a straight line. By comparing the slopes of the two lines, the equivalent weight, E, of the polymer was calculated using Eq. (14).

$$E, \text{ g/equiv.} = \frac{\text{slope of calibration curve, abs. units/equiv.}}{\text{slope of polymer curve, abs. units/g}} \quad (14)$$

From the equivalent weight, E, the polymer charge density was calculated using Eq. (15).

$$E = \frac{A(1-X) + M(\bar{X})}{X} \quad (15)$$



where A is the uncharged monomer molecular weight (71 g/mole), M is the charged monomer molecular weight (269 g/mole), and X is the charge density. A net cationic charge density of  $4.2 \pm 0.1$  mole percent was obtained for the polymer.

In order to obtain reproducible measurements with this procedure, it was necessary to thoroughly clean the polypropylene sample bottles before each use. Soaking the polypropylene sample bottles in 2M NaOH at 85°C overnight followed by rinsing two times in methanol and three times in distilled water produced a clean, nonwetable surface on the sample bottles and led to reproducible measurements.

#### ANIONIC CHARGE

The anionic charge on the polymer was measured using potentiometric titration. As discussed in the experimental section "Cationic Polyelectrolyte", anionic charge on the polymer would probably be the result of polymer hydrolysis, which would form carboxylic acid groups. These groups, if present, should exhibit a buffering capacity at low pH's which could be measured by potentiometric titration.

Specifically, the potentiometric titrations were performed by dissolving various amounts of polymer in 50 mL of 0.01M HCl and titrating these solutions with 0.1M NaOH while measuring the pH. By comparing the titration curves of the polymer solutions to that of blank (50 mL of 0.01M HCl), the amount of buffering could be measured. Figure 52 shows the potentiometric titration curves for two concentrations of the polymer solution and a blank. At low pH's, the polymer solution curves and the blank coincide. This indicates no buffering; thus, no hydrolysis or anionic charge. However, at high pH's, some buffering was observed which is indicative of tertiary amines. This was not expected,

since the polymer is supposed to have quaternary amine groups. Since the retention experiments were performed at low pH, the tertiary amine groups would be cationically charged and should behave like the quaternary amine groups.

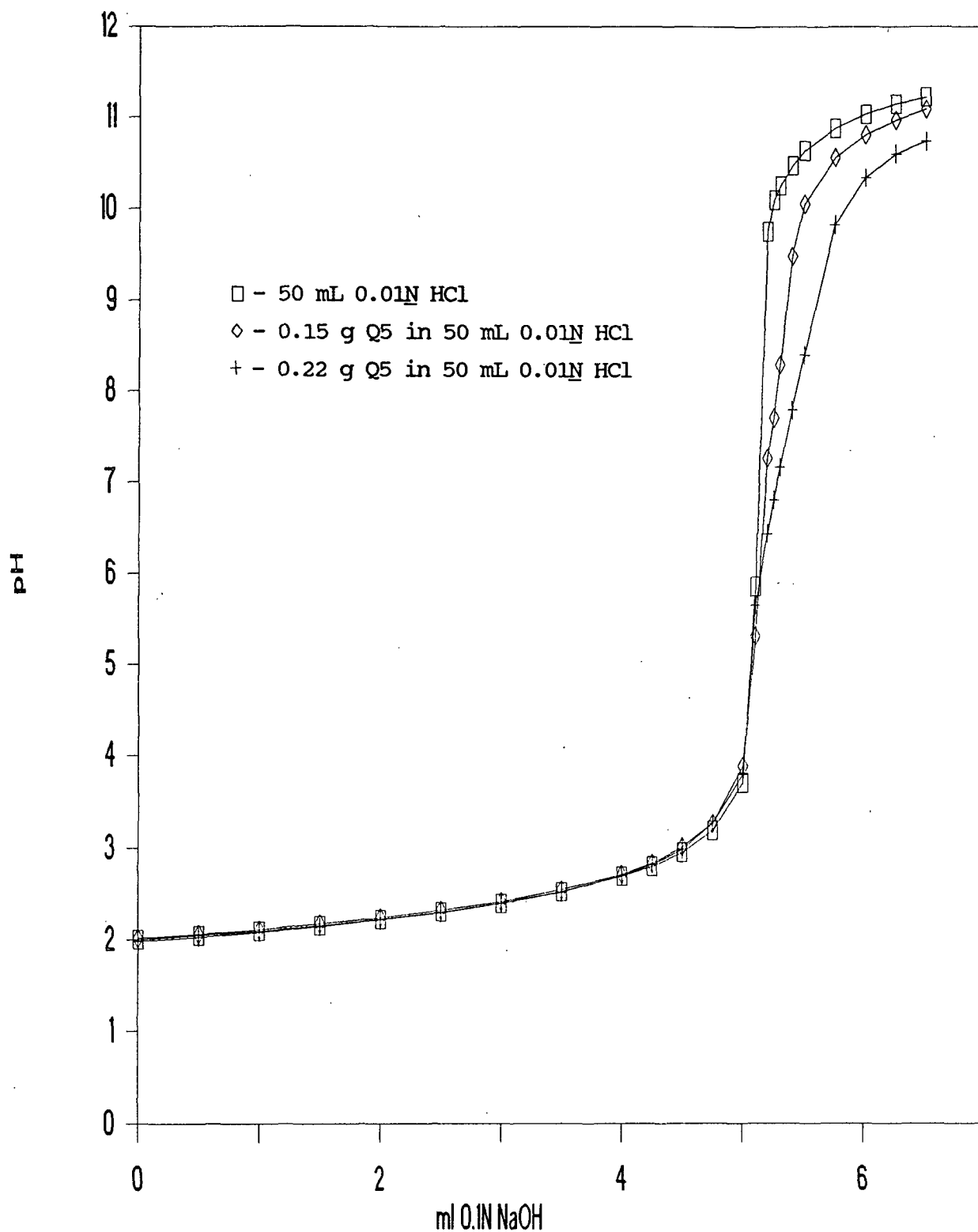


Figure 52. Potentiometric titration of polymer solutions.

## APPENDIX VI

### DILUTE ALUMINUM ANALYSIS

The aluminum concentration in the filtered drainage samples was measured by a procedure published by Fishman<sup>73</sup> as modified by Crow.<sup>22</sup> The procedure has been described in the experimental section "Aluminum Analysis".

Two reagents are needed for this procedure. The first reagent is a buffer solution containing 200 g of ammonium acetate plus 100 mL of concentrated ammonium hydroxide diluted to 1 L with distilled water. The second reagent is a chelating solution made by dissolving 10 g of 8-hydroxyquinoline in 25 mL of distilled water and then diluting to 1 L with distilled water.

The filtered drainage samples to be analyzed for aluminum concentration were placed in 50 mL volumetric flasks. When the retention run was conducted at  $10.0 \times 10^{-4} \text{M}$  Al, a 10 mL drainage sample was used. When the retention run was conducted at  $5.0 \times 10^{-4} \text{M}$  Al, a 15 mL drainage sample was used; and when the retention run was conducted at  $2.5 \times 10^{-4} \text{M}$  Al, a 25 mL drainage sample was used. One mL of the chelating solution and 10 mL of the buffer solution were added to each sample followed by shaking. Then, 5 mL of methyl isobutyl ketone was added and each sample was vigorously shaken for approximately 15 seconds. The aqueous and organic layers were then allowed to separate, and additional distilled water was added to bring the ketone layer up into the neck of the volumetric flasks. The samples were then allowed to sit for two days to reach equilibrium. Next, the absorbance of the ketone layer was measured at 450 nm in a 1-cm cuvet.

Aluminum concentrations were determined by comparison to standards prepared by the same procedure with solutions of known aluminum concentration. As shown

in Fig. 53, a linear relationship between absorbance and aluminum concentration is obtained for the standards.

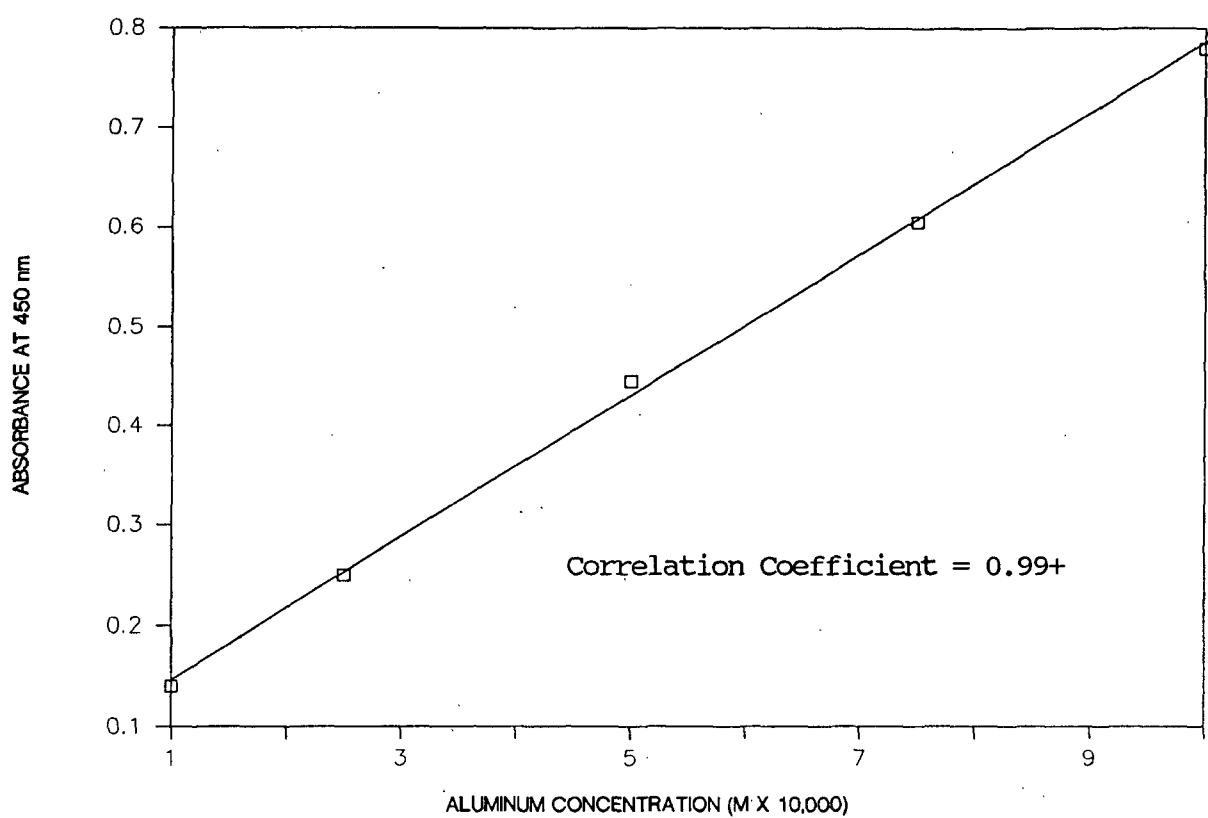


Figure 53. Aluminum concentration calibration curve.

## APPENDIX VII

### POLYMER ANALYSIS

The polymer concentration in the filtered drainage sample was determined by a modification of the colloid titration technique.<sup>69</sup> This procedure has been described in the experimental section "Polymer Analysis".

Three reagents were used in this procedure. The first reagent was an anionic polymer, potassium polyvinyl sulfate (PVSK), prepared at 2.0 mg/L. The second reagent was a cationic dye, o-toluidine blue (OTB), prepared at 12.4 mg/L. The third reagent was an aluminum complexing agent, maltol (3-hydroxy-2-methyl-4-pyrone), prepared at 0.12M.

For each retention run, two 5 mL aliquots of filtered drainage sample were analyzed for polymer concentration. The aliquots, with a polymer concentration less than 3.0 mg/L, were placed in disposable polypropylene test tubes. To these were added 0.625 mL of the PVSK solution, 0.625 mL of the OTB solution, and 0.50 mL of maltol. The test tubes were capped and mixed by inversion several times. After approximately 18 hours, the absorbances of these solutions were measured at 625 nm in a 10.0 mm cuvet.

Polymer concentrations were determined by comparison to standards prepared in the same manner. Standards were prepared at polymer concentrations ranging from 0 to 3 mg/L and aluminum concentrations ranging from 0 to  $1.0 \times 10^{-3}$  M Al. Figure 12 is a typical plot obtained using the standards. In order to determine the unknown polymer concentration, the aluminum concentration of the unknown must be known.

Standards were prepared for each set of retention experiments performed on the same day. This was because OTB slowly adsorbs onto the walls of the storage container resulting in different absorbance values each time the procedure is used. Also, the slope of the standard lines and the spacing at different aluminum concentrations slowly drift with time. Preparing a set of standards with each group of drainage samples was the best way to eliminate these variances.

In the polymer adsorption experiments, ultrafiltration was used to separate the unadsorbed polymer from the cationic surfactant. The ultrafiltration completely removed both the cationic surfactant and the aluminum salts from the polymer. Therefore, the polymer concentration measurements could be performed without the addition of maltol. In these experiments, ultrafiltration was performed on a 40 mL filtered drainage sample after which the polymer concentration was measured. The 40 mL sample was placed in a 60 mL polypropylene bottle and 4.0 mL of the PVSK solution and 2.5 mL OTB were added. The absorbance of this solution was then measured at 625 nm in a 10.0 cm path length, cylindrical spectrophotometric cell. Polymer concentrations were determined by comparing to standards of varying polymer concentration (0 to 3.0 mg/L) prepared in the same manner.

An important factor in obtaining good results was the use of clean polypropylene sample bottles or test tubes. Therefore, either new or freshly cleaned polypropylene sample bottles or test tubes were used. The method used for cleaning the polypropylene has been previously described in Appendix V under "Net Cationic Charge".

# APPENDIX VIII

## EXPERIMENTAL DATA: RETENTION EXPERIMENTS WITH ALUMINUM SALTS

Table 5. Aluminum chloride ( $2.5 \times 10^{-4}M$ ; 3.0 mg/L Q5).

pH	Aluminum Adsorption (mg/g cellulose)	Polymer Adsorption (mg/g cellulose)	Titanium Dioxide Retention (%)	Zeta Potential (mV)
4.0	0.15	0.48	18.0	21.0
4.0	0.15	0.49	17.5	21.9
4.4	0.24	0.45	10.4	35.1
4.4	0.26	0.45	9.6	33.2
4.55	0.31	0.37	9.1	36.2
4.55	0.29	0.38	9.0	37.6
4.7	0.61	0.35	4.5	39.5
4.7	0.60	0.35	4.2	40.5
5.0	1.46	0.17	5.0	42.0
5.0	1.49	0.16	4.8	44.0
5.5	2.01	0.12	2.5	40.0
5.5	1.99	0.10	2.3	41.0

Table 6. Aluminum chloride ( $5.0 \times 10^{-4}M$ ; 3.0 mg/L Q5).

pH	Aluminum Adsorption (mg/g cellulose)	Polymer Adsorption (mg/g cellulose)	Titanium Dioxide Retention (%)	Zeta Potential (mV)
4.0	0.20	0.38	14.2	22.9
4.0	0.20	0.38	15.0	23.9
4.4	0.61	0.32	10.3	34.5
4.4	0.59	0.34	10.8	35.9
4.55	1.05	0.24	6.7	37.0
4.55	1.04	0.21	5.8	37.0
4.7	2.23	0.13	4.3	42.5
4.7	2.26	0.15	5.6	41.0
5.0	3.45	0.10	2.6	46.0
5.0	3.48	0.10	3.3	44.0
5.5	4.00	0.07	3.4	42.0
5.5	4.01	0.05	3.1	42.0

Table 7. Aluminum chloride ( $10.0 \times 10^{-4}M$ ; 3.0 mg/L Q5).

pH	Aluminum Adsorption (mg/g cellulose)	Polymer Adsorption (mg/g cellulose)	Titanium Dioxide Retention (%)	Zeta Potential (mV)
4.0	0.31	0.27	11.8	28.3
4.0	0.33	0.25	10.8	27.9
4.2	0.43	0.19	10.1	30.4
4.2	0.41	0.20	9.8	29.2
4.4	1.10	0.07	6.9	33.5
4.4	1.06	0.03	9.1	33.0
4.55	2.55	0.05	5.0	39.5
4.55	2.47	0.06	3.0	40.5
4.7	4.37	0.04	3.2	44.0
4.7	4.38	0.04	3.2	44.0
5.0	6.41	0.05	3.2	47.0
5.0	6.44	0.04	3.0	48.0
5.5	7.18	0.03	3.0	43.0
5.5	7.21	0.04	3.4	41.0

Table 8. Aluminum sulfate ( $2.5 \times 10^{-4}M$ ; 3.0 mg/L Q5).

pH	Aluminum Adsorption (mg/g cellulose)	Polymer Adsorption (mg/g cellulose)	Titanium Dioxide Retention (%)	Zeta Potential (mV)
4.0	0.19	0.54	44.0	10.2
4.0	0.20	0.53	45.9	10.9
4.4	0.38	0.53	30.2	24.6
4.4	0.38	0.55	32.6	15.3
4.55	0.81	0.50	30.3	25.2
4.55	0.84	0.52	29.2	23.1
4.7	1.44	0.51	30.1	26.6
4.7	1.46	0.49	30.5	25.1
5.0	2.02	0.49	32.7	22.5
5.0	1.98	0.49	34.9	24.3
5.5	2.09	0.51	33.8	22.5
5.5	2.06	0.48	32.0	21.0



Table 9. Aluminum sulfate ( $5.0 \times 10^{-4}M$ ; 3.0 mg/L Q5).

pH	Aluminum Adsorption (mg/g cellulose)	Polymer Adsorption (mg/g cellulose)	Titanium Dioxide Retention (%)	Zeta Potential (mV)
4.0	0.29	0.45	40.8	12.1
4.0	0.27	0.44	39.3	10.5
4.4	0.66	0.43	30.0	23.1
4.4	0.68	0.43	26.0	18.3
4.55	2.14	0.44	24.3	27.3
4.55	2.12	0.40	25.7	25.3
4.7	3.22	0.44	24.8	29.6
4.7	3.22	0.43	25.2	29.4
5.0	3.88	0.51	28.9	28.7
5.0	3.91	0.49	30.0	29.5
5.5	4.17	0.54	34.6	26.1
5.5	4.18	0.56	33.5	25.3

Table 10. Aluminum sulfate ( $10.0 \times 10^{-4}M$ ; 3.0 mg/L Q5).

pH	Aluminum Adsorption (mg/g cellulose)	Polymer Adsorption (mg/g cellulose)	Titanium Dioxide Retention (%)	Zeta Potential (mV)
4.0	0.40	0.32	35.5	19.0
4.0	0.39	0.35	34.0	16.4
4.0	0.40	0.34	33.3	12.9
4.0	0.41	0.34	35.0	14.2
4.0	0.38	0.34	33.7	16.2
4.2	0.79	0.33	27.0	19.2
4.2	0.74	0.36	24.2	21.3
4.2	0.77	0.36	24.9	18.2
4.2	0.76	0.35	25.1	16.5
4.2	0.78	0.34	24.8	21.2
4.4	3.87	0.35	24.5	23.4
4.4	4.01	0.33	21.7	25.6
4.4	3.88	0.33	23.0	23.4
4.4	3.95	0.34	22.4	24.9
4.4	3.92	0.35	22.9	22.1
4.55	6.15	0.38	17.8	24.9
4.55	6.24	0.40	20.5	25.6
4.55	6.12	0.39	20.2	26.7
4.55	6.25	0.39	18.5	24.3
4.55	6.22	0.40	19.0	24.9
4.7	8.18	0.47	20.2	29.5
4.7	8.20	0.45	22.3	30.9
4.7	8.24	0.46	22.3	27.3
4.7	8.19	0.45	21.9	31.6
4.7	8.16	0.44	22.5	31.3
5.0	8.85	0.57	25.1	33.4
5.0	8.83	0.57	24.3	34.5
5.0	8.92	0.59	25.1	31.8
5.0	8.80	0.56	23.8	31.0
5.0	8.81	0.58	22.3	32.9
5.5	8.85	0.59	26.1	27.2
5.5	8.99	0.59	27.2	29.5
5.5	8.90	0.61	25.2	30.4
5.5	8.81	0.61	25.0	26.5
5.5	8.93	0.60	26.9	27.0

Table 11. Aluminum sulfate ( $10.0 \times 10^{-4}M$ ; 1.5 mg/L Q5).

pH	Aluminum Adsorption (mg/g cellulose)	Polymer Adsorption (mg/g cellulose)	Titanium Dioxide Retention (%)	Zeta Potential (mV)
4.0	0.39	0.24	19.8	15.1
4.0	0.38	0.24	18.5	11.6
4.2	0.74	0.26	13.1	19.7
4.2	0.76	0.23	13.4	18.1
4.4	3.83	0.19	12.8	24.1
4.4	3.95	0.21	12.4	22.0
4.55	6.17	0.26	9.8	25.6
4.55	6.28	0.24	10.2	24.3
4.7	7.92	0.30	11.2	31.2
4.7	8.10	0.31	12.1	28.7
5.0	8.70	0.38	12.4	30.1
5.0	8.82	0.35	12.7	28.9
5.5	8.90	0.41	14.5	28.2
5.5	8.95	0.39	15.3	25.4

APPENDIX IX

EXPERIMENTAL DATA: BASIC POLYMER ADSORPTION

Table 12. Equilibrium adsorption isotherm (0.01N KCl; 0.3% fiber consistency; pH 5.0; 120 min adsorption time).

Polymer Concentration		Polymer Adsorption (mg/g cellulose)	
mg/L	mg/g cellulose	fibers	fibers + titanium dioxide
1.5	0.5	0.45	0.46
1.5	0.5	0.45	0.48
3.0	1.0	0.91	0.95
3.0	1.0	0.92	0.94
7.5	2.5	2.11	2.33
7.5	2.5	2.15	2.34
15.0	5.0	3.62	4.28
15.0	5.0	3.63	4.23
30.0	10.0	7.25	7.55
30.0	10.0	7.30	7.57
60.0	20.0	7.98	8.29
60.0	20.0	7.94	8.21
120	40.0	8.00	8.35
120	40.0	8.03	8.40
240	80.0	8.25	8.60
240	80.0	8.30	8.60

Table 13. Variable polymer adsorption times (0.01N KCl; 3.0 mg/L Q5; 0.3% fiber consistency; 10% titanium dioxide addition based on OD fiber).

Time (min)	Polymer Adsorption (mg/L)		
	No Aluminum	10.0 x 10 <sup>-4</sup> M Aluminum Sulfate	
		pH 4.0	pH 5.5
0.25	1.80	1.08	1.53
0.50	1.86	1.50	1.71
1.0	2.18	1.85	1.98
3.0	2.52	2.25	2.40
10.0	2.70	2.67	2.69
30.0	2.79	2.75	2.73
60.0	2.84	2.79	2.84
120	2.85	2.82	2.85

APPENDIX X

EXPERIMENTAL DATA: RETENTION EXPERIMENTS WITHOUT ALUMINUM SALTS

Table 14. 3.0 mg/L polymer addition.

pH	Polymer Adsorption (mg/g cellulose)	Titanium Dioxide Retention (%)	Zeta Potential (mV)
4.0	0.58	49.9	-2.0
4.0	0.59	48.2	0.0
4.0	0.58	50.7	0.0
4.2	--	--	--
4.2	--	--	--
4.2	0.62	48.2	0.0
4.4	0.66	49.5	-3.1
4.4	0.66	50.8	-2.5
4.4	0.65	49.1	1.1
4.55	0.69	50.3	0.0
4.55	0.67	47.8	-0.5
4.55	0.68	48.3	0.0
4.7	0.67	48.3	+1.3
4.7	0.70	49.7	-0.8
4.7	0.67	49.0	+1.0
5.0	0.71	51.6	+0.5
5.0	0.68	48.9	0.0
5.0	0.70	49.8	0.0
5.5	0.68	48.3	-1.2
5.5	0.68	48.7	+2.0
5.5	0.70	48.0	-3.1

Table 15. 1.5 mg/L polymer addition.

pH	Polymer Adsorption (mg/g cellulose)	Titanium Dioxide Retention (%)	Zeta Potential (mV)
4.0	0.36	29.4	-3.4
4.0	0.37	28.1	-5.6
4.2	0.35	30.8	-6.7
4.2	0.37	29.9	-2.1
4.4	0.37	28.1	0.0
4.4	0.38	30.0	-4.2
4.55	0.36	27.5	-3.8
4.55	0.39	29.8	+0.8
4.7	0.39	31.2	-5.4
4.7	0.39	29.4	-2.1
5.0	0.38	29.5	0.0
5.0	0.39	30.4	-2.0
5.5	0.40	32.0	+1.3
5.5	0.39	30.3	-2.1

APPENDIX XI

EXPERIMENTAL DATA: RETENTION EXPERIMENTS WITH ADDITIONAL  
POLYMER ADSORPTION TIME

Table 16. Effect of increasing polymer adsorption time to 1 minute  
( $10.0 \times 10^{-4} \text{M}$  Al from aluminum sulfate; 3.0 mg/L Q5).

pH	Aluminum Adsorption (mg/g cellulose)	Polymer Adsorption (mg/g cellulose)	Titanium Dioxide Retention (%)	Zeta Potential (mV)
4.0	0.41	0.45	40.2	16.2
4.2	0.75	0.45	35.1	19.9
4.4	3.47	0.46	28.6	25.2
4.55	6.10	0.50	23.9	26.3
4.7	8.03	0.56	25.7	29.7
5.0	8.79	0.70	31.2	33.4
5.5	8.87	0.71	33.6	31.7



APPENDIX XII

EXPERIMENTAL DATA: RETENTION EXPERIMENTS WITH TYPICAL PARTICLE SIZE  
TITANIUM DIOXIDE

Table 17. Titanium dioxide retention when using a particle size typically used in papermaking systems ( $10.0 \times 10^{-4} \text{M}$  Al from aluminum sulfate; 3.0 mg/L Q5 polymer).

pH	Titanium Dioxide Retention (%)
4.0	43.2
4.0	44.5
4.2	34.2
4.2	38.7
4.4	30.2
4.4	32.4
4.55	30.0
4.55	27.1
4.7	33.3
4.7	32.0
5.0	37.8
5.0	38.7
5.5	39.1
5.5	39.6

APPENDIX XIII

EXPERIMENTAL DATA: RETENTION EXPERIMENTS AT VARIOUS DEGREES OF AGITATION

Table 18. Effect of agitation rate on titanium dioxide retention (3.0 mg/L Q5;  $10.0 \times 10^{-4} \text{M}$  Al from aluminum sulfate).

pH	Titanium Dioxide Retention (%)	
	500 rpm	1500 rpm
4.0	49.1	19.3
4.0	47.3	20.7
4.2	42.8	12.5
4.2	42.2	13.7
4.4	33.7	11.0
4.4	34.5	9.0
4.55	34.3	9.8
4.55	35.0	9.2
4.7	35.2	8.1
4.7	37.0	8.3
5.0	44.3	7.3
5.0	47.9	7.3
5.5	47.9	6.5
5.5	48.8	7.5

Table 19. Effect of agitation rate on titanium dioxide retention without polymer present ( $10.0 \times 10^{-4} \text{ M Al}$  from aluminum sulfate).

pH	Titanium Dioxide Retention (%)		
	500 rpm	1000 rpm	1500 rpm
4.0	15.3	12.0	7.9
4.2	--	5.9	--
4.4	--	3.2	--
4.55	5.1	2.8	0.7
4.7	--	0.0	--
5.0	--	2.0	--
5.5	4.3	2.1	1.1

APPENDIX XIV

EXPERIMENTAL DATA: ALUMINUM DESORPTION EXPERIMENTS

Table 20. Effect of aluminum desorption by acidification on polymer adsorption (3.0 mg/L Q5;  $10.0 \times 10^{-4}$  M Al from aluminum sulfate; 1.0 minute polymer adsorption time).

pH	Polymer Adsorption (mg/g cellulose)	
	Surfactant Alone	Surfactant + Acid
4.0	0.44	0.45
4.2	0.45	0.46
4.4	0.46	0.44
4.55	0.49	0.22
4.7	0.55	0.15
5.0	0.69	0.10
5.5	0.70	0.10