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The Effect of Aluminum Species and Cationic Starch
on Retention

By:

Kathleen R. Rutledge

A thesis submitted
in partial fulfillment of
the course requirements for
the Bachelor of Science Degree

Western Michigan University
Kalamazoo, Michigan
April 1989

Dr. Raymond Janes, Advisor

ABSTRACT

Aluminum sulfate, commonly known as alum, undergoes hydrolysis when placed in water and a variety of aluminum species are produced. The ionic charge of the species is dependent on pH. Research has shown that maximum adsorption occurs in the presence of $Al_8(OH)_{20}^{+4}$. Alum competes with other positively charged particles such as cationic starch for adsorption sites on fibers. Starch charge density and molecular weight govern the extent to which cationic starch adsorbs and bridges to fibers. This project is a study of the influence of cationic starch molecular weight and charge density, and aluminum species on retention.

The variables in the study were aluminum species (pH), starch molecular weight, and starch charge density. The pH levels were 3.5, 4.7, and 5.0 to produce the aluminum species Al^{+3} , $Al_8(OH)_{20}^{+4}$, and $Al(OH)_3$ respectively. Starch loadings that produced zero zeta potentials were determined for each set of conditions by using a zeta potential meter. The starch loadings were then used in Dynamic Britt Jar Retention Tests at their respective pH levels. A zeta potential of zero is believed to create conditions for optimum retention.

The results of this thesis suggested that maximum retention may occur near the pH of 4.7, that is, in the presence of $Al_8(OH)_{20}^{+4}$. In addition, it appeared that as pH increased the bridging mechanism became the dominant mechanism in producing optimum retention. Also, in the absence of alum, high molecular weight starch appeared to be necessary for obtaining retention of acceptable levels. This suggested again the importance of the bridging mechanism.

The key outcome of this study was that the prediction made by Crow and Stratton was supported, that is, as aluminum adsorption increases the starch configuration changes to one of loops and tails. The configuration thereby creates conditions more suitable for bridging and therefore, increased retention.

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INTRODUCTION

High first pass retention is a key factor in producing high quality paper at an attractive price. Increased ash content, paper machine efficiency, and production rate are significant cost saving results of increased fines and filler retention. Common problems resulting from low retention levels include increased fines content in the headbox, stuff-box, and wet-end circulation water. This buildup of fines retards sheet drainage thus limiting production rate and produces a poorly formed sheet with tendencies for two sidedness and variations in basis weight and ash. Long term retention problems lead to slime and deposit formation on the paper machine, which is then combated with costly chemicals and machine downtime (1). A contaminated paper machine system may also create a higher pollution load for the waste water treatment process, again producing unnecessary costs for the paper mill (2).

Many factors contribute to first pass retention including paper machine conditions and stock characteristics. On the microscopic level retention is believed to be a function of two basic mechanisms, filtration and adsorption (3). Filtration is responsible for retaining large particles while adsorption causes flocculation of colloidal particles in the stock by overcoming the negative electrostatic repulsive forces comprising the electrical double layers of the particles. An understanding of the basic mechanisms of

retention provide the papermaker with a foundation upon which to begin formulating a strategy to increase retention and in turn produce higher quality paper. This literature review discusses the basic concepts of retention, including the influences of the commonly used wet-end additives, alum (aluminum sulphate) and cationic starch.

THE MECHANISMS OF RETENTION

There are basically two mechanisms of retention: filtration and adsorption.

Filtration

The process of filtration describes the mechanical entanglement of fibers. These entangled fibers create a porous mat through which fines and filler pass if their dimensions are smaller than that of the drainage channels in the web and wire. The fines and fillers larger than the drainage channels are retained (4). Figure 1 demonstrates how the filtration and adsorption mechanisms are a function of particle size.

Filtration is affected by hydrodynamic forces created by foils and table rolls on the fourdrinier table. Larger particles experience greater hydrodynamic forces than do smaller particles. However, research shows that because larger particles have more points of attachment between fine particles and fibers the larger particles are affected less

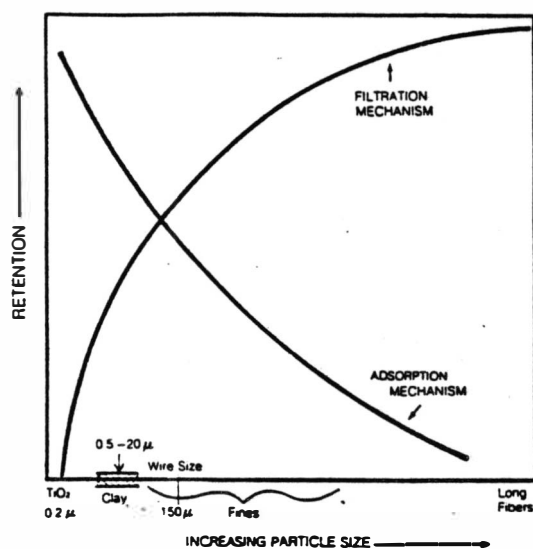


Figure 1. Effect of particle size on retention (3)

by the hydrodynamic forces than smaller particles. The forces also decrease retention because shear forces degrade retention aids physically and break bonds that retention aids form between fines and fibers (4).

Adsorption

The primary mechanism of fine and filler retention is believed to be adsorption. This mechanism is especially important in the retention of smaller particles. For titanium dioxide with an average particle size of 0.2 microns, it is estimated that 98% of retention is due to adsorption (3).

Almost all particles become charged when immersed in water, due to ionization of carboxyl groups or sulfonic acid groups on surfaces, specific adsorption of ions from solution, or isomorphous lattice substitution, as stated by Kaunonen and Springer (5). These charged particles attract a large number of counter ions. The ions immediately adjacent to the particle or surface are strongly attracted in a thin

layer called the Stern layer. The next layer, the Gouy-Chapman layer, increases in thickness and decreases in counter ion concentration as the distance from the particle increases. The outermost layer is the bulk of the solution and it contains an equal number of anions and cations (3,6). As a whole the system is known as the electric double layer. The electrical potential between the shear plane of the dense layer of attracted counter ions and the bulk of the system defines zeta potential (3,6,7). A pictorial description of zeta potential and electrical double layers is presented in Figure 2.

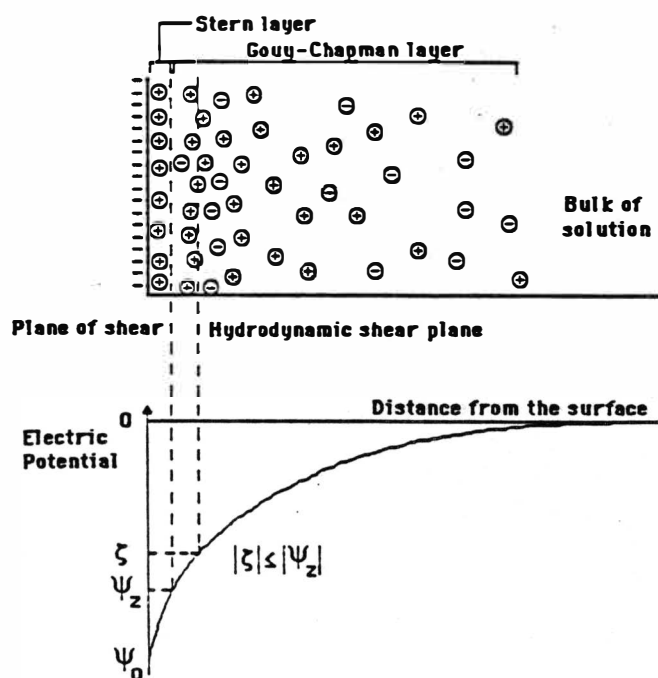


Figure 2. Electrical double layer and zeta potential (5)

Cellulose fibers and titanium dioxide characteristically are negatively charged when dispersed in water. Their like charges produce repulsive forces that prevent coagulation and keep particle floc dimensions to a minimum (6). The repeling

forces are long-range electrostatic or steric forces (8). The greater the charge, the larger the repulsive force and lower the tendency toward flocculation. A small degree of flocculation is needed to prevent fines and filler from being forced out of the sheet. Creation of attractive forces (short-range London Van der Waals forces) through introduction of cationic wet-end additives such as aqueous aluminum sulfate (alum), cationic starch, or positively charged polymers will reduce the forces of repulsion, thus decreasing zeta potential. Attractive forces allow large polymers to bridge fibers more effectively, therefore initiating flocculation (6,8). It is believed that maximum retention occurs when the zeta potential is near zero (3).

The theory of retention is derived from the classical DLVO theory (8). The theory is a quantitative explanation of how a lyophobic colloid undergoes flocculation upon the addition of an indifferent electrolyte. It explains that a higher potential at the surface of the particle will produce a higher potential throughout the double layer and therefore a larger repulsion between the particles (see Figure 3). Also, a lower concentration of indifferent electrolyte will cause the energy potential drop-off to be farther from the particle surface. Finally, the DLVO theory points out that greater attraction between macroscopic particles arises from a larger Hamaker constant (7).

A form of adsorption can be described as an ion exchange mechanism. This exchange, when applied to the formation of

paper, is the process of bridging and binding a polymer to a solid such as adsorbing a cationic aluminum species or starch onto cellulosic fiber. Adsorption levels are dependent upon the availability of binding sites and the binding capabilities of a polymer. Binding sites are the ionizable groups on the surface of fiber and filler particles. The ability of a polymer to bind is governed by its molecular weight, charge density (9) and configuration.

Because there is a potential for competition between solution components for adsorption sites, an understanding of the chemical and physical properties of the components is very beneficial in the attempt to understand the adsorption phenomenon. The next sections discuss the chemical and physical characteristics of aqueous aluminum sulfate and cationic starch, both of which are believed to compete for adsorption sites.

Aqueous Aluminum Sulfate Chemistry

Aluminum sulfate, $\text{Al}_2(\text{SO}_4)_3 \cdot (14-18)\text{H}_2\text{O}$, commonly known as alum, is one of the most widely used chemicals in the paper industry. Applications of alum in the paper industry range from raw water treatment to wet strength catalysis to recovery of solids in save-alls. Some of the most common reasons for using alum include rosin size precipitation, colloidal retention, drainage, and paper machine draw stabilization in low pH systems, along with ASA size retention in high pH systems.

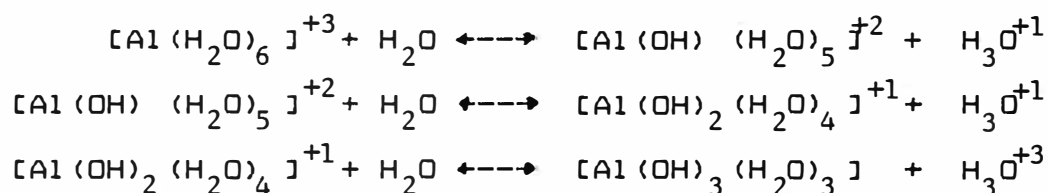
Although alum seems to be a simple salt, in water it can be found in forms such as a trivalent aluminum ion, alumina polymer, aluminum hydroxide precipitate, and anionic aluminate, depending upon the pH of the system (10).

Dissociation

In the crystalline form alum contains about 14 molecules of H_2O with each cation holding 6 molecules. The remaining water molecules are distributed around the anions in the lattice. Alum readily dissolves in water (11). Dissociation involving separation of oppositely charged ions occurs when alum is mixed with water. These ions then no longer influence each other. The degree of dissociation is a function of solute concentration and is assumed complete at 15 ppm or less when based on water content. The product of dissociation is hexahydrated aluminum, $[Al(OH)_6]^{+3}$, a very weak base.

Hydrolysis

When the product of dissociation $[Al(OH)_6]^{+3}$ undergoes hydrolysis it proceeds through three stepwise reactions as shown below (11). In each step a hydroxyl ion replaces a water molecule, and a hydrogen molecule is released.



As hydrolysis proceeds the cationic charge of the aluminum ion decreases until the formation of non-ionic, insoluble $\text{Al}(\text{OH})_3$ occurs (12).

Throughout this process a variety of alumina complexes are formed. Figure 3 shows the predominant alumina species over the pH range 4 - 11. These forms include; the soluble alumina ion (Al^{+3}), soluble alumina polymer ($[\text{Al}_8(\text{OH})_{20}]^{+4}$), insoluble aluminum hydroxide ($\text{Al}(\text{OH})_3$), and soluble aluminate ion ($[\text{Al}(\text{OH})_4]^{-1}$) (10). As the graph demonstrates, more than one chemical form of alumina can be present in the aqueous solution at the same pH. Each form has properties that will affect paper machine systems differently. It is important to know which species of alumina are present so that optimum papermaking conditions will prevail. However, it is important to realize that a shift in alum concentration may change the pH range in which given alumina ions are obtained. Also, a large increase in solution temperature will suppress the cationic charge of the alumina similar to the effect of high alum concentration on cationic charge(13).

Soluble Alumina Ion, Al^{+3} Below pH 3 the simple trivalent cation is the only species present in the water medium. The degree of hydrolysis of Al^{+3} in pure H_2O is limited by a change in pH which is the increase in hydrogen ion level. This level is set by hydrolysis reactions and sulfate ion interference. Sulfate ions may replace water and/or hydroxyl groups of the cation to form a more stable

sulfate complex. This inactivation process prohibits normal

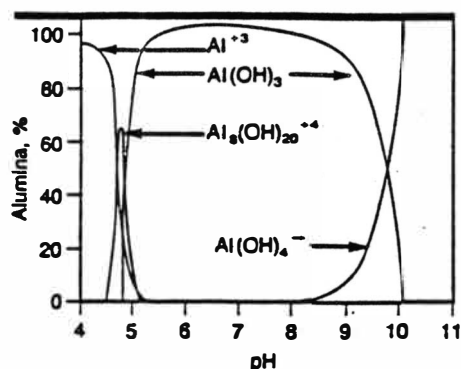
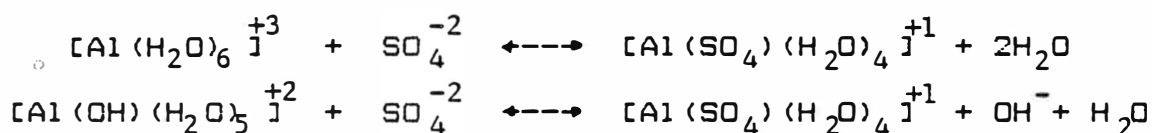


Figure 3. Predominant Alumina Forms (pH 4-11) (10)

aluminum or sulfate behavior. As shown in the stoichiometric equations of inactivation, the hydrogen concentration is reduced, thus creating a buffering action at equili-



rium (11). Figure 4 graphically demonstrates how a highly buffered system is resistant to pH upsets or stock variability.

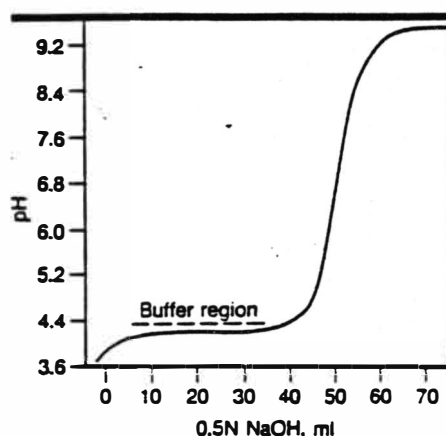


Figure 4. Buffering - An Effect of Alum (10)

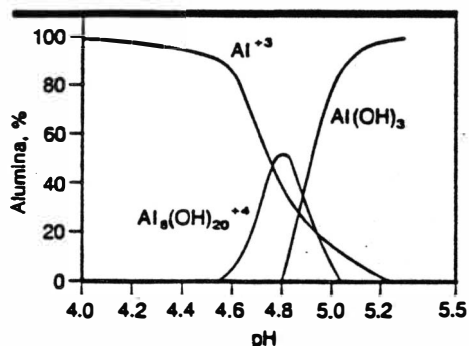


Figure 5. Predominant Alumina Forms (pH 4.0-5.5) (10)

A focused look at Figure 3 at pH 4.0 - 5.5, a common operating range for acidic paper machines, shows that in the buffer zone (generally pH 3.8 - 4.2) the predominant alumina species is soluble Al^{+3} (10). The high cationic charge produces a long-range attractive force. However, due to the lack of hydroxyl groups that promote hydrogen bonding, adsorption is weak. Only 5-10% of the trivalent ion is adsorbed onto fibers. The remaining percentage stays in the diffuse portion of the double layer (14).

Above pH 3 hydrolysis (the replacement of a water ligand with a hydroxide group) begins and AlOH^{+2} and other hydroxo-aluminum complexes form (15).

Soluble Alumina Polymer, $[\text{Al}_8(\text{OH})_{20}]^{+4}$ Between the pH values of 4.5 and 5.0 the most reactive form of alumina, $[\text{Al}_8(\text{OH})_{20}]^{+4}$, exists. Here hydrated hydroxy-aluminum ions dimerize and polymerize by the process of olation to produce

$[Al_8(OH)_{20}]^{+4}$, which is often referred to as a polynuclear species. Olation is the mechanism of an aluminum atom attaching to a hydroxyl group. The molecules are held tightly together by other aluminum atoms. Each aluminum atom gives up a bound H_2O molecule to form a Werner complex illustrated in Figure 6 (11). In the narrow pH range of 4.5 - 5.0 the polynuclear species is in equilibrium with the precipitate $Al(OH)_3$, therefore maximum concentration of

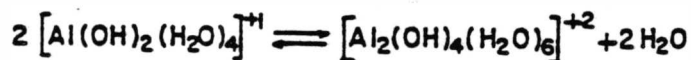
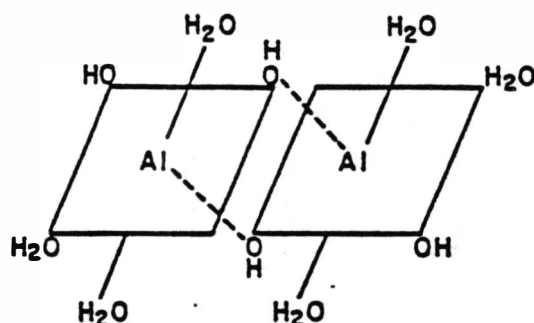


Figure 6. An Example of Olation Bonding (11)

$[Al_8(OH)_{20}]^{+4}$ occurs at the pH_p (pH of precipitation) (15). It has also been suggested that thermodynamically stable species in this range include Al_2 , Al_3 , and Al_{13} (12).

A sudden increase in pH, such as at a fresh water addition point, causes soluble Al^{+3} ions to change quickly to reactive alumina polymers and alumina hydroxide, $Al(OH)_3$.

The alumina polymer species possess a high ratio of hydroxyl groups which allow for strong adsorption to particles. The cationic charge contributes long-range

attraction with anionic cellulosic fiber together with charge neutralization. For these reasons the pH range of 4.0-5.0 is believed to be the most efficient range for fine and titanium dioxide retention during sheet formation (14).

Insoluble Aluminum Hydroxide, $\text{Al}(\text{OH})_3$ By viewing Figure 5 one can see that the pH 4.7 - 4.8 is the onset of insoluble, gelatinous aluminum hydroxide, $\text{Al}(\text{OH})_3$, formation. The pH of precipitation (pHp) at a given concentration occurs as shown in Table 2. The complex dominates in the pH 5 - 9. Because this insoluble alumina species is a very strong adsorber to stock components, it can be used in alkaline systems at low feed rates to decrease furnish charges. High feed rates promote aluminum hydroxide precipitation and deposit formation on the machine (10,14).

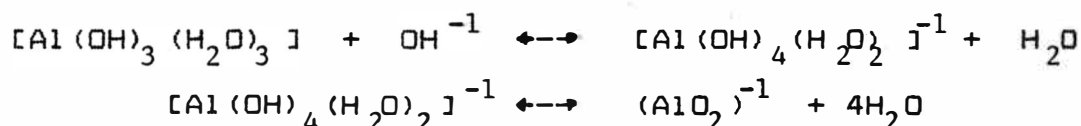
Table 1. Effect of alum concentration on pHp (16)

Aluminum Concentration, M	$\text{Al}_2(\text{SO}_4)_3$ pHp
1.0×10^{-4}	4.65
2.5×10^{-4}	4.55
5.0×10^{-4}	4.45
1.0×10^{-3}	4.26

As the empirical formula shows, aluminum hydroxide is non-ionic. This lack of cationic charge greatly reduces the ability of the precipitate to neutralize charges on fiber and

filler (14). However, a slight cationic charge may form due to the adsorption of aluminum hydrolysis products on the surface of $\text{Al}(\text{OH})_3$. This charge decreases as pH rises from 4.8 to 9.0 (10).

Soluble Aluminate, $[\text{Al}(\text{OH})_4]^{-1}$ Above pH 10, alumina is entirely in the soluble anionic form $[\text{Al}(\text{OH})_4]^{-1}$. Because this species contributes additional anionic components to the anionic fibers, the magnitude of the repulsive forces increases and the solution loses its coagulating efficiency. For this reason in the presence of alum, the pH range of 10 and greater is avoided. Aluminate is formed by the following hydroxylation reactions (11).



Starch

One of the most useful additives of the paper industry is cationic starch. When used in the wet end of the paper machine system it improves sizing efficiency, sheet strength, and retention. Cationic starch is a derivative of starch, a naturally occurring polysaccharide found in all vegetable plants (17).

Chemically, starches are similar to cellulose in that they are both polymers made up of anhydro-glucose ($\text{C}_6\text{H}_{10}\text{O}_5$) repeating units. However, in the cellulose polymer every second unit is rotated 180 degrees unlike the starch polymer in which there is no rotation. This characteristic of starch

exposes multiple sites for hydrogen to bond with cellulose and wet-end additives (18). Figure 7 demonstrates the differences in structures. The twisted configuration of glucose units in cellulose aids in molecular alignment with other similar chains to form crystallites. Because these microcrystalline regions are poorly soluble, cellulose is overall much less soluble than starch (19).

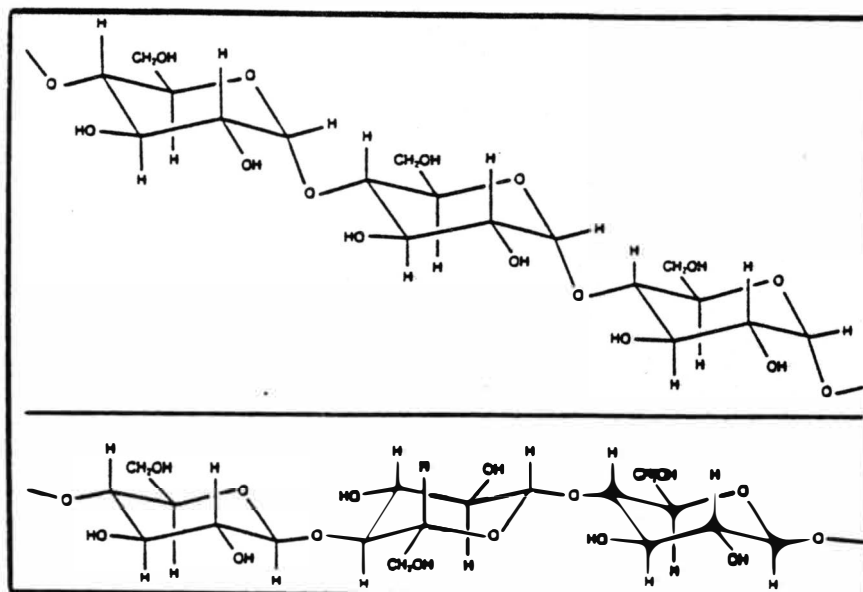


Figure 7. Starch (top) and cellulose (bottom) molecular structures (18)

All starches are composed of two fractions: amylose and amylopectin. A summary of characteristics for the two fractions is given in Table 2.

Amylose

Solid state amylose is an isotactic linear polymer consisting of 100-10,000 (1-4) linked α -D-glucopyranosyl units that may be helical in nature. This fraction has a graded series of molecular sizes including a mix of linear

and slightly branched chains and a few very long branches. Proportions of molecular sizes vary with the starch source and plant maturity (19).

Table 2. Properties of the Amylose and Amylopectin (19)

<i>Property</i>	<i>Amylose</i>	<i>Amylopectin</i>
General structure	Essentially linear	Branched
Color with iodine	Dark blue	Purple
λ_{max} of iodine complex	~650 nm	~540 nm
Iodine affinity	19-20%	<1%
Average chain length (glucose residues)	100-10,000	20-30
Degree of polymerization (glucose residues)	100-10,000	10,000-100,000
Solubility in water	Variable	Soluble
Stability in aqueous solution	Retrogrades	Stable
Conversion to maltose by crystalline β -amylase	~70%	~55%

Research proposes three configurations for amylose: helical, interrupted helix, and random coil (Figure 8). However, it has been found that in an aqueous solution at room temperature, steric factors hinder rotation about the D-glucosidic bonds and only the helical and interrupted helix structures may exist. The random coil structure will exist in a 'good' solvent or when the molecular weight of the chain is not in the range of 65,000 - 160,000 (19).

The linear chains of amylose consisting of α -D-(1-4) glucopyranosyl units create a less extended configuration than cellulose, therefore, amylose is poorly crystallized. The low level of crystallization allows for increased solubility (19).

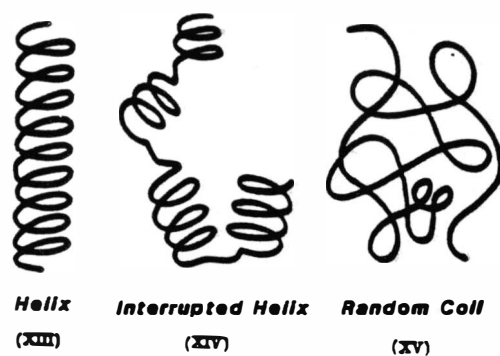


Figure 8. Proposed Models for Amylose

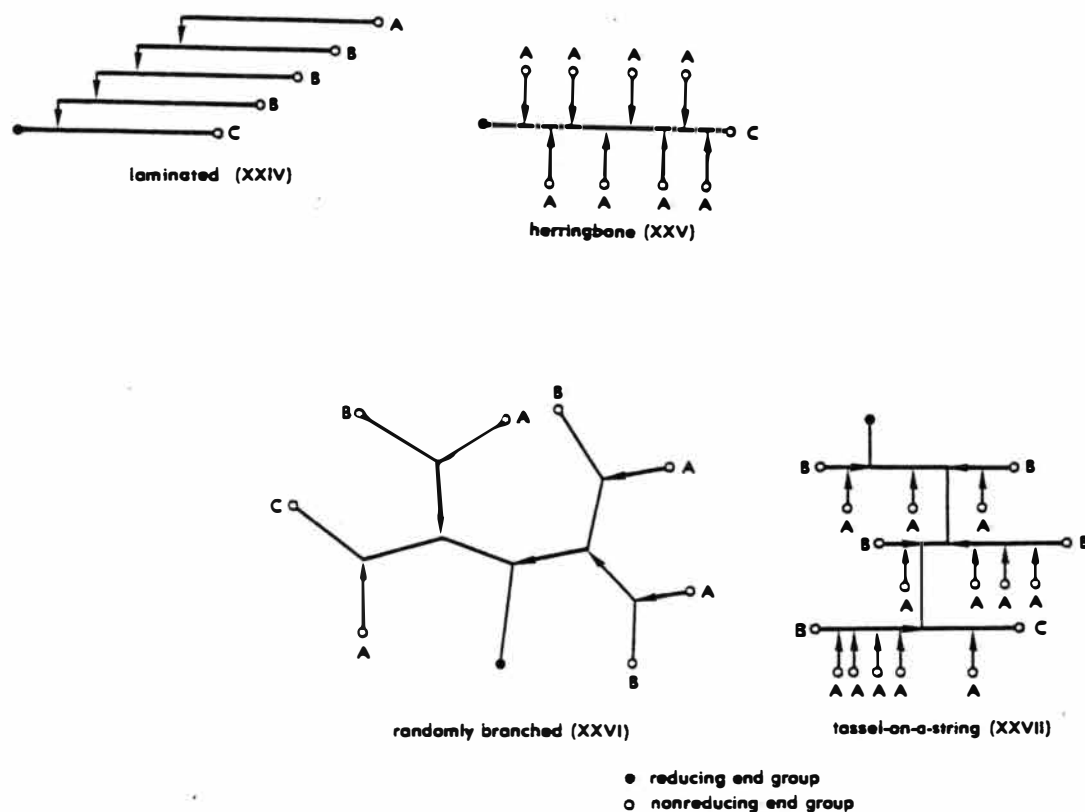


Figure 9. Proposed Models for Amylopectin

Amylopectin

Amylopectin is a branched, high molecular weight (10,000-100,000 D.P.) α -D-glucopyranosyl polymer linked by (1-4) bonds. Branches of amylopectin occur at O-6 at an average of one branch for every 18 to 28 α -D-glucopyranosyl units (18,19). For every branch point there is a branch end. Four amylopectin structure models are commonly proposed by researchers. The models include laminated, herringbone, randomly branched, and tassel-on-a-string (Figure 9).

The branched structure of amylopectin makes crystallization very difficult and, hence provides greater solution stability than is possessed by amylose. Crystallization may occur with low temperatures and time or very high amylopectin concentration. However, even a pure amylopectin fraction contains crystalline regions (19), although these may be dissolved easily by heating in water.

Molecules within a starch granule are hydrogen bonded, therefore, when submersed in water or any hydrogen bond-breaking solvent, the granules swell and disperse (19). Heating and agitation are necessary to completely solubilize starch. This process uncoils the molecules, making them more reactive to other solution components (18). Like cellulose fibers, starch molecules possess an anionic charge in water. Because the forces of these two components repel each other, retention during web formation is difficult. To overcome this problem cationic starch was developed (17).

Cationic Starch

Starch modified by grafting quarternary ammonium onto the starch molecule is one type of cationic starch (Figure 10). Other compounds may be grafted onto starch to vary the cationic charge and suitably fit the papermaker's needs. Starch derivatives that carry a fully substituted

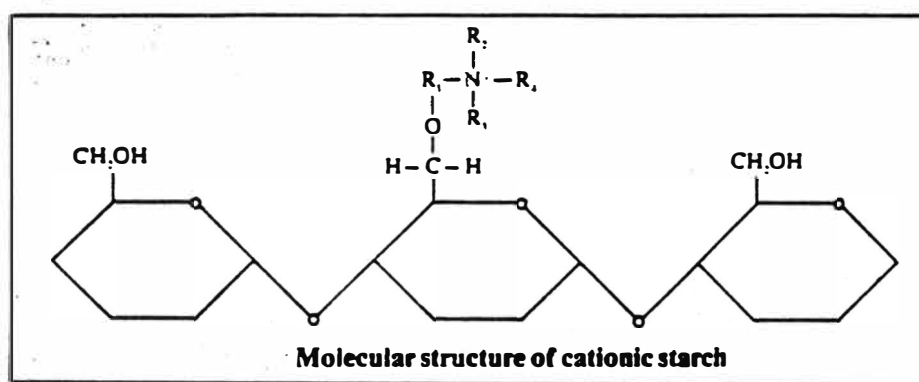


Figure 10. Molecular structure of cationic starch (17)

radical, such as quaternary ammonium, carry a formal positive charge over the entire pH range when the radicals are saturated with groups other than hydrogen. This type of modified starch becomes a cationic polyelectrolyte when dispersed in water (20).

In a stock solution the positively charged starch molecules are attracted to cellulosic fibers where they form both electrostatic and hydrogen bonds (17). The electrochemical affinity of cationic starch for negatively charged cellulose fibers, especially fines, results in nearly total irreversible adsorption of the modified starch. The starch

derivative behaves as an ionic bridge between fibers and fillers. The preferential adsorption of cationic starch onto fines results in increased fine retention (19).

The most important parameters which govern the performance of cationic starch as a retention aid are starch molecular weight and charge density or degree of substitution. Charge density strongly governs the way in which starch molecules attach to the surface of particles. Starches having a high degree of substitution adsorb in a relatively collapsed formation. The result is a reaction with counter ions on near-by particles to produce flocculation. A lower charge density allows the starch to adsorb in a loose manner and bridge between electrical layers of the particles in solution (9).

Molecular weight properties of cationic starch also influence adsorption. A short-chain polymer is able to adsorb in a flat configuration on a solid surface. A high-molecular-weight starch tends to adsorb with segments on a solid surface with loops and tangled ends sticking out into solution. Short-chain polymers with high charge density are often used to neutralize the charge of interfering substances, such as aluminum complexes and starches, to tie up dissolved interfering particles, and to control the number of binding sites available to the long-chain polymers (8).

The effects of cationic starch on retention vary with addition rate and are believed to produce maximum retention and drainage at addition rates between 0.3 and 0.5 percent.

Higher addition rates will cause retention to decline (17), although specific grades of paper may require other levels of addition. For example, Springer, Chandrasekaran, and Wegner (21) found that fines retention during paperboard formation improved at 1% addition and higher addition levels adversely affected retention.

Other cationic components within the stock solution, such as alum, are believed to compete with cationic starch for adsorption sites on cellulosic fibers (22). The next section of this literature review discusses the behavior and results that occur in a system of both aluminum and a cationic polyelectrolyte.

Cationic Polyelectrolytes and Adsorption

Aluminum Species Adsorption

As discussed previously and reaffirmed by Crow and Stratton's study (22), aluminum adsorption onto cellulose fibers occurs in a predictable manner directly related to the aqueous chemistry of the aluminum ion, especially pH and aluminum concentration (23).

Aluminum adsorption is low below the pHp where only the soluble aluminum species exists, and high above the pHp where the fibers became positively charged due to a layer of adsorbed aluminum precipitate (Figure 11). Aluminum precipitate is positively charged up to the pH 8.5-9.0 due to the adsorption of cationic aluminum species, however, the sulfate ion originating from aluminum sulfate reduces the cationic charge of the precipitate. Because the charge is

suppressed, the repulsion forces between adsorbed and unadsorbed aluminum are lessened and greater adsorption results (22,24). This is also evident as the concentration of aluminum is increased (Figure 11).

Polymer Adsorption

The adsorption of a polymer is dependent upon cation valence and concentration (22) and is independent of pH in the absence of aluminum.

Crow and Stratton's (22) research showed that throughout the entire pH range, polymer adsorption increases with an increase in polymer concentration at constant aluminum sulphate addition (Figure 12). However, as the charge on the fibers is neutralized, electrostatic attraction between the fibers and polymers is reduced, therefore, the fraction of polymer adsorbed decreases. This trend can be observed by a plot of zeta potential as in Figure 13. Crow and Stratton also concluded that the polymer adsorption rate is reduced throughout the pH range in the presence of aluminum salts.

Aluminum Species and Polymer Adsorption

Proximire and Stratton (24) state that at low pH values an increase in aluminum concentrations results in a reduction of polymer adsorption. This suggests that competition between cationic components for adsorption sites does occur as would be expected in an ion exchange adsorption method.

At high pH values where the aluminum adsorbs as a precipitate, polymer adsorption generally increases (Figure 14). Proximire and Stratton (24) propose that the

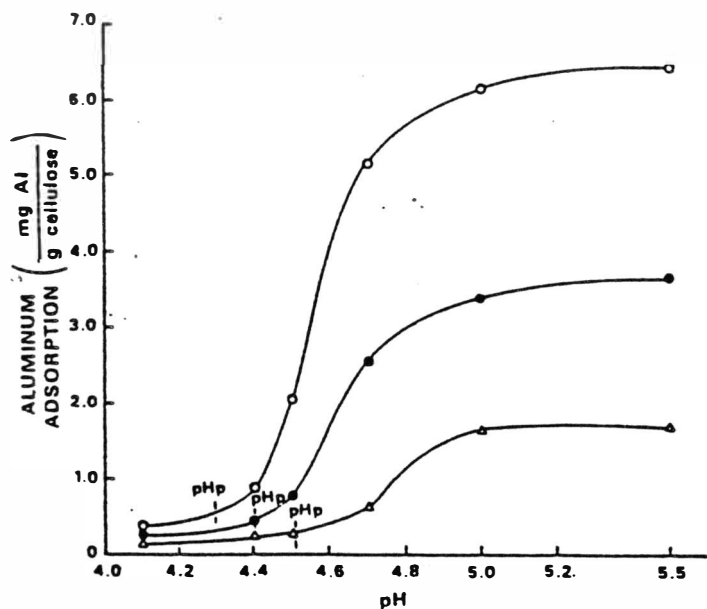


Fig. 11 - Aluminum adsorption as a function of pH and Al concentration

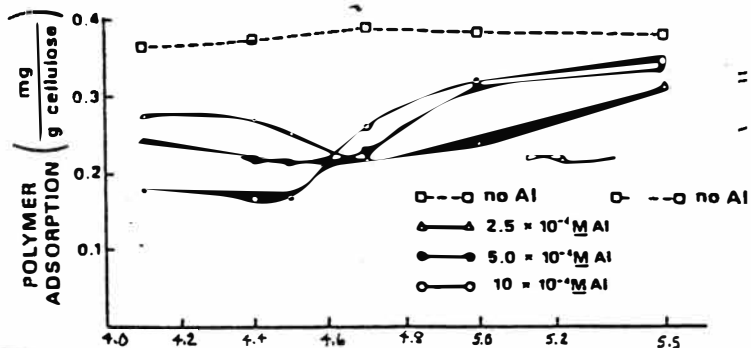


Fig. 12 - Polymer Adsorption as a function of pH and Al concentration

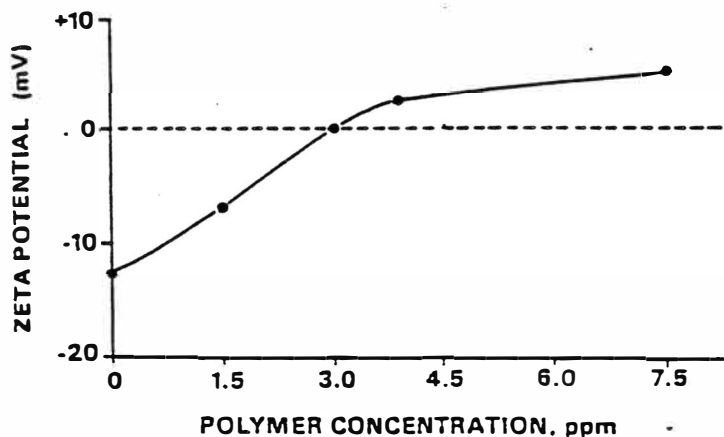


Fig. 13 - Zeta potential of fibers as a function of polymer addition in the absence of Al

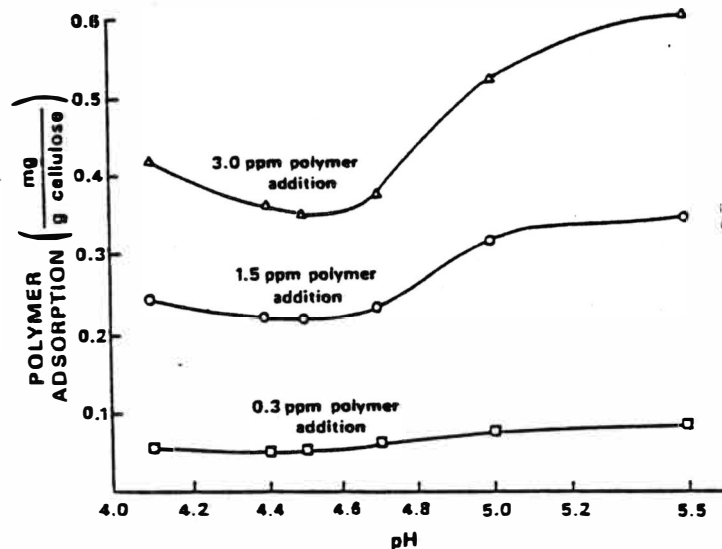


Fig. 14 - Polymer Adsorption as a function of pH and concentration

sulfate ions in the aluminum precipitate must act as additional adsorption sites for the polymer, therefore, the polymer is most likely adsorbing to the precipitate instead of directly to the fiber. It is important to note that these polymer to precipitate bonds are weaker and more susceptible to shear than the polymer to fiber bonds found in the lower pH range (24).

Adsorption and Retention

A study by Proximire and Stratton (24) show that filler retention generally follows polymer adsorption trends. As seen in Figure 15, at low pH values filler retention is good as a result of a moderate amount of directly adsorbed polymer and low zeta potentials. At high pH values, the filler retention is lower than that at low pH values because of positive zeta potentials and weaker polymer bonds, even though polymer adsorption is higher.

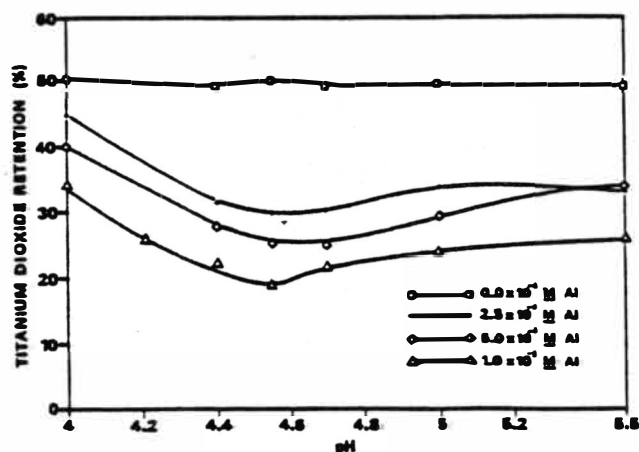


Figure 15. The effect of pH and aluminum concentration on titanium dioxide retention (24)

Based on their research, Crow and Stratton (22) predict improved retention as aluminum adsorption lessens the negative charge on fibers and decreases polymer-fiber attraction, thus changing the configuration of adsorbed polymer to longer loops and tails that enable better bridging. Above the pHp aluminum sulfate has only a small detrimental effect on polymer adsorption, but without knowing the configuration of the polymer on the surface of the adsorbed aluminum precipitate layer, Stratton and Crow state that it is impossible to predict retention levels under these conditions.

Electrokinetic theory suggests that overall retention should improve near zero zeta potential (isoelectric point) as this is where optimum coagulation of charged particles should occur (6).

Experimental Design

Problem Statement

The predictions presented by Crow and Stratton (22) and the electrokinetic theory together with a strong understanding of aqueous aluminum sulfate chemistry lay the foundation for further research of the effects of aluminum species and polymer characteristics on retention of fines and filler.

It is believed that adsorption is the primary mechanism in retention of fines and filler during web formation (8). Several researchers have shown that aluminum adsorption is a function of aluminum species and concentration where polymer

adsorption is a function of molecular weight and charge density. In an aqueous system the components compete for adsorption sites, and Crow and Stratton (22) state that aluminum salts are detrimental to polymer adsorption throughout the entire pH range.

Proximire (24) showed that titanium dioxide retention generally followed the polymer adsorption curve for all pH levels. From their studies, Proximire and Stratton could only predict that at low pH values the polymer-fiber attraction would allow the polymer to efficiently bridge particles and improve retention. Both of these studies were done with a low-charge density, high molecular polymer. The electro-kinetic theory also suggests that retention should be optimum at zero zeta potential since this is where optimum coagulation occurs (6).

With this background in mind, the objectives of the thesis were to study retention as a function of aluminum species (pH), polymer molecular weight, polymer charge density, and zeta potential and to test Proximire and Stratton's prediction on retention as stated above. The results of this project provide a better understanding of the relationship between the adsorption of aluminum species and polymer on cellulose fibers and retention, and also of one of the many phenomena of papermaking.

Experimental Approach

The experiment was designed to simulate a simple papermaking system at optimum retention conditions (near zero

zeta potential). First, addition levels of cationic starch that produce zero zeta potentials at a constant aluminum sulfate addition were determined. Zeta potentials were measured by a Laser Zee (tm) Model 500 instrument. Four different amylopectin (waxy maize) starches varying in charge density were evaluated, each at a pH of 3.5, 4.7, and 7.0. The pH levels were choosed because they represent points of maximum concentrations of soluble aluminum ion, alumina polymer, and insoluble aluminum hydroxide, respectively. The pH levels were controlled by NaOH and HCl only. Control levels with no alum were also determined for each starch. A flow diagram of the project was presented in Table 3 with a description of the cationic starch samples following in Table 4.

Each starch loading and its corresponding pH in a system of dionized water, bleached kraft pulp, alum, and titanium dioxide was tested for retention. The Dynamic Britt Jar was used because it simulates the turbulence experienced at the wet end of a paper machine and allows for the measurement of colloidal effects of fine particles without the effects of filtration (25). Retention was measured as the amount of filler and fiber that do not pass through the Britt Jar. Britt Jar retention tests were repeated three times for each experimental condition. The total number of retention tests equaled 57 (3 x 19). The significance of the results was determined by a linear regression analysis.

Table 3. Proposed Project Flow Chart

Starch	#1	#2	#3	#4	No Starch
mol wt	High MW	High MW	Low MW	Low MW	
chg den	High CD	Low CD	High CD	Low CD	
* pH					
	1 2 3 NA	1 2 3 NA	1 2 3 NA	1 2 3 NA	1 2 3
+ Starch Loading					
	1 2 3 4	1 2 3 4	1 2 3 4	1 2 3 4	
# DBJ Retn. Tests					
	1 2 3 4 5 6 7 8	9 10 11 12	13 14 15 16 17 18 19		
* 1 = pH 3.5, 2 = pH 4.7, 3 = pH 5.0, NA = No Alum (pH=4.7) + Cationic starch loading required to produce a zero or near zero zeta potential (kg/T)					
# Dynamic Britt Jar retention tests, one for each starch loading and one with no starch at each pH					

Table 4. Cationic Starch Sample Characteristics

Sample No.	Molecular Weight	% Ammonium Persulfate on D.S. Starch	% Nitrogen	Charge Density
39-II	High	None	0.1514	0.0140
39-IV	High	None	0.7498	0.0833
41-II	Low	0.10	0.1478	0.0136
41-V	Low	0.10	1.2373	0.1397

* High molecular weight refers to approximately 50 million.

+ Low molecular weight refers to approximately 1 million.

Experimental Methods and Materials

Base Stock Preparation

Three Valley Beater runs were made to a target freeness of 375 ml CS freeness, each with a 50-50 hardwood and softwood blend and 25% TiO₂ by weight. (The TiO₂ was an RPD (rutile pigment dry) sample donated by Du Pont.) The three batches were mixed together to produce a uniform master batch then refrigerated until needed. A small portion of this master batch was screened in the Dynamic Britt Jar to obtain fines for use in starch loading determinations. Another small portion was diluted to 0.1% consistency for the fines and filler fraction determination. The remainder of the master batch was diluted to 0.5% consistency with deionized water for Dynamic Britt Jar retention tests. The detailed preparation methods for these samples are given in Appendix I.

Cationic Starch Preparation

Four starches of varying molecular weights and charge densities were supplied in powder form by Grain Processing Corporation. The base starch was waxy maize, amylopectin. The cationic charge was of the quarternary type, thus the charge on the starch would not vary with changes in pH. Starch solutions were made to 0.5% solids and then diluted to 0.05% with deionized water for use in the starch loading determinations and retention testing. The starch samples were kept refrigerated overnight and allowed to warm to room temperature before being used. All starches were used within

48 hours in order to minimize error due to changes in the starch over time. Starch preparation details are given in Appendix II.

Starch Loading Determination

The object of determining starch loadings that produce zero zeta potentials is to create conditions that are thought to generate maximum retention, that is, have all charges neutralized.

A 500 ml solution consisting of 10 ml of fines obtained from screening master batch stock in the Dynamic Britt Jar, and 490 ml of deionized water was prepared for each starch loading trial. Two (2) ml of 5.00×10^{-6} M alum was added to the solution to make the alum concentration of the solution 1.0×10^{-8} or 0.007 lb alum per ton fiber. The pH was adjusted to either 3.5, 4.7, or 5.0 with HCl and NaOH. (Trials without alum were adjusted to a 4.7 pH.) A specific volume (between 0 and 5 ml) of 0.05% starch solution was mixed into the solution. The solution was then placed in the Laser Zee (tm) zeta potential voltage cell and the zeta potential determined. The procedure was repeated for every different starch loading trial for each starch, pH, and no alum condition. The average zeta potential for each starch loading trial was graphed. Starch loadings that produced zero zeta potentials were taken from the graphs. The procedure is explained in Appendix III.

Retention Testing Method

The Dynamic Britt Drainage Jar has been developed as a means for studying paper stock in the laboratory under conditions of controlled and graduated turbulence (2). In this experiment the stock solution, including alum and starch, was subjected to the range of turbulence (1000 rpm) experienced on a typical high speed paper machine.

The Dynamic Britt Jar was assembled as shown in Figure 16 with the swing-out base support to insure a constant distance of 1/8 inch between propeller blade and the screen. The three-bladed propeller has a 2-in. diameter and 30 degree pitch and was rotated counter clockwise. The stirring equipment consisted of an integrally-wound motor generator and servo feedback control. The apparatus was used both for the determination of the fines and filler fraction and retention.

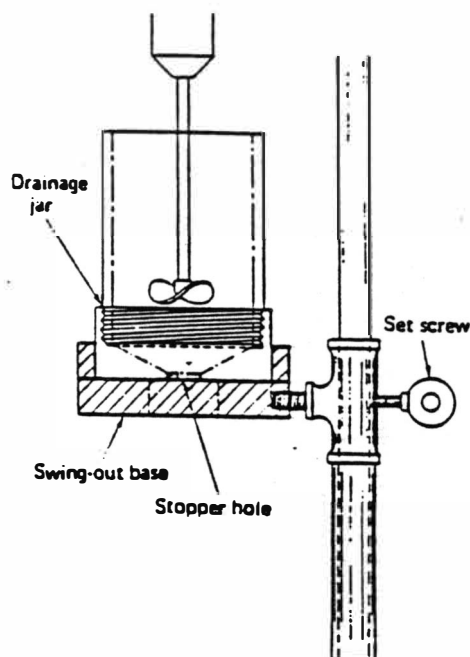


Figure 16. Diagram of Dynamic Britt Jar

For retention testing 0.5% consistency stock samples from the master batch were used together with 2 ml 5.00×10^{-6} M alum and the starch loadings previously found to produce zero zeta potentials. The solution then had an alum concentration of 1.0×10^{-8} M or 0.007 lb alum per ton fiber. pH levels were adjusted with HCl and NaOH to either 3.5, 4.7 or 5.0. (Runs without alum were adjusted to a 4.7 pH.) Three retention determinations were made for each set of conditions. The tests were conducted as specified in Appendix IV.

RESULTS

Table 5 is a summary of the average percent retention results for each starch and pH. The standard deviations for each average are also stated.

Table 5. Average % Retention Results

pH	HMW HCD	HMW LCD	LMW LCD	LMW HCD
3.5	50.42 \pm 10.00	46.11 \pm 3.42	46.19 \pm 5.89	51.92 \pm 3.83
4.7	59.16 \pm 13.52	50.76 \pm 4.28	48.99 \pm 4.23	55.00 \pm 1.85
5.0	53.88 \pm 3.24	53.48 \pm 2.63	47.63 \pm 2.91	53.44 \pm 9.23
N.A.	51.79 \pm 0.56	58.26 \pm 13.77	37.73 \pm 2.11	39.23 \pm 3.92

* HMW = high molecular weight LMW = low molecular weight
 HCD = high charge density LCD = low charge density
 N.A. = No alum present, pH 4.7

Figure 17 is a graphic representation of the average retention results. Figure 18 compares two starches with different charge densities. In contrast, Figure 19 compares two starches that differ in molecular weights. These graphs will be referred to in the discussion.

A regression analysis was run on all retention values with the exception of the no alum datum. The results are summarized in Table 6.

Table 6. Regression Analysis Results		
Variable	t-ratio	probability
pH	-1.83	0.076
molecular wt.	-2.11	0.042
charge density	-0.60	0.551
pH * MW	1.77	0.084
pH * CD	0.74	0.466
MW * CD	1.35	0.185
pH * MW * CD	-0.88	0.382

Figure 17. % Retention vs pH

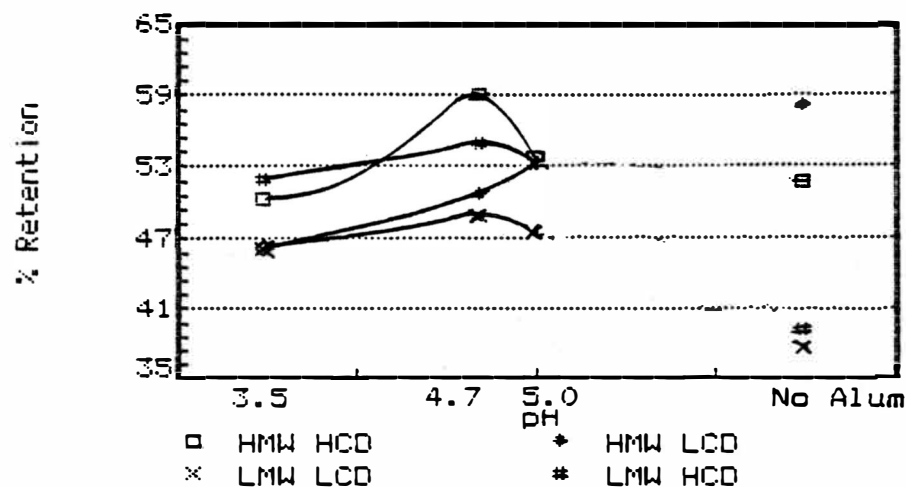


Figure 18. The effect of charge density on retention.

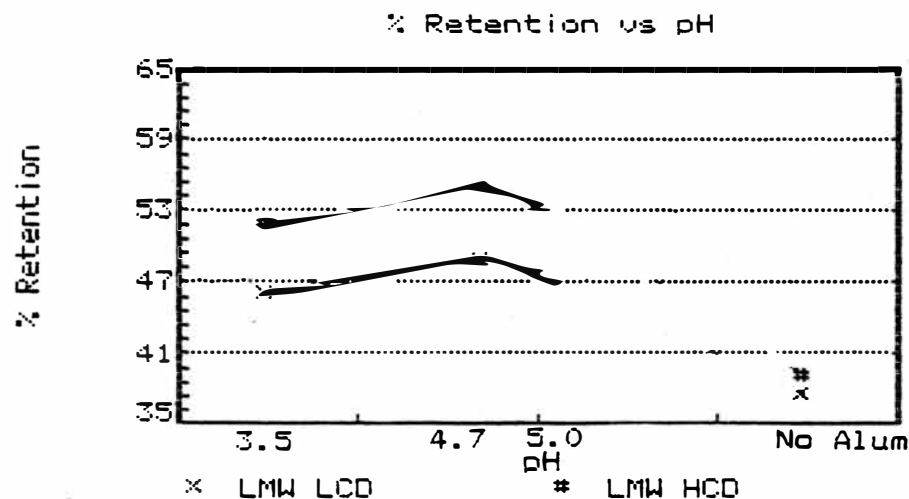
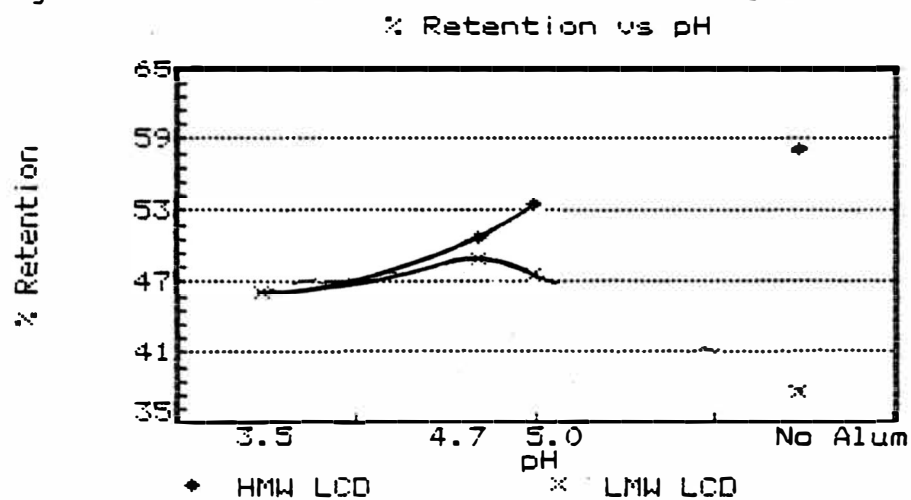


Figure 19. The effect of molecular weight on retention.



DISCUSSION

Effect of Aluminum Species

As seen in Figure 17, in the presence of alum, retention was minimum at pH 3.5 and increased to a maximum for 3 out of 4 starches at pH 4.7. When comparing this trend to the aluminum adsorption trend (Figure 11) it is clearly visible that minimum aluminum adsorption in the presence of the Al ion corresponds to minimum retention of fines and filler at very low pH values. Likewise, a large increase in aluminum adsorption in the presence of the $Al(OH)_8^{+4}$ species produced a large increment, actually a maximum, in retention at pH 4.7.

If this dependence on adsorption were to continue through pH 5.0, one would expect all of the retention values to continue rising similar to the high molecular weight-low charge density starch as seen in Figure 17. However, this does not occur. This may be due to the presence of the $Al(OH)_3$ precipitate at pH 5.0. This precipitate is believed to adsorb to the fibers and to create a gel-like shell that prevents starch from adsorbing directly on the fiber. Instead, the starch may adsorb onto the precipitate to form weaker bonds than fiber-starch bonds. This behavior was suggested and supported by the studies of Proximire and Stratton (24). The weaker bond may be less resistant to the high shear experienced in the Dynamic Britt Jar, therefore it is likely broken down to cause lower retention.

Effect of Charge Density

Figure 18 shows that in the presence of alum, a higher charge density starch generated higher retention levels. This effect suggests that even when the zeta potential was at or near zero in both cases, the higher charge density starch created stronger attractive forces that were able to resist shear better. The result was higher retention levels.

In the absence of alum, starch adsorption with neither high or low charge density was not adequate to produce strong enough bonding for any more than a low retention level. This effect is demonstrated in Figure 18 and shows that in general alum did not hinder adsorption but actually played an active roll in the adsorption mechanism. Even in the presence of the $\text{Al}(\text{OH})_3$ the sulfate ions in the precipitate appeared to act as additional adsorption sites for the cationic starch (24).

Effect of Molecular Weight

The results shown in Figures 17 and 19 suggest that in the absence of alum the low molecular weight starches appeared to be are neither able adsorb or bridge well enough to produce retention values comparable to those involving alum. However, for high molecular weight starches in the absence of alum, retention was comparable to, if not greater than, that generated with alum. This strongly suggests that bridging is the dominant mechanism when alum was not

available for interaction with cationic starch.

When comparing two starches that have equally low charge densities but distinctly different molecular weights, such as in Figure 19, the bridging mechanism appeared to be the governing mechanism in the absence of alum, and at pH 5.0 to a lesser degree. In the presence of $\text{Al}(\text{OH})_3$ aluminum adsorption is high, however it does not produce bonding that is as resistant to shear as that created by bridging, thus the higher molecular weight starch yields greater retention.

Figure 19 also suggests that as pH increases the bridging mechanism overpowers the adsorption mechanism. This hypothesis was signified by equal retention levels at pH 3.5 for starches of extremely different molecular weights but equal charge densities, followed by diverging retention as pH approaches the $\text{Al}(\text{OH})_3$ range (pH 5.0).

Regression Analysis

The regression analysis that was run on all of the data except those produced under the no alum conditions showed that three factors were significant in affecting retention at the 90% confidence level. The factors include pH (i.e. aluminum species), cationic starch molecular weight, and the interaction between pH (i.e. aluminum species) and molecular weight. The most influential of the three factors was molecular weight which is also the most important element in the bridging mechanism. The results of the analysis strongly support the effects of aluminum species and molecular weight

discussed previously.

The fact that charge density was not statistically significant arises from the large standard deviations in three of the high charge density starch retention values (see Table 5). Experimental and random error were the sources of the large deviations and are directly related to the low number of experiment repetitions. However, it is nearly impossible to rule out charge density as a significant factor because of statistics alone due to the presence of a strong background knowledge of the effects of charge density on adsorption.

CONCLUSIONS

From this study three conclusions about cationic starch-alum - fiber systems can be derived, all of which stress the importance of the adsorption and bridging mechanisms of retention. First of all, aluminum adsorption was an asset in achieving acceptable levels retention of fines and filler. The presence of alum in the papermaking system was necessary when using low molecular weight cationic starch.

Second, in the presence of alum, retention was minimum at very low pH values for all of the starches that were studied. This effect may have been caused by minimum adsorption of aluminum in this pH range.

Third, the polynuclear aluminum species $Al_8(OH)_{20}^{+4}$ which is usually created around pH 4.7 may possibly utilize both adsorption and bridging in promoting approximately maximum retention.

A hypothesis that can be drawn from this thesis was that in a alum - cationic starch - fiber system the bridging mechanism becomes the governing mechanism as pH increases. This may have been an effect of the presence of the aluminum polymer and precipitate in the pH range of 4.5-5.3.

The key outcome of this study was that the prediction made by Crow and Stratton (22) is supported, that is, as aluminum adsorption increases the negative charge on the fibers is lessened thus decreasing the cationic starch - fiber attraction. The configuration of the starch thereby

changes to one of more loops and tails which creates conditions more suitable for bridging to occur. The end result was improved retention in the presence of $[Al_8(OH)_{20}]^{+4}$ and a high charge density, high molecular weight cationic starch.

RECOMMENDATIONS

These experiments are several of hundreds of studies that could be done on aluminum species and cationic starch interactions and their effects on retention of fines and filler. It is one step towards a better understanding of the complex phenomena of retention. Although this study did not have the statistical significance to support all of the findings it did show many important trends.

The next step would be to repeat this study using 6-10 repetitions of each retention test instead of three repetitions. The results may prove to be more significant and also clarify some of the unexpected results seen in this study.

Finally, two other studies could be derived from this thesis. The first study would be to keep starch charge density constant and to vary pH and molecular weight. The second would be to keep molecular weight constant and vary pH and charge density. In both cases it would be useful to add one more pH such as 5.3 and to lower the Dynamic Britt Jar agitation to 500-750 rpm for testing. The latter may allow the researcher to more clearly see adsorption trends without having to overlook weak bonding.

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APPENDIX I

Preparation of Base Stock

A blend of 50% Eddy hardwood and 50% Dryden DCX softwood (180 g O.D. each) were beaten by a Valley beater to a target CS freeness of 375 ml. Approximately 25% TiO₂ and 3% formaldehyde was added to the stock and mixed in. Three beater runs were run by this procedure and then mixed together in a large barrel to produce an average freeness. The stock was then kept refrigerator at 8 degrees Celcius until needed.

Preparation of Stock for Zeta Potential Testing

Approximately three liters of the base stock were screened in a Dynamic Britt Jar and the filtrate collected. The percent solids of the well mixed filtrate was determined using the CEM device. The filtrate was refridgerated until needed.

Preparation of the Master Batch for Retention Testing

Previously prepared base stock was diluted with deionized water to a consistency of 0.5% in a 55 gallon drum. The stock was kept at room temperature and continuously agitated after preparation. The master batch was also used in the percent fines/filler determination (Appendix IV).

APPENDIX II

Cationic Starch Preparation

For each starch cook 1.4g of starch were dissolved under agitation in 200 ml of cold deionized water. Once the starch was dissolved the starch was heated on a steam bath at 90 C for 30 minutes under agitation. The starch sample was then covered with aluminum foil to prevent skinning and allowed to cool to room temperature. Next the starch was placed in a 250 ml volumetric flask and diluted to the mark with deionized water and mixed well. From this sample 50 ml was transferred by pipet to a 500 ml volumetric flask and diluted to the mark with deionized water. The samples were kept refrigerated overnight and allowed to warm to room temperature before being used for testing zeta potential. The percent solids of the 250 ml starch sample was determined by the CEM in order to calculate the solids of the 500 ml diluted starch sample.

All starch samples were used within 48 hours in order to avoid error due to changes in the starch over time.

Appendix III

Starch Loading Determination

Using a 60 ml syringe, 10 ml of prepared screened base stock were placed in approximately 490 ml deionized water, all in a 1000 ml glass beaker. After mixing the stock well the pH was adjusted to 4.0 using HCl. Next, using a 5 ml syringe, 2 ml of 5.00×10^{-6} M alum solution was added and mixed in well. The pH was adjusted again to either 3.5, 4.7 or 5.0 using HCl or NaOH. After proper agitation a starch sample (from the 500 ml flask) of known volume (between 0 and 5 ml) was added to the mixture by a syringe and agitated for one minute. Using a 35 ml syringe, a sample was transferred into the Laser Zee Meter voltage cell. The zeta potential reading was then taken as specified in the Laser Zee Meter instruction manual. Five or more readings were made from the same mixture with thorough rinsings with deionized water between each sample loading. New stock-alum solutions were made up each time the starch loading and/or pH was changed. The starch loading was calculated as follows:

$$\text{loading (lb/T)} = \frac{\text{x ml starch}}{10 \text{ ml stock}} * \frac{\% \text{diluted starch solids}}{\% \text{consistency of screened stock}} * 2000$$

Starch loadings determined for each starch at each pH were graphed against average zeta potential. The starch loadings at zero zeta potential were found on these graphs.

Appendix IV Dynamic Britt Jar Procedures

Fractionation Procedure

For the fractionation procedure, a sample of stock to be tested was adjusted to a consistency of about 0.1%. It is important to know the exact consistency of the sample and keep the sample agitated continuously. A 500 ml sample of the 0.1% consistency stock was placed in the Britt Jar and agitated at 1500 rpm for a few seconds to completely disperse the sample, then agitated at 750 rpm. The bottom orifice was opened and the filtrate was collected in a 2000 ml beaker. After drainage was complete 500 ml of wash water consisting of 0.01% TSPP, 0.01% Displex N-40 (at 40% solids), and 0.01% sodium carbonate was poured into the jar (with the bottom closed). Again agitation was briefly turned up to 1500 rpm and slowed down again to 750 rpm. The orifice was opened and the filtrate collected in the same beaker. This step was repeated until 2000 ml of filtrate, which contains the fine and filler fraction, was collected. The step was then repeated with water and the filtrate was collected in a clean glass beaker. This filtrate was observed for clarity and should have contained no appreciable amount of suspended matter. The solid residue of fiber on the screen was transferred to a weighed filter paper on a Buchner funnel, dried, and weighed again.

Fines and Filler Fraction Calculation

$$\frac{\% \text{ consistency}}{100 \text{ ml}} * 500 \text{ ml} = \text{grams solids}$$

$$\text{grams fines + filler} = \text{solids} - ((\text{fiber} + \text{filter}) - \text{filter})$$

$$\%(\text{fines} + \text{filler}) = (\text{grams fines} + \text{filler}) / \text{grams solids} * 100$$

Retention Test Procedure

Prior to running the retention test, the fines and filler fraction of the stock must be determined as described earlier. Also, the master batch must be prepared at a consistency of 0.5% as instructed in Appendix I and the exact consistency determined.

The apparatus for the retention test includes a rubber stopper placed in the bottom outlet of the jar. Attached to the stopper was a short glass tube (5/16" OD) connected to a rubber tube and medicine dropper. A pinch clamp was placed on the rubber tube to control the outlet flow.

For this experiment, 500 ml of well agitated master batch stock was poured into the jar with the pinch clamp closed. The pH was adjusted to 4.00 with HCl. Two (2) ml of $5.00 * 10E-6 \text{ M}$ alum was added by syringe and the pH was adjusted to either 3.5, 4.7, or 5.0 with HCl or NaOH, which ever was necessary. (If the test was to be done in the absence of alum, the pH was 4.7.) The stock was allowed to agitate at 500 rpm for 10 seconds before the starch was added. The volume of starch added was that determined to produce a zero zeta potential (Appendix III). The starch was allowed to mix for 10 seconds after which the agitator was

accelerated to 1000 rpm. After one minute a 100 ml sample was drained into an aluminum moisture can of accurately known weight. The can holding the sample was weighed and the weight recorded. Finally, after drying in an oven overnight and cooling in a desiccator, the dry sample was weighed.

% Retention Calculation

$$\text{total grams solids in sample} = \frac{\% \text{ consistency}}{100} * 500 \text{ ml}$$

$$\text{grams fines + filler} = \frac{\% \text{ fines + filler}}{100} * \text{grams solids}$$

$$\text{grams solids in can} = \text{total wet wt.} - \text{total dry wt.}$$

$$\% \text{ unretained} = \frac{\text{solids in can} * (500 + \text{starch volume})}{\text{grams fines + filler}} * 100\%$$

$$\% \text{ retention} = 100 - \% \text{ unretained}$$

Appendix V
Starch Loading Determination Results

Starch No.	pH	zeta potential (mV)	Loading (lb/T)
965-39-II	3.5	-2.20	14.12
	3.5	+9.70	28.25
	3.5	+11.0	56.50
	3.5	0.0	15.72
	4.7	-3.56	14.12
	4.7	+4.98	28.25
	4.7	+12.5	56.50
	4.7	0.0	17.97
	5.0	-13.8	14.12
	5.0	+13.0	56.50
	5.0	+20.0	113.0
	5.0	0.0	28.08
	No Alum	-7.42	42.36
	No Alum	+0.32	56.50
	No Alum	+1.22	84.75
	No Alum	0.0	53.58
965-39-IV	3.5	-2.80	2.17
	3.5	0.9	3.26
	3.5	+6.70	6.52
	3.5	+7.20	10.87
	4.7	-8.60	5.43
	4.7	-0.96	6.52
	4.7	0.0	7.61
	4.7	+2.40	8.70
	5.0	-19.50	7.60
	5.0	0.0	9.56
	5.0	+4.20	10.87
	No Alum	-23.20	6.52
	No Alum	-12.80	10.87
	No Alum	0.0	15.22
	No Alum	+22.90	21.74
965-41-II	3.5	-6.30	9.94
	3.5	0.0	17.40
	3.5	+3.90	24.86
	3.5	+14.50	49.72
	4.7	-6.30	12.43
	4.7	0.0	20.88
	4.7	+2.10	24.86
	4.7	+14.70	49.72
	5.0	-3.90	24.86
	5.0	0.0	28.84
	5.0	+12.60	49.72
	No Alum	-15.10	49.72
	No Alum	0.0	63.64
	No Alum	+11.20	74.58
	No Alum	+16.20	99.44

Starch No.	pH	zeta potential (mV)	Loading (lb/T)
<hr/>			
965-41-V	3.5	-1.80	7.29
	3.5	+10.50	9.72
	3.5	+17.20	14.58
	4.7	-11.60	6.07
	4.7	0.0	7.87
	4.7	+2.90	8.50
	4.7	+15.10	12.15
	5.0	-11.90	4.86
	5.0	0.0	8.75
	5.0	+10.90	10.90
	5.0	+21.80	21.80
	No Alum	-3.40	24.29
	No Alum	0.0	27.21
	No Alum	+2.10	29.16
	No Alum	+10.70	36.45
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Appendix VI
Dynamic Britt Jar Retention Test Raw Data

Key: starch 1 = HMW HCD, 2 = HMW LCD, 3 = LMW LCD
4 = LMW HCD, 5 = No Starch

pH 1 = 3.5, 2 = 4.7, 3 = 5.0, 4 = No Alum (4.7)

ROW	STARCH	pH	CAN WT	TOT WT	DRY WT	ML STRCH	SOLIDS	% RETN
1	1	2	59.09	139.16	59.21	25.0	0.119999	57.5715
2	4	3	60.16	177.65	60.29	25.5	0.130001	63.8910
3	2	4	60.04	156.56	60.16	47.0	0.119999	60.7066
4	4	2	60.41	171.86	60.56	24.0	0.150002	57.1365
5	5	3	60.32	169.70	60.51	0.0	0.139999	47.5345
6	4	2	60.16	191.40	60.34	24.0	0.180000	53.8153
7	3	3	61.01	170.11	61.18	85.0	0.170002	45.2032
8	3	3	59.78	172.27	59.96	62.0	0.180000	44.9654
9	5	2	60.51	158.23	60.65	62.0	0.140003	53.3962
10	5	2	60.20	163.40	60.36	0.0	0.160000	54.1147
11	2	1	60.28	202.44	60.51	41.0	0.230000	42.3946
12	1	4	60.85	173.91	61.01	53.0	0.160000	52.3179
13	4	2	60.46	171.05	60.62	24.0	0.160000	54.0629
14	4	2	60.15	193.94	60.35	32.0	0.199997	43.7510
15	5	2	61.00	169.66	61.16	47.0	0.160000	51.6537
16	5	3	60.78	177.81	60.98	0.0	0.200001	47.2915
17	3	4	61.10	182.95	61.27	183.0	0.170002	40.0836
18	5	1	60.13	163.36	60.29	0.0	0.160000	54.1035
19	4	1	61.47	166.07	61.62	22.0	0.149998	55.8125
20	4	3	60.52	187.77	60.71	26.5	0.189999	50.0704
21	3	3	60.23	165.01	60.39	85.0	0.160000	46.8381
22	1	4	60.96	183.04	61.13	53.0	0.170002	51.8641
23	1	3	60.28	158.87	60.42	33.0	0.139999	55.9803
24	5	2	60.11	170.02	60.32	0.0	0.209999	42.1207
25	5	1	60.23	168.19	60.41	0.0	0.180000	49.8491
26	1	4	60.46	169.92	60.62	53.0	0.160000	51.1982
27	3	1	61.11	181.02	61.28	51.5	0.169998	51.4601
28	5	3	59.08	158.01	59.27	0.0	0.139999	43.6329
29	5	2	60.14	159.97	60.32	0.0	0.180000	47.2721
30	3	4	60.03	163.99	60.19	188.0	0.160000	37.0891
31	1	1	60.39	165.53	60.60	11.0	0.209999	39.2429
32	2	1	60.32	190.64	60.52	41.0	0.200001	46.8075
33	3	2	60.16	164.03	60.32	62.0	0.160000	48.6231
34	3	1	60.99	166.61	61.16	51.5	0.169998	47.2619
35	2	3	59.78	166.03	59.92	73.0	0.139999	54.7176
36	1	2	60.64	193.39	60.67	25.0	0.029999	46.5106
37	3	1	60.45	171.98	60.65	52.0	0.200001	39.8372
38	4	3	60.13	184.02	60.33	26.5	0.200001	46.3709
39	2	2	60.84	190.26	61.04	47.0	0.200001	46.1101
40	3	3	60.18	167.34	60.33	35.0	0.150002	50.8541
41	1	3	60.27	160.32	60.43	33.0	0.160000	50.1466
42	2	2	60.99	180.37	61.15	47.0	0.160000	54.5244
43	2	3	60.77	173.62	60.93	73.5	0.160000	50.4677
44	1	3	61.10	168.47	61.25	33.0	0.150002	55.5230
45	4	4	60.12	199.09	60.35	82.0	0.230000	36.9861
46	4	4	60.12	173.02	60.32	82.0	0.200001	36.9487
47	1	1	60.03	175.15	60.20	11.0	0.170002	53.5163
48	4	4	60.38	190.32	60.59	47.0	0.209999	43.4340
49	4	1	60.15	179.32	60.34	22.0	0.139999	48.1644
50	3	4	60.49	161.25	60.65	183.0	0.160000	36.0201
51	1	1	60.45	173.15	60.60	11.0	0.149998	58.5124
52	2	4	61.04	174.69	61.14	47.0	0.099998	70.6540
53	1	2	60.81	166.48	60.90	25.0	0.090000	73.4003
54	2	3	61.46	168.20	61.60	73.5	0.139999	55.2628
55	5	1	60.52	166.79	60.66	0.0	0.139999	60.6666
56	4	1	60.98	182.69	61.16	22.0	0.180000	51.7981
57	2	1	60.96	179.42	61.14	41.0	0.180000	49.1331