4-1986

The Effects of Alum at Different pH Levels on ASA Sizing

James A. Farrand
Western Michigan University

THE EFFECTS OF ALUM AT DIFFERENT pH LEVELS ON ASA SIZING

By:

James A. Farrand

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

Western Michigan University
Kalamazoo, Michigan
April, 1986

Dr. Raymond Janes, Advisor

ABSTRACT

Alkenyl succinic anhydride (ASA) is a cellulose reactive size used in neutral to alkaline sizing. ASA is emulsified in cationic starch to help retain the ASA on the fiber and to protect the ASA from hydrolysis. The stability of the ASA emulsion is largely dependent upon temperature, pH, and shear.

While one of the advantages of alkaline papermaking is the elimination of aluminum from the process water, the addition of small amounts of alum has proven beneficial to some mills running ASA size. The advantages claimed by using alum are: improved sizing, improved retention, and improved runnability.

The aluminum species formed depends primarily upon pH. There are three pH regions of major concern: a low pH region (pH less than 4.3), an intermediate pH region (pH 4.3-5.0), and a high pH region (pH 5.0-8.0). The predominate aluminum species formed in these different pH regions are Al^{+3}, $Al_8(OH)_{20}{}^{4+}$, and $Al(OH)_3$, respectively. The effect of these three aluminum species on ASA sizing was studied to better define the role of alum in ASA sizing.

The results showed that in the low pH region alum improved sizing. In the intermediate and high pH region, the results showed that alum had little effect at low concentrations; however, at higher concentrations alum decreased sizing.

Keywords: Alkaline Papermaking, Alum, Aluminum, Alkenyl Succinic Anhydride (ASA), Sizing

TABLE OF CONTENTS

TABLE OF CONTENTS (Cont.)

INTRODUCTION

Alkenyl succinic anhydride (ASA) is a cellulose reactive size which has proven to be effective in neutral to alkaline papermaking. The elimination of alum in the papermaking process is one of the major advantages of alkaline sizing; however, the use of small to moderate amounts of alum has been shown to produce desirable effects in alkaline sizing with ASA. There has been much information published on alkaline papermaking and ASA sizing, but little work has been done studying how the various forms of aluminum perform in alkaline sizing. This thesis will study the effects of various forms of aluminum on the efficiency of ASA sizing. The goal is to gain a better understanding of the mechanisms involved in ASA sizing.

SIZING

Wetting of Paper

The papermaker and paper converter encounter a variety of processes that involve liquid-paper interactions. These operations include sizing, coating, printing and corrugating. The development of water repellency in paper and board is important for proper production control of these processes and also to ensure that end use specifications are met. Due to the importance of liquid-paper interactions, a discussion of the mechanisms involved is essential.

The degree of interaction between a liquid and solid is primarily due to the balance between the attractive van der Waals forces of the liquid molecules for themselves and for the solid. When the attractive forces between the liquid molecules (cohesion) are greater than the attractive forces between the liquid and solid (adhesion), the liquid will minimize its contact area with the solid. On the other hand, strong adhesional forces between the solid and liquid will cause the liquid to wet the solid. These two situations are illustrated in Figure 1a and 1b, respectively.

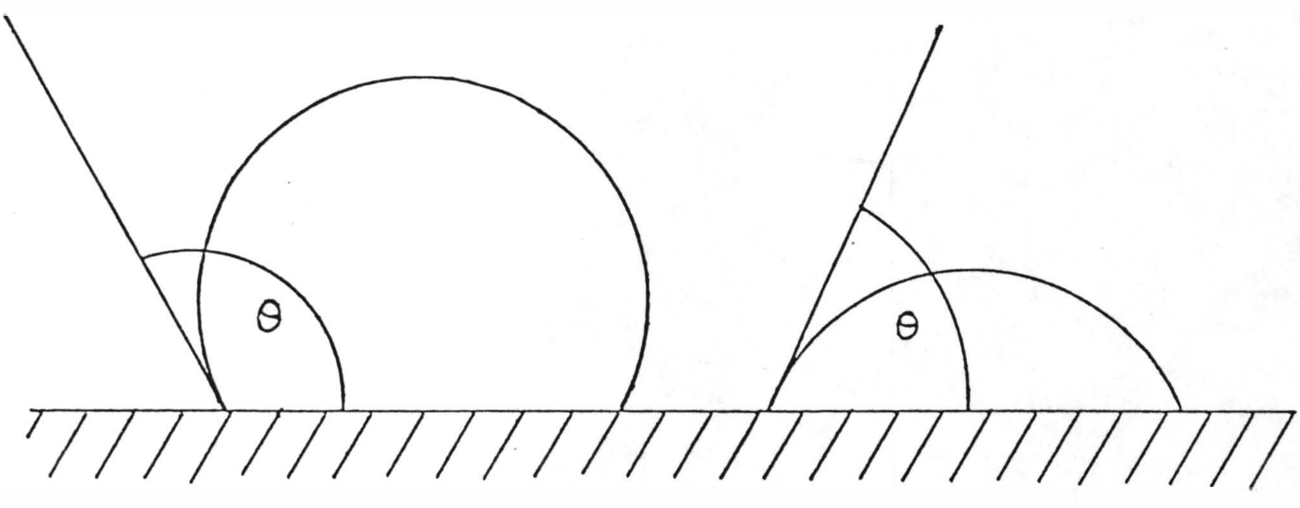


Figure 1. Examples of Liquid Wetting, Where (a) Cohesional Forces Dominate, (b) Adhesional Forces Dominate.

The contact angle is often used to quantify liquid-solid interactions. The contact angle (θ) of a liquid droplet on an ideal solid is measured through the liquid to a line drawn tangent at a point of contact of the liquid, solid and vapor interface as shown in Figure 1. A high contact angle is associated with strong cohesional forces and a low contact angle relates to strong adhesional forces. Angles less than 90° correspond to wetting of the solid and angles greater than or equal to 90° define non-wetting of the solid. A contact angle equal to 0° defines complete wetting while an angle equal to 180° defines non-wetting.

While the discussion up to this point is limited to ideal, smooth, flat, homogeneous and nondeformable surfaces, application of the contact angle concept is still very useful for understanding liquid-solid interactions with paper.(1)

Liquid Penetration

Another important aspect of liquid-solid interactions is the penetration of liquids into a porous (non-ideal) solid. The penetration of liquids is of general interest to the papermaker and is particularly relevant to paper sizing. The purpose of sizing is to modify the surface of the paper to control liquid penetration. The LaPlace Equation describes the capillary forces that control the penetration of a liquid into a porous solid.

$$\Delta P = \frac{2 \gamma_l \cos \theta}{r} \tag{1}$$

where ΔP represents the pressure differential across the meniscus of the liquid in the capillary. The difference in pressure is the driving force

for penetration. γ_l is the surface tension of the liquid, θ the contact angle and r is the radius of the capillary.

Equation (1) shows the relationship between the contact angle and liquid penetration. Equation (1) will generate a positive ΔP for angles less than 90°, thus, favoring liquid penetration. In order for sized paper to resist wetting, the contact angle must be greater than 90°.(1,2)

Another useful measurement describing liquid penetration is obtained from the Lucas-Washburn Equation which describes the rate of flow in a porous solid.

$$L^2 = \frac{\gamma_l r t \cos\theta}{2\mu} \qquad (2)$$

where L is the depth of liquid penetration, γ_l is the liquid surface tension, t is the penetration time, θ is the contact angle and μ is the liquid viscosity.(3)

Sizing Requirements

In order for a sizing agent to be effective (4) it must be:

1. Hydrophobic
2. Retained on the fiber
3. Distributed on the fiber
4. Anchored to the fiber

Sizing agents must be either hydrophobic in nature or contain a hydrophobic group which will reduce wettability. Most organic molecules containing more than 3-4 carbon atoms have portions of their molecules that differ chemically from other neighboring portions. This type of molecule must be able to adsorb onto the fiber surface to be an effective size. During the adsorption, the molecules usually preferentially orient themselves to yield

the lowest state of free energy. Generally, the polar part of the molecule will orient itself toward the fiber surface leaving the nonpolar (hydrocarbon) portion facing out. This outward orientation of the hydrocarbon group is desirable due to the weak interactions between liquids (especially water) and the hydrocarbon layer. This low interaction between the solid and liquid will probably result in a high contact angle or poor wettability. This is essentially the mechanism through which sizing agents operate.

The adsorbed molecules must be firmly anchored to the fiber, otherwise the molecules tend to reorient themselves when contacted with polar liquids such as water. The observed decrease in sizing when a sized paper is in contact with a liquid for a long period of time is believed to be partially due to this reorientation of the size molecules.

Water is also capable of penetrating paper by mechanisms other than capillary action. Water can move through the pores via intrafiber diffusion, vapor phase, and surface diffusion. It is postulated that these latter two processes occur more rapidly than capillary penetration; however, the bulk of the liquid penetrates into the pores by capillary action. (1)

Sizing Test Methods

The most commonly used test method for determining the degree of sizing is the Hercules Size Test (HST). The HST measures the penetration rate of the test liquids from the top to the bottom side of the paper or board substrate. A constant volume of test ink is applied to the top of the sheet. A photoelectric cell registers the drop in reflectance of the opposite side of the sheet as a function of time as the ink penetrates. When the reflectance drops to a preset percentage of the original (typically 80%), an automatic timer stops, indicating the end point.(3)

Standard test inks utilize formic acid solutions of typically 1% concen-

tration. A green dye which has no affinity for cellulose is used in conjunction with the formic acid.

Another useful test method for determining the degree of sizing measures the change in the contact angle with time. A controlled drop of liquid is placed on the surface of the paper through the use of a hypodermic needle. The drop is magnified and a horizontal line is placed at the base of the drop. At five to 60 second intervals, two tangents to the curve at the two points of contact with the baseline are drawn. The interior angle between the baseline and tangent is the angle of contact.(3)

The Cobb test method is also useful for measuring the degree of sizing. This test exposes a preweighed paper or board sample to water for a specified time period. A standard volume of water (100 cc) is poured inside a metal retaining ring which is clamped to the sheet. The retaining ring only allows 100 cm^2 of surface to be exposed to the water. After two minutes, the water is poured off and the free water is blotted from the surface. The sheet is reweighed to determine the amount of water picked up by the sheet.(3)

Other test methods include the total immersion test, edgewick test, and the pen and ink test.

ALKENYL SUCCINIC ANHYDRIDE

Structure and Properties

Alkenyl succinic anhydride (ASA) is a rapidly curing synthetic size which has proven to be effective in neutral to alkaline papermaking. ASA is also labeled as a cellulose reactive size because it is believed to form a covalent bond with cellulose. Cellulose reactive sizes were introduced to the paper industry in the 1950's and they have proven to be more effective than conventional sizing systems.(5)

The structure of ASA is shown in Figure 2. ASA is a dicarboxylic acid

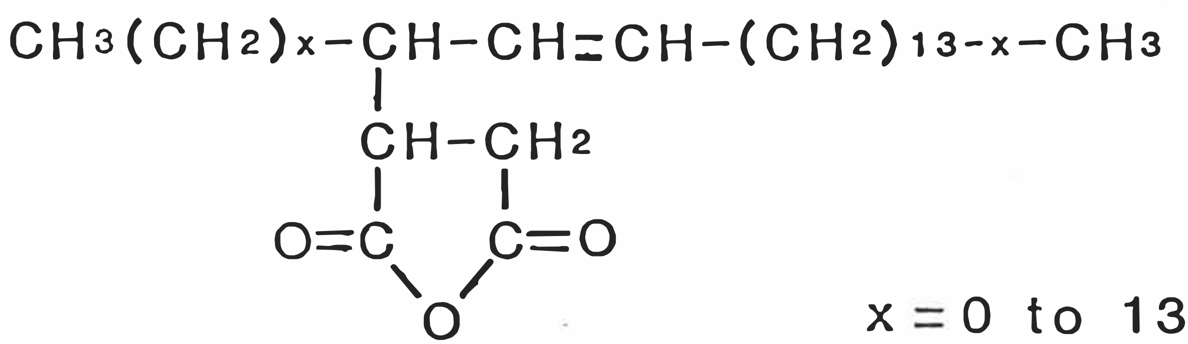


Figure 2. The Chemical Structure of ASA.

anhydride with a long hydrophobic side chain. The long chain hydrocarbon is typically 16 to 20 carbons in length and this part of the ASA molecule provides the hydrophobicity needed to lower the surface energy of the fibers. The succinic anhydride group provides the reactivity through which the ASA molecule can anchor itself to the fiber surface. The reaction between ASA and cellulose is shown in Figure 3.

ASA is a liquid at room temperature and since it is a nonionic organic compound it is insoluble in water. To make ASA compatible with the papermaking system, it must be prepared as an emulsion.(6)

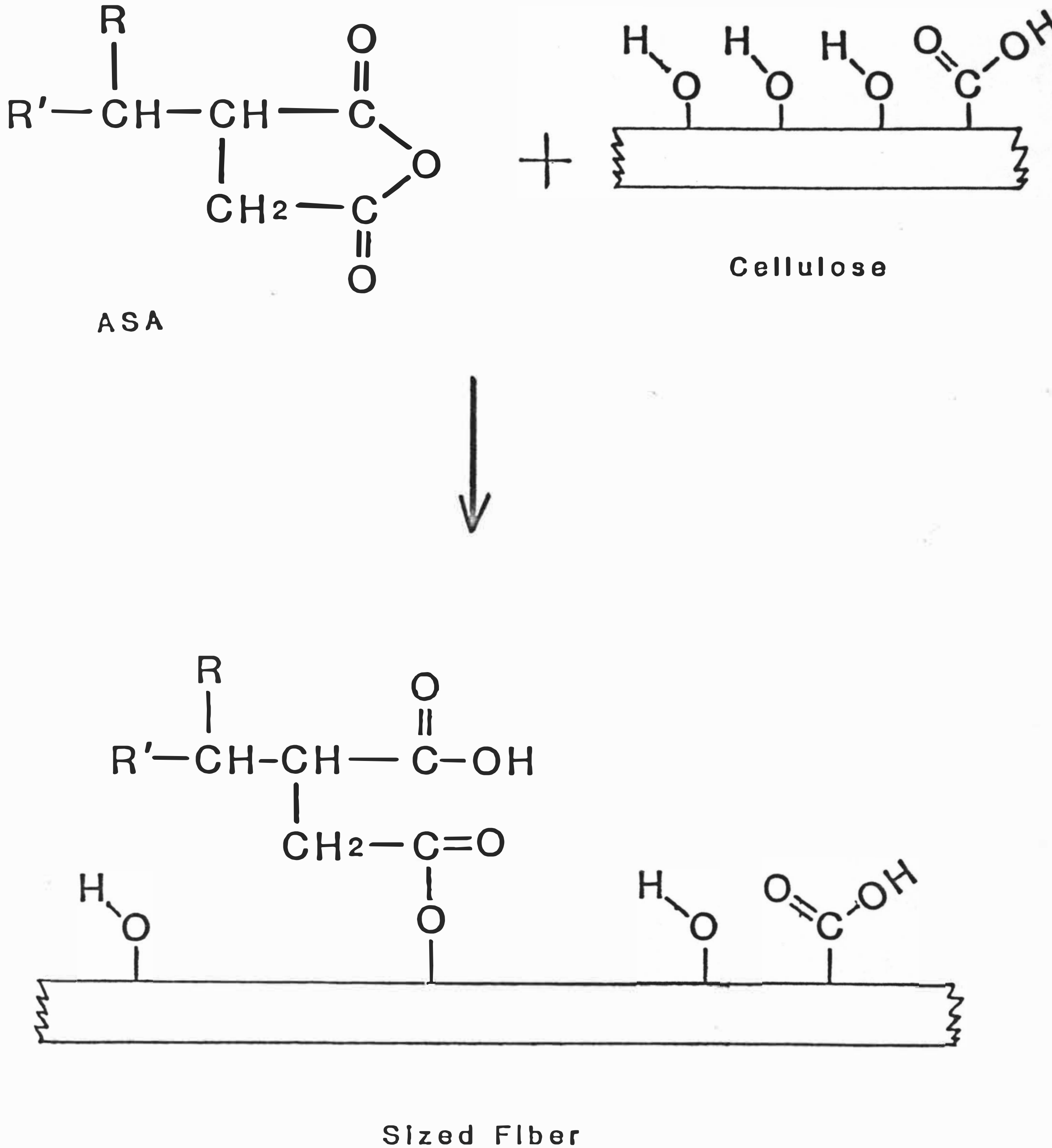


Figure 3. Reaction of ASA with Cellulose

Emulsification of ASA

Due to its insolubility in water, ASA must be added to the furnish as an emulsion. A surfactant is added to the ASA to reduce interfacial tension and to form an oil in water emulsion of good stability. ASA is typically emulsified in a cationic starch which imparts a net positive charge on the emulsion particles. The positive charge on the emulsion particle will help to retain the ASA on the fiber. The cationic starch also improves the mechanical stability of the emulsion and some believe it helps to protect the ASA from hydrolysis.

A typical emulsifier operates by injecting the ASA and emulsifying agent into a turbulent flow of starch and water to form the emulsion. Due to the reactivity of ASA with water the emulsification must be carried out at the mill and no more than a few hours before its application.

Hydrolyzed ASA is not effective as a sizing agent; therefore, as soon as the ASA is emulsified it starts to lose its sizing capability. The rate of hydrolysis of ASA is primarily dependent upon pH and temperature.

Hydrolysis of ASA

Wasser (6,7) showed that the hydrolysis rate of ASA is largely dependent upon temperature and pH. The effect of temperature on the hydrolysis rate of ASA is shown in Figure 4. As the temperature increases the rate of hydrolysis increases, doubling roughly for every ten degree (°C) increase. At room temperature (25°C) the hydrolysis rate is initially very slow, with complete hydrolysis occuring within 24 hours.

The pH of the emulsion also has a significant effect on the stability of the ASA as shown by Figure 5. As the pH increases above 3.5, the rate of hydrolysis increases rapidly, doubling roughly for every unit increase in

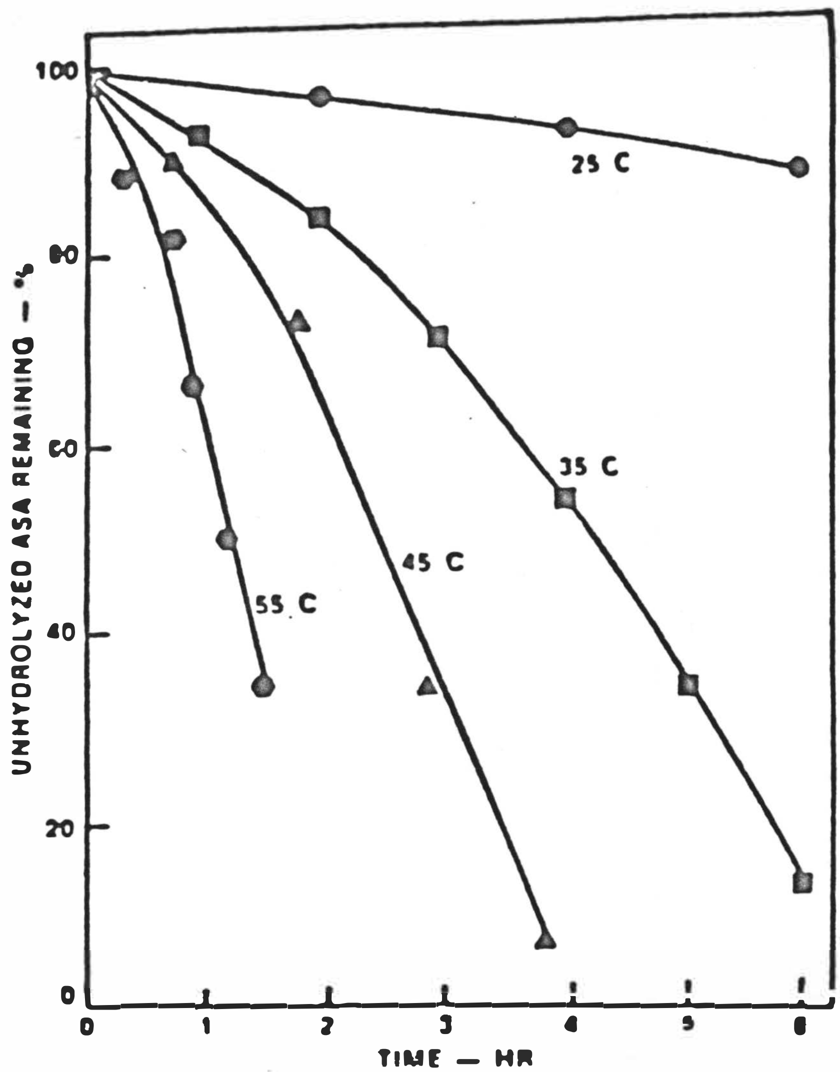


Figure 4. The Effect of Temperature on the Hydrolysis Rate of ASA (6)

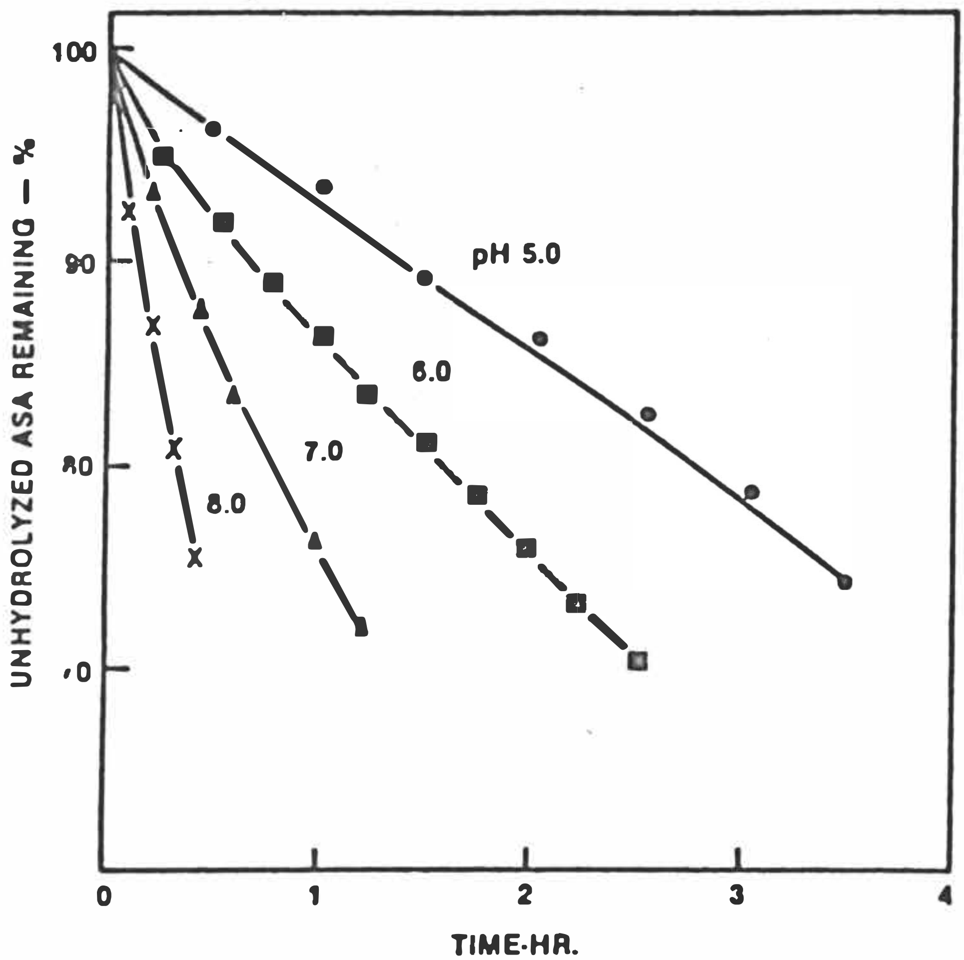


Figure 5. The Effect of pH on the Hydrolysis Rate of ASA (6)

pH. The maximum stability of the emulsion is in the pH range of 3.5 to 4.0. Thus, low temperature and low pH minimize the hydrolysis of ASA.

Emulsion Particle Size

Another factor affecting the stability of the ASA emulsion is the particle size. As the particle size of the emulsion decreases, the surface area of the ASA exposed to water increases thus increasing the rate of hydrolysis. However, this effect is relatively small in comparison to the effect of temperature and pH.(6)

The optimum particle size is determined more by the mechanical stability of the emulsion and its effect on sizing efficiency than by its effect on hydrolysis.(7) ASA emulsions give the best stability and performance when the particle size is between 0.5 and 3.0 microns.(8)

Rate of Cure

In the application of ASA, sizing does not develop until the dryer section. Under most conditions, sizing development (cure) is 80 to 100 percent complete on-machine or before the size press.(8) However, the ASA is still susceptible to hydrolysis until the water is removed from the sheet.

The time required to develop sizing decreases rapidly as the temperature in the dryer section increases. The rate of cure also increases as the pH increases; as does the rate of hydrolysis.(7) See Figure 6.

Normal operating conditions in a paper mill such as high stock temperatures and high pH are very favorable for hydrolysis. Since the sizing does not develop until the dryer section, any hydrolysis that occurs between the time of addition of the ASA emulsion and the time the web reaches the dryers is detrimental to sizing. However, the actual contact time on a paper machine from the fan pump to the dryer section is so short that the loss in

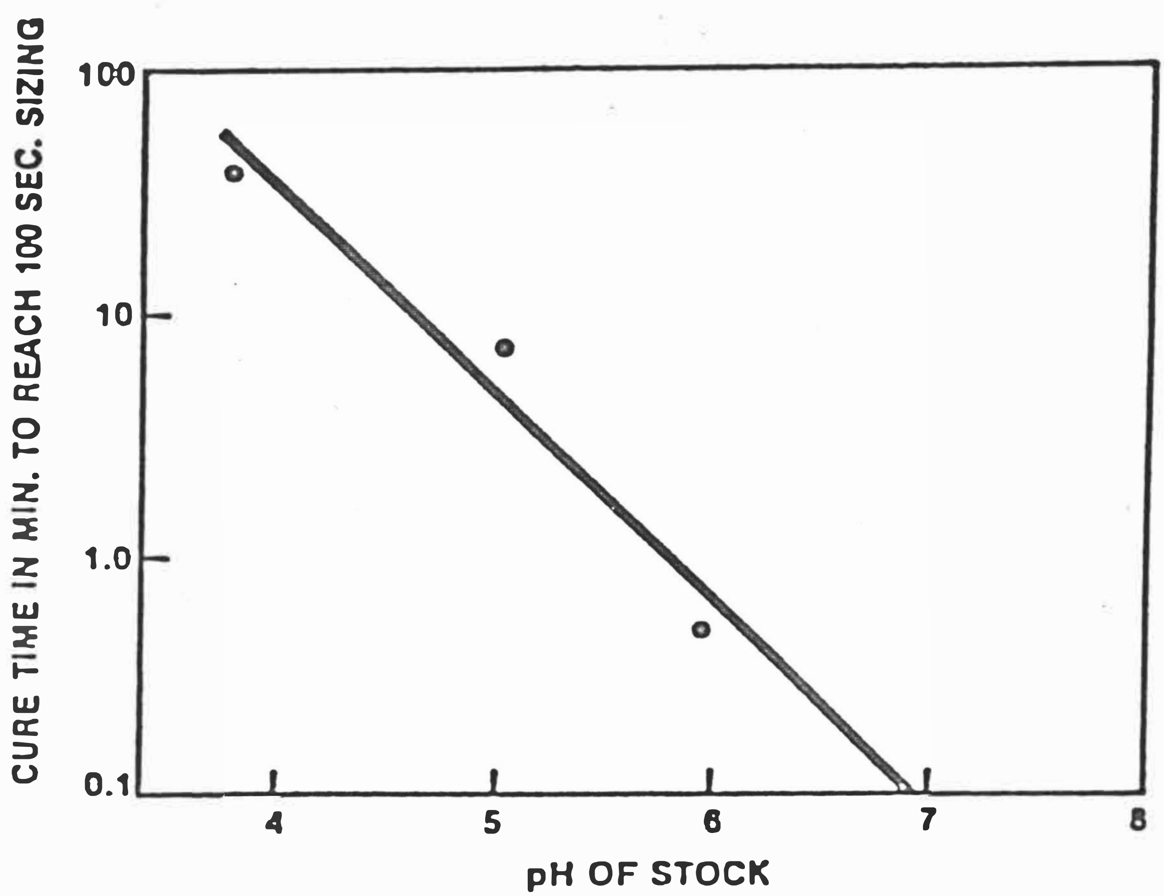


Figure 6. The Effect of pH on the Cure Rate of ASA Handsheets Dried to 4% Moisture at 90°C.(7)

sizing due to hydrolysis is insignificant.

Cationic Starches Used in the Emulsification of ASA

The effects of base starch and type of derivatization (tertiary amino or quaternary ammonium substituents) on ASA sizing was studied by Winters and Best.(9) They found that size emulsions prepared with quaternary ammonium-derivatized potato starch produced the best sizing, especially at high substitution levels. The quaternary potato starch was also more stable at high pH than tertiary corn starch. The cationic groups on the tertiary starches are cationic at low pH; however, as the pH increases the cationic charge decreases. The quaternary starch retains its cationic charge even at high pH. The superior performance of the quaternary ammonium-derivatized potato starch may be attributed to the fact that it remains cationic over a broad pH range. The effects of higher sizing with potato starches may also be assisted by higher molecular weight of the base starch.

Winters and Best (9) proposed the more stable cationic nature and higher molecular weight of the quaternary ammonium-derivatized potato starch improved the retention of the ASA emulsion on the fibers, thus improved sizing efficiency.

APPLICATION OF ASA

The application of ASA can present many problems to the papermaker, such as runnability, deposits, and press picking. However, most of the problems associated with ASA can be eliminated by gaining an understanding of ASA and its properties. Some of the main factors affecting the efficient use of ASA are: retention of the ASA emulsion on the fibers, point of addition and first pass retention.

Initially, the emulsion particles are retained on the fibers by electrostatic attraction. The positively charged emulsion particles are attracted to the negatively charged fibers. The retention of these relatively large emulsion particles can be severely affected by the harsh conditions found in a paper mill. High stock temperatures, shear, and recycling can lower the stability of the attached emulsion particles.(11)

The degree to which the ASA emulsion is retained on the fibers can be largely affected by the point of addition. ASA efficiency is optimized when the contact time with stock is minimized and mixing with stock is thorough and immediate. Typical addition points are at the screen inlet or fan pump inlet.(8)

First pass retention has also proven to be an important part of ASA sizing.(6,8,10,11) The fillers and fine particles adsorb cationic additives to a much greater extent than the long fibers because of their extremely high surface area. Fillers and fines not retained in the first pass will carry with them adsorbed ASA emulsion. Conditions of high temperature and shear found in a paper mill can destabilize the emulsion particles attached to these fillers and fines, especially with repeated cycling. By the time these particles are recycled, the ASA is likely to be completely hydro-

lyzed. Not only will low first pass retention reduce sizing efficiency, but the build-up of hydrolyzed ASA can cause runnability problems. The sticky nature of the hydrolyzate can cause build-ups in the headbox and picking at the press. Therefore, it is important to keep first pass retention as high as possible.

AQUEOUS CHEMISTRY OF ALUMINUM SALTS

Papermakers' alum, aluminum sulfate, has long been used in the manufacture of paper and paperboard. Even with its widespread use, our fundamental knowledge of the interactions of alum with other materials in the papermaking system is inadequate. A major factor which has inhibited the progress of investigations of these interactions is the complicated chemistry of the aluminum ion in aqueous solutions. Under the conditions used in the papermaking system, the aluminum ion can form a multitude of species including the simple trivalent cation, various hydroxo-aluminum complexes, and aluminum hydroxide precipitates.(12) In order to better define the type of aluminum species existing in the papermaking system and the type of interactions that are occurring, a discussion on aluminum chemistry is included.

The adsorption of cations such as the aluminum ion is a well-known property of cellulose fibers. The cations are adsorbed through an ion exchange interaction with surface groups, primarily carboxyl groups. When the pH increases, the carboxyl groups ionize and the adsorption of cations increases; however, this increase in adsorption was shown to play a minor role in the adsorption of aluminum species at high pH levels.(13)

Hayden and Rubin (14) identified five aluminum species for a non-complexing anion aluminum salt by using aluminum nitrate. The aqueous equilibria of aluminum from aluminum sulfate is considerably more complicated than aluminum nitrate due to the complexing effect from the sulfate ion. While the results obtained from the aluminum nitrate salt differ slightly from the aluminum sulfate salt, they are still very useful for describing alum applications. Hayden and Rubin concluded that their experimental data could only explain the presence of five aluminum species: Al^{3+},

$AlOH^{2+}$, $Al_8(OH)_{20}{}^{4+}$, $Al(OH)_3$, $Al(OH)_4^-$. The distribution of the aluminum species as a function of pH is shown in Figure 7.(14)

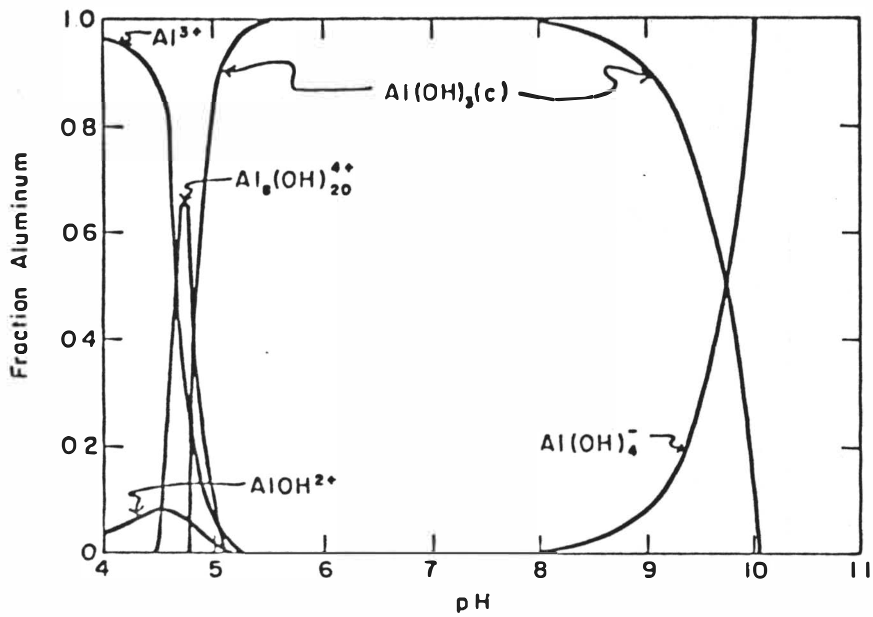


Figure 7. Distribution of 5.0 x 10^{-4} M hydrolyzed Aluminum (III) as a Function of pH.(14)

For the narrow pH range of 4.0 to 5.5, the bottom of Figure 8 shows the aluminum species distribution. It is possible to consider three distinct regions from pH 4.0 to 5.5: a low, intermediate, and high pH region.(19)

In the low pH region, below pH 4.3, Al^{+3} and $AlOH^{2+}$ are the only aluminum species present, where the trivalent cation Al^{+3} is the dominant species.(14) The top of Figure 8 shows the aluminum adsorption to be constant below pH 4.5. The adsorption of aluminum is affected primarily by pH and concentration. The adsorption of aluminum in the low pH region is independent of time and concentration.

In the intermediate pH region, there are three soluble aluminum species: Al^{3+}, $Al_8(OH)_{20}{}^{4+}$, and $AlOH^{2+}$. A majority of the total aluminum goes

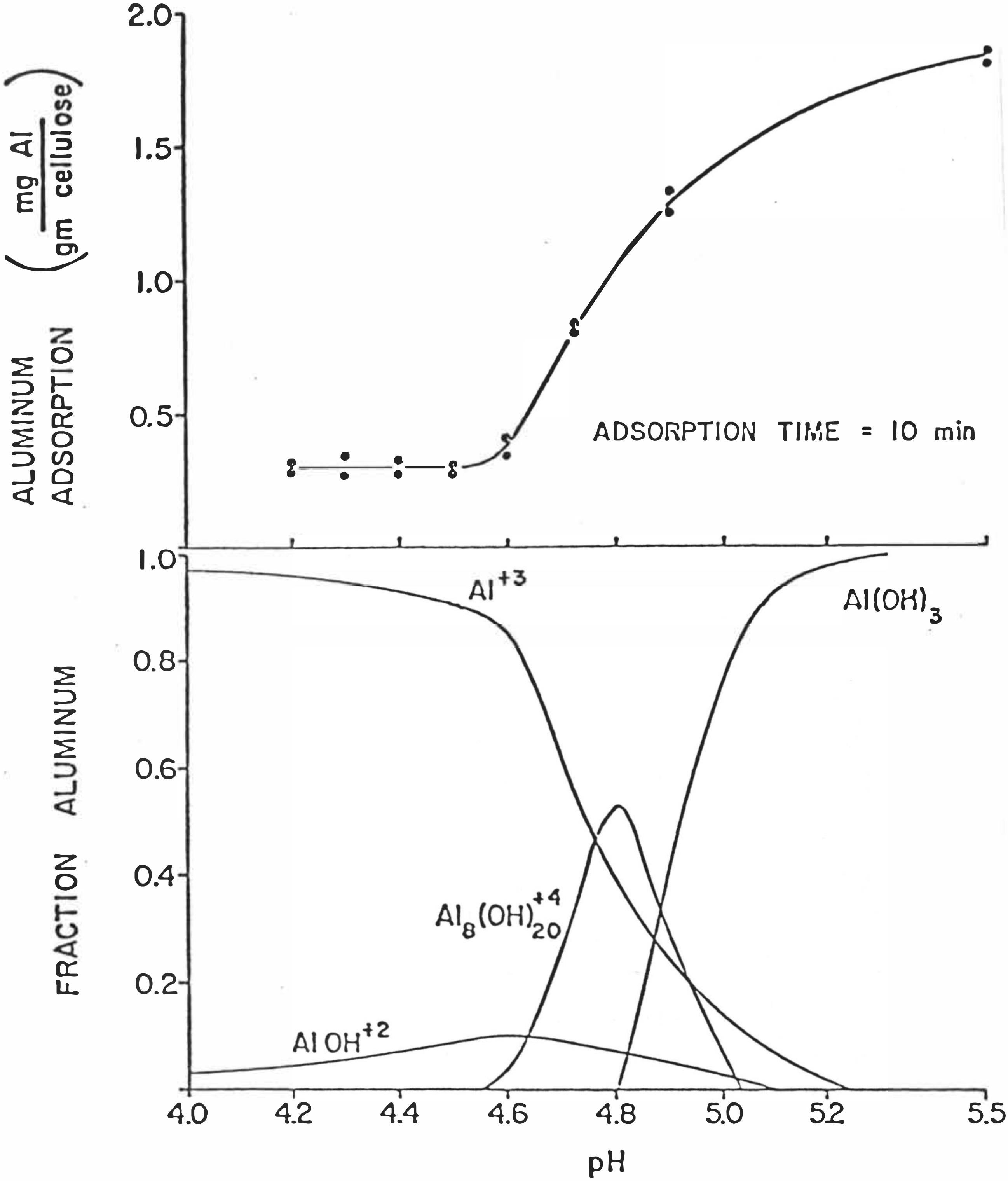


Figure 8. Top: Aluminum Adsorption as a Function of pH for $AlCl_3$
Bottom: Distribution of Aluminum Species as a Function of pH for $AlCl_3$.(12)

to form Al^{3+} and $Al_8(OH)_{20}{}^{4+}$. However, since there are eight aluminum atoms for every polynuclear molecule, the concentration of the $Al_8(OH)_{20}{}^{4+}$ is about the same as $AlOH^{2+}$ and considerably less than the concentration of Al^{3+}. It is important to note that the increase in adsorption in the intermediate pH region occurs before the pH of precipitate formation and coincides with the formation of the polynuclear species, $Al_8(OH)_{20}{}^{4+}$. From pH 4.2 to 5.0, the increase in adsorption is over 600%. The increase in adsorp- is due primarily to the formation of the polynuclear complex, $Al_8(OH)_{20}{}^{4+}$.(12)

Finally, there is the high pH region, where most of the aluminum hydrolyzes to form aluminum hydroxide precipitates. The increased adsorption of aluminum in this region is attributed to the formation of the colloidal $Al(OH)_3$ precipitate. Although the $Al(OH)_3$ precipitate is a neutral species, it exists as a positively charged species up to pH 8.5-9.0 due to the adsorption of hydrolysis products onto the precipitate.(12,13)

The colloidal precipitate is believed to adsorb onto the cellulose fibers at high pH. Arnson and Stratton (13) propose that as the precipitate accumulates at the fiber surface, it becomes enmeshed in the fibrillar structure of the fiber.

The complexing effect from the sulfate ion, as mentioned earlier, in aluminum sulfate makes the aqueous chemistry of alum more complicated than that predicted by the aluminum nitrate salt (Hayden and Rubin) and the aluminum chloride salt (Arnson). Arnson(12) shows the adsorption of aluminum from the alum solution to have the same pattern as the aluminum chloride, except the sulfate curve breaks upward before the chloride curve as shown in Figure 9. A proposed aluminum species distribution for aluminum sulfate is presented in Figure 10. Although this distribution curve has not been

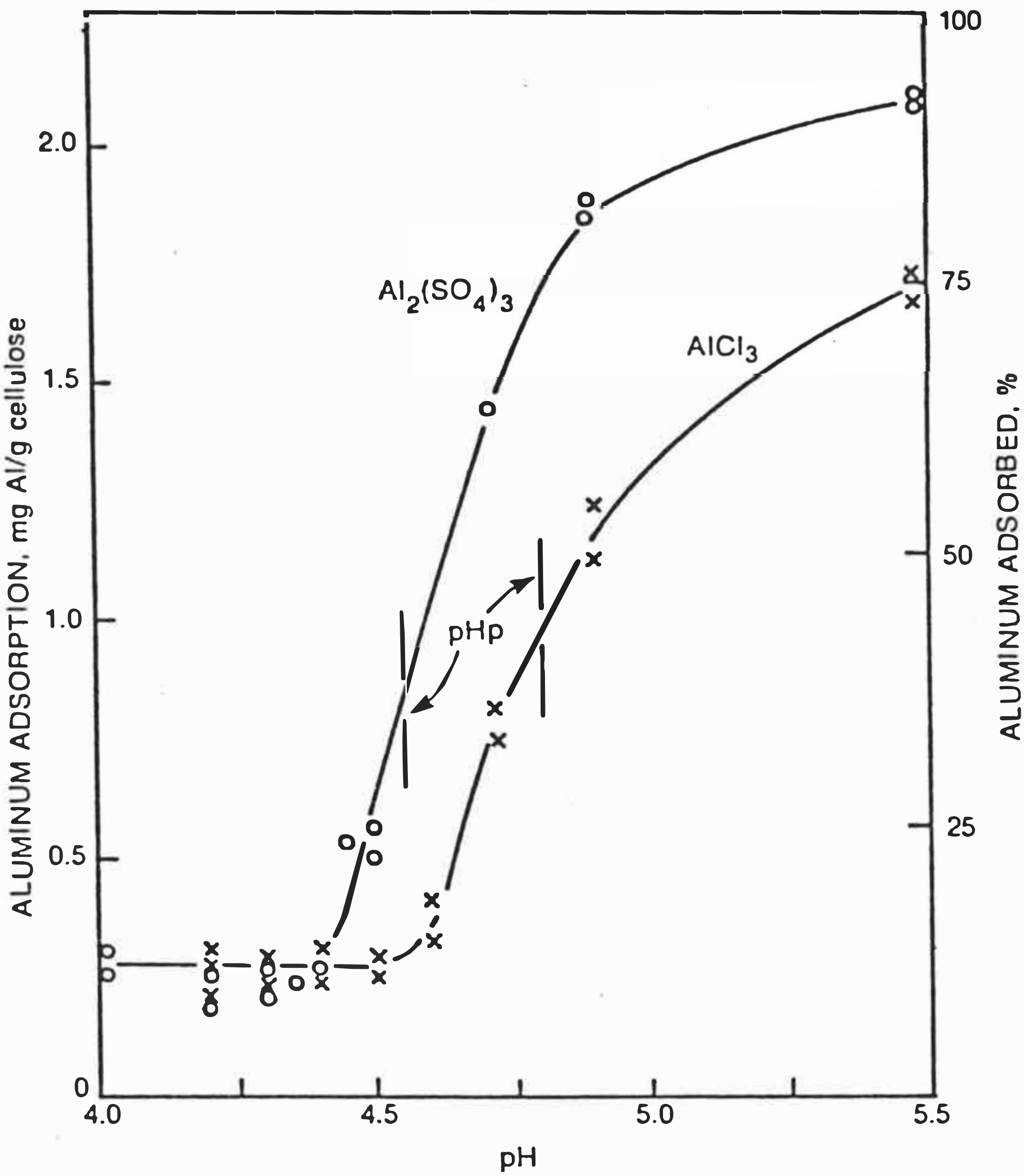


Figure 9. Comparison of Aluminum Adsorption for $AlCl_3$ and $Al_2(SO_4)_3$ (2.5×10^{-4}M). Solid Vertical Lines Denote the pH of Precipitate Formation (pHp) for each Aluminum Set.(12)

accurately determined, it can be seen that the distribution curves for aluminum chloride, aluminum nitrate, and aluminum sulfate are very similar.

The absorption and formation of each aluminum species is also a function of aluminum concentration as shown by Figure 11.

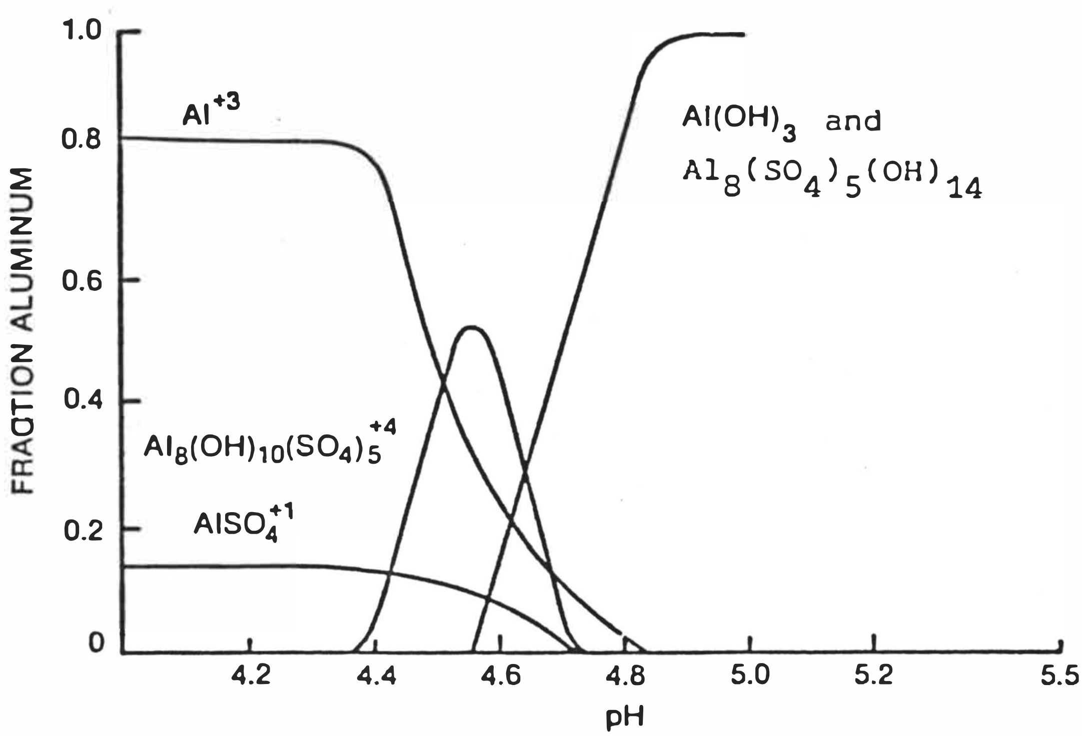


Figure 10. Proposed Aluminum Species Distribution for $Al_2(SO_4)_3$ (2.5×10^{-4}M).(12)

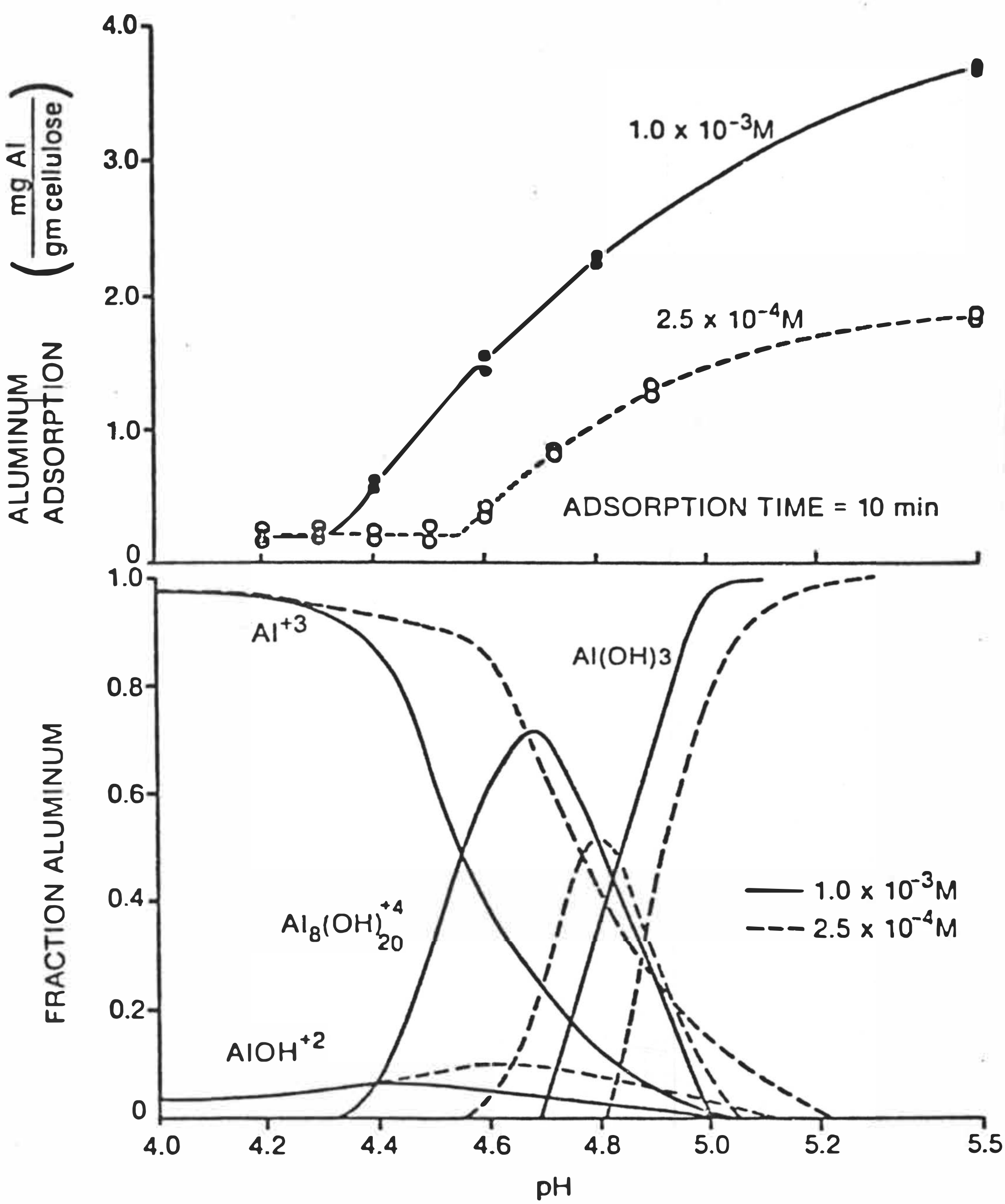


Figure 11. Top: Aluminum Adsorption as a Function of pH and Aluminum Concentration for $AlCl_3$.
Bottom: Distribution of Aluminum Species as a Function of pH and Aluminum Concentration for $AlCl_3$.(12)

THE EFFECT OF ALUM ON ASA SIZING

Alum has been commonly known as the papermaker's friend; probably because of its versatility in the well established rosin-alum sizing system. The sizing of paper with rosin and alum has a long and honorable history. However, there are many problems associated with acid papermaking, such as corrosion, impairment of paper permanence, lower strength and the exceeding of effluent limitations on dissolved aluminum. The disadvantages associated with acid papermaking are bringing about an increasing number of conversions to alkaline papermaking. While one of the main objectives of going alkaline is the elimination of aluminum in the papermaking process, some mills have found small levels of alum to be beneficial.

Meyer (15) showed that without alum, acceptable sizing levels can not be developed with ASA. On the other hand, some mills are currently applying ASA successfully without any alum.(16,17,18)

The role of alum in acid papermaking is fairly easy to predict and understand because of the cationic form of the alumina. The formation of aluminum hydroxide precipitate in alkaline conditions makes it more difficult to rationalize the effects of alum in alkaline papermaking. Alum, although it has no cationic charge under alkaline conditions, seems in many cases to improve the sizing efficiency and runnability of ASA.(6) The hydrolysis of ASA can lead to machine operability problems, especially press picking and deposits.

Press picking is believed to be due to nonreactive hydrolyzate which is not strongly bonded to the fiber and can pick out on a press roll.(10,11) Aluminum hydroxide is a sticky precipitate and the addition of alum has been shown to reduce the tackiness of the precipitate.(25) Calcium and

magnesium soaps of hydrolyzed ASA have been identified as causes for press picking; however, alum was shown to react preferentially over calcium and magnesium to produce a less tacky precipitate. Press picking tends to develop after sufficient time is allowed for the buildup of unretained free ASA-acid in the whitewater.(19)

Strazdins (20) showed that alum improved ASA sizing. Alum was also shown to improve drainage and retention of filler and increase the efficiency of an anionic retention aid. He proposed that alum improved ASA sizing because of better bonding and size orientation. Improvement in drainage and retention are believed to be due to a reduction of the electrokinetic charge on the fibers, thus allowing bridging. He proposed that the adsorption of alum reduced the electrokinetic charge.

THESIS PROPOSAL

Statement of Problem

The preceding literature analysis and inconsistent performance in the field have led to the conclusion that the explanations of the mechanisms involved with ASA sizing are inadequate and require further attention. This thesis is primarily concerned with the influence of various forms of alumina on ASA sizing.

Many of the authors reviewed in the literature state that the presence of small to moderate amounts of alum has proven beneficial to ASA sizing. The addition of alum has claimed to improve runnability, increase first pass retention, improve sizing efficiency, reduce the formation of ASA deposits and reduce press picking. In most cases, these advantages are based on very little, credible experimental evidence. Therefore, it can not be assumed that alum is solely responsible for these improvements in ASA sizing.

Due to the complex aqueous chemistry of alum, there is still a great deal of mystery as to the role of alum in ASA sizing. The formation of various aluminum complexes at different pH levels also contributes to the complexity of alum chemistry.

Strazdins (20) studied the charge of alum at different pH levels and determined that alumina that forms under alkaline sizing conditions has no titratable cationic charge. This is an important aspect of aluminum chemistry; however, it is more important to understand the relationship between alum and ASA.

Based on the above, this thesis proposes to study the effects of the various forms of alumina, at different pH levels, on the efficiency of ASA

sizing. Upon completion of this, it is hoped to better understand the mechanism(s) between alum and ASA.

Experimental Approach

The effect of the various forms of alumina on ASA sizing will be determined by the efficiency of the applied size. In order to study the effect of the various aluminum species it will be important to work in pH regions defining a particular dominant species. The efficiency of each aluminum species will be determined by the degree of sizing imparted to handsheets sized with ASA.

EMULSIFICATION PROCEDURE

Starch Preparation

The starch used in the ASA emulsion was Accosize 72, supplied by American Cyanamid. Accosize 72 is a cationic (quaternary amine) potato starch which is cold water soluble. This particular starch was in the flake form.

The starch was prepared at 5.0% solids in cold distilled water using a variable speed mixer. A standard mixing time of 25 minutes should be used when preparing the starch.

ASA Emulsification

The ASA used in the emulsion was Accosize 18, supplied by American Cyanamid. Accosize 18 contains a surfactant for emulsification. The ASA was emulsified in cationic starch using a Waring blender equipped with a glass jar. The following emulsification procedure and recommendations were obtained from Richard B. Wasser of American Cyanamid Company. Wasser has done some very important work with ASA and this emulsification procedure is the same as used by him. Wasser claims that the particle size of the emulsion produced by this procedure is in the optimum range of 1-3 microns.

The emulsification procedure is as follows:

1. Add 197.5 grams starch at 5.0% to the Waring blender and mix at high speed for 10 seconds.
2. Weigh 2.50 grams ASA by difference in a syringe.
3. Add 2.50 grams ASA to blender and mix at high speed for 2.5 minutes. The emulsion will then be at 1.25% ASA.
4. To prevent hydrolysis of ASA, adjust the pH of the emulsion to 3.5 to 4.0 and cool below 50°F.

Wasser said the emulsion should be stable for about eight hours.

In order to use the ASA emulsion in preparing handsheets, the emulsion

must be diluted to 0.25% ASA. Prepare the dilute 0.25% ASA emulsion by diluting 50 grams of emulsion at 1.25% ASA to a total of 250 grams with distilled water.

The starch to ASA ratio of the emulsion is 4:1. Typically a 2:1 starch to ASA ratio is used; however, since no internal starch or retention aid was used in the handsheet procedure, it was recommended by Wasser that the ratio be increased to 4:1 to improve retention of the ASA.

Emulsion Addition

The addition level of ASA was 3.6 #/ton (0.18%) based on a 2.50g O.D Noble and Wood handsheet.

2.5 x 0.0018 = 0.0045g ASA per sheet

0.0045g ASA/0.25% emulsion = 1.8g emulsion at 0.25% ASA per handsheet

The dilute emulsion was weighed by difference using a syringe and then injected into the stock under agitation.

FURNISH

The stock consisted of 75% bleached kraft hardwood and 25% bleached kraft softwood. The stock was refined to 323 CSF in deionized water with the Valley beater. The stock was thickened to approximately 3.5% consistency and was treated with 150 ppm biocide (Betz RX-41). The stock was stored in a refrigerator at 8°C to further preserve the furnish during the course of the semester.

HANDSHEET PROCEDURE

Figure 12 shows a schematic diagram of the handsheet procedure.

The consistency of the stock was adjusted to 0.25% in the Noble and Wood proportionator using deionized water. pH of the stock was adjusted with sodium hydroxide or sulfuric acid, as required.

Note: The pH of the stock was checked frequently as it will change as the stock mixes.

One liter samples of stock (2.5 grams O.D. fiber) were removed from the proportionator and placed under the "gang" stirrer for mixing. Typically the first and last one liter samples were controls, i.e. no alum was added. Alum was added to the other samples at the desired addition level from a stock solution of 1.0% alum (aluminum sulfate). The stock was allowed to mix for a standard time before making handsheets.

Note: The addition of alum to the stock may change the pH, so the pH of each sample was checked and readjusted if necessary.

After the stock was mixed under the "gang" stirrer, one sample was removed at a time and placed under a variable speed mixer, with moderate agitation.

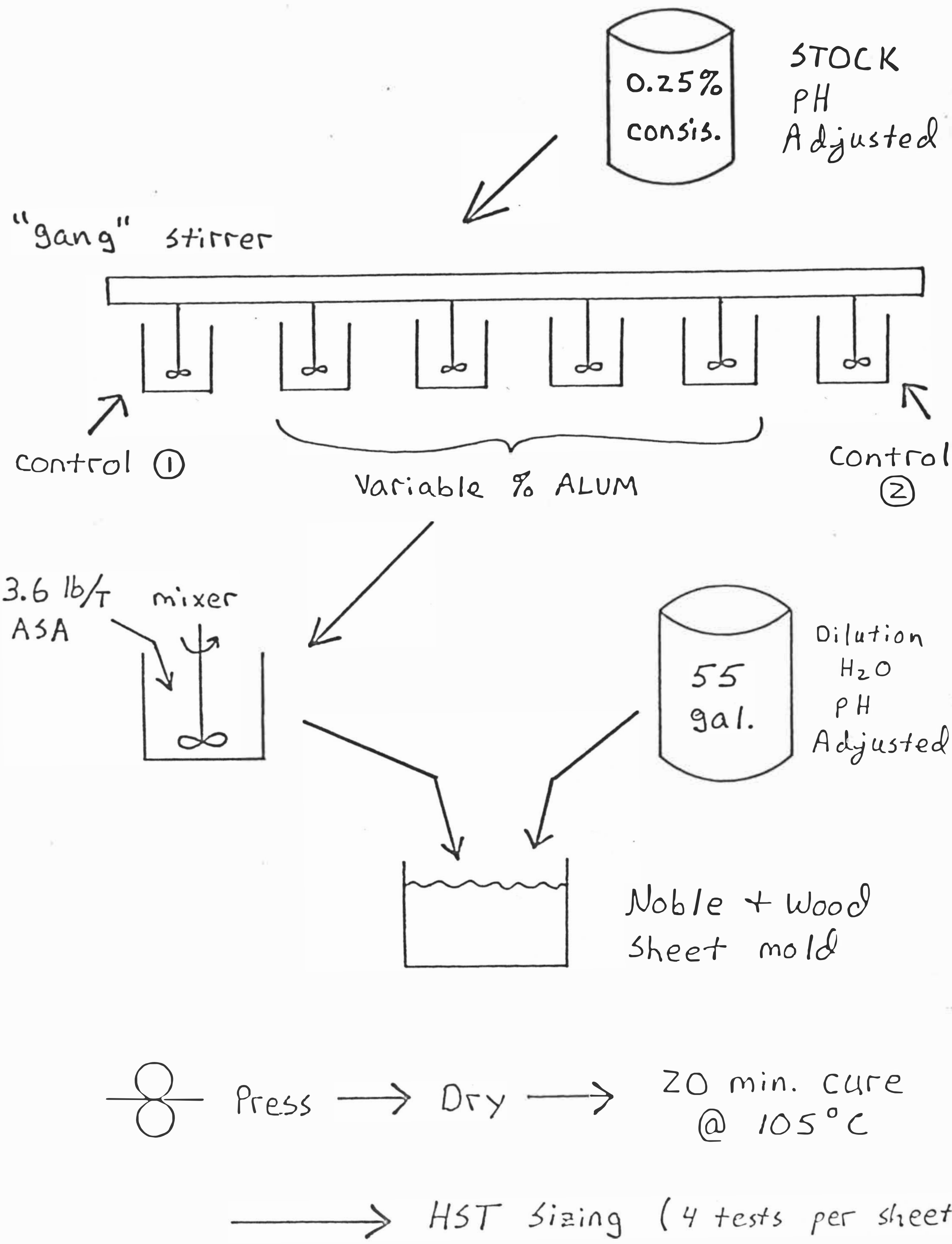
The Noble and Wood sheet mold was filled to the first dot with deionized water adjusted to the same pH of the stock.

Note: To provide a constant source of dilution water, a 55 gallon drum was filled with deionized water and adjusted to the proper pH.

3.6 #/ton ASA was added to the stock under agitation and mixed for 15 seconds. Immediately the stock was added to the sheet mold and mixed a standard number of times. Drain the sheet mold and press the sheet. Dry the sheet in the drum dryer for a standard number of times until the sheet "feels" dry.

After all the sheets were made in this manner, the sheets were placed between two pieces of blotter paper and placed in a convection oven at 105°C for

FIGURE 12
HANDSHEET PROCEDURE



20 minutes.

It was necessary to add this 20 minute cure since the ASA does not cure fast at a pH less than pH 6. Refer to Figure 6.

For handsheets made above pH 6, the ASA was cured by normal drying on the drum dryer. However, handsheets made below pH 6 will have very low sizing, if any at all, unless the sheets are cured for the additional 20 minutes. In order to be consistent, all handsheets were dried for an additional 20 minutes regardless of pH.

HANDSHEET TESTING PROCEDURE

1. The handsheets were conditioned for 24 hours prior to testing, in the paper testing laboratory at 50% relative humidity and 72°F.

2. Cut each sheet into four quarters.

3. Run a Hercules Size Test on each quarter following TAPPI Method T-530 pm-75. Hercules test ink #2 with 1% acidity was used. The Hercules size test meter was set at a 80% reflectance.

RESULTS

Presentation of Data

The results are presented graphically, showing the sizing level (seconds) plotted against some variable (typically percent alum). The average sizing value is represented by a dot through which a line has been drawn to represent the standard deviation of the average value.

The statistical significance of the results is very important. The significance test (see Statistical Analysis) can determine if the means of two samples are statistically different; however, the test cannot determine if the two means are equal. Therefore, if two or more means are statistically not different, this does not necessarily imply that they are equal.

Experimental Reproducibility

Figures 13 - 15 show the reproducibility obtainable with the handsheet procedure described earlier. Figure 13 shows that the sizing level from sheet to sheet is statistically not different. The average standard deviation for the six sheets is 17 seconds.

Figures 14 and 15 also show that the reproducibility between handsheets is statistically not different, except for the last sheet made in each case. The last sheet in both figures had a significantly lower sizing level than the previous sheets. It took approximately five minutes to make each handsheet. The average standard deviation of the results in Figures 14 and 15 is 41 seconds.

Results - Low pH Region

In the low pH region (pH 4.0), Figures 16 and 17 show that the addition of alum improved the sizing level with ASA. However, the sizing level was not

significantly affected by changing the addition level of the alum.

The controls made at the start and end of each run (Figures 16 and 17) were statistically not different; therefore, the two controls were averaged together and are represented by one data point.

The numbers below the data points on Figures 16 and 17 represent the order in which the sheet was made with respect to the first and second control. The first control being the first handsheet made in the run and the second control being the last sheet made in the run. The order in which the sheets were made was randomized in order to eliminate possible systematic errors.

Results - Intermediate pH Region

The results obtained in the imtermediate pH region (pH 4.8) are shown in Figures 18 - 20. The controls for Figures 18 and 19 were statistically different and therefore were not averaged. The controls for the data shown in Figure 20; however, were statistically not different and were averaged into one value.

The results shown in Figure 18 - 20 are hard to interpret due to the variability in the controls; however, the trends are consistent for each graph. The results show that at low levels (less than 1%), the addition of alum had no significant effect on sizing; however, as the percent alum was increased from one to two percent, the sizing appeared to decrease.

Results - High pH Region

The high pH region is defined as having a pH greater than 5.0 and less than 8.0.

The results are shown in Figures 21 - 27, where a majority of the work was done at pH 7; while the remaining work was done around pH 6.

Again, two controls were made, one at the beginning and one at the end of

each run. In every case but one, the first control (control 1) was higher than the second control (control 2). Figure 24, however, shows that control 1 was much less than control 2. Control 1 of Figure 24 is probably erroneous; this is based on the consistency of the other results.

Again, the results are numbered to show the order that the handsheets were made between the first and last control. It is important to note this order in the high pH region due to the consistently lower sizing level of control 2 compared to control 1.

The results showed that sizing was relatively unaffected by the addition of less than 1% alum. However, the addition of 1-2% alum tended to decrease the sizing level.

Figure 27 shows the results of a different study that was also done at the high pH region. For this study, a control was made adjacent with each sheet prepared with alum. This was done to eliminate the problem associated with the difference between the control made at the start and end of each run.

Again, the results showed that the sizing level of the controls decreased during the course of run. The results showed in this case that the addition of alum lowered the sizing level at all concentrations.

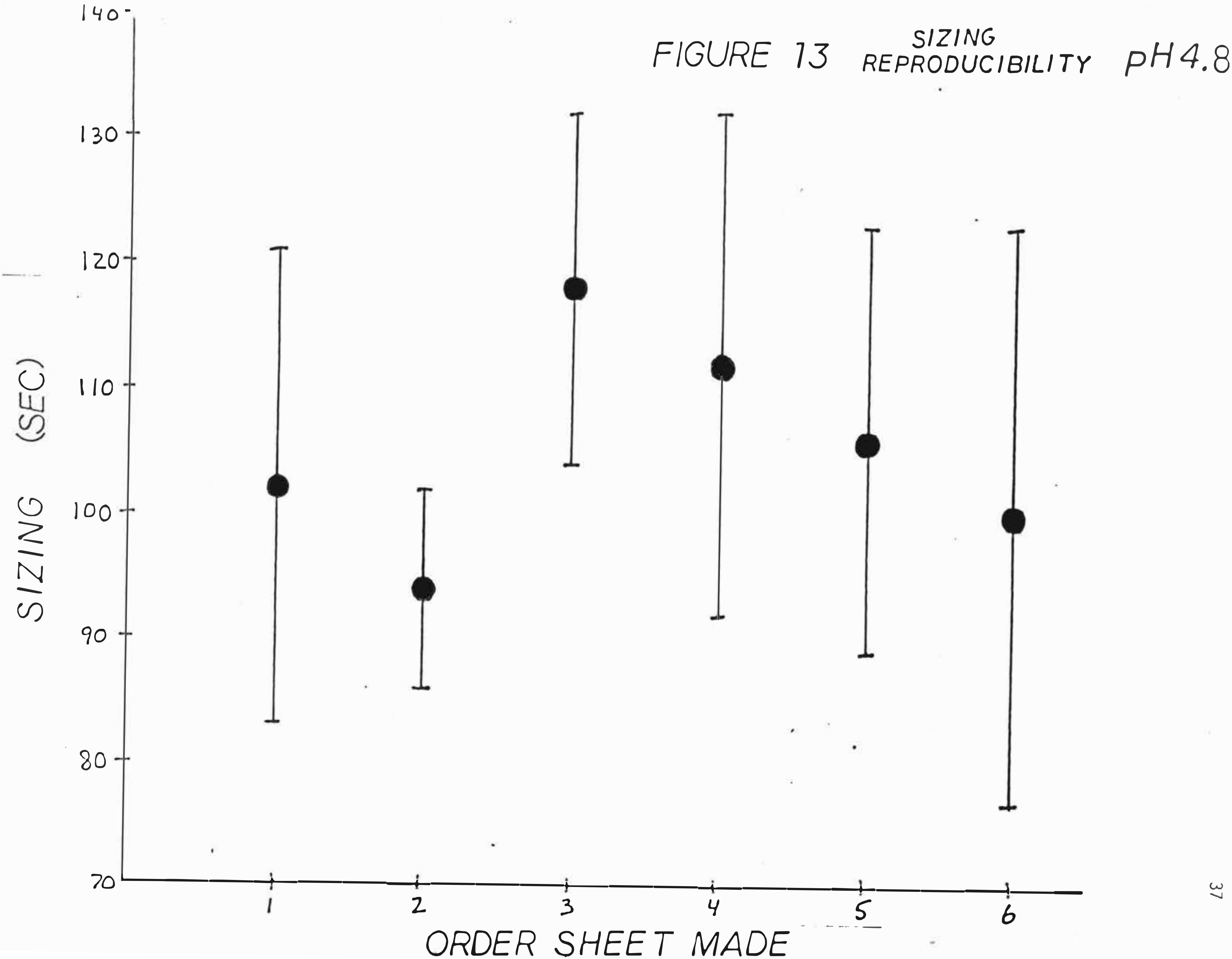


FIGURE 13 SIZING REPRODUCIBILITY pH 4.8
SIZING (SEC)
140
130
120
110
100
90
80
70
1
2
3
4
5
6
ORDER SHEET MADE

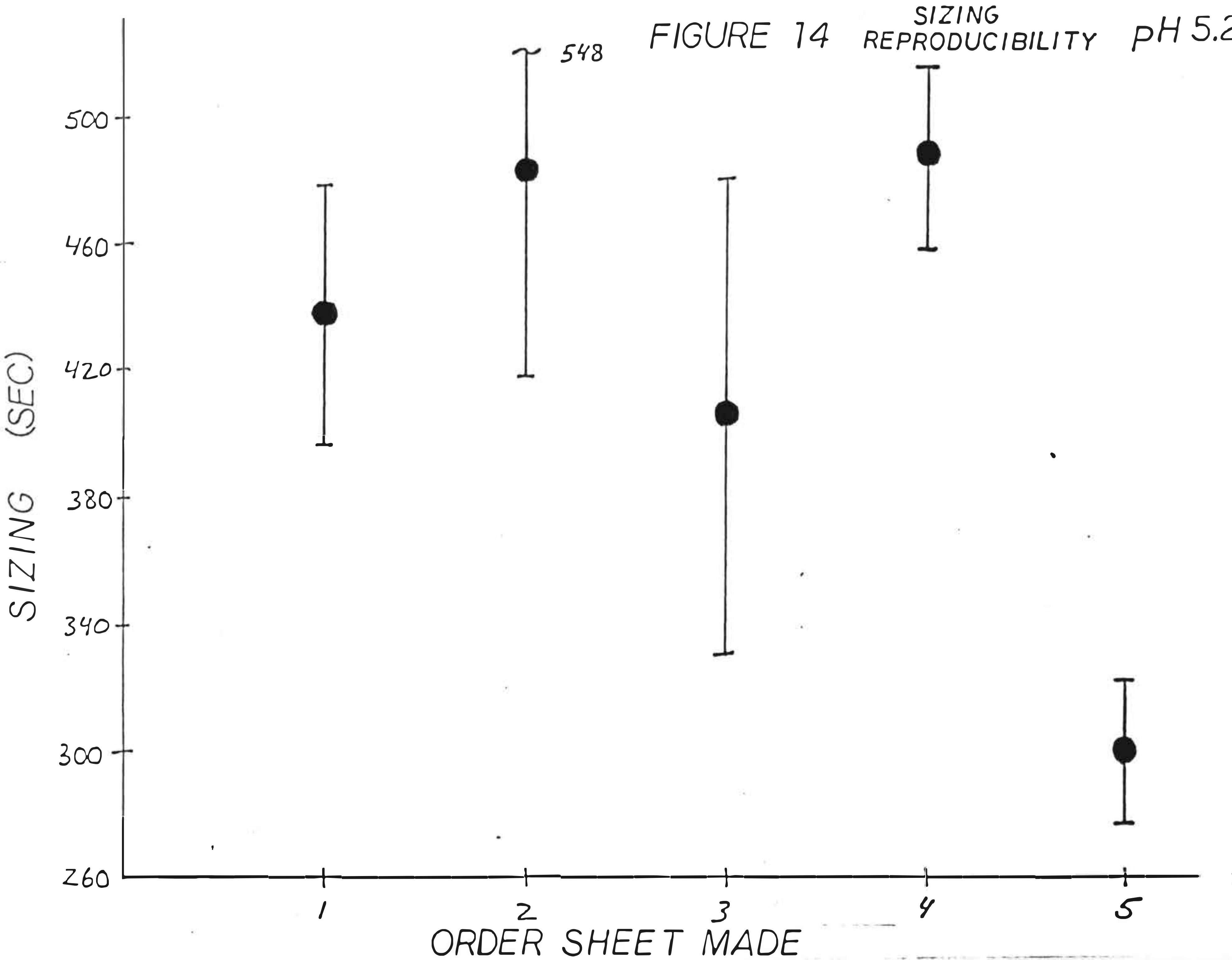


FIGURE 14 SIZING REPRODUCIBILITY pH 5.2
548
SIZING (SEC)
500
460
420
380
340
300
260
1
2
3
4
5
ORDER SHEET MADE

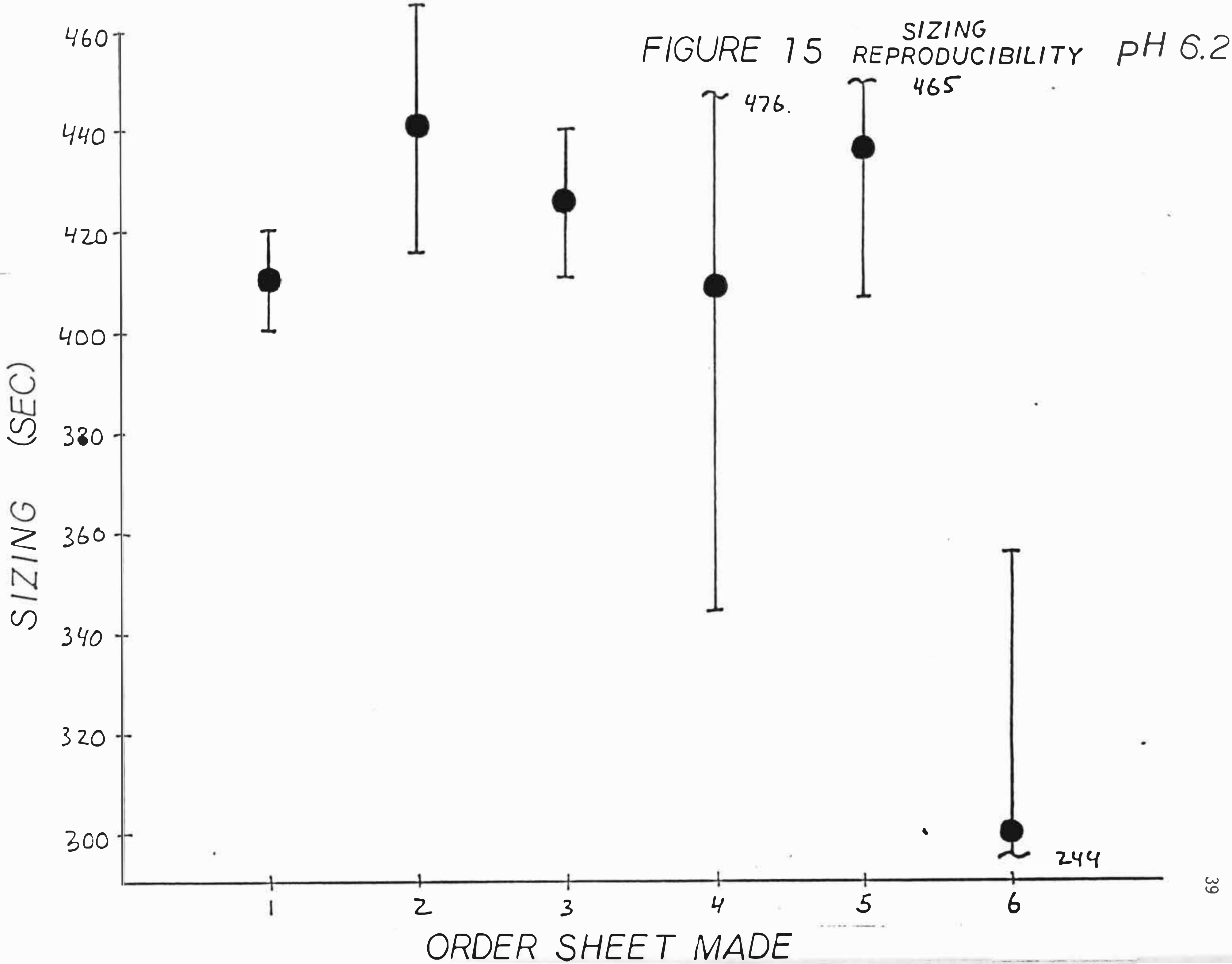
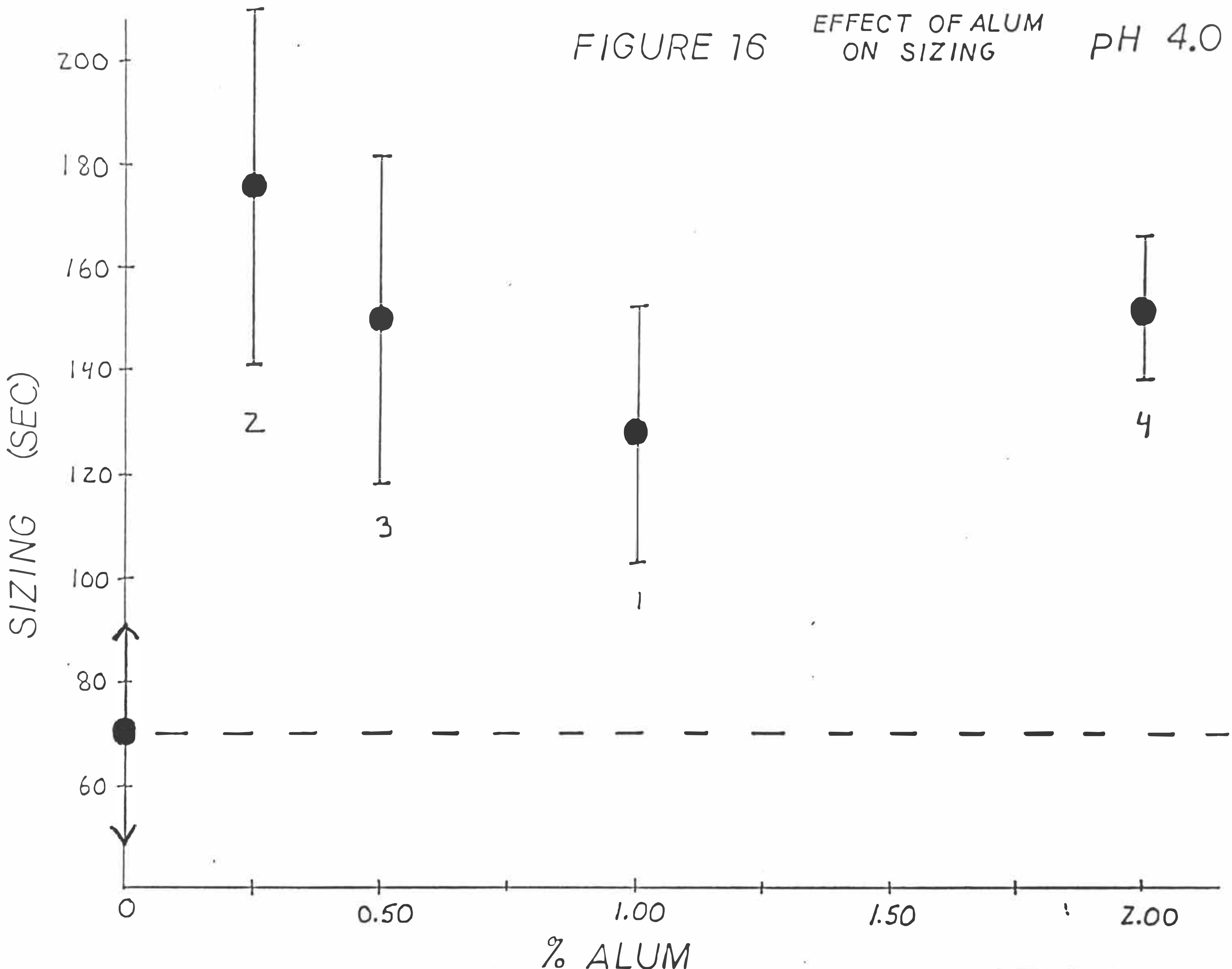


FIGURE 15 SIZING REPRODUCIBILITY pH 6.2
SIZING (SEC)
460
440
420
400
380
360
340
320
300
476.
465
244
1
2
3
4
5
6
ORDER SHEET MADE

FIGURE 16 EFFECT OF ALUM ON SIZING PH 4.0



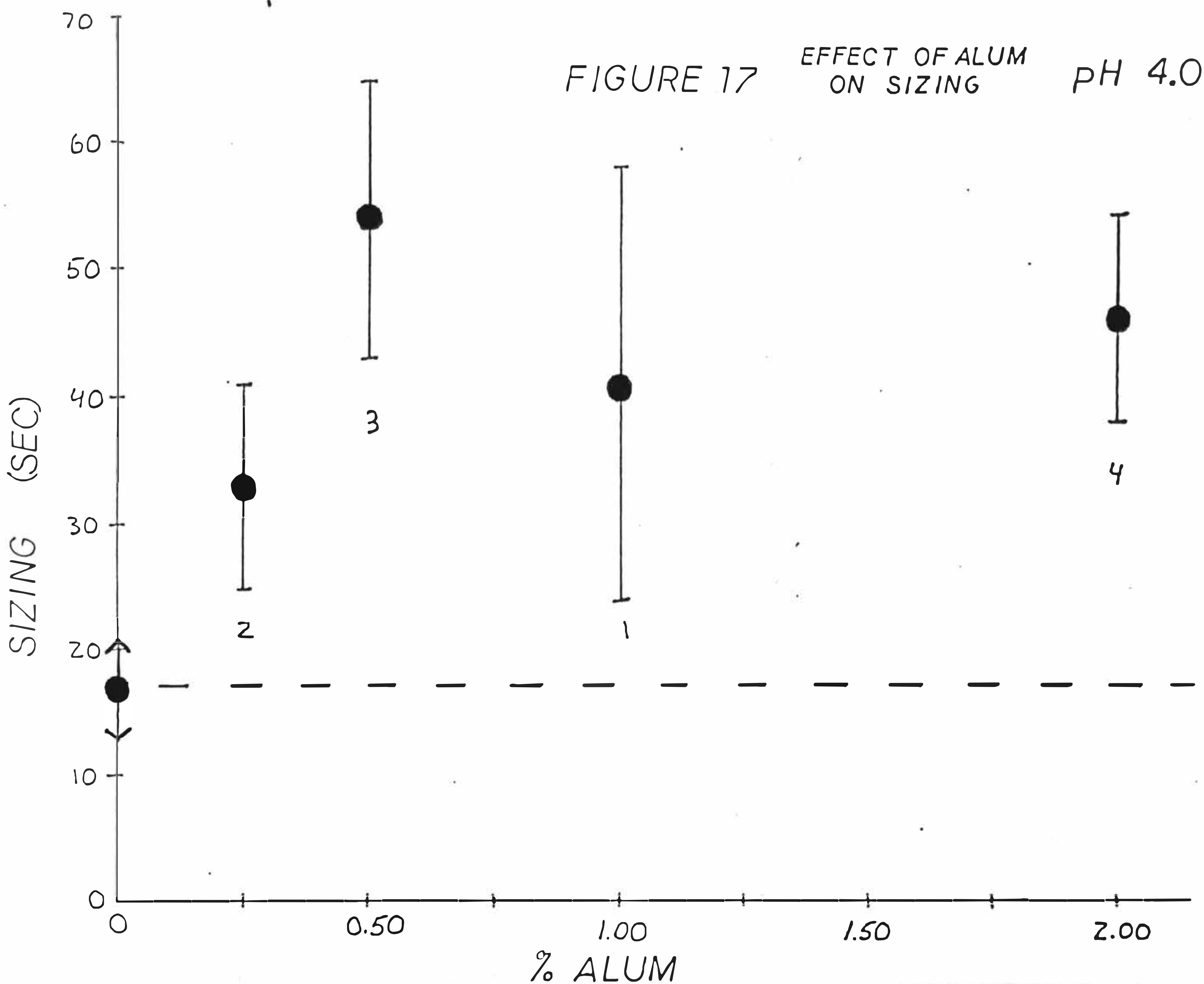


FIGURE 17
EFFECT OF ALUM ON SIZING
pH 4.0
SIZING (SEC)
70
60
50
40
30
20
10
0
0
0.50
1.00
1.50
2.00
% ALUM
2
3
1
4

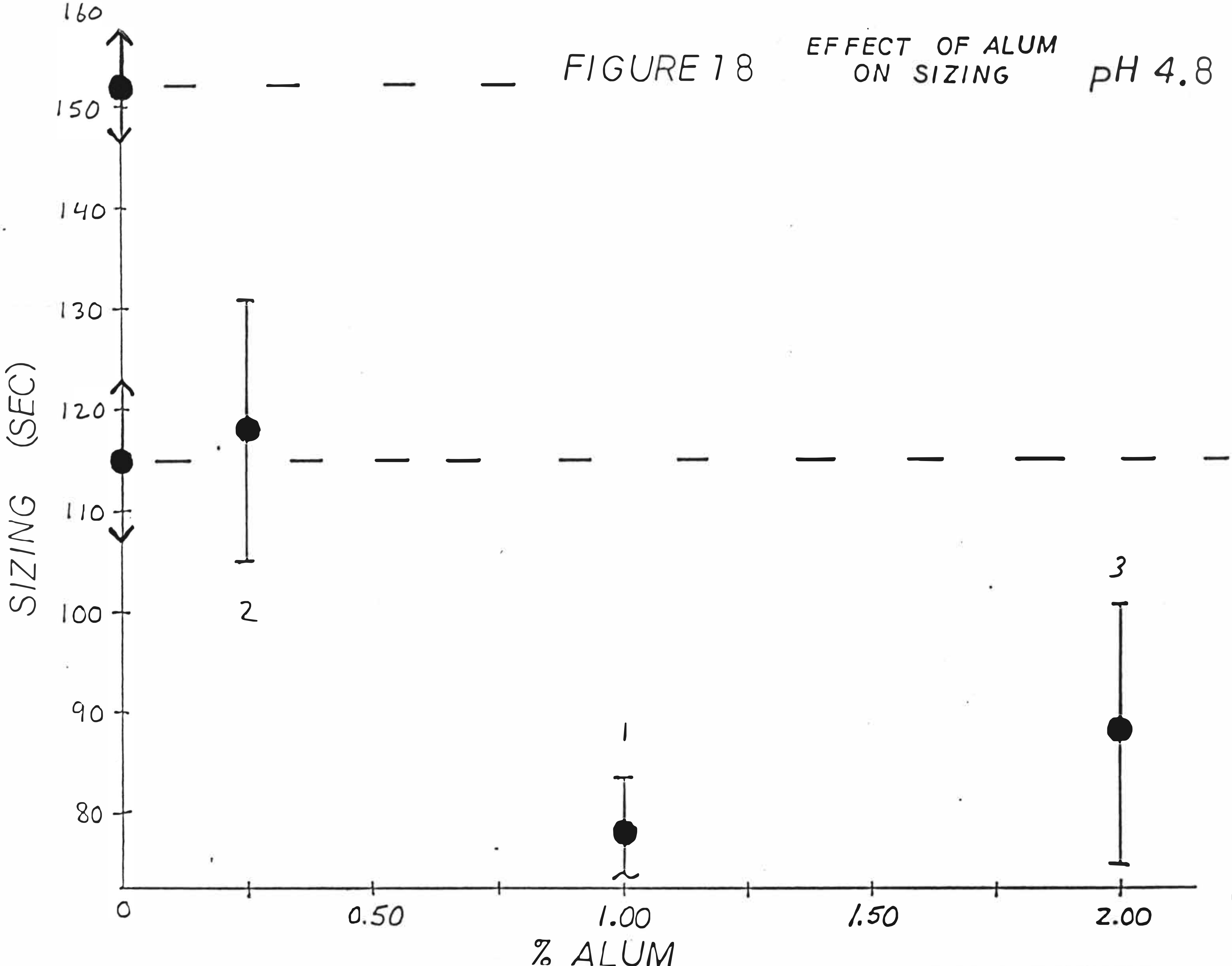


FIGURE 18
EFFECT OF ALUM
ON SIZING
pH 4.8
160
150
140
130
120
110
100
90
80
SIZING (SEC)
0
0.50
1.00
1.50
2.00
% ALUM
1
2
3

FIGURE 19 EFFECT OF ALUM ON SIZING pH 4.8

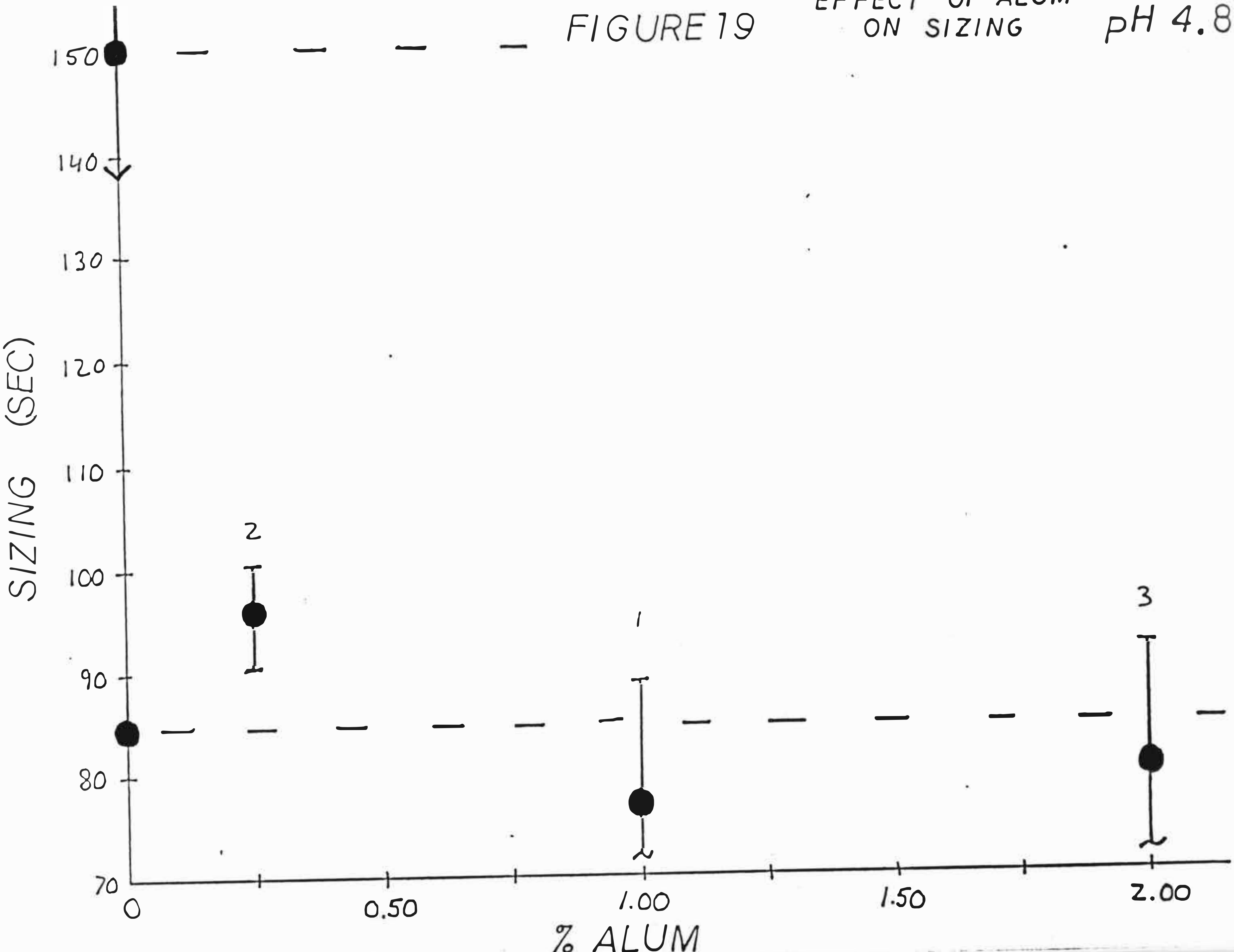


FIGURE 20 EFFECT OF ALUM ON SIZING pH 4.8

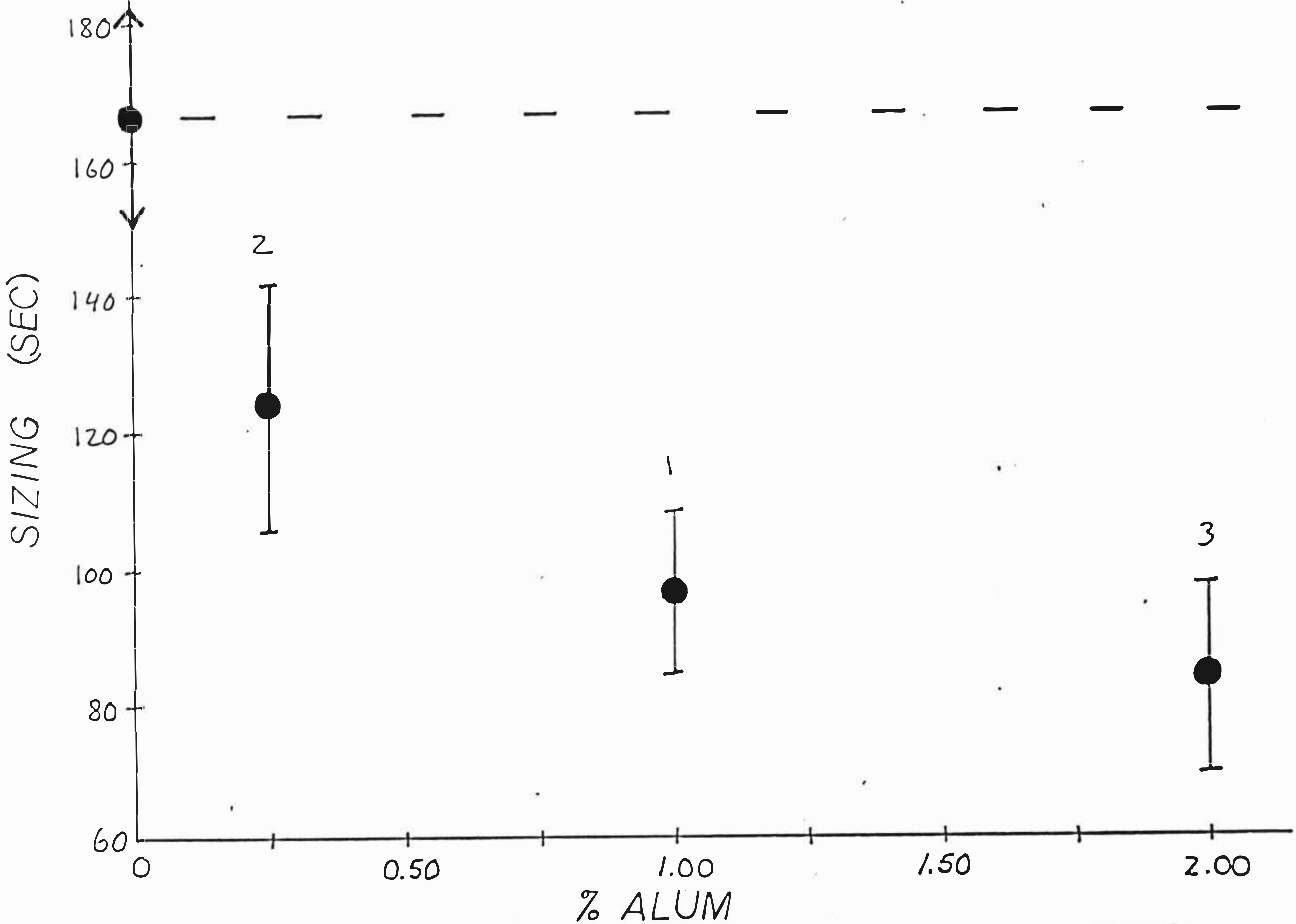


FIGURE 21

EFFECT OF ALUM ON SIZING pH 7.0

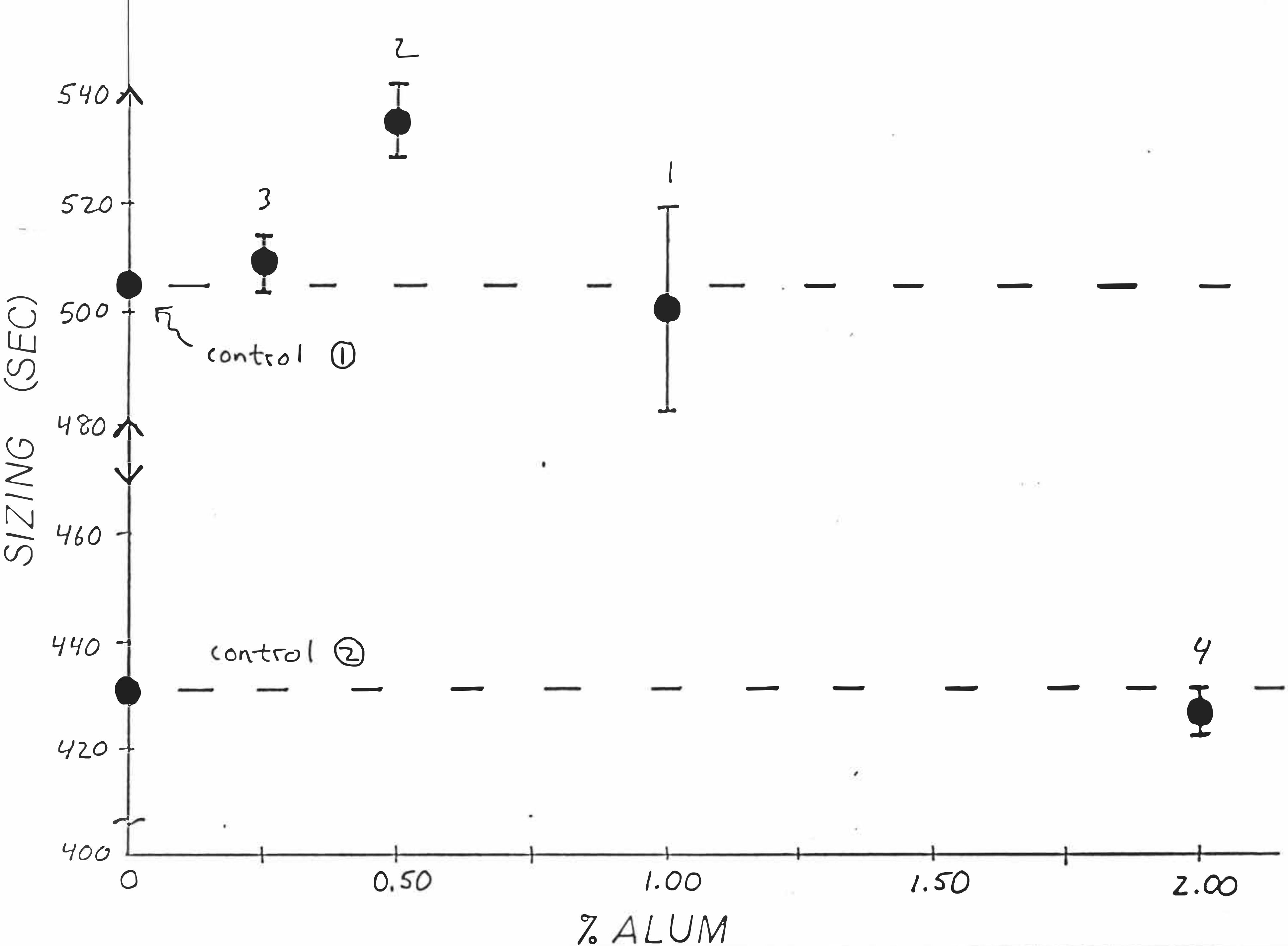
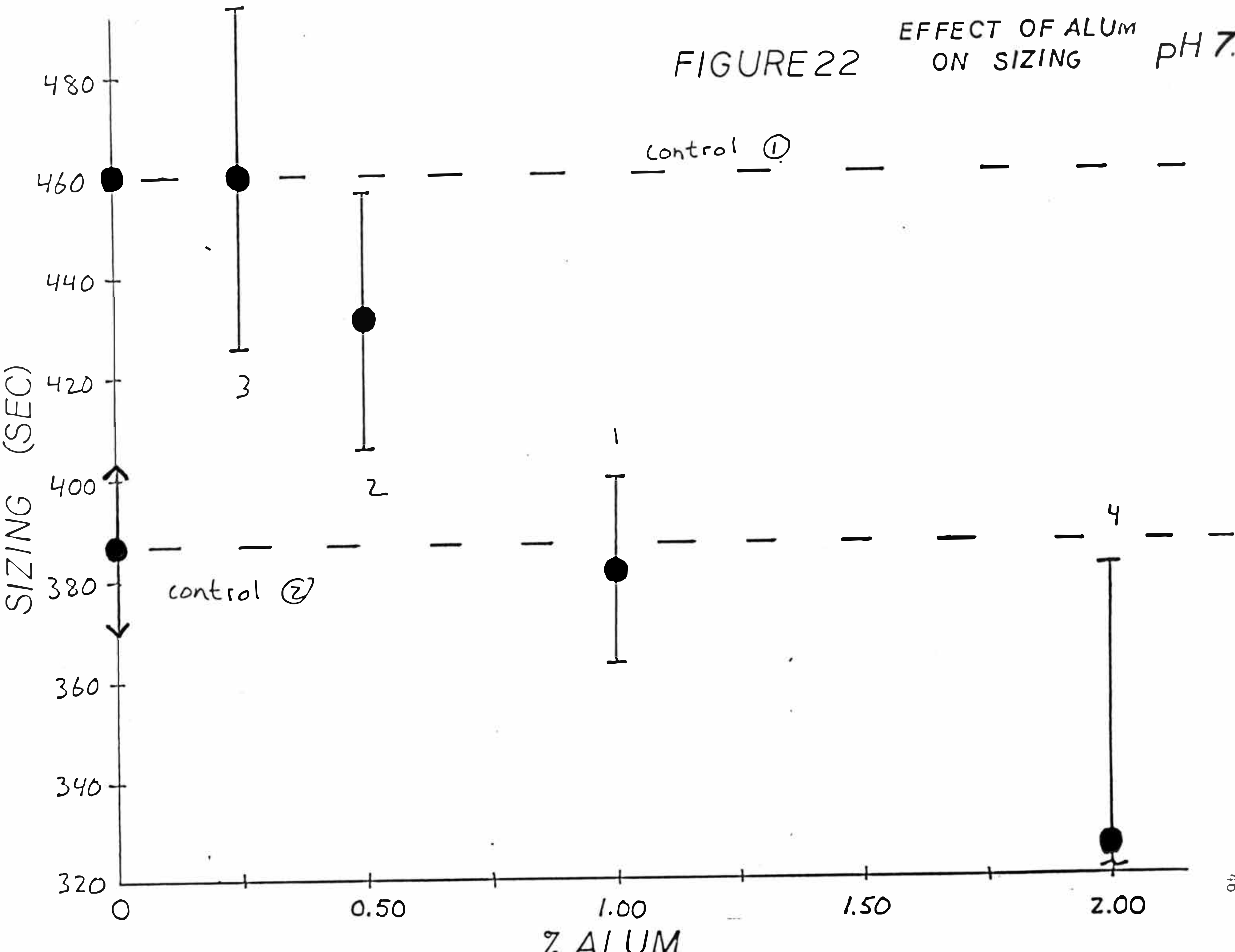


FIGURE 22

EFFECT OF ALUM ON SIZING pH 7.0



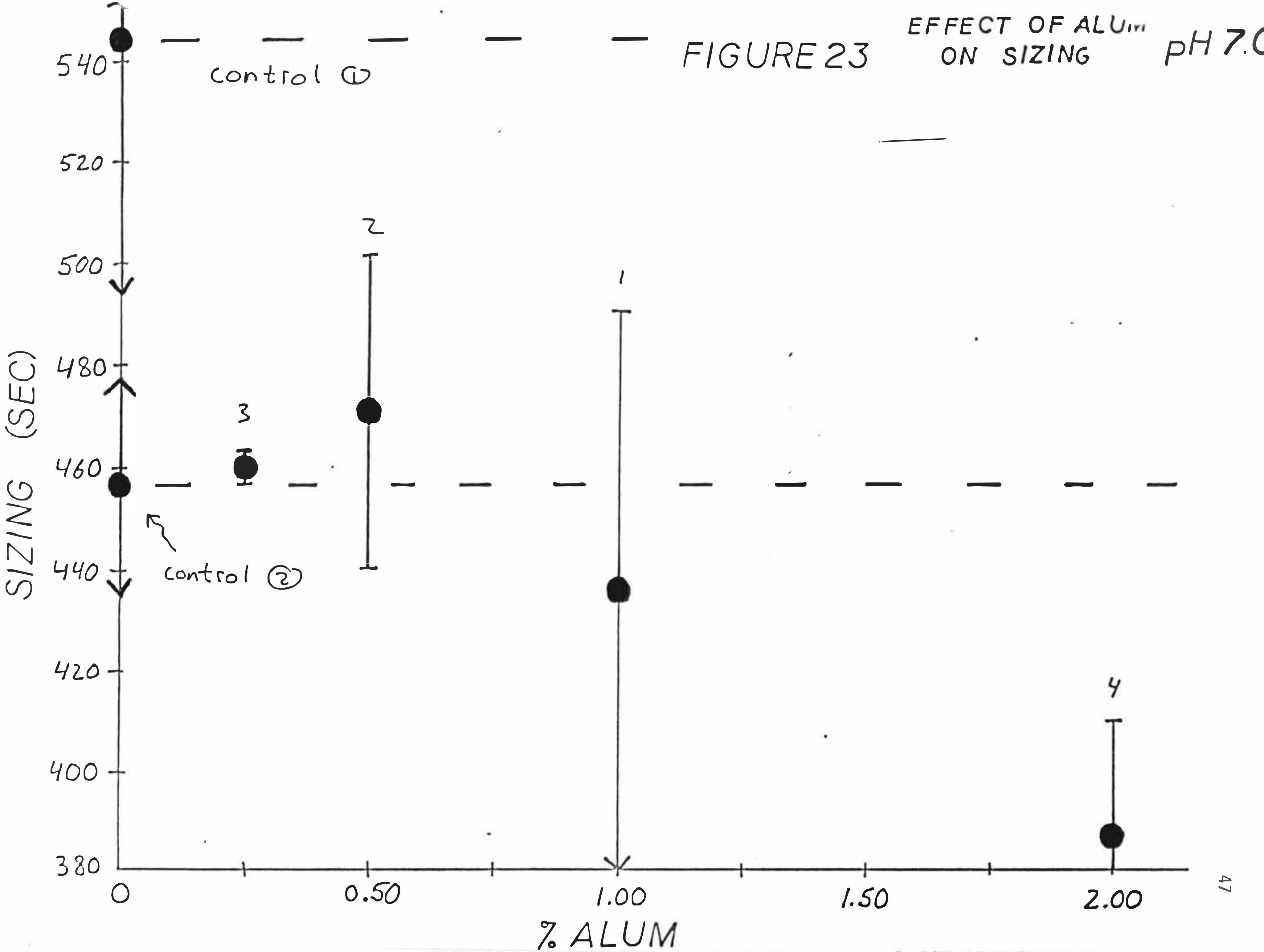


FIGURE 23
EFFECT OF ALUM ON SIZING
pH 7.0
control ①
control ②
1
2
3
4
540
520
500
480
460
440
420
400
380
SIZING (SEC)
0
0.50
1.00
1.50
2.00
% ALUM

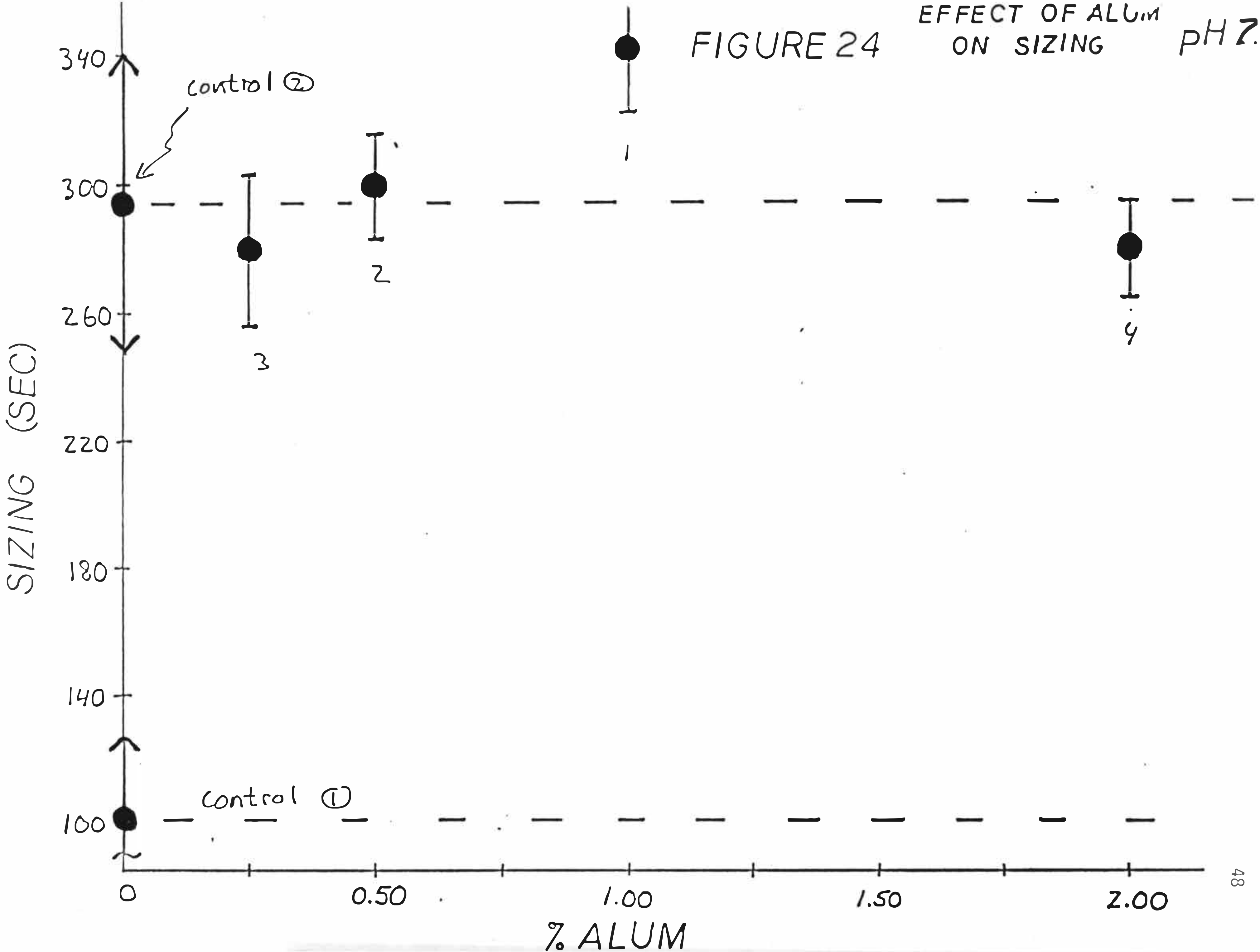
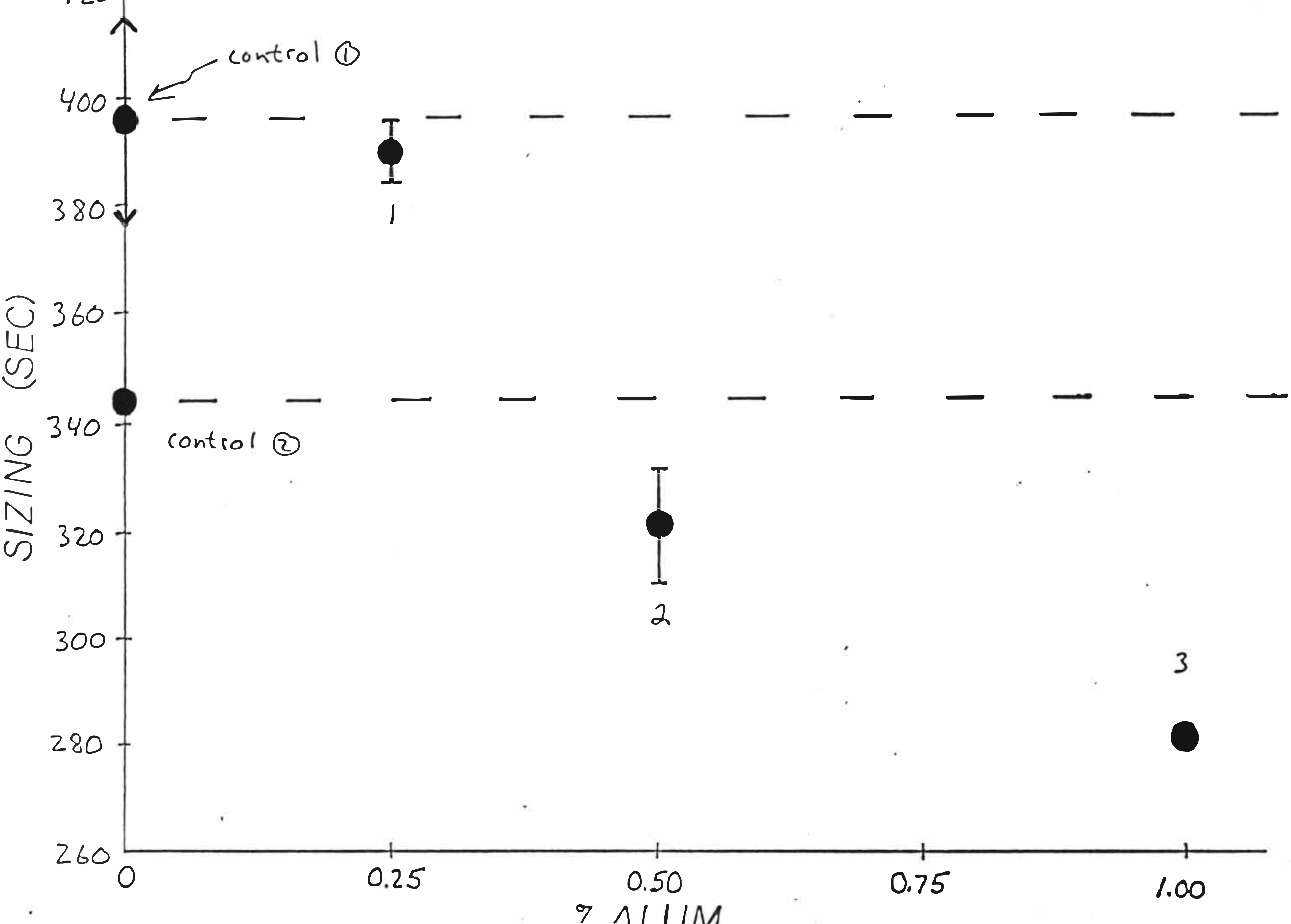


FIGURE 24 EFFECT OF ALUM ON SIZING pH 7.0

FIGURE 25 EFFECT OF ALUM ON SIZING pH 6.4



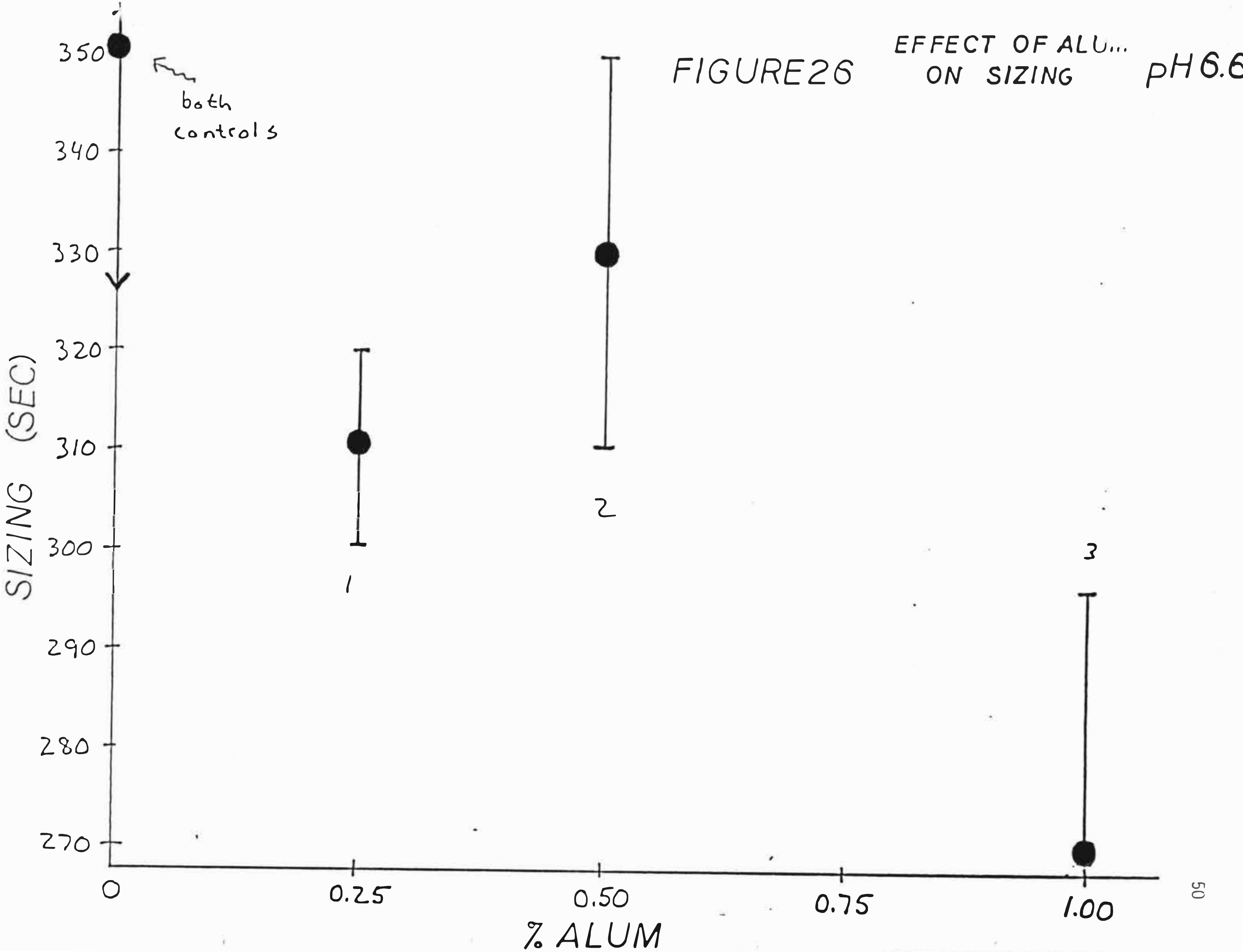


FIGURE 26
EFFECT OF ALU...
ON SIZING
pH 6.6
both controls
SIZING (SEC)
350
340
330
320
310
300
290
280
270
1
2
3
0
0.25
0.50
0.75
1.00
% ALUM

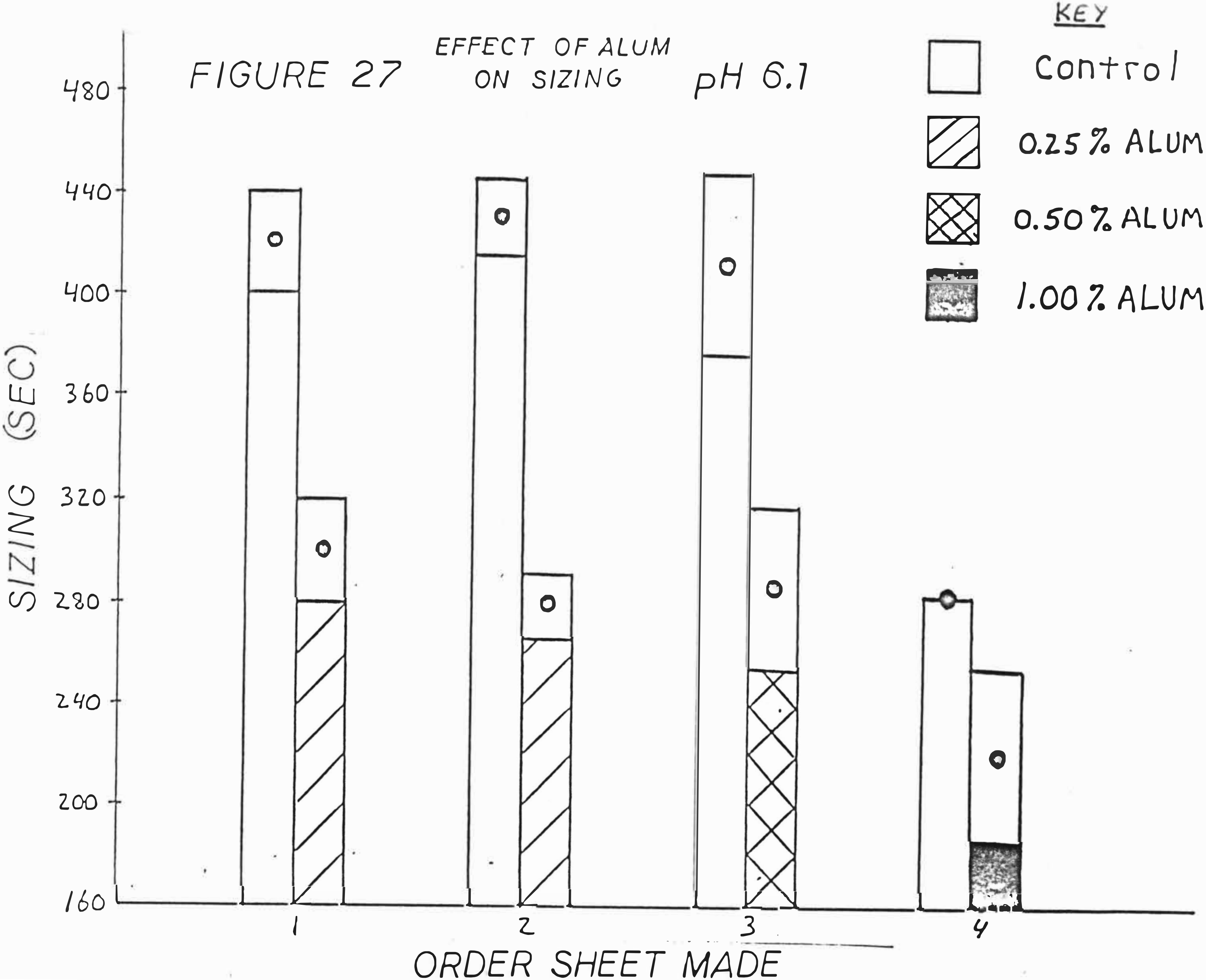


FIGURE 27
EFFECT OF ALUM ON SIZING
pH 6.1
KEY
Control
0.25 % ALUM
0.50 % ALUM
1.00 % ALUM
SIZING (SEC)
480
440
400
360
320
280
240
200
160
1
2
3
4
ORDER SHEET MADE

DISCUSSION OF RESULTS

The results are broken up into three separate groups:

1. Low pH region (pH 4.0)
2. Intermediate pH region (pH 4.8)
3. High pH region (pH 5-8)

The three different pH regions represent three distinct aluminum species of major concern. In the low pH region (pH 4.0), the dominate aluminum species present is the trivalent cation, Al^{+3}. In the intermediate pH region (pH 4.8), the major aluminum species present are Al^{+3} and the aluminum complex $Al_8(OH)_{20}{}^{+4}$. However, the presence of the +4 aluminum complex is of primary concern. In the high pH region (pH 5-8), the aluminum exists primarily as aluminum hydroxide precipitate, $Al(OH)_3$.

In the past, a major problem involving work with ASA has been due to the variability in emulsion quality and reproducible sizing. While the work done in this thesis was very careful, problems with reproducibility were still encountered. The results showed that sizing was generally reproducible within a run; however, reproducibility between runs was impossible. Typically, the standard deviation of sizing values within a run was in the range of 10-40 seconds.

One problem encountered, especially at the higher pH region, was the variation between controls. Typically the control made at the end of the run had a lower sizing level than the control made at the start of the run. This decrease in sizing could be due to the hydrolysis of ASA.

While there were some problems with reproducibility, the author believes that the trends observed were significant.

Low pH Region

The results obtained in the low pH region (pH 4.0) showed that alum improved sizing. Changing the concentration of alum, however, had no significant effect on the sizing level. This result is consistent with the work done by Arnson (12), in that the adsorption of the aluminum trivalent cation onto the cellulose was independent of concentration (see Figure 8). The exact mechanism through which the alum operates at this low pH is very difficult to understand. It is possible that the high charge density of the Al^{+3} ion improves the retention of the ASA emulsion on the fiber. On the other hand, the increase in sizing with alum could be attributed to the (SO_4^{-2}) counterion and not the Al^{+3}. It is also possible that there was some interaction between the aluminum cation and the sulfate anion.

Intermediate pH Region

The results from the intermediate pH region (pH 4.8) showed the effect of the aluminum complex $Al_8(OH)_{20}^{+4}$ on sizing. The presence of the aluminum complex had no significant effect on sizing at low concentrations; however, at higher concentrations (1-2% alum), sizing decreased. The decrease in sizing could be attributed to the interference of the aluminum complex with ASA sizing. The aluminum complex is a very large, bulky cation and the adsorption of this complex onto the cellulose may interfere with ASA bonding. The complex may cover-up or consume reaction sites on the cellulose which would normally be available to react with the ASA. While the complex carries a +4 charge, due to the size of the complex the charge density is much less than the Al^{+3} ion.

The decrease in sizing at higher alum concentrations agrees with the work done by Anrson.(12) Arnson showed that at pH 4.8, the adsorption of the complex

increased with concentration. Therefore, we should expect with increased adsorption at higher concentrations, the interference with sizing will be greater and the sizing will decrease.

High pH Region

The results obtained at the high pH region (pH 7.0) were similar to those found at the intermediate pH region. The alum had little effect on sizing at low concentrations; however, at higher concentrations of 1-2% alum, sizing decreased. Here again, the adsorption of the aluminum hydroxide precipitate increases at higher concentrations.(12)

The adsorption of aluminum above pH 5, still increases due to the formation of the aluminum hydroxide precipitate. See Figure 8. The aluminum hydroxide precipitate is a very fine colloidal precipitate which can become immeshed in the fibrillar structure of the cellulose. The adsorption of the precipitate onto the fiber may cover up reaction sites and therefore interfere with ASA bonding.

It is obvious from the results that alum does not improve sizing with ASA under neutral conditions. These results contradict some of the effects found by using alum in the paper industry. Some paper mills claim that the addition of alum improves: sizing, runnability, and retention of filler and fines under neutral to alkaline conditions. However, the results of this thesis show that alum has no beneficial effect on ASA sizing under neutral conditions. In fact, alum was shown to decrease sizing.

The positive effects of alum shown in neutral to alkaline sizing with ASA must be explained by some other mechanism than alum itself. It is important to remember that the sizing system used in this thesis was very pure, i.e. there was no retention aid, internal starch, filler, white water, etc. used. The

system was kept pure to identify the role of alum on ASA sizing by eliminating other variables.

The application of ASA on an actual papermachine is much more complex. The positive role that alum plays, as seen by the industry, may be due to charge neutralization. The author believes that the alum may possibly tie up the anionic "trash" existing in the process water. If the alum ties up the anionic "trash" in the system, it will no longer be able to react with the ASA. The ASA is then retained on the fiber, where it is desired.

CONCLUSIONS

1. At the low pH region (pH 4.0), the addition of alum improved the sizing with ASA. There was no effect of increasing the alum concentration on sizing.

2. At the intermediate pH region (pH 4.8), the addition of alum had no significant effect on sizing at low concentrations; however, at higher concentrations (1-2% alum) the sizing tended to decrease.

3. At the high pH region (pH 6-7), the results were similar to those at the intermediate pH. The addition of alum had no significant effect on sizing at low concentrations; however, at higher concentrations (1-2% alum) the sizing tended to decrease.

4. There appears to be no reason to add alum to an ASA system at neutral to alkaline conditions. While a very pure system was used in this study, the role of alum in a more complex system as a papermachine requires further research.

RECOMMENDATIONS

The purpose of this study was to better define the role of alum in ASA sizing. While the results of this study provided possible explanations of the mechanisms involved between alum and ASA, it is obvious that much more work is required. The following work is recommended with the hope that the mechanisms involved with ASA sizing will be better defined.

1. A good starting point for follow up work would be to start at the beginning. The variables involved in preparing the emulsion and making handsheets need to be better defined. It is important to have reproducible sizing with ASA before we go on to study the effects of other variables.

2. The role of alum in neutral to alkaline sizing still requires further work. While the results of this study showed alum to be detrimental to ASA sizing in a very pure system, it would prove very meaningful to repeat this study with a more complex system. A complex system containing filler, retention aid, internal starch, and white water would correspond more closely to actual papermachine conditions. Although alum showed to lower sizing at pH 7.0, the results may be different with a complex system. To eliminate problems associated with handsheet work, a machine run is recommended.

3. The retention of fillers and fines in ASA sizing is believed to be very important to the performance and runnability of ASA. A study showing the relationship of fillers and fines with ASA sizing would be very useful. A possible study would be to fractionate the pulp into a pulp free of fines. Handsheets prepared with the fines-free pulp could be compared to handsheets prepared with stock containing fines. The sizing level of the two different conditions should help to define the effect of fines and fillers on sizing.

4. The order of addition of alum is also an important variable. This thesis showed the effects of alum added to the thin stock (0.25% consistency). It would be interesting to see the effect of alum added to thick stock. Alum could also be added before filler is added and after filler is added.

REFERENCES

1. L.J. Stryker, "The Wetting of Paper", 1983 Sizing Seminar, TAPPI Notes, p. 1.

2. Joseph Marton, "Fundamentals of Rosin Sizing", 1985 Advanced Topics in Wet End Chemistry, TAPPI Notes, p. 29.

3. F.L. Kurle, "Sizing Test Methods," 1983 Sizing Seminar, TAPPI Notes, p. 9.

4. D.H. Dumas, "Alkaline Sizing - The Papermaker's New Friend?", 1979 Papermaker's Conference, TAPPI Notes, p. 67.

5. Henry G. Brink, "Alkenylsuccinic Anhydride Sizing in Alkaline Papermaking", 1983 Alkaline Papermaking Seminar, TAPPI Notes, p. 15.

6. Richard B. Wasser, "Sizing with ASA: Its Properties and Application," 1985 Advanced Topics in Wet End Chemistry, TAPPI Notes, p. 45.

7. Richard B. Wasser, "The Reactivity of Alkenyl Succinic Anhydride: Its Pertinence to Alkaline Sizing, 1985 Alkaline Papermaking Seminar, TAPPI Notes, p. 17.

8. Charles E. Farley, "Optimizing an ASA Sizing System for Fine Papers, 1985 Alkaline Papermaking Seminar, TAPPI Notes, p. 73.

9. J.C. Winters and R.W. Best, "Cationic Starches in ASA Sizing Systems," 1985 Alkaline Papermaking Seminar, TAPPI Notes, p. 51.

10. David H. Dumas, "An Overview of Cellulose Reactive Sizes," TAPPI, 64(1):43 (1981).

11. David H. Dumas, "An Overview of Cellulose Reactive Sizes", 1983 Sizing Seminar, TAPPI Notes, p. 85.

12. Thomas R. Arnson, "The Chemistry of Aluminum Salts in Papermaking", 1983 Sizing Seminar, TAPPI Notes, p. 45.

13. T.R. Arnson and R.A. Stratton, "The Adsorption of Complex Aluminum Species by Cellulosic Fibers", 1983 Papermakers Conference, TAPPI Notes, p. 37.

14. P.L. Hayden and A.J. Rubin, "Systematic Investigation of the Hydrolysis and Precipitation of Aluminum (III)", Aqueous - Environmental Chemistry of Metals, Ann Arbor, Ann Arbor Science, p. 317, 1974.

15. Roland F. Meyer, "Conversion to Alkaline Sizing - Case History at Appleton Papers, Roaring Spring Mill", 1983 Sizing Seminar, TAPPI Notes, p. 93.

16. R.E. Freis, "Deposit Control in Alkaline Papermaking Systems", 1983 Alkaine Papermaking Seminar, TAPPI Notes, p. 93.

17. Thomas A. Sanford, "Conversion to Alkaline Papermaking: One Mill's History", 1983 Alkaline Papermaking Seminar, TAPPI Notes, p. 81.

18. James E. Beatty, "Alkaline Papermaking: Appleton's Decade of Problem Solving Success", Pulp and Paper, 57(12):86 (1985).

19. Robert E. Scalfarotto, "Remedies for Press Picking Boost Efficiency of ASA Synthetic Sizing", Pulp and Paper, 59(5):126 (1985).

20. E. Strazdins, "Role of Alum in Alkaline Papermaking", 1985 Alkaline Papermaking Seminar, TAPPI Notes, p. 37.

21. Burington and May, Handbook of Probability and Statistics with Tables, Sandusky, Handbook Publishers, Inc., 1953, p. 185.

APPENDIX I

Statistical Analysis(21)

The following is a significance test for difference between means of two samples.

Let $\overline{x}_1$ and $\overline{x}_2$ be the means of two independent samples of sizes n_1 and n_2 for normal populations, with corresponding sample variances $(s_1)^2$ and $(s_2)^2$. It is desired to test whether the samples come from the same normal population, or not. The quantity:

$$t = (\overline{x}_1 - \overline{x}_2)[(n_1 + n_2 - 2)\, n_1\, n_2]^{\frac{1}{2}} \,/\, [(n_1 + n_2)(n_1\,(s_1)^2 + n_2\,(s_2)^2)]^{\frac{1}{2}}$$

is distributed according to the t-distribution with $m = n_1 + n_2 - 2$ degrees of freedom. Select a level of significance ϵ . If the value of t calculated from the samples exceeds t_ϵ , the hypothesis that the two samples come from the same normal population would be rejected at the level ϵ .

APPENDIX II

DATA FOR SIZING REPRODUCIBILITY

Data for Figure 13: Sizing Reproducibility @ pH 4.8

Conductivity = 7.4 micromhos
Emulsion made @ 10:18
Emulsion diluted @ 10:21

order made	sheet wt. (g)	time	%alum	no. samples	ave. HST	standard deviation
1	2.69	10:37	1.00	4	102	19
2	2.70	10:45	1.00	4	94	8
3	2.71	10:52	1.00	4	118	14
4	2.70	11:01	1.00	4	112	20
5	2.70	11:08	1.00	4	106	17
6	2.70	11:17	1.00	4	110	23

Data for Figure 14: Sizing Reproducibility @ pH 5.2

order made	sheet wt. (g)	no. samples	ave. HST (sec)	standard deviation
1	2.55	3	438	41
2	2.59	4	482	66
3	2.56	4	406	75
4	2.57	3	488	29
5	2.56	4	300	23

Data for Figure 15: Sizing Reproducibility @ pH 6.2

order made	sheet wt. (g)	no. samples	ave. HST (sec)	standard deviation
1	2.59	3	411	10
2	2.55	4	441	25
3	2.61	4	426	14
4	2.57	4	409	67
5	2.60	3	436	29
6	2.57	4	300	56

APPENDIX III

DATA FOR LOW pH REGION

Data for Figure 16: Effect of alum on sizing @ pH 4.0

Conductivity = 33 micromhos

order made	sheet wt. (g)	%alum	no. samples	ave.HST (sec)	standard deviation
1	2.68	0.00	4	86	31
2	2.59	1.00	4	128	25
3	2.62	0.25	4	176	34
4	2.62	0.50	4	150	32
5	2.64	2.00	4	152	14
6	2.63	0.00	4	55	3

Data for Figure 17: Effect of alum on sizing @ pH 4.0

Conductivity = 33 micromhos
Emulsion made @ 8:52
Emulsion diluted @ 9:14

order made	sheet wt. (g)	time	%alum	no. samples	ave. HST (sec)	standard deviation
1	2.56	9:23	0.00	4	19	3
2	2.64	9:28	1.00	4	41	17
3	2.64	9:33	0.25	4	33	8
4	2.62	9:37	0.50	4	54	11
5	2.65	9:42	2.00	4	46	8
6	2.70	9:46	0.00	3	14	1

APPENDIX IV

DATA FOR INTERMEDIATE pH REGION

Data for Figure 18: Effect of alum on sizing @ pH 4.8

Conductivity = 6.6 micromhos
Emulsion made @ 10:10
Emulsion diluted @ 10:50

order made	sheet wt. (g)	time	%alum	no. samples	ave. HST (sec)	standard deviation
1	2.65	10:38	0.00	4	148	20
2	2.67	10:45	1.00	4	78	6
3	2.64	10:50	0.25	4	118	13
4	2.64	10:56	0.00	4	115	8
5	2.67	11:01	2.00	4	88	13
6	2.67	11:06	0.00	4	156	29

Data for Figure 19: Effect of alum on sizing @ pH 4.8

Conductivity = 6.6 micromhos
Emulsion made @ 10:10
Emulsion diluted @ 11:25

order made	sheet wt. (g)	time	%alum	no. samples	ave. HST (sec)	standard deviation
1	2.68	11:36	0.00	4	83	6
2	2.72	11:42	1.00	3	77	12
3	2.66	11:47	0.25	4	96	5
4	2.66	11:52	0.00	4	84	11
5	2.67	11:57	2.00	4	80	12
6	2.67	12:01	0.00	4	150	12

Data for Figure 20: Effect of alun on sizing @ pH 4.8

Conductivity 7.4 micromhos
Emulsion made @ 10:18
Emulsion diluted @ 10:21

order made	sheet wt. (g)	time	%alum	no. samples	ave. HST (sec)	standard deviation
1	2.56	10:33	0.00	4	174	30
2	2.58	10:40	1.00	4	97	12
3	2.47	10:49	0.25	4	124	18
4	2.49	10:57	0.00	4	148	14
5	2.56	11:05	2.00	4	84	10
6	2.50	11:13	0.00	4	178	17

APPENDIX V

DATA FOR HIGH pH REGION

Data for Figure 21: Effect of alum on sizing @ pH 7.0

Conductivity = 57 micromhos
Emulsion made @ 11:52
Emulsion diluted @ 12:24

order made	sheet wt. (g)	time	%alum	no. samples	ave. HST (sec)	standard deviation
1	2.72	12:32	0.00	4	505	36
2	2.71	12:33	1.00	4	501	18
3	2.71	12:42	0.50	2	535	7
4	2.71	12:47	0.25	3	509	5
5	2.73	12:52	2.00	3	427	4
6	2.70	12:57	0.00	4	430	51

Data for Figure 22: Effect of alum on sizing @ pH 7.0

Conductivity = 57 micromhos
Emulsion made @ 3:20
Emulsion diluted @ 3:25

order made	sheet wt. (g)	time	%alum	no. samples	ave. HST (sec)	standard deviation
1	2.60	3:32	0.00	3	460	2
2	2.60	3:37	1.00	4	382	19
3	2.57	3:44	0.50	4	432	26
4	2.58	3:50	0.25	4	460	34
5	2.59	3:55	2.00	4	327	56
6	2.58	4:00	0.00	4	387	17

Data for Figure 23: Effect of alum on sizing @ pH 7.0

Conductivity = 37.5 micromhos
Emulsion made @ 3:20
Emulsion diluted @ 4:28

order made	sheet wt. (g)	time	%alum	no. samples	ave. HST (sec)	standard deviation
1	2.62	4:33	0.00	4	544	50
2	2.64	4:39	1.00	4	431	55
3	2.65	4:45	0.50	4	472	31
4	2.63	4:49	0.25	3	460	3
5	2.64	4:54	2.00	3	387	22
6	2.61	5:00	0.00	3	457	21

APPENDIX VI

DATA FOR HIGH pH REGION (cont.)

Data for Figure 24: Effect of alum on sizing @ pH 7.0

Conductvity = 220 micromhos
Emulsion made @ 11:00
Emulsion diluted @ 11:01

order made	sheet wt. (g)	time	%alum	no. samples	ave. HST (sec)	standard deviation
1	2.68	11:07	0.00	4	100	27
2	2.68	11:12	1.00	4	342	21
3	2.66	11:17	0.50	4	299	16
4	2.67	11:22	0.25	4	280	24
5	2.67	11:26	2.00	4	280	15
6	2.64	11:32	0.00	4	295	40

Data for Figure 25: Effect of alum on sizing @ pH 6.4

Conductivity = 1.9 micromhos

order made	sheet wt. (g)	%alum	no. samples	ave. HST (sec)	standard deviation
1	2.62	0.00	2	396	19
2	2.63	0.25	2	390	6
3	2.64	0.50	2	322	11
4	2.63	1.00	2	282	3
5	2.63	0.00	2	344	0

Data for Figure 26: Effect of alum on sizing @ pH 6.6

Conductivity = 2.8 micromhos

order made	sheet wt. (g)	%alum	no. samples	ave. HST (sec)	standard deviation
1	2.64	0.00	2	334	8
2	2.66	0.25	3	311	9
3	2.66	0.50	4	330	19
4	2.66	1.00	4	270	27
5	2.64	0.00	2	368	4

APPENDIX VII

DATA FOR HIGH pH REGION (cont.)

Data for Figure 27: Effect of alum on sizing @ pH 6.1

order made	sheet wt. (g)	%alum	no. samples	ave. HST (sec)	standard deviation
1	2.66	0.00	2	420	20
1A	2.54	0.25	3	301	20
2	2.61	0.00	2	430	16
2A	2.51	0.25	2	279	13
3	2.69	0.00	3	411	35
3A	2.43	0.50	4	285	32
4	2.68	0.00	2	282	2
4A	2.46	1.00	4	218	37