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THE EFFECT OF INCREASING CALCIUM ION
CONCENTRATION ON ALKYL KETENE DIMER SIZING EFFICIENCY

By:

Lance M. Merrell

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

Western Michigan University
Kalamazoo, Michigan
April, 1983

ABSTRACT

This thesis is a study of the relationship between calcium ions and the effectiveness of an alkaline sizing agent. Relationships between the increasing calcium ion concentration of a pure system and the sheet sizing based on the Hercule Size Tester are developed. It was determined that low addition levels of calcium ions increased the level of sizing developed and excessive calcium contents caused sizing response to deteriorate. Proposed mechanisms for this determination involve the compression of the fiber's electrical double layer at low concentrations of calcium, and an adsorption competition between the size and calcium where high concentrations of calcium ions are found.

High variability in sizing existed within a large majority of the handsheets produced. Standard error for handsheet sizing reproducibility averaged around twenty percent. It is suggested that a handsheet sizing method be developed with reduced variability so that the pertinent results are not concealed by excessive error.

Keywords: Alkaline Sizing, Closed Systems, Handsheet Sizing, Statistical Analysis.

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INTRODUCTION

The utilization of calcium carbonate in alkaline papermaking is of primary importance when discussing the economic incentives for a conversion from rosin/alum sizing to alkaline sizing. The possibility for loadings of up to 35% exists and have become a reality in some mills to date.

Where acid systems are forced to close up their wet ends, in order to reduce effluent volumes and contamination of waters due to heavy aluminum concentrations, certain ionic species are found to build in the system as a function of the degree of closure. To consider an alkaline system in the same vane would be total speculation, but if any ionic buildups would occur within a closed alkaline system they would probably be certain species of ionic calcium compounds.

The alkaline sized systems all have one major requirement to fulfill before the system works effectively, that being size retention. If the size is for some reason displaced from the fiber surfaces in the wet end of a papermachine and consequentially not retained in the sheet entering the presses, the size will recirculate within the system and perhaps, with enough time, react with water and form the hydrolyzate product. This product has a tendency to pick out in the wet presses, build up on the forming table and cause overall poor machine runability.

The effect of calcium ions on size performance is studied here with respect to a pure handsheet system. The thrust of this work hinges on the reliability of making reproducibly sized handsheets from purified long softwood fibers.

GENERAL SIZING THEORY

Sizing is the process with which the rate of an aqueous liquids' penetration into paper or paperboard is inhibited. This is a temporary, time dependent condition that has been imparted to a web through either a surface treatment or an internal addition of a material that provides the fibers with a low surface energy coating. This results in the formation of a high contact angle when high surface energy liquids contact the fibers.¹ The angle of contact between a liquid and a solid substrate is found in the Washburn Equation to relate to the rate of liquid penetration through the cosine of the contact angle.

$$\frac{dl}{dt} = \frac{l}{4} - \frac{\gamma r \cos \theta}{\eta l}$$

l = distance of penetration
 η = viscosity of liquid
 γ = surface tension of liquid
 r = average pore radius in sheet
 θ = contact angle

Figure 1: The Washburn Equation

The Washburn Equation also illustrates that the average pore radius will directly effect the penetration rate of a liquid. Thus, by controlling the sheet formation through refining, it is possible to close these pores and inhibit the penetration of liquids.² The important factor here is the combination of both the contact angle and the pore radius as they contribute to sizing development. The application of a film forming material such as starch to the surface of a fibrous web has the advantage of blocking or

reducing pore radius which provides contact angle.³

For an internal sizing agent to be effective it must: 1) be of low free surface energy, 2) be retained on the fibers, 3) have even and uniform distribution, and 4) anchor to cellulose in such a way that the aqueous liquids cannot later displace them.^{4,5} This method of sizing, being applied in an aqueous medium, is effected directly by the water quality variables involved in papermaking; namely pH, conductivity, hardness, acidity and/or alkalinity.⁶ The quantity of filler used in papermaking also adversely affects sizing due to the increase in surface area of the sheet with increasing filler content.³

ACID SIZING

Prior to 1807, the application of sizing materials utilized a tub sizing procedure to apply a glue to the surface of the sheet. That year, Morris Illig developed an engine sizing process through which he precipitated a rosin soap onto the fibers.¹ Although this process of rosin sizing has been refined and modified since those early days, it continues to be an effective tool for making many grades of coated and uncoated papers and paperboards.

Rosin-alum sizing has been called acid sizing because of the 4.0–6.0 pH range that it is most effective at. Most mills using this method usually run their machines between 4.0 and 4.8 pH with papermakers alum being the chemical for pH control. The addition of rosin to a papermaking system followed by the addition of alum, forms an aluminum–rosinate precipitate that is cationic and easily retained on negative cellulose fibers. The size of the rosin-alum floc is very important to the sizing efficiency of the system and the smaller flocs are found to be optimum for this system due to the high surface area of the particles. These flocs must first be retained on the fibers in the wet end. In the dryers, the rosin precipitate melts and flows over the fibers where it is anchored through the electrostatic attraction of the multivalent alumina ions. The final step in this mechanism occurs when the hydrophobic fatty acid groups orient in such a way to provide hydrophobicity to the fibers beneath the area swept by the fatty acid tail.

The important controlling factor in rosin sizing that is perhaps too often overlooked is the total acidity of the system.⁷ This is a measure of the quantity of multivalent cations present in the system and is measured by titrating a sample of the system's water with NaOH. Due to the hardness,

acidity, and/or alkalinity of the fresh water, the total acidity of the system is variable and is thus dependant on the quantity of alum added, and not the quantity that is added for pH control alone. Since rosin must be anchored to the fibers (through multivalent alumina ions), it is imperative that there be a sufficient quantity of these ions present. In a system with highly acidic fresh water, the control of pH with alum does not offer enough of these ions to promote efficient sizing. In these cases an alum demand can be developed through the addition of NaOH back in the system. For efficient acid sizing, total acidity should be considered, and it should be understood that this property of the system is relatively independent of pH (Figure 2).

Acid Closure

The production of paper has always been a heavy user of fresh water supplied by lakes, rivers, streams, and wells. The effluent produced in the pulping, bleaching, and papermaking operations has historically been returned to the land with little or no treatment prior to its return. As agencies were formed to protect the environment, the paper industry was directed to clean up the waste water, and reduce the overall quantity of the effluent returned. In order to reduce the quantity of the effluent being generated, it became necessary to reduce the amount of fresh water being used, and to supplant it with recirculated mill water. As the papermakers began closing up flow loops and substituting mill water for fresh water around their papermachines (in areas such as showers and dillution points), they found economical benefits in the savings of fiber, filler and other wet end additives. Energy savings were realized when the decrease in cold fresh water supplied reduced the amount of wet end steam that is typically required to reach papermaking temperatures.⁸ A limit to the amount of white water recirculation was found

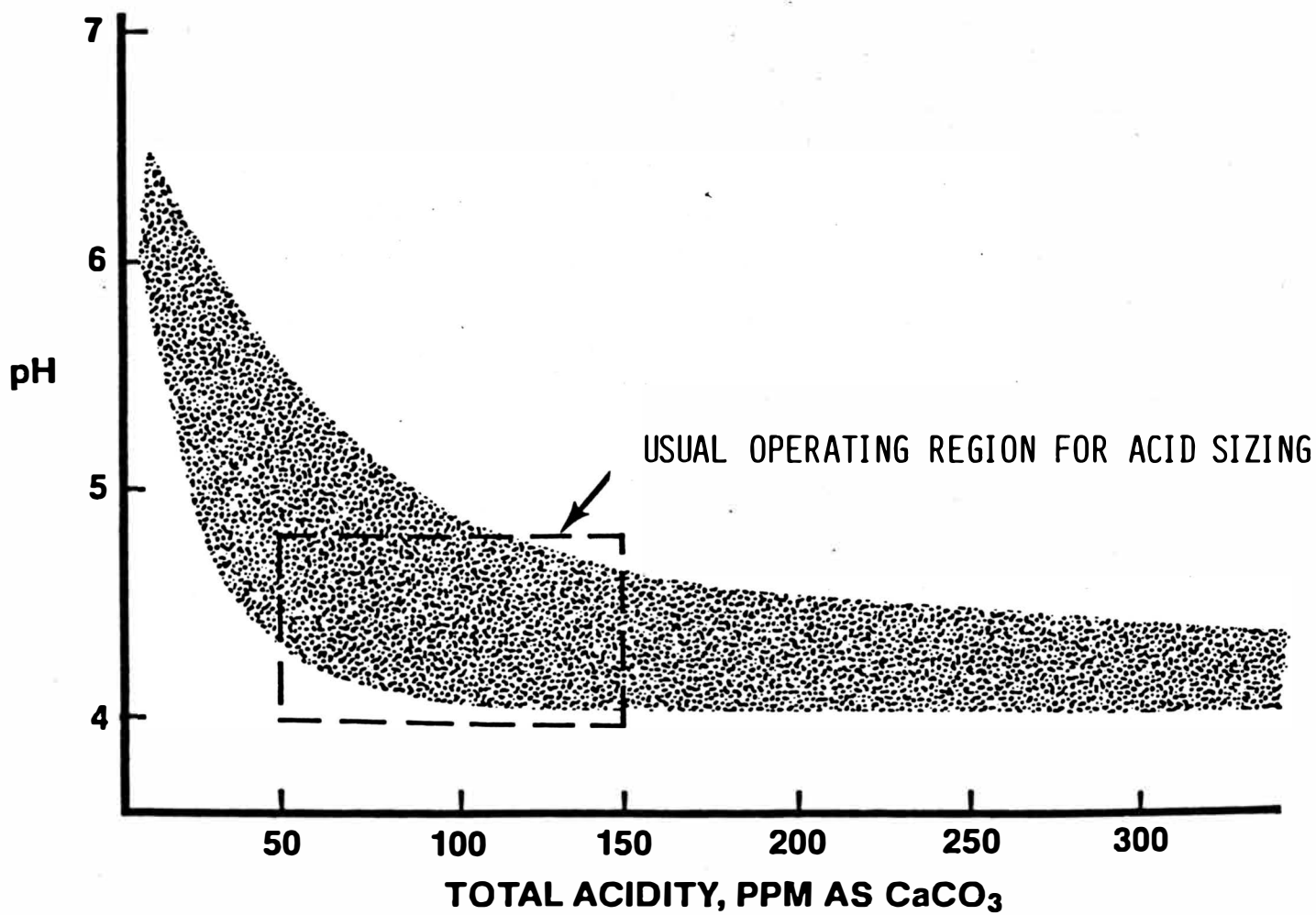


FIGURE 2: pH - TOTAL ACIDITY RELATIONSHIP³

to be around 0.6% of the total headbox flow due to the moisture in the paper entering the dryers.⁹ This means that it is possible to recirculate 99.4% of the total headbox fluid flow by closing the wet end until the only water entering the system is equal to the amount that leaves by evaporation through the dryer section.

In an acid sized system, the salt concentration in solution is found to be a function of the additives, the fresh water hardness, and the degree to which the wet end is closed. The addition of papermakers alum has been previously discussed, but the ionization of aluminum sulfate was not mentioned. Figure 3 illustrates the dissociation and equilibrium conditions of this chemical as it is related to the systems pH. Due to the complexity of the acid papermaking system, changes in pH can upset the equilibrium balance so as to effect sizing, color, retention and machine runnability.¹⁰ As the degree of closure of an acid system increases, the amount of electrolyte in solution is found to increase exponentially (Figure 4). This factor of electrolyte enrichment is a ratio of the electrolyte concentration in the recycled system to that of the fresh water.¹¹ In a system that recirculates 75% of its headbox flow, the enrichment factor is found to be equal to three. When 95% recycle is achieved, the electrolyte concentration is found to be 20 times that of the fresh water. Not only will this chemical build-up modify the behavior of most wet end chemicals, but when solubility limits are exceeded the system will begin to salt out at a rate equal to the rate of the electrolyte addition.¹² This results in build-ups associated with the formation of scale, felt filling, and suction roll plugging. In the prevailing environmental climate of today, it is highly probable that governmental rules and regulations will continue to force the paper industry into greater mill closure. In light of the troubles caused by the extensive closure of acid

systems, long range solutions and/or alternatives must be determined today. One method found to reduce the build-up of electrolytes is the elimination of alum altogether, through sizing in the neutral to alkaline pH ranges using cellulose reactive sizing agents.

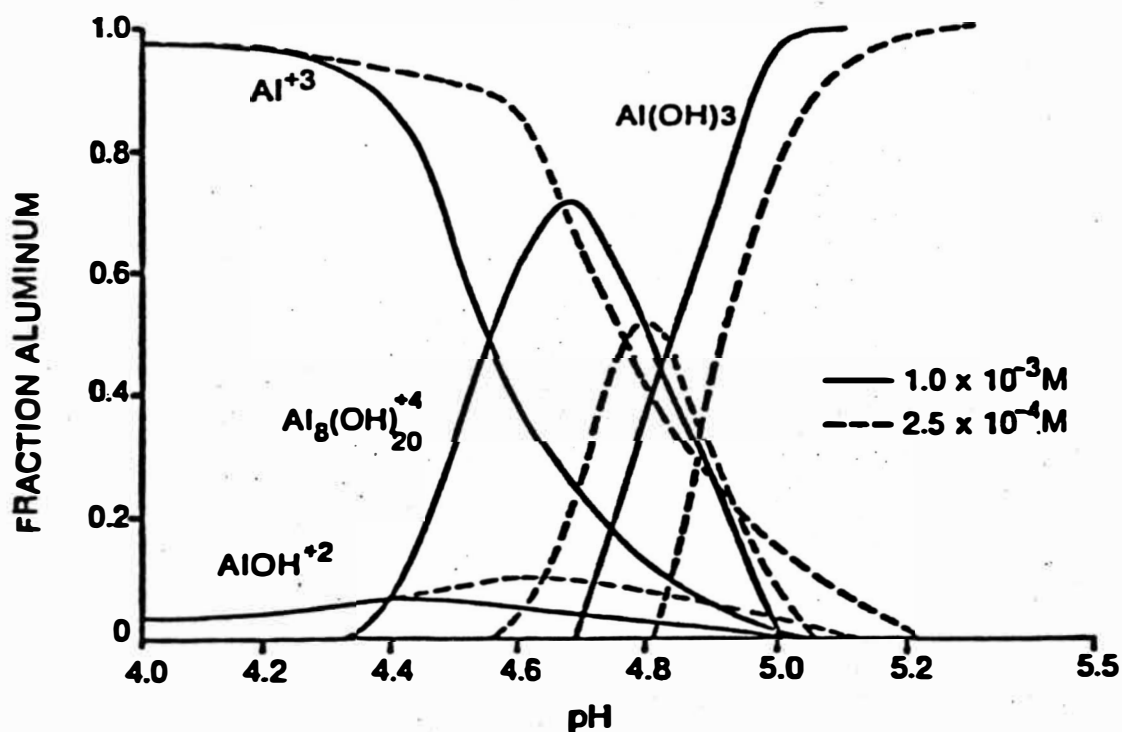
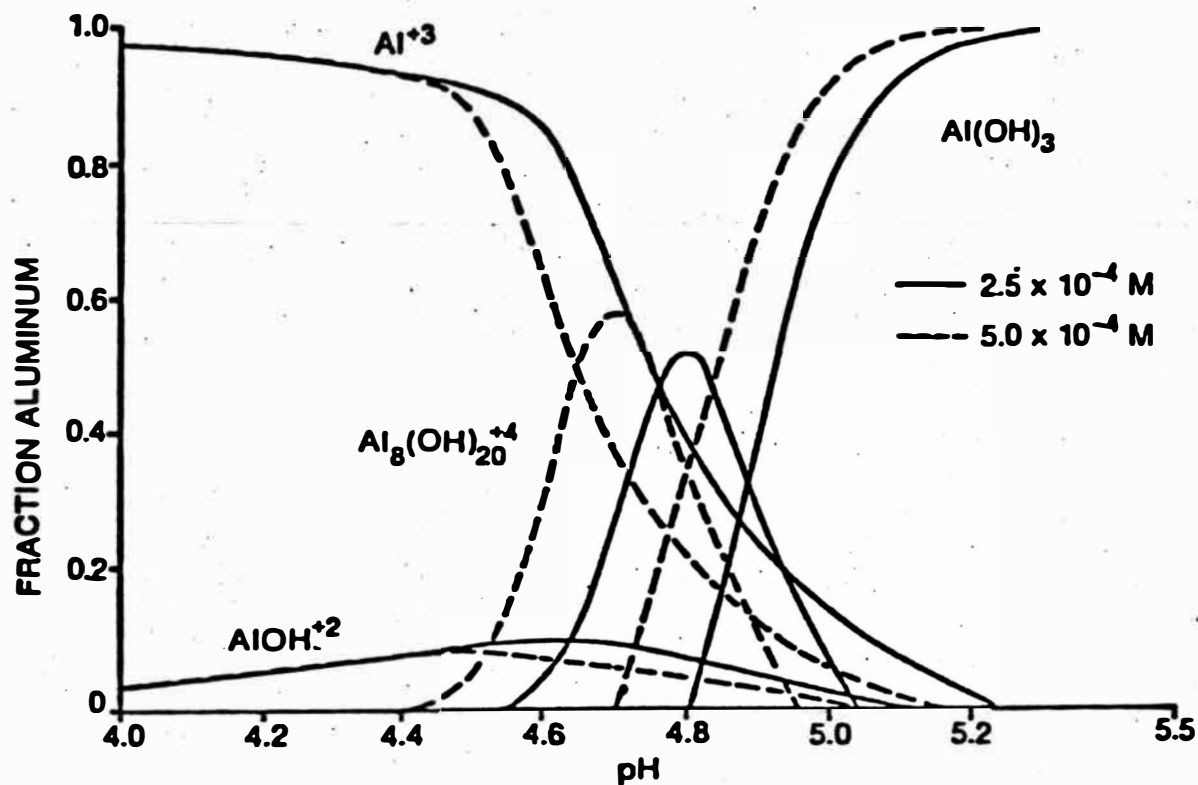
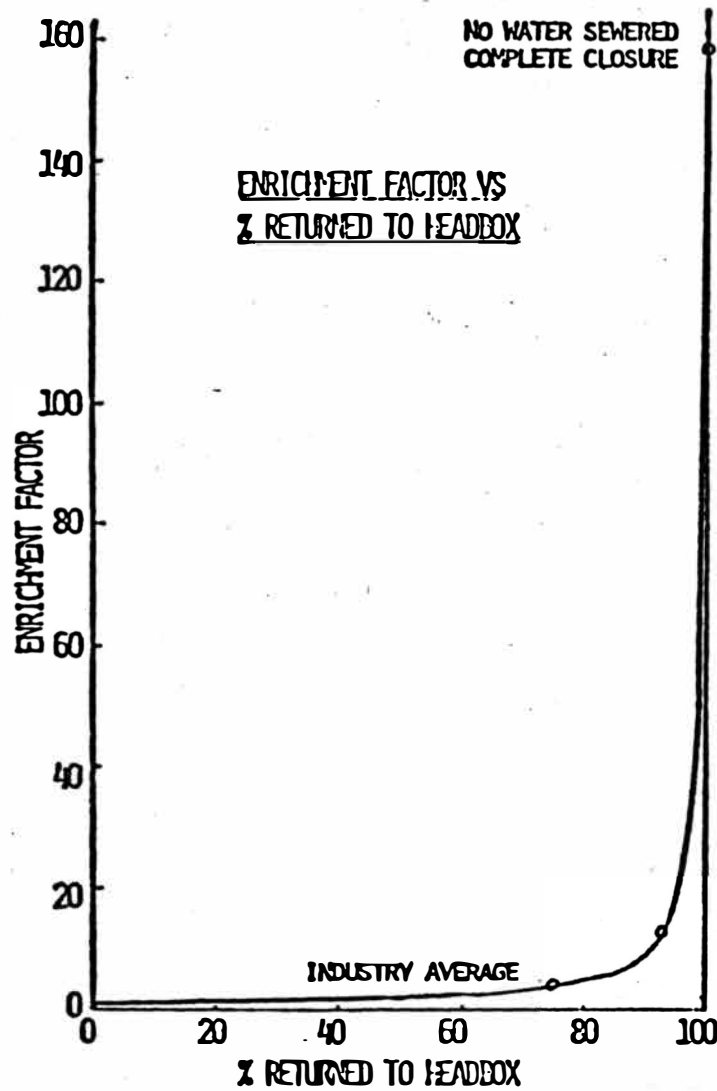


FIGURE 3: DISTRIBUTION OF ALUMINUM SPECIES AS A FUNCTION OF pH AND ALUMINUM CONCENTRATION AT pH 4.0-5.5



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FIGURE 4: ENRICHMENT FACTOR AS A FUNCTION OF THE PERCENTAGE OF THE TOTAL HEADBOX WATER FLOW THAT IS RETURNED TO THE HEADBOX.

ALKALINE SIZING

Cellulose Reactive Sizes

In contrast to the ability of alum to anchor rosin size to cellulose, mainly through Van der Waals forces, the reactive sizes form covalent bonds with cellulose. There are many different types of organic compounds that will react chemically with cellulose and form a hydrophobic surface on the fibers. Of these there are only two types that have had successful industrial applications, the anhydrides and the ketene dimers.⁴ This has resulted from roughly 25 years of trial and error associated with developing an optimum sizing agent while minimizing the effects of hydrolysis and reaction time. Both the cellulose reactive group and the hydrophobic group (or groups) are key to sizing efficiency.

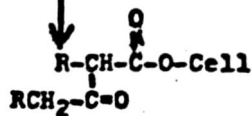
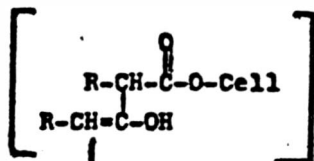
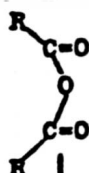
The primary reactive groups are the anhydride, associated with both the alkenyl succinic anhydride and the stearic anhydride, and the lactone ring associated with the alkyl ketene dimers (Figure 5). Both will react with cellulose and water equally as well, and they must be protected in the wet end by emulsifying them with materials that are attractive to cellulose fibers. Since fibers are electronegative by nature, the use of cationic materials for the reactive size emulsion has been adapted. It is important to note that the anhydride is quicker to react with both water and cellulose than is the lactone ring. The unique traits associated with the cellulose reactive groups can be both advantageous and detrimental to a papermaking system. The major advantage stems from the rapid reactivity of these groups and their ability to set and provide contact angle before the size press, which aids in controlling size press pick-up. The reaction of these groups

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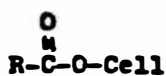
FIGURE 5: COMMERCIAL SYNTHETIC SIZES

Alkyl Ketene Dimers $R = C_{14}H_{29}-C_{16}H_{33}$ 

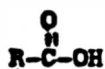
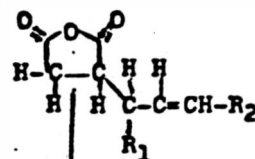
Cell-OH

Stearic Anhydride $R = C_{15}H_{31}-C_{17}H_{35}$ 

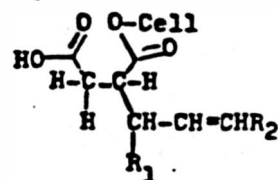
Cell-OH



+

Alkenyl Succinic Anhydrides $R_1 = \text{CH}_3, \text{CH}_3\text{CH}_2-$ $R_2 = C_{12}H_{25}-C_{16}H_{33}$ 

Cell-OH



with water forms a sticky hydrolyzate that generally results in runnability problems.

The Alkaline Papermaking System

The conversion from acid papermaking to alkaline papermaking involves the transformation of a complicated chemical system to a relatively simple system, void of the complexed aluminum chemistry (Table 1). The fact that the alkaline system is quite simplistic in comparison helps stabilize the fragile mechanism of additive and filler retention. The most important additive is the alkaline size emulsion, which upon reaction with water forms the hydrolyzate product that interferes with machine runnability and the degree of sizing. This hydrolyzate product forms whenever the emulsion is broken, or there is enough time for the functional groups to react with water. Both of these are found to occur when the retention of the size is affected by some type of chemical imbalance within the system. Dumas⁴ identifies the size retention as the weakest link in the alkaline sizing mechanism, and suggests that the size be first set on the long fibers since they are most easily retained.

In a similar article, Dumas⁸ stated that during pressing and drying, the retained sizing material is believed to form a monomolecular layer over the sheets surface as the ketene dimer melts and flows over the surface of the fibers. It is at this point that the size begins to react with the cellulose and permanently anchors itself to the fibers. It has been reported that the quantity of stearic acid required to produce a monomolecular layer is only 0.06% of the total weight, or 1.2 lbs/ton.⁷

Papermaking Problems in Alkaline Systems

As mentioned earlier in regards to the size retention mechanism, the

TABLE I

ACID PAPERMAKING RAW MATERIALS

<u>Process Primary</u>	<u>Performance Secondary</u>	<u>Product Primary</u>	<u>Performance Secondary</u>
Water	Retention* Aids	Pulp	Sizing Agent
	pH Modifier*	China Clay	Rosin/Alum
*Alum			

ALKALINE PAPERMAKING RAW MATERIALS

<u>Process Primary</u>	<u>Performance Secondary</u>	<u>Product Primary</u>	<u>Performance Secondary</u>
Water	Retention Aids	Pulp	Sizing Agent (AKD or ASA)
		Filler- CaCO ₃	

hydrolysis of the cellulose reactive group can gravely effect the alkaline system. Aside from the reduction in the degree of sizing, the hydrolyzate product that is retained within the sheet is found to be loosely held on the fibers and thus picks out easily in both the wet and smoothing presses. Also, deposits of the hydrolyzate are found to cause other machine operating problems. In his extensive experience at the Wolvercote Paper Mill (United Kingdom), Riddell⁶ found the optimization of the alkaline retention mechanism to be one of the more difficult problems in this type of papermaking. Hoppe¹⁴ suggests that the most difficult aspect of alkaline sizing is the controllability of the sizing value. He found that the sizing was not incremental with the quantity of addition, but more on the line of on/off control. Either there was plenty of sizing or there was none.

The chalk filled alkaline sheet looks to be wetter at the couch roll than it actually is. Bryson¹⁰ found this artificial wetness caused the dry

line to appear to be about two feet further down the fourdrinier than it actually was. Paiste¹⁵ found the dewatering kinetics of the sheet to be much different than that of an acid formed sheet. These changes may cause initial operating difficulty, but once the machine crew adjusts to this new method of papermaking these problems will soon diminish.

Benefits of Alkaline Papermaking

The benefits associated with alkaline papermaking have been reported in the more recent technical bulletins.^{4,6,8,15-20} Of the numerous associated benefits, four stand out as key areas to investigate when considering a switch to alkaline; 1) the utilization of calcium carbonate as a filler, 2) the reduction in energy requirements from the stock preparation area to the reel, 3) the system cleanliness, and 4) the reduction in effluent loads and required treatment of the effluent produced. For a mill to find due cause to make the move from acid to alkaline papermaking, only one of these four major benefits need be fully developed due to the intimate relationship of each to the others. The use of calcium carbonate in the alkaline sized system is a key consideration in the content of this investigation.

The Use of Calcium Carbonate

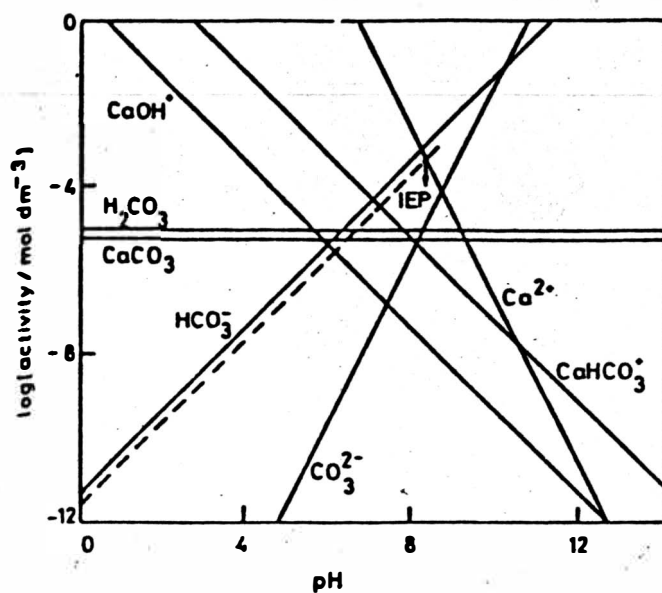
In the acid sized system, operating in the 4.0-6.0 pH range, calcium carbonate cannot be used due to its conversion to CO_2 which causes foam and the loss of the material as a filler.¹⁹ The use of calcium carbonate in the alkaline system ($\text{pH} > 7.0$) is not only chemically feasible, but very economical to the papermaker. Dumas⁸ claims that loadings of 25-30% are possible while still maintaining adequate strength properties, and showing improvements in bulk and smoothness for printing. Penniman¹⁹ states that as much as 34% chalk whiting has been used in a Scottish mill maintaining excellent

physical properties, good uniformity, and of extreme importance today, a substantial cost reduction. Due to the problems associated with abrasion in the wet end, something that only recently has surfaced in the literature,^{17,21} these high filler loadings are not without detrimental factors. The use of calcium carbonate in systems of this sort also have the inherent advantage of buffering the system to between 7.5 and 8.3 pH.^{6,12} If the wet end closure continues to underscore the objectives of the industry for environmental reasons, the effect of the high CaCO_3 loadings on alkaline sizes and other wet end additives should be thoroughly investigated.

Calcium Ion

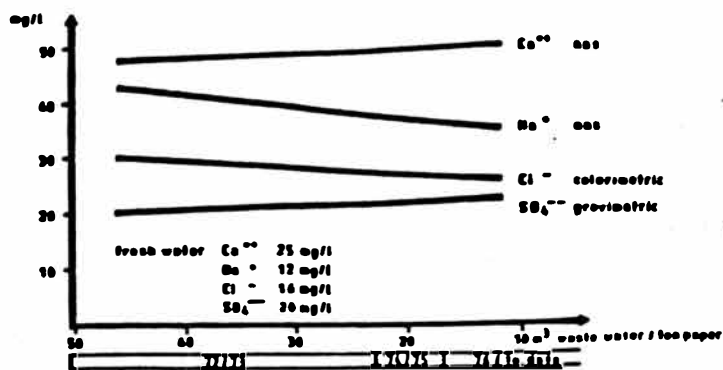
Dunlop-Jones²¹ found the dissociation of calcium carbonate to be a function of pH (Figure 6). Penniman¹⁹ claims that even though the calcium carbonate is only slightly soluble in water, the number of ions in solution is far greater than with clay and titanium dioxide solutions. In systems of high CaCO_3 loadings one would thus expect to see an increase in the calcium ion concentration. Hoppe¹⁸ found this not to apply. Even with a decrease in the fresh water usage he did not show evidence of an increase in the calcium ion concentration (Figure 7). As shown in the section under acid closure, the build-up in the ionic concentration does not increase rapidly until a level of closure in excess of 90% is achieved. In this article by Hoppe, he at no point mentions the size of this system, and thus the percent closure cannot be calculated. Figure 7 clearly shows the increase in the calcium ion concentration over and above that contained in the fresh water. Beach¹⁶ claims that the build-up of metallic ions and their complexes is extremely low in an alkaline system, but again the degree of closure is not mentioned in this analysis.

Both calcium and barium ions have been found to have the highest relative affinity for the carboxyl groups of cellulose than any other cation.²² In a study by Davison,²³ a radioactive cationic wet strength agent adsorbed on the fiber surface, was found to be in equilibrium with the same wet strength agent in solution. This was found to be readily displaced by simple cations like calcium. The fact that the calcium ions can displace such things as wet strength agents adsorbed on the fiber surfaces, is of key concern where calcium ions are present in high concentrations.



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FIGURE 6: IONIC CONCENTRATIONS IN CALCITE SOLUTIONS

FIGURE 7: INCREASE IN HARDNESS WITH CLOSURE¹⁸

PRESENTATION OF PROBLEM

In today's alkaline systems the use of calcium carbonate has already reached levels of nearly 35%. In areas where the fresh water hardness is high it is possible that the concentration of calcium ions in the white water could reach levels detrimental to the system. As mills begin to close the wet end of alkaline papermachines, in order to further reduce energy costs and to reduce the quantity of effluent, they may eventually reach a point where the exponential increase in ionic substances is found.

The key component in the mechanism of alkaline sizing is the adsorption of the cationic emulsion onto the electronegative fibers. If excessive levels of calcium ions are found in an alkaline sized system, it may be possible that this cationic emulsion will be displaced from the fiber surface or that the initial competition for adsorption sites will prevent the size from adsorbing onto fiber surfaces in quantities required for sufficient sizing. These factors could cause an increase in the hydrolyzate concentration in the system which would effect both the sizing efficiency and the machine run-ability.

This thesis is an investigation into the effects of increasing calcium ion concentration on the alkyl ketene dimer sizing effectiveness.

EXPERIMENTAL DESIGN

The purpose of this study is to identify whether or not calcium ions in a neutral system will affect the alkyl ketene dimer sizing performance. Through the course of this investigation an attempt will be made to develop both a time dependent and a time independent mechanism to explain the behavior of this proposed adsorption competition. Handsheets will be made using 100% bleached softwood long fibers using variations in the quantity of calcium ions in solution, the order of addition of both the calcium ions and the size, and the time for adsorption to occur. Handsheets will be pressed and dried, and tested for the degree of sizing using the Hercules Size Tester. The filtrate from the handsheets will be tested for calcium ion concentration using a displacement EDTA titration.

The data analysis will be based on the variation in sizing due to changes in the system. The major thrust of the investigation will hinge on the variation in sizing due to the concentration of calcium ions, adsorption times, and orders of addition of the calcium ion and the alkyl ketene dimer.

EXPERIMENTAL MATERIALS AND PROCEDURES

Materials

Fiber Preparation. One hundred percent bleached softwood kraft pulp was refined in the Valley beater in accordance with TAPPI Standard T200 OS-70 using distilled water. Using the Clark Classifier Procedure (T233 OS-75), the shortest fiber fractions were separated from the whole and discarded. The remaining fibers were then thoroughly washed with distilled water and concentrated to about 10% consistency. At this point the stock was soaked in 2N HCl for approximately 30 minutes under constant agitation for the sole purpose of displacing as many adsorbed ions from the stock as possible. This two liter acid bath of about 200g fiber required 40-50 gallons of distilled water to wash the fiber free of the acid. The fiber was washed repeatedly until the filtrate approached pH = 5.0, which was roughly the distilled water pH.

Chemical Preparation: Calcium. To obtain ionic calcium in pure form, it was necessary to use a calcium salt that had a high dissociation constant. Calcium chloride dihydrate of assay between 78 and 74% CaCl_2 was prepared in high solution concentrations. These solutions were later diluted to strengths which allowed for ease of addition with low standard errors. Strong and weak solutions were checked for accuracy with EDTA titrations.

Chemical Preparation: Size. An alkyl ketene dimer emulsion (Hercon 40) was supplied by Hercules Incorporated for use in this thesis. The emulsion is supplied at 15% total solids. Due to the weight of each handsheet, it was necessary to dilute the size to 0.015% so that a 10ml aliquot would give an addition level equal to 1.5 lbs/ton. To weigh one gram of size for dilution to one liter, a one milliliter pipet was charged and a weight by difference

method of determination was used. When this chemical was diluted in the handsheet system, it was equivalent to 0.75 ppm based on total mass. To prevent the size from losing its reactivity due to hydrolysis, it was necessary to use the size within four hours of its dilution to 0.015%.

Chemical Preparation: Water. The water used in the primary investigation of this thesis was held constant in terms of pH, conductivity, and temperature. Distilled water was standardized in batches of 55 gallons through adjustments with NaOH to $\text{pH} = 7.2 \pm 0.1$ followed by NaCl addition to adjust the conductivity to roughly 30 micromhos. The earlier experimental work may have been somewhat affected through distilled water variations in the three control parameters, since only five gallons of distilled water were drawn off of the major system at a time.

Procedure

Handsheet Formation. The development of a reproducible handsheet procedure for the Buchner funnel (based on uniform sizing with a cellulose reactive size) was found to be a necessary requirement since system purity was essential in this study. A detailed outline of the handsheet procedure can be found in Appendix II.

Where sizing is concerned, it is mandatory to have uniform formation. Due to the relationship between stock consistency and formation, it was necessary to increase the volume of the Buchner funnel so that the consistency of two grams O.D. fiber was roughly 0.1%. The funnel was fitted with a 150 mesh wire to insure complete retention of all fibers in the stock.

Sizing Testing

After the handsheets had conditioned for roughly 12 hours in a constant temperature and humidity room, the sizing levels were analyzed using the

Hercules Ink Penetration Tester (HST). Hercules number two acid ink was used as the penetrant. During the initial stages of this investigation, reflectance curves were run to help isolate the level of size addition required to achieve a 100-200 second sizing target. The penetration rate can in this way be separated from the level of sizing achieved as Figure 8 shows for subset A of Series in Appendix III. Once the level of sizing required was reached at 80% reflectance, the 80% reflectance endpoint was held constant.

Water Analysis

For each subset of handsheets produced, the filtrate from one handsheet was saved for testing. The calcium ion concentration was determined through the use of EDTA titrations run in triplicate. The pH was checked to guard against large fluctuations due to high calcium chloride addition levels, and conductivity was determined to act as a cross check with the titration results. For this pure system the conductivity was found to be a quadratic function of the calcium ion concentration (Appendix IV).

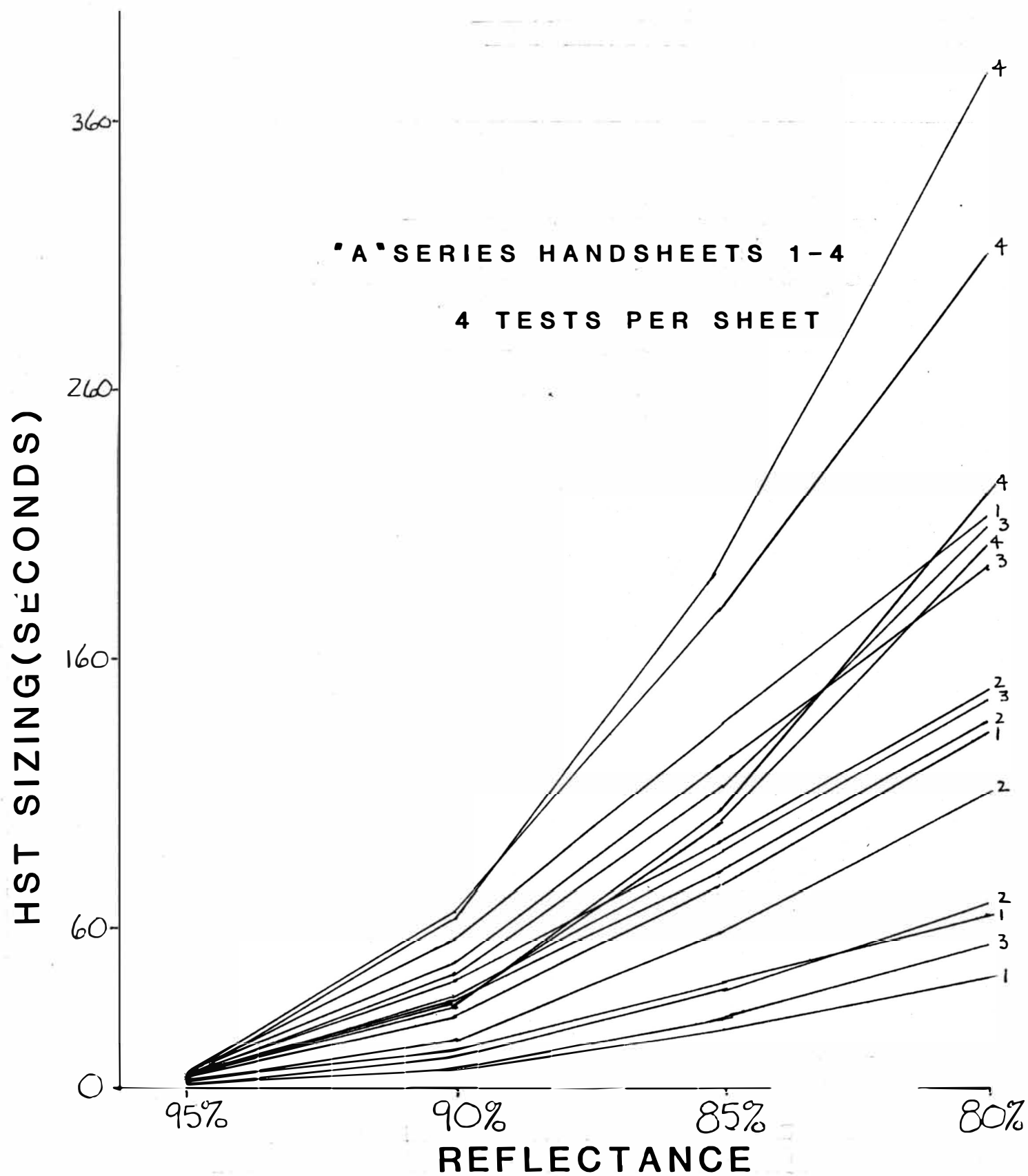


Figure 8: Acid Ink Penetration Rates for Subset A of Appendix III

PRESENTATION OF EXPERIMENTAL RESULTS

Primary Investigation: The Role of Calcium Ions on Sizing Effectiveness

The addition of calcium ions to the handsheet system was through the use of a solution of calcium chloride. To eliminate the variations in calcium ion concentration due to the variations in the total volumes of each system, calcium ions were added as a percentage of the fiber mass, as opposed to a parts per million basis. The molar concentrations in the filtrates were checked and recorded as the levels of addition.

The first set produced (Series A of Appendix III) consisted of seven subsets, of three and four handsheets each, having consecutive increases in the addition level of calcium ions at a constant 1.52 lbs/ton addition level of size. The time interval from initial dilution of the size to the final handsheet provided with 200% calcium, exceeded the allotted four hours initially set to reduce the effects of hydrolysis formation. Thus, the last three subsets having the highest concentrations of calcium in solution, had been made with the most hydrolyzed size. To guard against the alkyl ketene dimer hydrolysis, it was therefore important to make the remaining sets with alternating addition levels of calcium (as opposed to consecutive addition levels).

The remaining sets produced (B, C, and G Series of Appendix III) were made with a different batch of purified fiber that had been refined, classified, and acid washed in exactly the same manner as the Series A stock. It later appeared that this stock was not completely rinsed clean of the excess acid which may have had an effect on the adsorption characteristics of the fibers.

Due to an observed decrease in the sizing response of the blanks of both

Series B and C (Appendix III), an increase in size addition level for Series G was used. The new level of 1.9lbs/ton was still not enough to equal sizing levels previously attained, but due to shortages in purified fiber and available time it was not possible to continue this line of investigation.

For a history of the trial and error of developing a handsheet sizing method for this work, see the section entitled "Problems Associated with Initial Stages".

DISCUSSION OF RESULTS

The change in the degree of handsheet sizing as a result of increasing the concentration of calcium ions in the system is shown in Figures 9 and 10. Although the quantitative reproducibility of this work is lacking between trials, certain trends can be readily identified in overall view of the results. Since each curve has its own unique behavior in response to certain levels of calcium addition, it is not applicable here to discuss the effects of specific concentrations. An analysis of the trends however, can handle all curves simultaneously without biasing the results.

Analysis of Decreasing Sizing Response

The loss in sizing at high levels of calcium addition is consistent throughout this work. The fact that this occurred repeatedly in these pure systems, suggests that there existed a competition between the systems cationic materials.

These materials (calcium ions and the cationic emulsion size) undoubtedly have different relative affinities for cellulose fibers. Since the cationic size was present in each trial to the same extent in each of the systems, it can be argued that the affinity of calcium for the fibers was stronger than the affinity of the size for fibers. It is proposed that as calcium begins to surround the fiber surfaces it becomes more difficult for the size to find a site to adsorb onto the fibers. This caused a decrease in adsorbed sizing agent as the calcium ion concentration was increased within the system. Assuming the calcium ionic affinity for cellulose is greater than that of the cationic size, it is probable that since the size was added to the system before calcium once the size is displaced from the fiber surfaces

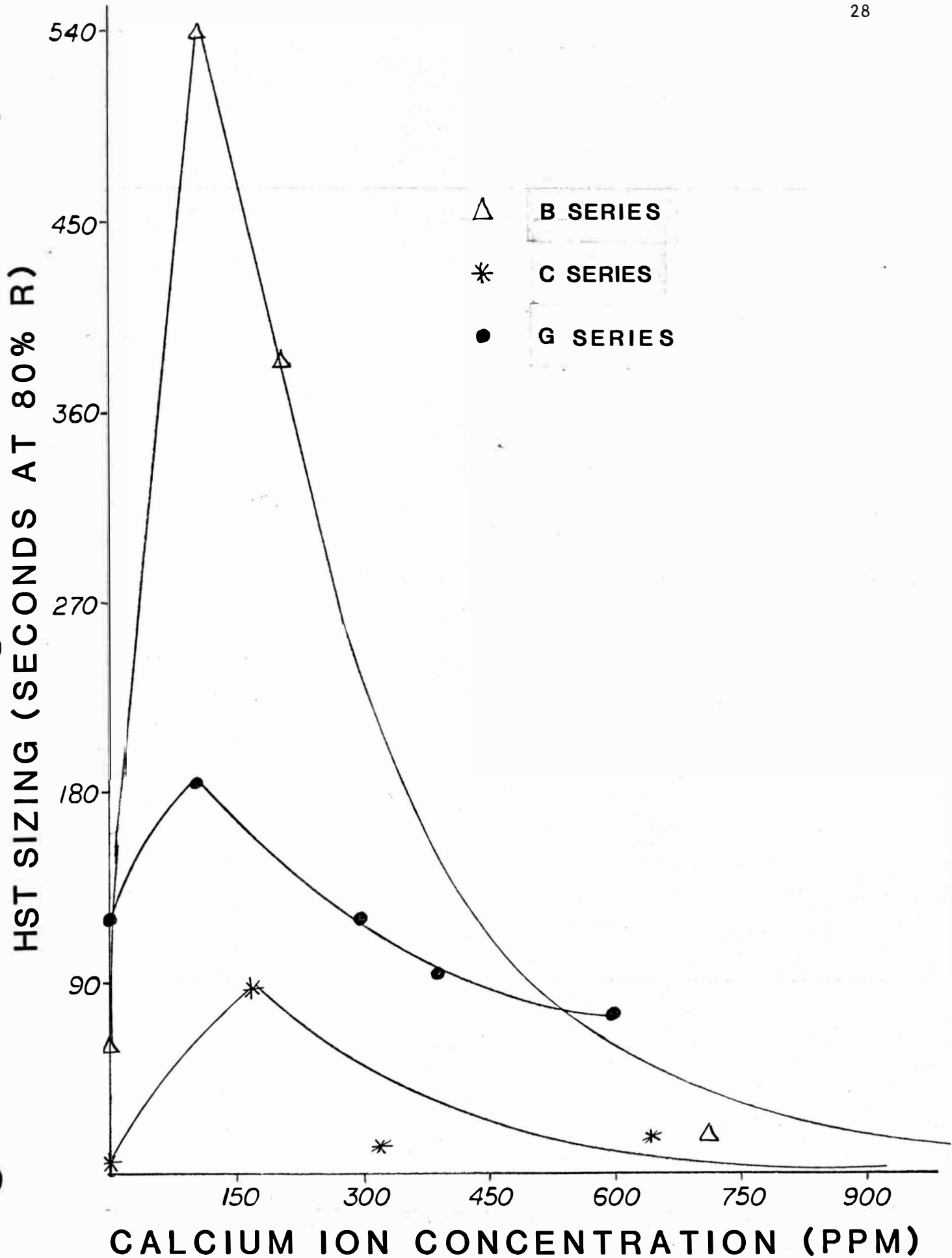


Figure 9: Calcium Effect on Sizing

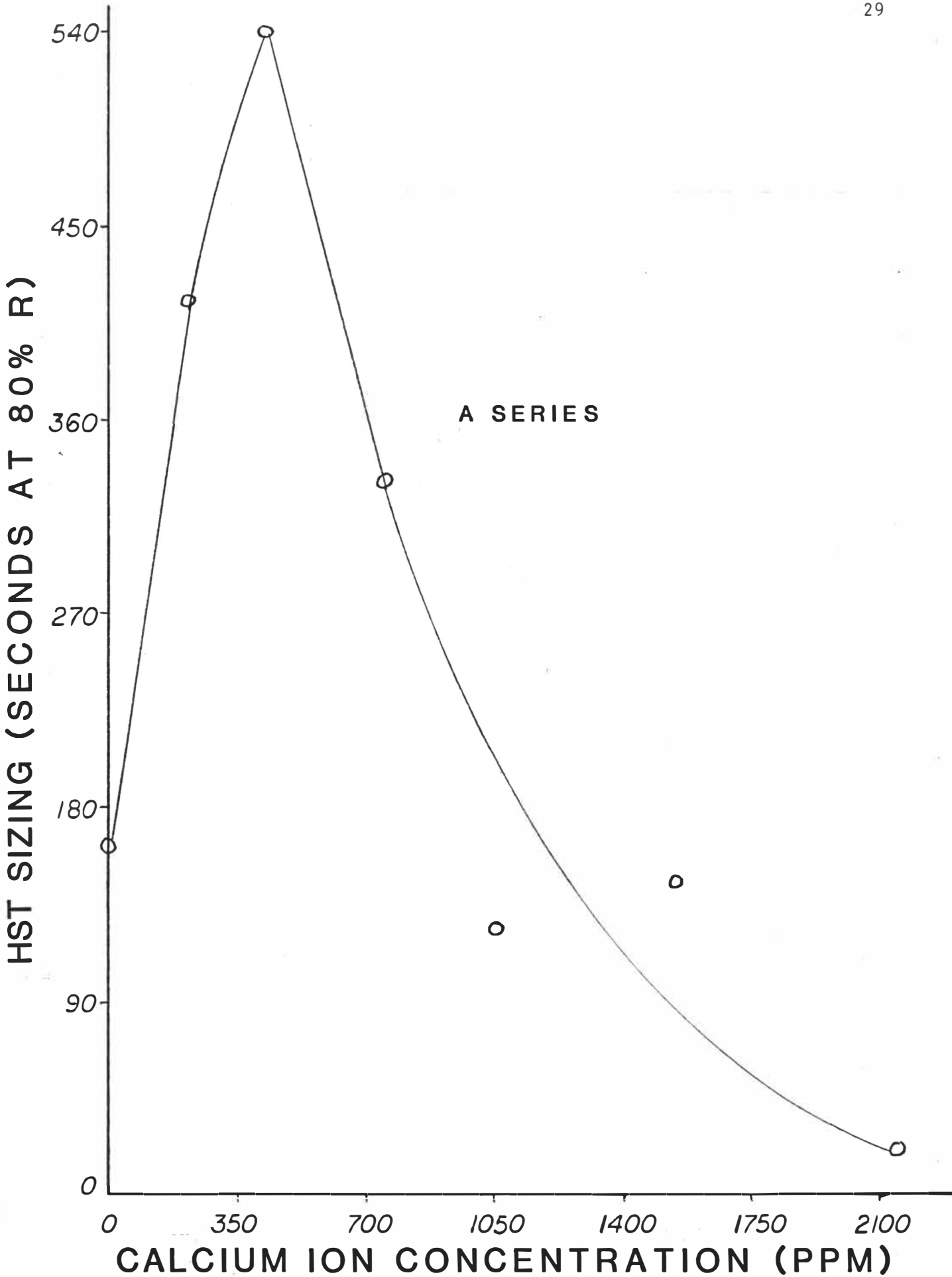


Figure 10: Calcium Effect on Sizing

it becomes more difficult for readsorption to take place while calcium ions are in command of the system. This competition probably exists with all cationic inorganic materials, but since alkaline systems utilize calcium carbonate as a filler, the calcium ions can easily be the dominant cations in the system. Mill fresh water supply can also add to the concentration of calcium ions as observed in areas where high hardness is present.

The combination of high fresh water hardness and high filler loadings of calcium carbonate in an alkaline system may be harmful to the adsorption of the sizing agent resulting in: a) higher size level requirements; b) losses in sizing extremes; and/or c) an increase in the hydrolyzate formation.

Analysis of Peaks in Sizing Response

All peak levels of sizing were obtained at low addition levels of calcium ions. The difference between the position of the peaks in Series A (Figure 10) compared to that of the other three series ran (Figure 9) was most probably related to the variation between the stocks used. Through the analysis of this trend it is evident that the low addition levels of calcium chloride had increased the level of sizing over that realized in the pure case. In the previous discussion of the sizing loss due to excessive calcium chloride addition levels, it was stated that the sizing response was an indication of the retention of the size onto the cellulose fibers. With this in mind, it appears that the pure case (absence of calcium ions) does not have the superior adsorptive capacity, but rather the systems containing low levels of calcium chloride in solution have the best potential for size retention. To explain this phenomenon with something more substantial than conjecture, extensive laboratory analysis would be required.

It is a well known fact that adding salts to certain papermaking systems

changes the retention mechanisms. This is explained through analysis of the system's zeta potential, where the addition of salts tend to cause the compression of the electrical double layers of the particles. The net result of this compression is a decrease in the electrostatic repulsion between particles and a corresponding increase in the systems retention ability. This, it can be argued, applies to the systems under investigation since the initial low levels of this calcium salt have in fact increased the attraction of the cationic size for cellulose. In the pure case, the size (at equilibrium with the fibers) could probably be rinsed from the fibers to a certain degree. This theory of electrical double layer compression due to calcium chloride additions can be tested through analysis of the electrophoretic mobility of particles within the system. This analysis was unfortunately beyond the scope of this thesis, due to the absence of fines within the system.

Statistical Analysis of Data

Through the use of the hierarchical design for the analysis of variance (commonly referred to as the nested design) support for the conclusion that calcium ions do indeed effect the sizing response was attempted. This design, as expanded upon in Appendix V, analyzes the variations in the fixed variable A (calcium concentration - referred to as a subset) and the random variable B (reproducibility of sizing between handsheets within each subset). In this analysis, the F statistic is calculated for the null hypothesis test where H_0 is rejected if $F_{calc} > F$. In the first case, $H_0 : \tau_i = 0$, tests to see if the variation between subsets is zero when H_0 fails to be rejected. Since the initial objective was to prove that differences in sizing responses due to changes in calcium addition levels exist, it was hoped that this part of the

analysis would reject the null hypothesis with a high level of significance. In case 2 the null hypothesis, $H_0 : \sigma_{\beta}^2 = 0$, tests if the variation (within each subset) between the sheets differs to an extent greater than the variation of tests within each sheet. The acceptance of H_0 would indicate that there were no significant deviations within each subset.

The data tabulated in Appendix VI shows the F statistic for both cases one and two followed by the significance of F. This significance is the fractional acceptance region for H_0 . The analysis shows that for each series the Case 1 acceptance region was at the most 7.1%, or in other words, the statistical evidence indicated a difference between subsets for each series ran. The analysis of the Case 2 data indicates that (asside from Series A - Limit 1) the variation between the sheets within each subset exists to a significance of better than 99%. Therefore, although it is statistically possible to say that differences between the subsets exist, it is not possible to say that these variations found in sizing were due solely to the changes in calcium addition levels.

SUMMARY

To study the effect that a change in a chemical component within a papermaking system (as pure as it may be) has on the sizing response of that system, a control of sizing under constant conditions is of utmost importance. Where handsheet sizing is concerned, a number of major obstacles must be overcome to establish a control system. Sheet formation, retention of materials, variability of water temperature, pH and ionic strength, and the minute concentrations of additives required in making a sized handsheet are all major wet lab variables that must be minimized to achieve reproducible sizing in handsheet making devices. To compound the problem further, the rate of sizing development has been found to be a complexed function of the sheet moisture content at time equal zero of the drying cycle, the rate of water removal from the sheet, time and temperature interactions during final curing, and temperature differences during drying between the opposing sides of the sheet. If all of this variation could be reduced to within acceptable levels of uncertainty, the addition of a chemical component to the system would probably result in the alteration of any number of control parameters causing diminished certainty as to the actual isolated effect of that certain chemical's interaction. For example, in this work the addition of calcium chloride was found to effect the systems pH and ionic strength, but changes in zeta potential and perhaps fines retention (although the fines content was undoubtedly very small) went virtually unnoticed and/or undetectable.

The largest uncontrolled variables that had undermined results of this work with excessive levels of variance were the drying and curing rate differences between the handsheets. Although, again difficult to prove, sheet moisture variations and size distributions due to poor formation had un-

doubtedly added to the excessive variance statistically found between sheets within the subsets.

Regardless of this excessive variation, it seems quite logical that the increase in sizing at low levels of calcium addition are a result of the compression of the electrical double layer. At high levels of calcium addition, a decay in the sizing response may indicate that a competition exists between these cationic materials for adsorption sites on cellulosic surfaces. Although this is not statistically acceptable, the numbers indicate that these trends exist, without exception.

The overall scope of this work has shown that, in the general case, the presence of calcium ions in a papermaking system (utilizing an alkyl ketene dimer emulsion size) effects the sizing response of the paper in ways dependent on the concentration of the calcium ions in solution. In today's alkaline systems the use of calcium carbonate filler at high levels of loading results in the addition of calcium ions to the systems. Dunlop-Jones and Jaycock²¹ examined the equilibrium concentrations of ionic species found within a pure solution of calcium carbonate. They found that the systems pH drifted for as long as four months before equilibrium was attained. Figure 6 shows the dependence of the ionic nature of a calcium carbonate solution on pH. With this in mind it seems probable that in actual mill applications the constantly changing ionic nature of the wet end of a paper machine may alter the size retention level in the wet end enough that sizing peaks and/or decays may occur. Sizing variations could also be strictly a result of changing the filler content or perhaps altering the water supply to one of a different hardness. This analysis also indicates that if systems of this sort move toward increased closure, although buildups in ionic species will probably not occur, the thermodynamic condition of the system (since equilibrium

never exists) would probably be altered to some extent and again directly effect sizing.

The reproducussions of lowering the size retention level in the wet end are in terms of the increased recirculation of the sizing agent causing the hydrolyzate product to form and the decreased sizing level obtained. Machine runability problems can results anywhere from the buildup of the hydrolyzate product on the fourdinier table, to press picking, to increases in size press pickup and even off machine with poor performance in the finishing operations.

CONCLUSIONS

The conclusions for this investigation are as follows:

1. The addition of large quantities of calcium ions to a pure papermaking system caused the sizing response to deteriorate.
2. Low calcium ion additions increased the sizing effectiveness of the system.
3. Handsheets made in the Buchner Funnel had high variabilities in sizing within the sheets.
4. Handsheet reproducibility was difficult to obtain with the method of sizing used here.

RECOMMENDATIONS

In this experimental work, every precaution was taken to eliminate uncontrolled variables that arose in the wet lab formation of a sized handsheet. The drying rate of these handsheets by the method used here, does not seem to be held at a constant and hence reproducibility between handsheets did not exist in the statistical analysis. Therefore, a detailed study of pressing/drying interactions would be extremely useful for future handsheet sizing studies. It is possible here that different press/dry mechanisms would prove best for sizing with rosin/alum, alkyl ketene dimers, and alkenyl succinic anhydrides, since they differ from each other by so much in terms of reactivity.

The investigation into the reason for the peak sizing levels found in this work through the use of zeta potential analysis may shed more light onto the complexity of the wet end competition between cationic particles for cellulose surface adsorption sites.

A study of possible ionic buildups that may occur in a calcium carbonate filled system as white water closure nears 100% would shed light on an area that may not be a concern at the present, but will undoubtedly concern paper-makers as effluent laws become more stringent.

PROBLEMS ASSOCIATED WITH INITIAL STAGES

Preliminary Investigation: Calcium Adsorption Time

The initial portion of this work was designed to test the theory of adsorption and displacement for time dependency and addition order of the adsorbants. The time required to achieve full (or maximum) adsorption of calcium ions in solution was first investigated so as to give a base time for the remainder of the investigation. Solutions of calcium chloride were prepared so that the final systems of fiber, water, and calcium chloride remained at 250 ppm Ca^{2+} .

Initial handsheets produced using the procedure outlined in a previous thesis²⁴ were found to be inadequate in terms of the quantity of fiber and the consistency of formation. Two grams oven dry fiber was found through trial and error to be sufficient in terms of forming a mat of substantial integrity, but the volumetric limit of one liter capacity for the Buchner funnel could not be exceeded. This system, with formation at 0.2% consistency, was at that time found to be the most feasible.

During this period of trial and error with consistency and bulk, six handsheets were made with calcium ions present in the concentration of 250 ppm based on the volume of the system. The calcium was given thirty seconds to adsorb onto the fiber, at which time the handsheet was produced. The effluent from each handsheet was tested for calcium ion concentration using EDTA displacement titrations. These six systems had effluent concentrations of 257.5 ± 3.6 ppm Ca^{2+} . From this result it was decided that no noticeable adsorption of the calcium ions were detectable. To be sure of these results, fourteen handsheets were made again under constant addition levels of 250 ppm

Ca^{2+} . Given various times for adsorption ranging from one to sixty minutes, with reproductions of two sheets at each level, it was hoped that calcium ion adsorption onto cellulose would be detectable. Again this procedure showed no detectable signs of this adsorption.

At this point, further investigation into the purification of the fibers through acid treatment uncovered the treatment with HCl previously outlined in the materials section of this report. Prior to this, only a rinse with 0.06M HCl had been used to cleanse the fibers. After the stock had been properly steeped in HCl, the adsorption of calcium ions were again tried. Following this trial it was decided that the adsorption level of calcium was not quantitatively detectable under these conditions and using these procedures of effluent analysis.

Preliminary Investigation: Sizing Level Required

For control purposes a sizing level of roughly 200-300 seconds HST sizing under pure conditions (ie, fiber and size in distilled water only) was set as a goal. At this time the effects of drying rate, drying duration, temperature of drying, and sheet temperature gradient were not considered. Only later did it become very evident that these factors had tremendous effects upon the sizing levels of the handsheets, to the effect that each handsheet had its own conditioning and curing history.

The first series of handsheets produced with various levels of alkyl ketene dimer emulsion (Hercon 40) were done in sets of two with addition levels ranging from zero to 15 lbs/ton active chemical based on a 2.0g O.D. handsheet (70 lbs/ream at 24 x 36 x 500). The size was prepared at a dilution of 0.0525% by weight and had to be used within two hours due to its reactivity with water. Twenty handsheets were made within this time frame,

and after drying the sheets in sets of four on the hot plate at ten minutes per side, the sheets were given two hours to condition prior to testing. The sheet weight distribution of this set was much greater than expected at $2.12g \pm 3.14\%$. Table II shows the sizing distribution of a part within this set that was important in determining the level of Hercon required. Although the distribution of sizing levels throughout each sheet was high, it appeared that an addition level between two and three pound per ton would be sufficient.

TABLE II

SIZE LEVEL ANALYSIS

Sheet	Weight (Grams)	Hercon 40 #/T	HST (Seconds) 95% R			
			Felt Side		Wire Side	
1A	1.96	0.00	---- No Sizing ----			
2A	1.70	1.27	0.2	0.2	0.2	0.2
3A	1.86	1.16	0.3	0.8	0.2	0.2
4A	2.06	2.15	63	150	90	19
5A	2.10	2.11	1.9	7.5	4.3	2.4
6A	2.10	3.14	193	650	560	340
7A	1.85	3.57	338	281	389	512
8A	1.79	4.95	493	463	530	346
9A	2.28	3.89	1300+	1040	1000+	1000+
0A	2.28	4.84	330	110	1054	135

At this stage it was determined that pressing and drying techniques had to be stabilized to reduce the variation in sizing between handsheets at constant sizing levels. Coefficients of variation in sizing of from 0.30 to 0.80 were found over a range of pressing/drying techniques analyzed, accounting for some 90 handsheets (Appendix I). These techniques all utilized the hot plate for drying with variations in time and temperatures. As it turned out, the use of the hot plate was the major source of the sizing variation. Since moisture variations between handsheets could not realistically be

eliminated through constant pneumatic pressing between blotter paper, the handsheets could not realistically be dried under constant rates. Thus, a trial was carried out to test the sizing variability of sheets air dried for 24 hours and conditioned at 105°C for ten minutes. With the level of sizing stabilized to 1.52 lbs/ton \pm 2.0%, it was possible to produce a sized sheet with the coefficient of variation of about 0.20. During the initial stages, front to back variations in sizing were evident. By testing only the wire side of the sheets, four tests could be averaged together with a net reduction in the coefficient of variation of each set.

APPENDIX I

SIZING VARIATIONS DUE TO DIFFERENCES IN PRESSING, DRYING AND CONDITIONING METHODS

A. H Series

Pressing: Pneumatically with fresh blotter paper
Drying: Hot plate - medium heat - five minutes per side
Conditioning: 105°C for ten minutes
Size Level: 1.98 lbs/ton
Testing: All wire side

Sheet	Weight (g)	HST Sizing at 95% R			
		Observations (Seconds)			
1	2.41	11	15	21	257
2	2.45	477	1430	240	-
3	2.42	32	176	687	95
4	2.51	988	583	-	-
5	2.38	787	-	-	-

$$\begin{aligned}\text{Set: } \bar{X} &= 414 \\ \sigma &= 120 \\ \sigma/\bar{X} &= 0.290\end{aligned}$$

B. Q Series

Pressing: Groups of two with hand roller (repeated twice with fresh blotter paper)
Drying: Hot plate - wire side down - high heat - five minutes
Conditioning: 105°C for ten minutes
Testing: Wire side

Set	Sheet	Weight (g)	(lbs/ton) Sizing	HST Sizing at 80% R			
				Observations (Seconds)			
A	1	1.97	1.80	482	420	33.8	513
A	2	1.96	1.81	47.8	43.1	8.3	43.9
B	3	1.97	1.73	68.8	25.5	156	660
B	4	1.97	1.73	16.0	3.3	2.0	4.3
C	5	1.97	1.65	5.3	1.9	1.2	2.2
C	6	1.98	1.65	3.6	11.1	4.1	3.3

Set	\bar{X}	σ	σ/\bar{X}
A	199	86.0	0.432
B	117	85.3	0.729
C	4.1	1.2	0.288

C. R Series

Pressing: Hand roll between blotters - five passes

Drying: Hot plate - wire side down - low heat - ten minutes resting
two minutes

Size Level: 1.54 lbs/ton

Testing: Wire side

Sheet	Weight (g)	HST Sizing at 90% R			
		Observations (Seconds)			
1	2.00	137	150	300	590
2	1.97	95	112	305	134
3	1.98	84	260	360	77

$$\begin{aligned}\text{Set: } \bar{X} &= 217 \\ \sigma &= 46.1 \\ \sigma/\bar{X} &= 0.212\end{aligned}$$

D. A Series

Pressing: Pneumatic press with blotter paper

Drying: Air dry for 24 hours

Conditioning: 105°C for ten minutes

Size Level: 1.50 lbs/ton

Testing: Wire side

Sheet	Weight (g)	HST Sizing at 80% R			
		Observations (Seconds)			
1	--	212	131	40	64
2	--	109	148	68	136
3	2.05	208	53	193	144
4	2.06	201	310	377	220

$$\begin{aligned}\text{Set: } \bar{X} &= 163 \\ \sigma &= 23.9 \\ \sigma/\bar{X} &= 0.147\end{aligned}$$

APPENDIX II

PROCEDURE FOR PRODUCING SIZED HANDSHEETS IN A BUCHNER FUNNEL

A. Materials

Buchner Funnel: Sizes may vary.

Filtering Flask: Volumes may vary

Funnel Extention: Custom fit plexiglass tube with rubber gasket attached near bottom to act as a seal between funnel and extention.

Handsheet Wire: Custom sized to funnel I.D.; mesh may vary

Level: Bubble type

Chemical Additives

Water Supply

Stock Supply

B. Procedure

As in all handsheet making procedures, formation is of primary importance. It too is a well known fact that formation is critical where sizing is concerned. The use of an extention for the Buchner funnel is for the sole purpose of reducing the consistency of the system to allow for formation uniformity. The degree of dilution is limited, however, by the capacity of the filtering flask. Drainage will begin, in this method, with the first addition of liquid to the funnel, and thus it is important to pre-wet the wire already in place within the funnel with roughly 100ml fiber free water. The extention should have a very flat bottom to hold out water from under the extention. Prior to the addition of any stock to the funnel, a level of some sort should be used to align the funnel so that drainage is uniform across the wire. When the stock is added, allow a consistent quantity to gravity drain prior to the introduction of the vacuum. This will allow an even mat to form which is not overly concentrated in the center, which otherwise may be the case. Do not add stock to the funnel if a vacuum exists in the flask below prior to addition. If this (or any other hand sheet) procedure is to be used for sizing comparisons, it is essential that consistent pressing, drying and conditioning procedures are used. It is suggested that air drying be considered for alkaline sized handsheets, followed by a ten minute condition of the sheets at 105°C.

APPENDIX III
EXPERIMENTAL DATA
A Series

Subset	Sheet	Weight Grams	Calcium Level		HST Sizing at 80% R Observations (Seconds)				\bar{x}	Sheet σ	σ/\bar{x}	\bar{x}	Subset σ	σ/\bar{x}
			% on Fiber	PPM										
A	1	0.00			212	131	40.0	64.0	112	44.5	0.398			
A	2	0.00			109	148	68.0	136	115	20.5	0.178			
A	3	2.05			208	53.0	193	144	150	40.4	0.269			
A	4	2.06	0.0%	0	201	310	377	220	277	47.3	0.171	163	23.9	0.147
B	5	2.02			444	258	517	281	375	72.7	0.194			
B	6	2.02			300	617	458	382	439	77.9	0.177			
B	7	1.98			144	240	702	1029	529	238	0.450			
B	8	2.01	22.8%	235	388	266	418	215	322	56.0	0.174	416	57.3	0.138
C	9	2.01			541	466	1137	1354	874	253	0.290			
C	10	2.03			234	258	147	227	216	27.9	0.129			
C	11	2.00			275	955	336	377	486	182	0.375			
C	12	2.04	42.4%	428	425	1071	579	280	589	198	0.337	541	97.1	0.179
D	13	1.99			612	748	792	951	775	80.7	0.104			
D	14	2.01			139	249	131	146	166	32.4	0.195			
D	15	2.00			93.0	190	80.0	290	163	56.4	0.346			
D	16	2.04	73.8%	741	172	232	208	216	207	14.7	0.071	328	72.2	0.220
E	17	2.04			184	172	121	114	148	20.4	0.138			
E	18	2.02			186	91.0	142	124	136	22.9	0.168			
E	19	1.99	104%	1052	56.0	116	49.0	148	92.2	27.6	0.300	125	13.6	0.109
F	20	2.03			18.0	20.0	17.0	22.0	19.2	1.28	0.067			
F	21	2.05			173	291	416	330	302	58.3	0.193			
F	22	2.07	152%	1554	181	103	110	105	125	21.7	0.174	149	40.4	0.271
G	23	2.03			17.5	8.2	72.0	37.4	33.8	16.3	0.482			
G	24	2.02			2.3	2.9	3.3	2.0	2.6	0.3	0.155			
G	25	2.05	211%	2148	27.5	28.0	30.0	26.4	28.0	0.9	0.032	21.5	6.2	0.288

APPENDIX III

EXPERIMENTAL DATA

B Series

97

Subset	Sheet	Weight Grams	Calcium Level		HST Sizing at 80% R				Sheet			\bar{X}	σ	σ/\bar{X}	\bar{X}	σ	σ/\bar{X}
			% on Fiber	PPM	Observations (Seconds)				\bar{X}	σ	σ/\bar{X}						
A	1	2.11			8.2	7.3	3.1	6.5	6.3	1.3	0.206						
A	2	2.06			81.5	21.1	8.0	44.6	38.8	18.6	0.479						
A	3	2.11	0.0%	0	62.9	25.5	22.0	29.1	34.9	10.9	0.312	26.7	7.4	0.277			
B	4	2.12			2.2	1.4	0.9	0.6	1.3	0.4	0.308						
B	5	2.08			0.8	1.0	1.3	0.4	0.9	0.2	0.222						
B	6	2.08	266%	2783	0.9	0.6	1.0	0.8	0.8	0.1	0.126	1.0	0.1	0.142			
C	7	2.04			460	498	158	202	330	101	0.306						
C	8	2.04			1267	1426	707	324	931	294	0.316						
C	9	2.08	10.4%	106	564	516	146	222	362	121	0.334	541	126	0.233			
D	10	2.10			5.1	2.5	3.0	5.3	4.0	0.8	0.200						
D	11	2.08			0.5	0.7	0.4	0.6	0.6	0.1	0.167						
D	12	2.13	165%	1728	2.2	1.9	1.7	2.2	2.0	0.1	0.050	2.2	0.5	0.227			
E	13	2.05			205	367	222	417	303	60.8	0.201						
E	14	2.09			264	168	691	227	338	138	0.408						
E	15	2.06	19.9%	206	254	526	961	421	516	178	0.345	385	70.0	0.182			
F	16	2.07			16.4	18.5	30.5	22.3	21.9	3.6	0.164						
F	17	2.7			34.6	22.2	43.4	25.9	31.5	5.5	0.175						
F	18	2.08	68.6%	710	7.2	6.0	6.2	6.4	6.4	0.3	0.047	20.0	3.7	0.185			
G	19	2.06			49.7	15.4	34.2	32.7	33.0	8.1	0.245						
G	20	2.08			126	72.2	34.5	60.5	70.8	24.3	0.343						
G	21	2.11	0.0%	0	234	107	152	235	182	36.6	0.201	95.3	23.3	0.244			

APPENDIX III

EXPERIMENTAL DATA

C Series

Subset	Sheet	Weight Grams	Calcium Level		HST Sizing at 80% R Observations (Seconds)				\bar{x}	Sheet σ	σ/\bar{x}	\bar{x}	Subset σ	σ/\bar{x}
			% on Fiber	PPM										
A	1	2.08			2.0	2.7	1.6	1.9	2.05	0.27	0.132			
A	2	2.04			19.3	16.8	20.6	19.9	19.1	0.94	0.049			
A	3	2.11	0.0%	0	8.7	5.4	3.5	8.0	6.40	1.38	0.216	9.19	2.38	0.259
B	4	2.12			0.1	0.3	0.4	0.2	0.25	0.07	0.298			
B	5	2.08			0.2	0.2	0.2	0.0	0.20	0.00	0.000			
B	6	2.12	519%	5475	0.1	0.2	0.2	0.1	0.15	0.03	0.222	0.20	0.03	0.141
C	7	2.08			80.3	96.7	87.6	50.2	78.7	11.6	0.147			
C	8	2.04			123	112	44.3	404	171	92.0	0.538			
C	9	2.07	15.3%	167	23.6	15.8	13.6	9.7	15.7	3.38	0.215	88.4	32.3	0.365
D	10	2.13			0.1	0.3	0.3	0.2	0.22	0.06	0.250			
D	11	2.08			0.2	0.2	0.2	0.3	0.22	0.03	0.132			
D	12	2.05	332%	3466	0.3	0.3	0.3	0.3	0.30	0.00	0.000	0.25	0.02	0.0081
E	13	2.11			10.1	10.7	5.4	3.9	7.52	1.95	0.259			
E	14	2.09			5.9	5.0	3.0	7.1	5.25	1.00	0.190			
E	15	2.08	30.5%	319	12.3	17.7	29.2	44.4	25.9	8.20	0.317	12.9	3.71	0.288
F	16	2.08			0.6	0.6	0.7	0.8	0.68	0.06	0.081			
F	17	2.10			0.6	0.3	0.5	0.4	0.45	0.07	0.166			
F	18	2.09	221%	2312	0.4	0.3	0.4	0.4	0.38	0.03	0.076	0.50	0.05	0.096
G	19	2.09			7.4	2.7	1.7	6.3	4.52	1.59	0.352			
G	20	2.05			5.4	5.8	4.8	7.2	5.80	0.59	0.102			
G	21	2.05	62.5%	644	41.7	45.9	49.7	25.6	40.7	6.12	0.150	17.0	5.55	0.326
H	22	2.08			2.0	3.1	3.0	2.5	2.65	0.29	0.109			
H	23	2.05			0.9	0.7	0.9	0.7	0.80	0.07	0.084			
H	24	2.06	149%	1530	0.6	0.6	0.5	0.7	0.60	0.06	0.078	1.35	0.30	0.244
I	25	2.07			0.5	0.8	1.0	1.7	1.00	0.29	0.294			
I	26	2.09			0.9	1.0	1.1	2.3	1.32	0.38	0.286			
I	27	2.09	103%	1067	1.7	1.4	1.9	2.3	1.82	0.22	0.120	1.38	0.18	0.130
J	28	2.05			6.6	2.1	1.1	2.0	2.95	1.43	0.485			
J	29	2.09			1.1	0.6	0.6	0.8	0.78	0.14	0.179			
J	30	2.07	0.0	0	2.1	1.8	1.7	3.1	2.18	0.37	0.170	1.97	0.149	0.249

APPENDIX III
EXPERIMENTAL DATA
G Series

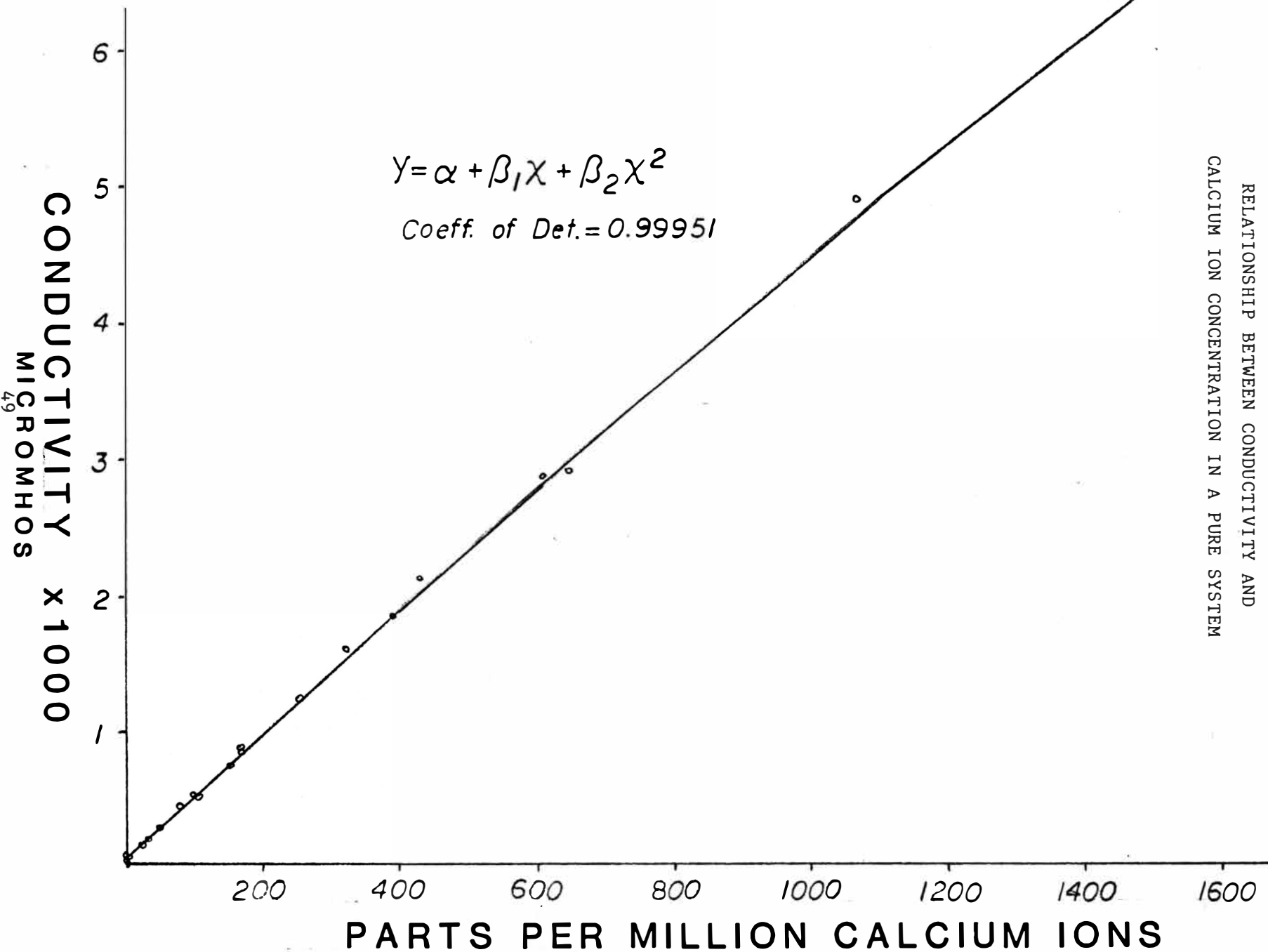
Subset	Sheet	Weight Grams	Calcium Level Conductivity (Micromhos)	HST Sizing at 80% R Observations (Seconds)				\bar{x}	Sheet σ	σ/\bar{x}	\bar{x}	Subset σ	σ/\bar{x}
A	1	1.80	33	3.3	28.1	17.5	11.0	15.0	6.06	0.404			
A	2	1.84	32.5	35.5	25.4	18.4	38.5	29.4	5.34	0.182			
A	3	1.82	33	9.1	15.8	21.9	11.4	14.6	3.25	0.223	19.7	3.24	0.164
B	4	1.77	520	115	207	137	220	170	29.8	0.175			
B	5	1.83	530	245	85.3	153	184	167	38.4	0.230			
B	6	1.80	520	202	246	281	150	220	32.7	0.149	185	17.7	0.096
C	7	1.76	900	277	73.1	68.8	115	133	56.5	0.425			
C	8	1.81	990	112	59.8	96.4	82.7	87.7	12.8	0.146			
C	9	1.75	100	131	192	194	65.1	146	35.3	0.242	122	20.1	0.165
D	10	1.77	1925	43.6	116	39.8	54.0	63.4	20.6	0.325			
D	11	1.78	1925	139	143	152	138	143	3.68	0.026			
D	12	1.83	1725	78.9	60.1	53.5	121	78.4	17.5	0.223	94.9	13.2	0.139
D	13	1.79	2800	136	147	116	213	153	27.2	0.178			
E	14	1.81	2800	56.1	22.8	36.8	24.7	35.1	8.84	0.252			
E	15	1.82	2800	31.5	21.3	38.7	70.1	40.4	12.2	0.302	76.2	18.8	0.247
F	16	1.78	46	476	293	221	159	287	79.2	0.276			
F	17	1.81	39	164	81.6	84.8	168	125	27.6	0.221			
F	18	1.81	38.5	326	210	284	205	256	34.0	0.133	223	33.2	0.149

APPENDIX IV

RELATIONSHIP BETWEEN CONDUCTIVITY AND
CALCIUM ION CONCENTRATION IN A PURE SYSTEM

$$Y = \alpha + \beta_1 X + \beta_2 X^2$$

Coeff. of Det. = 0.99951



APPENDIX V

HIERARCHIAL DESIGN FOR ANALYSIS OF VARIANCE

A. Expected Mean Squares in the Two-Stage Nested Design

E(MS)	A Fixed / B Random
$E(MS_A)$	$\sigma^2 + n\sigma_{\beta}^2 + \frac{bn\sum\tau_i^2}{a-1}$
$E(MS_{B(A)})$	$\sigma^2 + n\sigma_{\beta}^2$
$E(MS_E)$	σ^2

B. ANOVA Table With Computational Formulas

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square
A (Case 1)	$\sum_i \frac{y_{i..}^2}{bn} - \frac{y_{...}^2}{abn}$	a-1	MS_A
B within A (Case 2)	$\sum_i \sum_j \frac{y_{ij.}^2}{n} - \sum_i \frac{y_{i..}^2}{bn}$	a(b-1)	$MS_{B(A)}$
Error	$\sum_i \sum_j \sum_k y_{ijk}^2 - \sum_i \sum_j \frac{y_{ij.}^2}{n}$	ab(n-1)	MS_{B_E}
Total	$\sum_i \sum_j \sum_k y_{ijk}^2 - \frac{y_{...}^2}{abn}$	abn-1	

C. Calculation of F Statistic

Source of Variation	F Calc
A (Case 1)	$MS_A / MS_{B(A)}$
B within A (Case 2)	$MS_{B(A)} / MS_E$

APPENDIX VI

ANALYSIS OF VARIANCE: TESTS OF SIGNIFICANCE

USING SEQUENTIAL SUMS OF SQUARES

SERIES A - Limit 1

Source of Variation	Mean Square	Degree of Freedom	F Calc	Significance of F
A (case 1)	545526.04	6	14.3175	0.000
B within A (case 2)	38102.04	14	1.6116	0.101
Error	23641.71	63		

SERIES A - LIMIT 2

Source of Variation	Mean Square	Degree of Freedom	F Calc	Significance of F
A (Case 1)	399613.44	6	2.5341	0.071
B within A (Case 2)	157692.10	14	5.9820	0.000
Error	26360.98	63		

SERIES B

Source of Variation	Mean Square	Degree of Freedom	F Calc	Significance of F
A (Case 1)	574505.99	6	7.5063	0.001
B within A (Case 2)	76536.26	14	3.1947	0.001
Error	29357.03	63		

SERIES C

Source of Variation	Mean Square	Degree of Freedom	F Calc	Significance of F
A (Case 1)	8786.79	9	3.2689	0.013
B within A (Case 2)	2688.02	20	3.0815	0.000
Error	872.31	90		

SERIES G

Source of Variation	Mean Square	Degree of Freedom	F Calc	Significance of F
A (Case 1)	65889.89	5	6.3477	0.004
B within A (Case 2)	10380.19	12	3.4870	0.001
Error	2976.78	54		

The statistical analysis was done on the Western Michigan University computer through the use of a statistical program entitled the "SPSS BATCH SYSTEM". The program did not have any way of handling unbalanced subsets such as those found in Series A (four groups of four handsheets and three groups of three handsheets), so the Series A data was biased in two different ways. By discarding one handsheet randomly from each of the four subsets containing four handsheets, a total of 256 permutations arise. To logically bias this data set so that only two runs of data analysis were required, the handsheets were selectively omitted from the data. The first analysis of Series A - Limit 1 discarded one handsheet in each subset that gave that subset the lowest standard error. The second analysis of Series A - Limit 2 discarded one handsheet from each subset that gave that subset the highest standard error. This biasing had no startling effect on the outcome of the data analysis, although logical differences were found between the two limits.

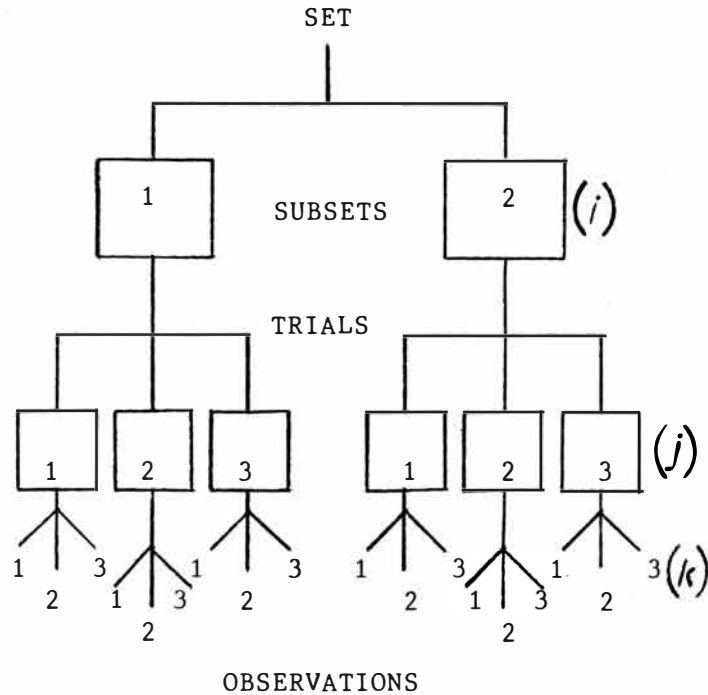
APPENDIX VII

INSTRUCTIONAL GUIDE FOR USE OF "SPSS BATCH SYSTEM"

ANALYSIS OF VARIANCE FOR A NESTED DESIGN

For a nested design with the following configuration, a data set and corresponding input file should be available on DISK.

Nested Design Configuration



Data File Format

A disk file should be constructed as follows:

Observations	V1	V2	V3
1	1	1	$Y_{(1,1,1)}$
2	1	1	$Y_{(1,1,2)}$
3	1	1	$Y_{(1,1,3)}$
.	.	.	.
.	.	.	.
.	.	.	.
ijk-2	i	j	$Y_{(i,j,k-2)}$
ijk-1	i	j	$Y_{(i,j,k-1)}$
ijk	i	j	$Y_{(i,j,k)}$

Example: If $i=2$, $j=3$, $k=3$, there would be 18 total observations called $Y(1,1,1)$ through $Y(2,3,3)$

The data set would appear as:

Observation	V1	V2	V3
1	1	1	$Y(1,1,1)$
2	1	1	$Y(1,1,2)$
3	1	1	$Y(1,1,3)$
.	.	.	.
.	.	.	.
.	.	.	.
15	2	2	$Y(2,2,3)$
16	2	3	$Y(2,3,1)$
17	2	3	$Y(2,3,2)$
18	2	3	$Y(2,3,3)$

Input File Construction

While in Monitor, type "MAKE (FILE NAME).DAT"

The computer will respond with a *

Type "I" followed directly by the first character of the file to be made, and a carriage return after each line is complete. When the file is finished type the following:

"(ESC)(ESC)" - Alt modes / may appear as \$\$

The computer will respond with *

Type: "EX\$\$"

A file is now formed under the name (FILE NAME).DAT

The file to be created is as follows (line numbers should not be typed):

1. "RUN NAME" type heading of analysis
2. "PAGESIZE" "57" (the magic number)
3. "VARIABLE LIST" "V1,V2,V3" (or any name appropriate)
4. "INPUT MEDIUM" "(DATA FILE).DAT" (data file input)
5. "INPUT FORMAT" "FIXED(DATA FILE FORMAT)"
6. "MANOVA" "V3 BY V1(1,i) V2(1,j)/"
7. "DESIGN=V1 VS 1, V2 W V1=1 VS WITHIN/"

If V1,V2,V3 were named, use these names in the design (i and j are the numbers these letters represent).

Instructions for Running SPSS

In Monitor type "R SPSS"

The computer will reply with *

Type "(NEW FILE NAME).OTA=(FILE NAME).DAT"

The computer will reply with a response of reading from a file called NONAME and claim "END-OF-FILE WAS ENCOUNTERED ON INPUT MEDIUM"

This will be followed (after a delay) with *

Type: Control Z " Z"

A file of the SPSS run is now under the name (NEW FILE NAME).DAT and can be run off on a hard copy terminal, a CRT, or queued to the line printer.

LITERATURE CITED

1. Griggs, W. H., Crouse, B. W., TAPPI 63 (6):49 (1980).
2. Neuphor Sizing Handbook, Hercules Inc., revised 2/82.
3. Pexol Sizing Handbook, Hercules Inc.
4. Dumas, D. H., TAPPI 64 (1):43 (1981).
5. Strazdins, E., TAPPI 64 (1):31 (1981).
6. Riddell, M. C., "A Decade of Experience with Alkaline Papermaking", in "1979 Papermakers Conference Proceedings", TAPPI, Atlanta, 1979, pp. 87-95.
7. Schwalbe, H. C., "Nonfibrous Materials", Pulp and Paper Manufacture, second edition: Volume III, "Papermaking and paperboard Making", pp. 35-53.
8. Dumas, D. H., "Alkaline Sizing: The Papermakers New Friend?", in "1979 TAPPI Annual Meeting Proceedings", TAPPI, Atlanta, 1979, pp. 67-72.
9. Alexander, S. D., Dobbins, R. T., and Roscoe, R. W., "The Influence of Dissolved Electrolytes in a Closed Paper Mill System", in "1975 TAPPI Papermakers Conference Proceedings", TAPPI, Atlanta, 1975, pp. 93-99.
10. Bryson, Hugh R., Paper Trade Journal 162 (20):26 (October 15, 1978).
11. Alexander, S. D., Dobbins, R. J., TAPPI 60 (12):121 (1977).
12. Tosh, C., Paper 195 (5):37 (May 18, 1981).
13. Listed in text as footnote 4.
14. Hoppe, J., Karle, R., Wochbl. Papierfabrik. 102 (23/24):883 (1974).
15. Paiste, D. P., TAPPI 64 (4):97 (1981).
16. Byrson, H., Paper 195 (6):24 (June 22, 1981).
17. Beach, E., "Alkaline Papermaking - The Wet End", Paper presented at the 1982 Kalamazoo Pima Conference, Three Rivers, MI, October 1982.
18. Hoppe, J., Karle, R., "Reflections on Neutral System with the Production of Woodfree Papers", in "1980 Papermakers Conference Proceedings", TAPPI, Atlanta, 1980, pp. 223-228.
19. Penniman, John G., Paper Trade Journal 162 (3):31 (July 1, 1978).

20. Penniman, John G., Paper Trade Journal 164 (15):14 (August 15, 1980).
21. Dunlop-Jones, N., Jaycock, M. J., Paper Trade Journal 195 (10):34 (October 30, 1981).
22. Harris, M., Sookne, A. M., "Base-Exchange Properties", Cellulose and Cellulose Derivatives, Copyright 1954, pp. 208-215.
23. Davison, R. W., "Adsorption of Radioactive Kymene 557 by Cellulose Surfaces in Dilute Aqueous Pulp Slurries", Hercules Inc. Trade Report (Unpublished).
24. Brannstrom, Kevin J., "The Effects of Complex Aluminum Species from Aluminum Chloride and Aluminum Sulfate on Rosin Sizing", Senior Thesis, Western Michigan University, April 1982.