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Addition of Ba (Oh)2 To A Closed White Water System as a Means of Controlling Acidity and Sulfate Ion Build Up

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ADDITION OF $Ba(OH)_2$ TO A CLOSED WHITE WATER
SYSTEM AS A MEANS OF CONTROLLING ACIDITY
AND SULFATE ION BUILD UP

by

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ABSTRACT

In an effort to reduce the intake of fresh water into a mill a greater quantity of white water must be recycled to meet the demands of production. Unless some action is taken, continued reuse of the water produces a badly deteriorated papermaking system.

It is believed that the build up of free acid and sulfate ions from the addition of papermaker's alum causes the degradation. A bench trial using a Noble and Wood handsheet maker capable of recirculating white water was used to duplicate such a deteriorated system and then to restore it with the introduction of $Ba(OH)_2$. The hydroxides would neutralize the acidity while the barium would precipitate the sulfate, giving a fine white pigment: a filler formed _in situ_.

An offset furnish consisting of equal amounts of bleached hardwood and bleached softwood kraft was prepared for use. Pexol was added at the rate of 1% based on O.D. fiber content and alum was added at the rate of 2%. Deionized water was used in the beater and as make up water in the sheet mold. No other water was added to the closed system. 5% $Ba(OH)_2$ was introduced into the system following its deterioration.

White water tests showed immediate reduction in the total acidity and sulfate ion concentration. Handsheet tests revealed improvements in opacity, brightness and sizing with only moderate decrease in tensile, despite

the increased ash content. A slurry solids check indicated virtually a complete precipitation of all barium added. Retention of $BaSO_4$ averaged about 88%.

The theoretical feasibility of such a reaction is now a reality. Results were favorable but the economics involved were not. So, other less costly and less efficient means of controlling the papermaking system will be utilized for now.

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INTRODUCTION

Influenced by popular support for pollution abatement and spurred
on by state and federal regulations regarding conservation, the pulp
and paper industry has found it necessary to increase its efforts to
reduce the quantity and improving the quality of emissions to land,
air, and water by increasing the recycling and reusing of its raw ma-
terials. This effort demands a greater understanding of the numerous
variables involved; for to close a system and allow only limited flows
in or out is not an easy task. In a closed system the conditions
affecting it are dynamic; the concentration of chemicals involved is
changing, temperature is changing, acidity is changing, solids content
is changing, etc. These changes can adversely affect the system and in
turn the product being made. Only through investigation can information
be collected which will aid in comprehending the interrelationships in-
volved and in devising means for control and improvement.

LITERATURE SURVEY

Water and Its Reuse

Comparative water requirements show that the pulp and paper in-
dustry is among the top four industrial categories that require large
amounts of water. Based upon total water needs for all industry, paper
and allied products utilize 14.7% of the total. Being cognizant of the
value of good water and its conservation dictates that water can be re-
used as much as possible before being eliminated. Only thirty-five
years ago it was generally believed that water could not be reused with-
out sacrificing too much of the quality of paper. Currently the paper
and allied industry reuses 191% of its water intake (1). Yet in the
interest of water conservation and in preparation for future needs this
may not be enough.

Reuse of water serves many purposes, among which are conservation
of water, reduction of the amount of waste in compliance with state and
federal pollution regulations, conservation of heat, and conservation of
fiber and other raw materials. In a closed system, the rich white water
can be used in the beater and for stock dilution prior to its passage
to the headbox. When this water demand is satisfied the remaining white
water, together with any remaining lean water, is sent to a save-all. The
save-all effluent is used in the sprays and showers and when necessary
for make-up. Otherwise, it is sewered.

Theoretically, it would be possible to completely close a mill or
machine system so that the required make up water would be used only to

replenish that which is retained by the finished paper and that which is lost by evaporation. However, this is difficult to achieve in practice, because conditions may be created that favor the growth and accretion of slime forming micro-organisms, drainage problems could become more acute and sheet formation may be adversely affected, odor problems may likely develop or become more troublesome, showers would tend to plug more frequently, color and grade changes prevent carry-over to another run, and most important, the quality of the paper produced would most likely deteriorate. So in practice, mills are discharging some of their used water to avoid these problems.

Sizing, Hypothesis

Sizing is one area of paper quality which shows marked changes with increasing reuse of water. In fact, a brief survey of resource material indicates that 100% recirculation of white water may lead to badly deteriorated sizing and sheet strength unless more and more sizing chemicals are added or some of the offending chemicals are neutralized, or, as in normal practices, some of the accumulated chemicals are purged from the system. As of this writing, two experimental trials based on 100% closed white water systems bear out the above expectations (2, 3).

Since the filler and fines content of white water tends to level out while sizing decrease continues, it is believed that the build-up of free acid and sulfate ion from the addition of papermaker's alum cause the real harm. On production runs with partially closed white water systems, NaOH is added to neutralize the system, thus preventing acid build-up. But nothing is done about sulfate ion concentration. True, in a partially

closed system the build-up may not be too great; however, in a fully closed

system the concentration may become sufficient when considered as part of

all the ions competing for positions during the alum-rosin interaction

to produce poor sizing. To test this hypothesis it would be necessary to

remove the sulfate ions from the system and check the results of sized

sheets. Investigation of available chemicals for the removal job yielded

$Ba(OH)_2$ as a possibility. Barium would precipitate the sulfate in the

white water system, forming $BaSO_4$ in situ. This fine, white solid could

be retained as a filler or separated from the system to be used as a pig-

ment for coating. The anion portion of $Ba(OH)_2$, namely the hydroxides,

could effectively control the acidity and thus eliminate the need for NaOH

addition. The overall reaction should look something like this:

$$Al_2(SO_4)_3 + H_3O^+ + Ba(OH)_2 + Rosin\ soap \longrightarrow$$
$$Al\ (Resinate)\downarrow + BaSO_4\downarrow + H_2O$$
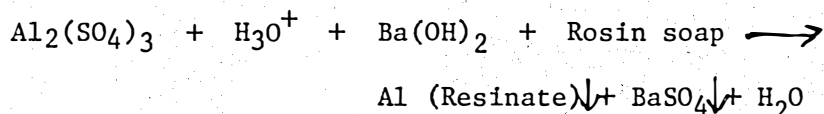
Before formulation of any kind of experimental procedure can begin,

a better understanding of sizing; its history, mechanism and limitations,

must be obtained through a thorough literature search. In addition, re-

search must be done on the acceptability of $Ba(OH)_2$ as an active ingredient

in the proposed reaction. If $BaSO_4$ is to be used as a filler, a basic under-

standing of loading is needed and, in particular, the potential of $BaSO_4$

as a filler must be established. Other uses might prove to be more feasible,

so uses in other areas should be considered. In order that this "shot gun"

approach to sizing improvement be accepted, it must be economically plau-

sible, so a cost analysis must be included to investigate this.

Sizing, Surface and Internal

Cellulose is a very hydrophilic substance and pulp fiber surfaces have a high specific surface energy. Thus, water readily wets these surfaces. The porous structure or paper makes it act like a sponge in the presence of liquids and hence it must be treated with various sizing agents to impart repellency.

When an aqueous liquid is placed on the surface of paper, it must first wet the fibers, after which it is drawn into the sheet structure by the capillary action of the pores or spaces between the fibers. In addition, the liquid tends to spread out on the surface of the sheet. Liquid can also penetrate into the paper and along its surface by paths through the fibers themselves by diffusion.

Regardless of the structure of paper, a sizing agent should make the fiber surfaces hydrophobic, so that the contact angle between the aqueous liquid and the fiber wall is very high thus resisting penetration and feathering. Thus, any effective sizing agent must either be hydrophobic or contain a hydrophobic substituent group. These must become oriented on the cellulose substrate so that the hydrophobic groups become the exposed surface. The sizing agent should be applied in such a way as to become strongly attached to the fiber. Finally, the sizing material should be well distributed over the fiber surface in something less than complete monolayer coverage yet still sufficient to effect good sizing and a high contact angle.

Papermaking terminology calls paper which has no sizing at all, water leaf; increasing degrees of sizing are termed lightly-sized or slack-sized; and well sized or hard-sized.

Nearly all grades of paper are sized to some extent to meet definite requirements. This is done through two principal processes: surface sizing and internal sizing. External or tub sizing (as surface sizing is also called) is as old, historically, as paper itself. When paper was invented in China, it was treated with sizing solutions of glue or other adhesives to improve its writing characteristics. Basically, surface sizing involves the application of a sizing agent to the surface of the partially dried web and is done in a size tub, size press or on the calender. Surface sized papers generally also contain internal size.

Internal sizing, also known as engine or beater or wet-end sizing, consists of mixing a sizing agent with a fibrous furnish and then forming the entire mass into a sheet containing a relatively uniform distribution of fibers and sizing agent. Treatment of paper with internal sizing agents not only affects sizing, but it also has a definite effect on the other properites of paper. Large amounts of some sizing agents are detrimental to both optical and physical properties. Rosin size and paraffin wax are the principal materials used for internal sizing. Other materials used include asphalt and synthetic sizing agents like hydrocarbon resins, various polymers and other chemically reactive materials.

Rosin

Most internal sizing is done with rosin size because it is relatively cheap, reliable and reasonably effective. A 1960 survey of U.S. paper mills reported that 162,000 tons of rosin and rosin size were used for sizing. This is about half of the total tonnage of sizing materials consumed that year (4).

In 1807 the rosin sizing process was introduced by Moritz Illig of Germany. Illig demonstrated that resistance to the penetration of water in paper could be accomplished by co-reacting rosin size with paper-maker's alum (aluminum sulfate) to produce rosin size precipitate in situ which becomes "fixed" to the pulp fibers. This precipitate becomes the actual sizing agent in the dried sheet.

Rosin is a brittle, yellow or amber-colored natural resin. The three types of rosin are designated as gum rosin, wood rosin and tall oil rosin. Modern refining processes have made them essentially equivalent from the viewpoint of sizing efficiency. Gum rosin is obtained by tapping live southern pines from early spring to late fall; the oleoresin that exudes is collected and steam-distilled to yield rosin and turpentine. Wood rosin is obtained from stumps and roots which are chipped and then solvent-extracted to yield rosin and turpentine. Tall oil rosin is obtained as a by-product when pulp is made from southern pine by the kraft process. Black, foamy alkaline tall oil skimmings from spent cooking liquor are neutralized, washed and then vacuum-distilled to yield rosin and fatty acids.

Chemically, rosin is a glassy, amorphous material that softens at temperatures between 75 and 95°C. It consists primarily of several different monocarboxylic resin acids of alkylated hydrophenanthrene structures having the empirical formula $C_{19}H_{(27 \text{ to } 33)}COOH$ (M.W. 302.24). The resin acids are divided into two general structural types, abietic and pimaric. These acids have varying degrees of unsaturation and chemical reactivity. Their carboxyl substituents are sterically hindered so that they are considerably weaker than acetic acid. The bulky hydro carbon portion of a resin acid provides considerable shielding of the relatively small polar carboxyl group. Thus, when properly oriented, these molecules serve as very effective hydrophobic coating for surfaces. Resin acids are soluble in most organic solvents, but are essentially insoluble in water. The resin acid component of rosin accounts for about 90% of the total material. The remainder consists of neutrals such as resinous alcohols, esters, ketones, fatty compounds and various hydrocarbons.

Rosin is converted into rosin size by cooking with alkali in either an open or a pressure cooker to produce a product containing varying amounts of "free" rosin depending on the degree of saponification of rosin by alkali; either sodium carbonate or sodium hydroxide may be used. Important characteristics of rosin size are total solids content, free rosin content and alkalinity.

Industrial suppliers have modified rosin and rosin size to improve such properties as softening point, resistance to oxidation, color, stability, handleability and sizing efficiency. Sizing efficiency is accomplished with

a better base rosin coupled with additives which yields a much smaller

particle size, is more effective against agglomeration and is easier to

attach to the fibers.

Development of fortified rosin size was done by incorporating a

certain amount of the maleic anhydride or fumaric acid adduct of rosin

to the final product. The levopimaric acid in the size adds two car-

boxyls making a total of three acid carboxyl groups per molecule. In-

creased reactivity increases efficiency, especially in hard-to-size sys-

tems. Commercial fortified sizes are sold under the names of "Pexol",

"Mersize", and "Cyfor".

Since high free rosin produces better sizing and uses less alum

to set, a protected rosin size was introduced which employs a protective

colloid to prepare highly stable size containing as high as 90% free ro-

sin. Advantages over ordinary rosin size include non-interference of cal-

cium or magnesium ions, better sizing at lower acidity and no special pre-

cautions necessary in diluting or handling. Commercial names of this type

of size are "Bewoid" and "Prosize".

Choice between the various types of commercial sizes available or of

mill made size (Delthirna process) depends largely on the grade of paper

being made, the requirements necessary, and the local conditions that pre-

vail. Commercial types may be supplied dry or in paste form depending on

the needs of the mill. For additional discussion on the types of sizes

consult Casey (5) and Schwalbe (6).

Alum (M.W. 666.41) is made from bauxite or high-alumina clay which is digested for several hours with sulphuric acid. The product when dried is aluminum sulfate, $Al_2(SO_4)_3$, with 14 to 18 molecules of water of crystalization. Only 20% of the alum used today is dried; the rest is shipped in liquid form as a 50% solution.

When dissolved in water, alum dissociates into sulfate ions and hexahydrated, trivalent aluminum ions that undergo successive stages of hydrolysis as follows:

$$Al_2(SO_4)_3 \cdot 18 \, H_2O + H_2O \longrightarrow 2 \, Al(H_2O)_6^{+3} + 3 \, SO_4^{-2} + 6H_2O$$

$$Al(H_2)_6^{+3} + H_2O \longrightarrow Al(OH)_5^{+2} + H_3O^{+1}$$

$$Al(OH)(H_2O)_5^{+2} + H_2O \longrightarrow Al(OH)_2(H_2O)_4^{+1} + H_3O^{+1}$$

$$Al(OH)_2(H_2O)_4^{+1} + H_2O \longrightarrow Al(OH)_3(H_2O)_3 + H_3O^{+1}$$
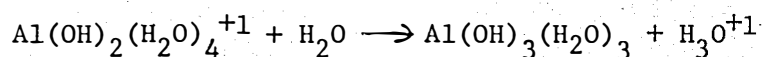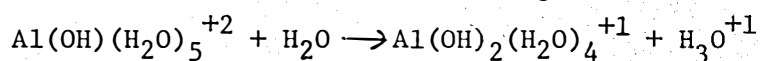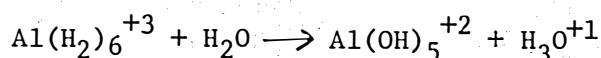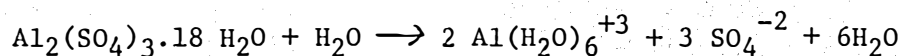
Increased acidity produced by these reactions limits the degree of hydrolysis. A 2.5% pulp slurry in distilled water, alumed to a pH of 4.5, represents a system involving perhaps 20% first-step hydrolysis (7). The acidic system buffers at a pH of about 4.0 because of hydrolysis equilibrium and because of the in-activation of some of the trivalent aluminum species by complexation with sulfate ions (8).

An alumed system, therefore, contains a small amount of active acidity (pH) and a large reserve of potential acidity. This acidity serves to acidify the sodium resinate present in the size and to neutralize any alkaline materials in the pulp and water suspension. Important points to consider so far as the composition of an alum solution is concerned are total solids content, pH value, total acidity and alumina content.

An aqueous dispersion of rosin size consists of suspended particles 0.1 to 0.5 in diameter, soap micelles perhaps 50 A in diameter, and individual resinate ions. The pH of this system ranges from 8.0 to 9.5 depending on the concentration of the dispersion with less than 1% hydrolisis of the resinate (7). Depending on the degree of saponification, the suspended particles are composed of rosin neutrals and free resin acids. Since the usual sizing process is below the critical micelle concentration for resin acids, only suspended particles and individual ions will be present.

Alum

To get desired results, the rosin size must be precipitated onto the fibers. Unless this is done a good portion of the size will be washed from the sheet and little change in water holdout will be noticed. Acids, acid salts or salts of alkaline earth metals can be used but sizing is not as good nor as permanent as that obtained with alum. Generally, reports show decreasing effectiveness in order of alum salts, chromium, iron manganese and nickel.

Papermakers traditionally refer to aluminum sulfate as "alum" although it is not true alum at all. Because it is similar in appearance and effect to one of the true alums, aluminum potassium sulfate, which was originally and commonly used to precipitate size, the name "stuck".

Rosin and Alum Addition

The amount of rosin size used depends upon the functional require-
ments demanded of the paper as well as the efficiency of the sizing
process. Amounts vary from 0% size in absorbent papers to 5% size in
some specialty grades. It has become an established fact that sizing
does not increase in direct proportion to the amount of sizing agent
added. Greatest change per increment of additional size is obtained in
a range of about 0.75 to 1.5% size based on pulp weight. Above this
range efficiency decreases, but end use may demand that greater amounts
be used.

Theoretically, approximately 0.3 pound of alum would be required to
precipitate one pound of rosin size as aluminum resinate. However, in
practice, a ration of alum to rosin varies from 1 to 1 to 3 to 1. The
ratio depends upon the amount of size used, the character of stock being
used, the character of the water used and the amount of water reused.

It is desirable to add the size and the alum at an early stage to
provide for their uniform distribution in the pulp slurry, as well as
adequate time for size precipitate formation. Addition of both chemical
reactants prior to final pulp refining is not advisable. Usual procedure
has rosin size addition preceding alum addition; however, reversed order
may give better results in some systems, especially those with hard water.

Chemistry of Internal Sizing

Although the Illig sizing reaction has been in use for some 150 years, it is not completely understood. Originally, sodium or potassium salts were reacted with rosin until neutral. The resulting rosin size was added to the pulp in the beater and precipated with alum. This was considered to be simple double decomposition where water-repellent aluminum resinate was precipitated and soluble alkali sulfate would be formed as a waste by-product.

Later on it was found that satisfactory sizing would also result if some of the rosin was not fully saponified. To explain this, Wurster in 1879 stated that sizing was due to the precipitation of free rosin and that alum was merely a rosin precipitant; the incidental aluminum resinate that was formed was believed to be inactive (9).

Price's (10) study of rosin precipitates showed that chemical composition varies over a wide range without affecting sizing efficiency. Aluminum diresinate, aluminum monoresinate, and free rosin have been found present in rosin size precipitates.

Since the initiation of the rosin sizing process, the literature on paper sizing has become voluminous. Most of it is the result of a controversy which has persisted between proponents of the colloidal theory and the proponents of the ionic theory as related to the role of dissociated alum.

Sieber (11), Ostwald and Lorenz (12) were among the first to ex-
plain the sizing reaction in terms of colloid chemistry. Basically they
believed that sizing occurred because of the reaction between the nega-
tively charged rosin particles, negatively charged fibers and the positively
charged colloidal aluminum hydroxide; alumina, formed by the hydrolysis of
alum. The alumina particles are attracted to the negatively charged pulp
fibers. When a sufficient amount has been attracted, the fibers take on
a positive charge and these attract and hold the negatively charged rosin
particles to form a water-repelling complex.

Ostwald and Lorenz (12) show that the best sizing was obtained at the
isoelectric point; too little alumina left the fiber and rosin size nega-
tively charged, while too much alumina made them positively charged. Each
condition yielded poor sizing. According to theory, a pH below 4.0 gives
unsatisfactory sizing because no alumina is formed (11). Some alumina is
present at a pH of 10, but is ineffective as a fixing agent because of the
stabilizing action of hydroxyl ions on the rosin size. Martin and Willets
(13) found that all alum added to a pulp furnish is adsorbed as alumina up
to an addition up to about 4.0%; beyond this amount efficiency decreased.
Increased beating, increased stock dilution and increased temperature ap-
pear to favor the adsorbtion of alumina by cellulose (5).

In general, anions tend to lower the positive charge on alumina,
making it less effective as a "fixer" between rosin and cellulose. Although
some sulfate ion is necessary for the coagulation of rosin-alumina complex

on the fibers, the sizeable build-up in a white water system accounts
for the lowered sizing value (14). Thus, alum produces alumina and
supplies sulfate ions for its coagulation with rosin size and cellulose.

Along with the others, Calkin (15) supports the colloidal theory
of rosin sizing first presented by Lorenz in 1923. It is his contention
that alumina binds rosin to the fibers by electrostatic forces as well
as orienting it so that the hydrophobic end protrodes outward away from
the fiber.

It was Price (16) who said that alumina, as such, was not part of
the regular size precipitate. Alumina, she maintained, may be formed by
the reaction of excess alkali in an alumed system and may be coprecipi-
tated with rosin, but this alumina has no beneficial effect on sizing
and may when present in excessive amounts be detrimental. The fact that
the greatest amount of alumina is formed at a pH of 6 whereas the best
sizing is obtained in a system where the pH is in a range of 4.5 to 5.5.
This gives further evidence that alumina is not the active fixing agent.

Consequently, another theory developed to explain the bonding me-
chanism; the aluminum ion theory. Price (17), Davison (18) and others
believe that precipitation proceeds by the simple interaction of cationic
and anionic species. The hydroxyl groups on hydrolyzed aluminum ions may
be replaced by anions, provided their coordination ability is stronger than
that of hydroxyl ion or if their concentration is sufficiently higher.
Thus, in the presence of resin acid anion, various aluminum rosin salts

may depending upon the molar ratios of the reactants. Ekwall and Bruun (19) concluded from their studies that under ideal conditions the sizing material is dibasic aluminum monoresinate. Guide's (20) work on reaction products showed that the size precipitates were not stoichiometric compounds but coprecipitates of several compounds dependent on the abietate-to-aluminum ratio and is independent of pH. It is not unreasonable to assume that polymeric products may also result from the alum precipitation of rosin size since some Al-O-Al bonds would be expected to fulfill maximum coordination of the aluminum. Steric hindrance would become a factor when considering the feasibility of a cross-linked structure (7).

Chemical analysis and solvent extraction have suggested that size precipitate is an equimolar mixture of free rosin acids and aluminum diresinate (17). Davison's (18) infrared- and thermal-pyrolysis data revealed the presence of 1.2 molecules of free resin acid, leaving 1.9 resinate groups associated with each aluminum atom in the precipitate as indicated by the following formula:

$$Al(Ab)_{1.9}(OH)_{1.1}(H_2O)_{1.7} + 1.2 \text{ Hab} + 0.6n$$
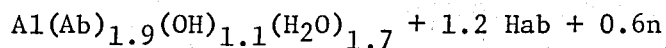
Further chemical analysis demonstrates the absence of aluminum hydroxide as an independent molecular species; further refuting the old alumina theory (7). Examination of rosin size precipated in water containing common impurities such as hardness or alkalinity reflects the effect of environmental influences and can easily be explained by the ionic mechanism (18).

The two theories become fused at this point since proponents of the ionic theory lend support to the electrostatic theory of Ostwald and Lorenz [12] to explain the mechanism for retention of the rosin size precipitate on the cellulose.

Since both aluminum diresenate and free resin acid are very insoluble in water, they aggregate to form precipitate particles. Neutrals are also precipitated and have resinate ions attached to the particle surfaces. The aluminum salts on the precipitate particles makes them positively charged in water while cellulose pulp surfaces possess a negative charge even in the presence of alum [21, 22]. Rapid growth of size precipitate particles is terminated by the attraction and retention of cellulose. Thode and co-workers [23] were among the first researchers to endorse this theory and regard alum as the agent creating a positively charged rosin size precipitate. Based on his study, Guide [20] concludes that retention of size precipitate is a strong function of the electrokinetic potential of the precipitate particles which in turn depends upon the composition of the precipitate, the pH of the slurry, and the presence of ions in the system.

Improved electrokinetic techniques have led investigators to revise the simple electrostatic concept to encompass recent findings. Micro-electrophoresis applied to a system of cellulose fines yielded Strazdins [24] results which he believes controls the rate of interaction of oppositely charged colloids. The electrokinetic surface charge acts like a "valve"

that regulates the sizing reaction. Strazdins finds that a low level

of counterions can be beneficial because of the moderating effect on

the positively charged hydrated aluminum. This moderating effect tends

to prevent excessive agglomeration of the size particles allowing a

more uniform distribution on the fiber surfaces.

Vandenberg and Spurlin (22) report that various wood pulps contain

up to 0.5% anionic, water-soluble ployuronides that are readily absorbed

by the rosin size precipitate and cellulose. The action of these water

solubles is to moderate the positive charge of size precipitate particles

while exerting a protective colloid action that decreases agglomeration

of these particles. Thus, a more even distribution of finer particles

over the fiber surfaces is permitted.

Attachment of the rosin size precipitate to cellulose may depend on

simple physical adsorption or electrostatic attraction. Permanent bonding

results from the role of the pulp's carboxyl content in covalent bonding

or in the coordination of aluminum ions located on the surfaces of precipi-

tate particles. Aluminum may also coordinate to cellulose hydroxyl groups.

Beyond this chemical bonding activity, some physical bonding may occur

since the tacky rosin derivatives readily stick to various surfaces.

Thus, the short range Van der Waals forces are the most probably

source of ultimate bonding. Strazdins (24) postulates that the long range

electrostatic forces are superimposed on the Van der Waals forces. Van-

derberg and Spurlin (22) believe actual chemical binding is the result of

salt formation and chelation of uronic acid groups. Thomas (25) suggested

the inclusion of a hydroxyl group from the cellulose into the olated

dimer of aluminum monoresinate. The work of Yiannos (26) supports the

idea that the aluminum resinate is chemically bound to the fiber surface

through acidic carboxyl groups or similar exchange sites. Cobb and Lowe

(27), similarly, believe that the aluminum-rosin complex is bound to the

fibers through the coordinate valences of the aluminum ion.

A review of the proposed chemical mechanisms of the rosin sizing

process shows a good deal of overlap in certain areas. As predicted by

Griffin and Little in 1894 the true theory may lie between the two ex-

tremes. Proponents of ionization must admit some effective colloidal

precipitation and colloidal proponents must admit some ionization (9).

Fiber Coverage By Size Precipitate

Size particles, after drying, are distributed in a discontinuous,

latticelike, stratified formation throughout the sheet partly covering

the fibers and partly filling the voids between the fibers (28). Barthel

(29) and other investigators corroborate this description through their

use of the electron microscope. Davison (18) and Hock (30) report that

the sized pulp fibers appear speckled with tiny (o.1 diameter) roundish

particles, distributed singly and in clusters. Examination of samples

dried at elevated temperatures revealed a flattening of the particles

as the precipitated material fused, flowed and spread over the fiber sur-

face losing a good deal of individual distinction (18). Thus, it would

appear the degree of sizing depends on the number of particles inter-

mixed with fibers and their proximity to one another.

Factors Affecting Sizing

Nearly all components on the furnish affect the sizing value.

Physical conditions to which the stock is subjected, such as amount of

beating, temperature of the stock, order of addition of components,

andling of stock on the wire and conditions of pressing and drying all

influence sizing results.

1. Pulps

There is a great difference between pulps in respect to their ease of

sizing. An approximate correlation exists between pulp sizeability and

pulp impurities content. Unbleached pulps, in general are easier to size

then bleached ones. Cotton linters, a relatively pure form of cellulose,

are extremely difficult to size. Wilson (31) believes that the ion ex-

change properties of pulp determine the number of bonds available for fix-

ing rosin size precipitate on the fibers and that the greater exchange

potential of the impure pulps explains their ease of sizing. Also, the

presence of natural resins in unbleached pulps improves sizing they are

basically sizing agents themselves.

2. Fresh and White Water

(Acidity and Alkalinity)

The pH of a pulp slurry has a profound effect on sizing development and

can cause premature precipitation of rosin size. Maximum sizing is achieved

at a certain pH which varies slightly with environmental factors according

to Watkins (32). Casey (5) states the best and most efficient sizing is

obtained at a pH between 4.5 and 5.5 at the wire. Extremes in system pH

must be avoided since neither yield good sizing. Precipitation of rosin

size with acid alone gives only negligible sizing. Alkaline consumption

of aluminum ions results in poor sizing when alkalinity becomes excessive.

Strazdins (24) found good correlation between sizing efficiency and pH.

Guide's (20) studies showed that a high positive charge on size precipi-

tate was favored by a low pH (approximately 5.0).

Lewis and Bowman's work (2) with a 100% closed white water system led

them to believe that free acid, not sulfate ion concentration, was the

offender causing strength and sizing deterioration. Britt (7) concurs with

this finding. Watkins (32) discussion of the adverse effect of high total

acidity on sizing development lends further support. Total acidity, as de-

termined by titration, depends on the amount of alum added in order to re-

duce the pH to the desired level. Continued water recycle may lead to a

highly buffered system requiring larger amounts of alum to reduce the pH.

If such a system develops, the large quantity of aluminum in various

stages of hydrolysis causes a high total acidity and reduces sizing.

In order to reduce the undesirable effects of an improper pH either

an acid or alkali substance is added to the system. Addition of low cost

H_2SO_4 lowers the pH to the desired range with at times improved sizing

results (17). To improve a pH that is too low, a small amount of alkali,

usually NaOH, can be metered in. This has the desired result of raising

the pH for improved sizing as well as reducing equipment corrosion, extending wire life and improving sheet strength and permanance. Sodium aluminate, an alkaline source of alumina, is used in combination with alum for precipitation of rosin size with good results over a wide range of pH.

A total acidity of 50 to 200 ppm is acceptable for white water in a recirculated system. Higher values of 400-800 ppm can cause poorer sizing due to lower rosin retention. W.M.U.'s pollution study (3) encountered poor sizing at high acidity.

(Calcium Salts)

Excessively hard water is objectionable to the sizing process. Jayme and Arledter (33) maintain that a small amount of calcium is not objectionable as it acts as an electrolyte promoting sizing. Calcium resinate is an ineffective sizing agent and has a floc size too small for good retention (24). Price (34) contends the effect of hard water on sizing depends somewhat on the pH of the system. If softening is not feasible, treatment with H_2SO_4 or alum prior to size addition is helpful.

(Aluminum Content)

Excess alum should be avoided. A residue of 5 to 10 ppm aluminum at a pH of 4.5 in white water is recommended (6).

(Sulfate Ion Concentration)

A high concentration of sulfate ions reduces the coordination of rosin with aluminum and depresses the electric charge (6). Cobb and Lowe (27) maintain that the organic ions such as oxalate, citrate, tartrate and the

inorganic ions, sulfate and phosphate may become detrimental at suffi-

cient concentrations. Guide (20) favors a low concentration of easily ab-

sorbed anions in the sizing suspension and emphasized the elimination

of such species as sulfate. Casey (5) feels the circulation of too much

white water is harmful because excess sulfate ion build-up in the system.

Wilson (35) presented evidence that large quantities of sulfate and other

inorganic anions are detrimental to sizing. Collins, Davis, and Rowland

(36) find that sulfate anion reduces electrophoretic mobility of alumina

flocs formed by aluminum chloride while Thode and co-workers (23) have

shown that excessive sulfate ion decreases net surface potential. Van-

denberg and Spurlin (22) note similar findings. Strazdins (24) is of the

opinion that the reduction in electrokinetic charge of aluminum ion by

sulfate counterions does not necessarily mean a loss in its available

positive charge and a commensurate loss in sizing. As noted earlier, he

feels rather that the sulfate ion controls the rate of interaction of the

various species. Before a final judgment can be made about the sulfate

ion's role, consideration of environmental factors are necessary. Such

things as pH, concentrations of chemicals used, rate of mixing, colloidal

state of rosin, contact time and desired longevity of paper produced must

be taken into account (37). Strazdins (24) does feel that under condi-

tions where the pulp furnish contains inorganic salts, highly negative

residual lignins, other coordinating organic acids and fillers, most of

which heavily tax the cationic nature of the added alum, a build-up in

sulfate content could further aggravate the serious shortage of the positive charges and be detrimental to sizing.

Lewis and Bowman (2) found a continual increase in sulfate ion concentration over the course of their run, yet maintain that total acidity was the real offender. The W.M.U. study (3) had sulfate ion concentrations on the range of 500-1500 ppm and noticed some sizing decrease.

To combat the effects of excessive sulfate ion concentrations, general practice dictates the sewering of some white water. Some mills replace some alum with sodium aluminate to lower the rate of sulfate build-up. Schwalbe (6) mentions the use of calcium hydroxide to neutralize sulfate ions.

3. Rosin Size

The type of rosin size used makes a good deal of difference in the sizing results. While regular size exhibits good sizing under most conditions, fortified size, with its higher anionic charge, lowers the positive charge of the alumina to give a more uniform distribution of smaller size particles and, thus, better sizing. With varying mill conditions and varying pulp sizing requirements the right size must be selected to meet these needs.

4. Additives and Modifiers

Many modifiers have been introduced into the pulp slurries in hopes of improving sizing efficiency. They include carboxymethyl cellulose, urea-formaldehyde and other wet-strength resins, starch and natural gums.

Following the findings of Vandenberg and Spurlin (22) such things as gum arabic and pectin were added. It is believed these additives improve the degree of dispersion of the size precipitate and improve its distribution on the fibers.

5. Fillers

Fillers have an adverse effect on sizing. Some are reactive with alum. Because to this it is generally best to add them after the rosin size and alum.

6. Physical Treatment

As a general rule, more beating gives higher sizing. This is due partly to the decrease in porosity of the paper and partly to the increased exposure of greater fiber surface. With extensive beating a bit more rosin size should be used or the regular dosage will be precipitated too sparsely to be fully effective.

If insufficient time is allowed for distribution of size before alum addition, uneven sizing will result. Contact time between rosin size and fibers should be sufficiently long to allow mixing but not excessive for once alum is added undue delay is bad.

Good distribution is obtained at a consistency of 4 to 6% where intermolecular distances are of reasonable length. Foaming in the system tends to concentrate size at the surface of the air bubles and therefore inhibits distribution.

7. Temperature

Good results with rosin sizing are more difficult to achieve in warm water than in cold. Many mills have encountered severe reductions in sizing efficiency when their wet ends operate at higher temperatures. Price (38) studied temperature effects in a range of 16° to 50^oC and found lowest temperatures gave best results. Where possible, temperatures should be maintained below about 35^oC (5). If this is not possible, the time during which size and alum are both present in the heated stock should be minimized.

8. Sheet Formation

Nearly all variables in the wet end operation affect the formation of the finished sheet and, therefore, sizing. Retention of fiber and filler fines has a considerable effect on results and their recirculation from save-alls can bring noted sizing improvements. Two-sidedness is a problem with sizing too and differences in sizing are apparent.

Wet pressing can help sizing or hurt it. Variation in the treatment of the two sides of the sheet sometimes shows up as two-sidedness. Uneven pressing across the sheet results in uneven sizing.

9. Drying

Elevated-temperature drying of sized paper improves the degree of sizing obtained. Davison (18) states that better mobility of the size precipitate during high temperature drying explains improvement. At elevated temperatures the size precipitate tends to spread and further polymerize leading to better fiber coverage. A reorientation of polar substitutes

occurs making the sized surfaces more hydrophobic and immobile, giving a well-bonded, protective coating. This anchors the precipitate in a position which gives a high, stable contact angle. Electronmicrographs illustrate these changes (18,30).

Jayme and Arledter (33) investigated the sintering temperatures of various rosin sizes. For a fully saponified rosin a temperature of 123°C was required. A size with a free rosin content of 37% needed 117°C while one with a free rosin content of 66% needed 112°C. All three sizes gave about 50% higher sizing values when dried at 140°C instead of 100°C. Davison (18) found that a fully saponified rosin size acidified with acid and then with alum had a sintering temperature of 68° - 75°C and upon analysis 79% free rosin acid.

The proper drying rate and temperature profile needed to promote maximum sizing depends on production requirements, environmental conditions and equipment limitations. If temperature is raised too rapidly, rosin size precipitate attachment to the fibers will be disrupted by the action of escaping vapor. Migration of the precipitate may occur under severe conditions. A graduate temperature increase is desirable as the web proceeds through the dryers with maximum temperature being reached when the sheet solids are in the 45 to 55% range.
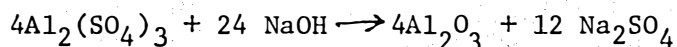
Streaky sizing can be prevented by control of dryer felt dryness across the machine width and by uniform paper felt draws (6).

10. Calendering

Machine calendering of a sized sheet will substantially lower the degree of sizing. Loss varies with the degree of sizing and the grade and weight of the paper. Supercalendered sheets pretreated with steam often show improved sizing.

Sodium Aluminate

Sodium aluminate, $Na_2Al_2O_4$, is an alkaline source of alumina containing about three times as much alumina as alum. This alumina is in the form of a negative radical. Used in conjunction with alum, sodium aluminate offers independent control of the pH and the amount of alumina added to the system. For an equivalent amount of alumina, sodium aluminate plus alum adds only 1/4 the amount of sulfate ion as is added by alum and sodium hydroxide, as shown below.

$$Al_2(SO_4)_3 + 3\ Na_2Al_2O_4 \longrightarrow 4Al_2O_3 + 3Na_2SO_4$$

$$4Al_2(SO_4)_3 + 24\ NaOH \longrightarrow 4Al_2O_3 + 12\ Na_2SO_4$$
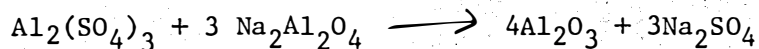
Product bulletins (39) claim better, more uniform sizing because of less acidity and a lower sulfate ion concentration; increased retention due to its coagulating qualities; improved formation with less two-sidedness; a cleaner machine system with less fines deposition; improved paper strength because of a higher residual pH in the finished paper; lower foaming tendency of the slurry; and reduced corrosion in the water system because of higher pH.

Improved sizing development at a higher pH has been reported by Chene (40), and Coursault (41) when using an alum-aluminate system. Dohne and Libby (37), using a recirculated white water system, produced satisfactory sizing with 2.5% of a 100% free rosin size, 0.5% sodium aluminate and 1% alum at a pH just under 6. Another study obtained good results by precipitation of 2% of 10% free rosin size with 0.7% sodium aluminate and 1.8% alum at a pH just over 6. Without white water recirculation sizing took place at a pH as high as 8.

Addition may be made prior to refining to aid pulp swelling. The alum is added last after the rosin size. Others recommend the reverse order with sodium aluminate last to the fan pump. Amounts range from 0.1 to 0.5 with anything over that being rare. Optimum pH for sodium aluminate used in sizing is in the vicinity of 5.5 - 5.7.

Sodium aluminate may be obtained in granular form and then dissolved on location in water to form a 5 to 15% solution. It may also be purchased in liquid form with elimination of the solution make-up equipment.

The effectiveness of sodium aluminate depends on the environmental conditions encountered. Excessive agitation should be avoided when mixing or handling since carbon dioxide precipitates alumina. Since it is an alkaline product, care should be taken to prevent contact with eyes, skin or clothing. Because of its rather high cost only limited addition in severe cases is sensible.

Fillers and Loading

Formed _in situ_ with the addition of $Ba(OH)_2$ to the alum-rosin

system, $BaSO_4$ has the potential of being a filler. It is good then

to consider fillers and loading in general and then consider the possi-

ble usage of barium sulfate as such a filler.

Loading or filling means the incorporation of inorganic materials

into the fibrous web to improve the quality of the paper by filling the

voids between the fibers and making a smoother more even sheet surface.

Fillers are used in amounts varying from 2 to 40% of sheet weight with

4 to 15% being a good average. They may be added dry to the beater or

be slurried and the metered into the beater or mixing chest. Calcium

carbonate and calcium silicate can both be prepared by _in situ_ methods

in the beater; thus, forming pigment directly in the stock (5).

Suitable pigments improve brightness and opacity, basis weight,

sheet density, softness, smoothness, finish, and ink receptivity and

printability. They also improve the appearance and absorbency of paper as

well as increasing the density. Less pitch trouble is encountered in pa-

per stocks containing appreciable amounts of filler.

Use of a high percentage of filler results in certain undesirable

effects, chief of which are a decrease in internal strength due to the

reduction of fiber-to-fiber bonding and a decrease in sizing, especially

above the 10 to 15% range. Bulk is decreased since pigment is heavier

than fiber consequently increases weight more than thickness. A high

concentration of filler on the felt side and a low content on the wire

side causes marked two-sidedness. Poor attachment of filler in the web

can cause dusting. Poor retention interferes with efficient machine

operation and good paper quality.

Willets (<u>42</u>) states that the perfect filler should have the following

characteristics:

1. It should have a reflectance of 100% in all wave lengths

   of light.

2. It should have a high refractive index.

3. It should be free of grit or extraneous matter and

   have a particle size distribution of close to 0.3μ,

   approximately half the wave length of visible light.

4. It should have a low specific gravity and be soft

   and nonabrasive.

5. It should be able to impart to paper a surface cap-

   able of taking any finish from the lowest matte to

   the highest gloss.

6. It should be chemically inert and insoluble.

7. It should be reasonable in price.

8. It should be completely retained.

High pigment retention is desirable from the standpoint of reducing

pigment loss, especially the expensive ones. With the use of an efficient

water system retentions as high as 85 - 95% are obtained with the average

around 60 to 70%. Many pigment properties affect retention; among them are solubility, specific gravity, particle shape and size and degree of dispersion. Other additives in the system do affect retention. Practical knowledge indicates that retention increases with increased sheet weight, increased stock refining, increased sizing, increased fiber length of stock, increased recirculation of white water and increased temperature. Retention decreases with increased machine speed, increased suction, increased dilution of stock, increased shake, increased size of wire mesh and higher pH values.

Casey (5) includes a list of theories which explain retention. Among them are filtration of particles at the interstices between fibers, mechanical attachment of pigment to imperfections in fiber wall surfaces, adsorption of pigment on the fiber surface, capillary attraction of the pigment in the pores of the fiber, diffusion of pigment into the lumens of the fibers and coflocculation of pigment with rosin precipitate or fiber debris. Haslam and Steele (43) found filler to be retained by filtration (a small amount), coflocculation (a large amount), and mechanical attachment (about 30%). Martin and Willets (13) emphasize colloidal factors involving alumina and electrostatic attraction. Hemstock and Swanson (44) believe the theories of stability of various colloids are directly applicable to filler retention. Johnson (45) concluded from his work that the electric charge of both fiber and pigment affect retention.

Opposing retention forces is the shearing stress of the water as it flows out of the forming mat.

Alum aids retention through simple flocculation. It acts to aggregate the finer pigments into larger particles which can be more readily filtered out in the wet sheet. Beyond flocculation, alum in its alumina form is adsorbed by the negative fibers, making positive sites which attract and hold negatively charged fillers. Alum alone is not as effective as alum and alkali as little alumina is formed. pH should be maintained between 5 and 6 for maximum retention.

Fillers should be furnished to the beater before alum is added in order to insure even distribution before flocculation is begun. Alum should be added to the system at a point of maximum dilution and sufficient time allowed for floc formation.

$BaSO_4$, M.W. 233.43

Specific investigation of $BaSO_4$ is now in order. If evaluation of its use as a filler proves discrediting, other uses must be considered.

$BaSO_4$ is available as the ground, natural mineral, barite, or as an artificially precipitated material, blanc fixe. The precipitated filler is obtained by reacting sulfuric acid with barium carbonate or barites or it is the by-product in the manufacture of hydrogen peroxide. Blanc fixe is occasionally produced in the beater by reacting barium chloride and sodium sulfate.

It is one of the heaviest white pigments, practically insoluble in water and not attacked by acid or alkali. $BaSO_4$ has a refractive index of 1.64 while cellulose's is 1.53, clay's is 1.56, and TiO_2's is 2.70.

The scattering coefficient of blanc fixe is no better than most clays. Brightness or reflectance at 457 mu is comparable to TiO_2 at about 95%. Particle size is 0.5 or about twice the optimum of 0.25. Particle shape is cylindrical or acicular. Abrasiveness is comparable to clay and slightly less than TiO_2. $BaSO_4$'s high specific gravity, 4.35, results in poor retention and two-sidedness. It has the lowest specific volume (0.22) of all fillers. Consequently, $BaSO_4$ is rarely used as a filler in North America and then only in specialty printing and art papers that are required to lay flat (46). None of its properties, including cost, indicate any appreciable use as a filler beyond quite limited and specialized application (47).

By far the largest use of purified blanc fixe is for coating photographic papers. Because of its properties, it gives good opacity, high brightness and an improved surface at a reasonable price. $BaSO_4$ is also used in x-ray photography for purposes of medical diagnosis. Its use as an adulterant or filler for rubber, paint, oil cloth and linoleum requires little or no purification. Oil-well drilling make use of its share of $BaSO_4$. Artificial ivory is made in part of blanc fixe.

$Ba(OH)_2$ $8H_2O$ M.W. 315.50

Barium hydroxide is a white or transparent crystalline substance which is moderately soluble in water (1 gram dissolves in 11.6 ml of water). It forms a strong alkaline aqueous solution considered moderately basic when
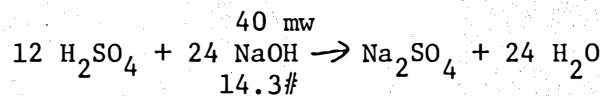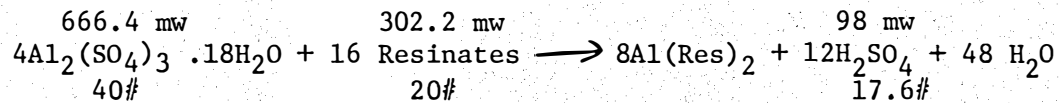
compared to sodium hydroxide. Care must be taken when handling this chemical for basic solutions are very caustic and the barium ions are poisonous.

Cost Analysis

In order for this application of $Ba(OH)_2$ to the white water system to be accepted if it does prove to be effective, the cost of such an application must be reasonable. To be reasonable it must be comparable to the current price structure for a given degree of sizing.

Calculations are made using a 1% rosin 2% alum make-up and is based on one ton of bone dry paper. The conventional rosin-alum process neutralized with sodium hydroxide would have the following cost:

$$\underset{40\#}{\underset{666.4 \text{ mw}}{4Al_2(SO_4)_3 \cdot 18H_2O}} + \underset{20\#}{\underset{302.2 \text{ mw}}{16 \text{ Resinates}}} \longrightarrow 8Al(Res)_2 + 12H_2SO_4 + \underset{17.6\#}{\underset{98 \text{ mw}}{48 H_2O}}$$

$$12 H_2SO_4 + \underset{14.3\#}{\underset{40 \text{ mw}}{24 \text{ NaOH}}} \longrightarrow Na_2SO_4 + 24 H_2O$$

Alum   40# X \$4.30/100# = \$1.72   Total Cost   \$5.01/ton of paper

Rosin 20# X \$13. /100# = \$2.60

NaOH14.3# X \$4.80/100# = ___.69

Substitution of sodium aluminate for part of the alum added would give these results. (0.5% of sodium aluminate and 1.0% of alum)

$$\underset{20\#}{\underset{666.4 \text{ mw}}{4Al_2(SO_4)_3 \cdot 18H_2O}} + \underset{10\#}{\underset{218.3 \text{ mw}}{3 Na_2Al_2O_4 \cdot 3H_2O}} + \underset{20\#}{\underset{302.2 \text{ mw}}{16 \text{ Resinates}}} \longrightarrow$$
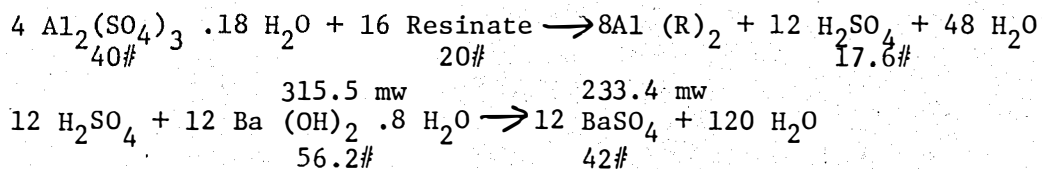
$$8 Al(R)_2 + 15H_2O + 3 Na_2SO_4$$
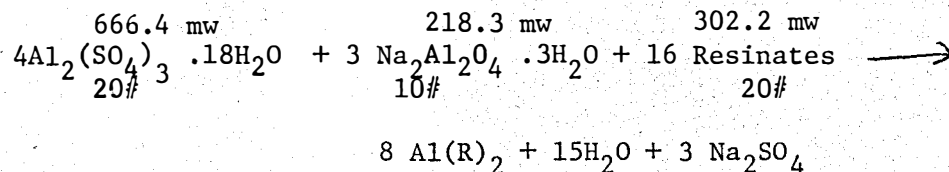
Alum 20# X \$4.39/100# = \$0.86

NaAluminate 10# X \$8.50/100# = \$.85 Total Cost \$4.31/ton of paper

Rosin 20# X \$13/100# = \$2.60

Addition of $Ba(OH)_2$ to the rosin-alum system would give the cost breakdown below if all the $BaSO_4$ could be utilized. For a given basis weight the filler retained would replace a certain amount of fiber thus reducing the overall cost of the finished paper.

$$4 \; Al_2(SO_4)_3 \cdot 18 \; H_2O + 16 \; \text{Resinate} \longrightarrow 8Al \; (R)_2 + 12 \; H_2SO_4 + 48 \; H_2O$$
$$\underset{40\#}{} \qquad \underset{20\#}{} \qquad \qquad \underset{17.6\#}{}$$
$$315.5 \; mw \qquad\qquad 233.4 \; mw$$
$$12 \; H_2SO_4 + 12 \; Ba \; (OH)_2 \cdot 8 \; H_2O \longrightarrow 12 \; BaSO_4 + 120 \; H_2O$$
$$\underset{56.2\#}{} \qquad\qquad \underset{42\#}{}$$

Alum 40# X \$4.30/100# = \$+1.72

Rosin 20# X \$13/100# = +2.60   Total Cost \$7.82/ton of paper

$Ba(OH)_2$ 56.2# X \$12/100# +6.75

$BaSO_4$ 42# X \$7.75/100# = -3.25

The cost does seem reasonable if 100% of the $BaSO_4$ is retained in the sheet and no further work needs to be done to separate it from the white water system for some other use. To assume 100% retention of $BaSO_4$ is a bit optimistic and therefore, further costs would be encountered in the separating process.

EXPERIMENTAL PROCEDURE

Schedule

Control sheets will be made first using beaten pulp only and these will be used for comparison with all other work. Secondly, sheets made with pulp and sizing materials will be made using recirculated white water for a check of strength and sizing decrease with continued recycling. Thirdly, $Ba(OH)_2$ will be added with pulp and sizing materials to demonstrate its effect on the recirculated system.

Furnish

The pulp used will be a blend of 50% bleached hardwood kraft and 50% bleached softwood kraft. No broke will be used. A Canadian Standard Freeness of 375 to 400 ml will be achieved. No filler, other than $BaSO_4$, will be used. Sizing materials consist of 1% Pexol and 2% alum based on the weight of fibers. $Ba(OH)_2$ will be added in varying amounts (0 to 5%) and will be added in different order with sizing materials.

Water

Deionized water will be used for the beater make-up. Deionized water will be used initially for sheet formation and then it will be recirculated with no fresh water addition.

Procedure

Pulp is to beaten in a Valley beater following the specifications outlined in T 200ts-61 with 460 grams of OD fiber used. This gives a consistency of about 2%. After a sample of pulp is removed, rosin will be added to the beater and allowed to mix.

Enough stuff will be placed in the proportioner for 3 sheets (6 - 8 grams OD fiber) and the alum will be added and mixed. Addition of alum and $Ba(OH)_2$ will be varied during that part of the experiment but all additions will be made in the proportioner. Sheet formation will be done with a Noble and Wood Handsheet unit capable of recirculating white water.

The press and dryer drum will be utilized to more closely approximate machine conditions. The dryer temperature should be maintained at 150° - 180°F to effect good sizing. Probably two passes of the sheet will be necessary. Once made and dried the sheets will be conditioned in the humidity room for 6 hours prior to testing.

Testing

While sheets are being made, a check of temperature, pH, total acidity, and sulfate ion concentration in white water will be made. Sulfate ion concentration is checked with the Betz sulfate ion test. Total acidity is determined by titration with 0.02 N NaOH using phenolthalene as an indicator.

Water hardness will be checked with an EDTA titration.

Filtered solids in a given weight of slurry will be dried in an oven at 105°C for determination of total solids. The dried solids will then be ashed to determine the amount of pigment material in the solids.

Conditioned sample sheets are to be tested for brightness, (T 452m-58), opacity (T 452m-60), sizing using the Hercules sizing test, tensile using the Instron tensile tester, basis weight, and ash (T 413ts-66).

Data

All data will be recorded in tabular form for further study and analysis. Any changes made in this tentative procedure will be described. Comments of particular interest will be noted.

EXECUTED EXPERIMENTAL PROCEDURE

Stock Preparation

Five hundred grams of oven-dry fiber were furnished to the Valley beater. This was an equal mixture of Q 90, a bleached softwood kraft, and Allied hardwood, a bleached hardwood kraft. The Q 90 had an A.D. moisture content of 7.3% while the Allied hardwood had a 6.5% content.

Once in the beater, enough deionized water (pH 7.2) was added to allow relatively unrestricted flow. After sufficient time had elapsed for adequate fiber dispersion, weights in the amount of 6000 grams were applied to the beater arm. One hour and twenty minutes of beating time were necessary to reduce the Canadian Standard Freeness from 735 ml to 395 ml. Slurry temperature increased from $21^{o}C$ to $24^{o}C$ during that time. A solids check showed the slurry to have a consistency of 1.9%.

Approximately 1600 grams of slurry (30 grams of O.D. fiber) were then removed from the beater for later experimental use. To the remaining stock (470 grams of O.D. fiber) 4.70 grams (1% based on the weight of O.D. fiber) of Pexol was added and allowed to mix with the weight removed from the beater arm. The pH of this mixture was 8.2. No other additions were made at this time.

Sheet Formation and Sampling

Following a thorough rinsing of the Noble and Wood handsheet maker

with deionized water, approximately 20 liters of it were placed in the
white water holding tank. This amount was sufficient for sampling with-
out endangering the supply necessary for sheet formation toward the
end of the sheet making schedule. No other water was added to the system.
Sulfuric acid (8.4 ml of concentrated acid) added to the water lowered the
pH from 7.2 to 5.1.

The sheet-making schedule was arranged as follows: Set 0, control
sheets with only stock being used; Set 1, stock with rosin present; Sets
2-27, stock with rosin present and alum (2% based on O.D. fiber) added in
the proportioner; Sets 28-30, stock with rosin present, alum and then
$Ba(OH)_2$ (5% based on O.D. fiber) mixed in proportioner; Sets 31-33, stock
with rosin present, $Ba(OH)_2$ and then alum added; Sets 34-35, stock with
rosin present, alum (1% based on O.D. fiber) and sodium aluminate (0.05%
based on O.D. fiber) mixed. In an effort to better illustrate the effects
of a 100% closed white water system on paper quality only every 5th set
was saved from Sets 2-27, i.e., Sets 2, 7, 12, 17, 22, 27. The discarded
sets were made in similar fashion to those that were saved.

For each set ten grams of oven-dried fiber (530 grams of slurry) were
placed in the proportioner and allowed to disperse in a total of 4 liters
of slurry. 10 grams of fiber would give 3-2.5 gram handsheets for testing
and a sample for a solids check. A 2.5 gram Noble and Wood handsheet is
equivalent to a 42# sheet 25 X 38-500.

Chemical additions to the proportioner were made according to the schedule and the stuff was mixed for 3-4 minutes prior to use. A pH check was made at this time. 2% alum based on 10 grams of O.D. fiber weighed 0.2 grams and 5% $Ba(OH)_2$ weighed 0.5 grams. 1% alum amounted to 0.1 gram while 0.1 ml of 68.5% sodium aluminate liquid gave the desired 0.05% or 0.0005 gram.

Using the small Noble and Wood measure (about one liter), a quantity of slurry was transferred to the sheet mold which had been previously filled to the appropriate mark with white water. After good mixing, a pH check was made and then the sheet was formed on the screen while the water returned to the white water tank. No external suction was applied during the formation of any sheet. Once drained, the sheet while still on the wire screen was pressed and then given two passes through the dryer. The sheet was peeled from the wire, identified and those so designated were saved. After a wash in an acid cleaning solution the screen was rinsed in deionized water and replaced in the sheet mold. The process was then repeated.

A sample of slurry was taken from the proportioner following formation of the third sheet and saved. The remaining slurry was drained on a wire screen with the water returning to the white water tank. The stock was discarded and the screen replaced in the sheet mold. A sample of the white water was saved after the set was made. No slurry sample was taken from Sets 29 or 32 and no white water samples were taken either. The entire

process was repeated with stock and chemicals being mixed in the proportioner with recirculated white water pumped from the white water tank.

White water temperature ranged upward from $25^{\circ}C$ to $27^{\circ}C$ during the sheet forming. Dryer temperature varied from $105^{\circ}C$ to $115^{\circ}C$. The white water remaining in the holding tank was under constant agitation to prevent settling. Otherwise, processing variables were unchanged.

Testing

Handsheets were conditioned for 12 hours at $72^{\circ}F$ ($20^{\circ}C$) and 52% relative humidity prior to testing. A standard size sample was cut from each sheet for a basis weight check and other samples were cut to size as prescribed by the several testing methods.

Non-destructive tests were run first on the handsheet samples. Brightness was tested according to Tappi Standard T 452 m 58 while opacity was tested following T 425 m 60. Basis weight of the conditioned samples was measured as a 3-sample average weight. A moisture content check was made.

The destructive tests included the tensile test using the Instron Tensile Tester and the procedure outlined in its manual. A full scale load of 20 kg was used. The sizing test was run on the Hercules Sizing Tester because of its simplicity and dependability. Procedure was carried out as described by the manufacturer. The number two ink used had a 0.99% acidity and an optical density of 0.43. Ash was run according to Tappi Standard T 413 ts 66.

Where applicable a check of both the wire side and the felt side of a sheet was made, i.e., sizing, brightness etc. The value recorded was an average of both values.

Tests for hardness, total acidity, and sulfate ion concentration were run on white water samples saved during sheet making. Water hardness of the deionized water was checked with an EDTA titration. Total acidity as determined by titration with 0.02 N NaOH and phenolthalene as an indicator, was tested on each white water sample. Also on each sample a Betz Sulfate Ion Test was done to determine quanitatively the sulfate ion concentration.

A total solids check was run using the slurry sample saved during sheet making. A 300 gram sample of slurry was filtered in a Buchner funnel and dried to constant weight at 103°C. After weighing, the samples were ashed at 995°C, desicated and weighed to determine pigment content.

RESULTS AND DISCUSSION

TABLE I

Summary of Results

GROUP	OPACITY/# SHEET WT.	BRIGHTNESS	ASH,%	TENSILE/# SHEET WT.	SIZING SEC.
1-C	2.01	65.4	0.21	0.232	0.35
2-R	1.93	67.2	0.27	0.229	0.55
3-R + A	2.24	65.7	0.21	0.220	223.69
4-R+A+B	2.30	66.0	2.66	0.217	123.49
5-R+B+A	2.34	66.7	4.44	0.213	102.29
6-A+NA+R	2.10	64.5	1.38	0.235	106.81

C = Control, R = Rosin alone, R+A = Rosin + Alum, R+A+B =
Rosin + Alum + $Ba(OH)_2$, R+B+A = Rosin + $Ba(OH)_2$ + Alum,
A+NA+R = Alum + Sodium Aluminate + Rosin.

Examination of the test results as summarized in the table above gives

substance to the theoretical formation of $BaSO_4$ in the 100% closed white

water system of a papermaking operation through the addition of $Ba(OH)_2$.

Ash, which serves as an indicator for the amount of pigment present in a

sample, shows a ten fold increase above the natural ash content of the

control group (1) when $Ba(OH)_2$ was added to the first grouping (4) and

a 20-fold increase in the second grouping (5). Opacity exhibits an ex-

pected overall improvement when $BaSO_4$ is present in the sample. Brightness,

likewise, shows improvement over the unfilled samples. Tensile decreases with the introduction of a filler into the web structure. Sizing in Groups 4 and 5 where $BaSO_4$ is present is markedly higher than the control group with no sizing, yet considerably below the average for Group 3, the rosin + alum group.

While the average results of the rosin and alum group (3) appear favorable in the summary table, a closer inspection of the results from which those averages came show some unfavorable trends developing. Graphs 1 and 2 of Sheet Samples portray the deterioration of the papermaking system as exhibited by the samples.

TABLE 2

Sheet Test Results

SET	BASIS WT. 25X38-500	OPACITY	OPACITY/# SHEET WT.	BRIGHTNESS	TENSILE Kg	TENSILE/# SHEET WT.	SIZING SEC.	ASH, %	pH @ PROPORTIONER CONSISTENCY	pH @ WIRE CONSISTENCY
0	41.09	92.4	2.01	65.4	9.40	0.23	0.35	0.21	6.0	5.8
1	49.10	94.9	1.93	67.2	11.26	0.23	0.55	0.27	6.8	5.7
2	47.25	96.1	2.03	65.5	11.06	0.23	198.98	0.16	4.3	5.1
7	48.76	95.3	1.95	67.4	10.83	0.22	231.18	0.26	4.3	4.9
12	46.70	94.3	2.01	67.2	10.73	0.23	221.63	0.20	4.4	4.7
17	45.38	94.7	2.09	66.4	9.20	0.21	201.78	0.21	4.5	4.6
22	37.61	96.2	2.46	64.4	8.76	0.23	170.21	0.21	4.5	4.7
27	40.63	93.0	2.29	64.1	8.23	0.20	118.38	0.23	4.5	4.7
28	40.57	94.1	2.31	66.3	8.80	0.22	117.75	2.06	4.8	4.7
29	42.96	94.5	2.20	66.4	10.33	0.24	134.60	2.53	5.1	4.8
30	38.58	94.2	2.40	65.3	7.23	0.19	110.12	3.39	5.8	4.8
31	39.83	94.5	2.37	66.4	7.90	0.20	98.33	4.39	5.8	4.9
32	41.41	96.2	2.35	66.8	8.76	0.21	101.81	4.77	6.2	5.2
33	43.31	96.9	2.30	66.9	9.80	0.23	106.73	4.16	6.2	5.5
34	41.16	95.9	2.33	64.3	9.46	0.23	95.55	1.59	5.6	5.7
35	52.52	97.7	1.86	64.6	12.73	0.34	118.07	1.17	5.6	5.8

Moisture content of conditioned sheet samples 5.61%

Opacity shows an increase during the rosin alum additions probably
due to the flocculation of fines and subsequent retention of them in
the sheet. Brightness exhibits an initial increase and then rapid de-
crease as recirculation continued. Sizing also showed improvement to a
maximum followed by a decrease. Tensile became moderately lower as the
acidity and sulfate concentration of the system increased. From Graph
#3 of the White Water Test Results total acidity and sulfate ion concen-
tration increase constantly during the rosin + alum additions, while pH
decreases rapidly to a minimum and then begins a gradual rise. The ash
content remained relatively steady, depicting the natural ash content of
the fiber.

These findings concur with those found in the W.M.U. Study, the
Lewis and Bowman Study and general mill experience. Recirculation of all
or a large part of the white water in a papermaking system results in a
general deterioration of paper quality unless something is done to re-
store good conditions.

Introduction of $Ba(OH)_2$ into the papermaking system yielded immediate
results and brought about at least partial recovery of the system. Be-
sides improving the deteriorated system, the precipitation of $BaSO_4$ and
its inclusion in the sheet gave extra benefits. Opacity showed an improve-
ment over the unfilled sheet, yet took an unexplainable dip when pigment
content was the highest. Possibly the method of comparison, dividing the
value obtained from the opacimeter by the sheet weight, was improper but

because of the wide variation improvement, a dip, and then continued improvement at a lesser rate. The rate of deterioration of sizing was halted by the $Ba(OH)_2$ addition. An increase followed and then a slight decrease set in but this was during the time when maximum filler was present in the sheet. Tensile increased initially after introduction of the $Ba(OH)_2$. Its graph then became an inversion of the ash content curve decreasing as the pigment content increased and visa versa. The pH curve on Graph #3 continued to rise, however, at a slightly faster rate. Both total acidity and sulfate ion concentration began an immediate decline with the introduction of $Ba(OH)_2$ and continued to fall with each addition. No doubt sheet improvements were the result of a much improved white water system brought about by the neutralization of excessive acidity and precipitation of the sulfate ions.

Stoicheiometrically, 0.50 gram $Ba(OH)_2$ should produce 0.37 gram of $BaSO_4$ when reacted in an excess of sulfate ions. This $BaSO_4$ was formed in a slurry containing 10 grams O.D. fiber so this would mean that with complete precipitation and good mixing filler content would be 3.70%. From Table #3, the Slurry Solids Content, the average ash content of those samples where $Ba(OH)_2$ was added was 3.89%. Subtracting the average natural ash content of 0.22% from the total ash content, 3.89%, gives 3.67% or the $BaSO_4$ content. When the experimental error in weighing and the carry-over of $BaSO_4$ to the next two handsheet sets is considered, it can be assumed

TABLE 3

SLURRY SOLIDS CONTENT

SAMPLE SET	FILTERED SOLIDS, gm	ASH, gm	ASH, %
0	0.5673	0.0012	0.21
1	0.8215	0.0023	0.25
2	0.7978	0.0016	0.20
7	0.8993	0.0017	0.19
12	0.8823	0.0024	0.27
17	0.8543	0.0013	0.15
22	0.7163	0.0023	0.32
27	0.7843	0.0018	0.23
28	0.7743	0.0257	3.32
30	0.7288	0.0284	3.90
31	0.7413	0.0334	4.51
33	0.7838	0.0302	3.85
34	0.7388	0.0065	0.88
35	0.9683	0.0082	0.85

(no samples taken for sets 29 or 32)

TABLE 4

WHITE WATER TEST RESULTS

SAMPLE	pH	TOTAL ACIDITY	SO_4ppm
Deionized H_2O	7.2	1 drop	4
pH corrected H_2O	5.1	0.4 ml	12
After set 2	5.6	0.04ml	28
After set 7	4.8	1.02ml	48
After set 12	4.3	2.6 ml	72
After set 17	4.5	3.1 ml	84
After set 22	4.6	3.7 ml	104
After set 27	4.7	4.2 ml	124
After set 28	4.7	3.8 ml	104
After set 29	4.8	3.7 ml	–
After set 30	4.9	2.9 ml	68
After set 31	5.0	2.4 ml	48
After set 32	5.2	2.2 ml	0
After set 33	5.8	1.8 ml	48
After set 34	5.9	1.5 ml	84
After set 35	5.9	1.3 ml	92

(Water hardness of deionized water 1.82 ppm (as $CaCO_3$)

that virtually 100% of the barium was percipitated. The range upward

of the barium sulfate content in these samples could be the result of

inadequate mixing in the proportioner or possibly some of the barium

did not precipitate until it reached the white water holding tank and

was subsequently returned to the proportioner.

Retention of $BaSO_4$ is one of the major problems preventing its

greater acceptance as a filler and test results here obtained support

this. An average of 3.48% ash was found in test samples containing

filler. Again, subtracting the natural ash, 0.21%, from the total puts

the $BaSO_4$ content at 3.27%. If it is assumed that 3.70% would repre-

snet 100% retention, then the actual average retention is 88.4%. The

range, however, is from 49.7% to 123.0%.

When the samples are divided into groups as in the Summary Table

according to chemicals added and order of addition, Group 5 has a de-

finite edge over Group 4. In Group 5 $Ba(OH)_2$ was added prior to the alum

addition while in Group 4 the addition was reversed. If the $Ba(OH)_2$ is

added first, $BaSO_4$ has a chance to precipitate and become mixed in the

slurry before the alum is introduced. The pigment may become attached

to the size precipitate and hence have a higher retention. This is in

accord with the writings of Casey. Granted the build-up of $BaSO_4$ from

earlier sets undoubtedly had an effect but it does seem feasible and the

reduction of ash in Set 33 supports this concept. Graph 4 gives a sum-

mary of ash content.

pH can play an important role in such things as retention, sizing and sheet strength. Retention of fines and fillers in an alumed system is supposed to be greatest in a pH range of 5 to 6 while sizing conditions are optimum in a range of 4.3 to 5.0. Sheet strength improves with increasing pH. Graph 5 depicts the changing pH's of slurry samples taken from the proportioner (consistency: 0.25%) and the sheet maker (consistency: 0.025%).

Not as yet mentioned is Group 3 on the Summary Table. Rosin was the only chemical added and there was a slight increase in the degree of sizing; probably induced by the acidified system. Opacity was slightly less than the control set and tensile was about the same. However, brightness and ash were quite high. This may be the result of the flocculation of fines and their retention in the sheet.

Also not as yet mentioned is Group 6, the sets containing rosin plus alum and sodium aluminate. There is also some carry-over of $BaSO_4$ from the previously made sets but the amount of it present was decreasing. Sizing made an improvement over the previous sets despite the presence of filler. Brightness increased with decreasing $BaSO_4$ loading. Opacity was about equal to the opacity value of the control group. Tensile showed improvement. Total acidity continued to decline but at a slower rate while sulfate ion concentration began to climb. pH of the white water leveled off, pH of the stock slurry also began to level off.

CONCLUSIONS

Addition of $Ba(OH)_2$ to a no purge white water system does seem to be an effective means of controlling total acidity and sulfate ion concentration while obtaining $BaSO_4$ in the process. Its introduction stopped the deterioration of the papermaking system and brought about its recovery.

Results demonstrate that there may well be an advantage in forming the $BaSO_4$ pigment prior to alum addition. Retention may well be increased. 100% recirculation of white water will affect retention further by returning the unretained filler to the slurry where it can be retained during subsequent formation.

The improvement of sheet properties with the presence of $BaSO_4$ helps to improve its acceptability. Better opacity, improved brightness and better printability all enhance its approval.

Further testing needs to be done as a follow-up to this feasibility study. Bench trials using various chemical combinations and quantities could produce the optimum conditions necessary to obtain maximum benefit from $Ba(OH)_2$ addition. A pilot trial simulating actual production conditions would produce results which could further demonstrate the applicability of such a process. Safety studies must be done to determine its acceptance from a health standpoint.

Public consciousness of and concern for strong conservation practices has made it necessary for industry to make the most of the raw materials it uses and to return them to nature in the best condition possible. This practice promotes investigation for new methods of maintaining raw materials in a useable state. $Ba(OH)_2$ addition is the result of one such investigation.

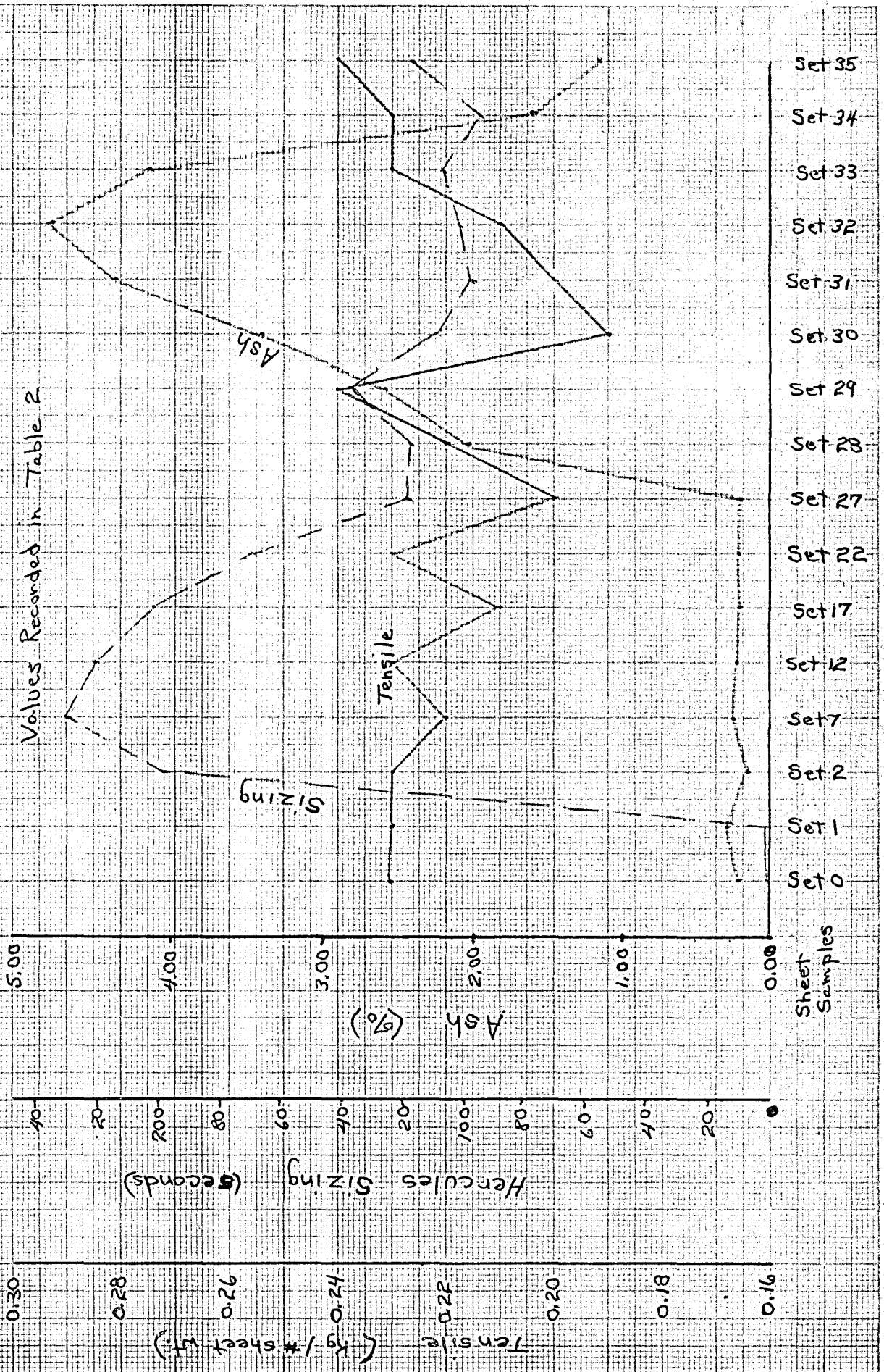#1 Graph of Sheet Samples

Values Recorded in Table 2
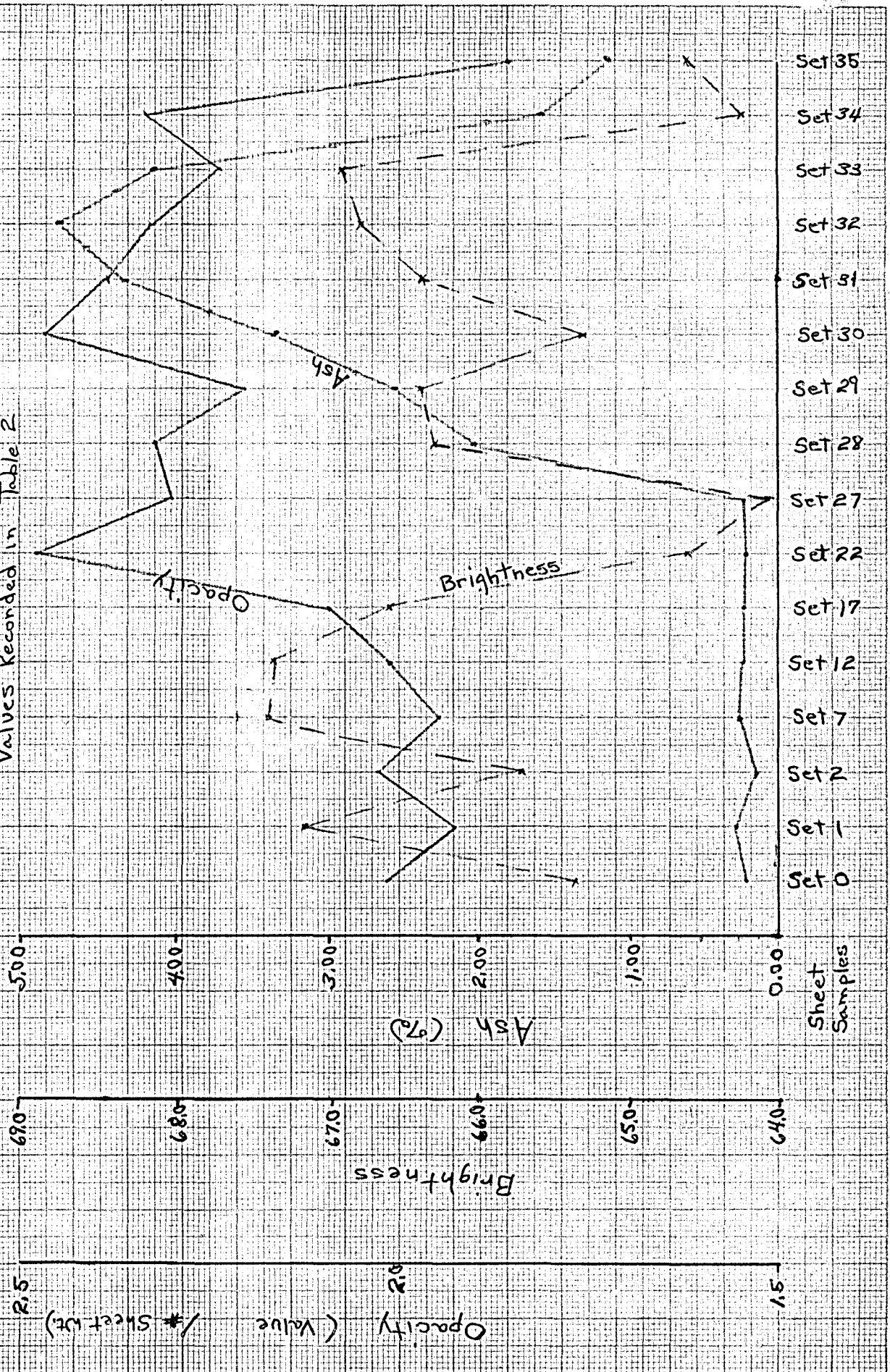
#2 Graph of Sheet Samples
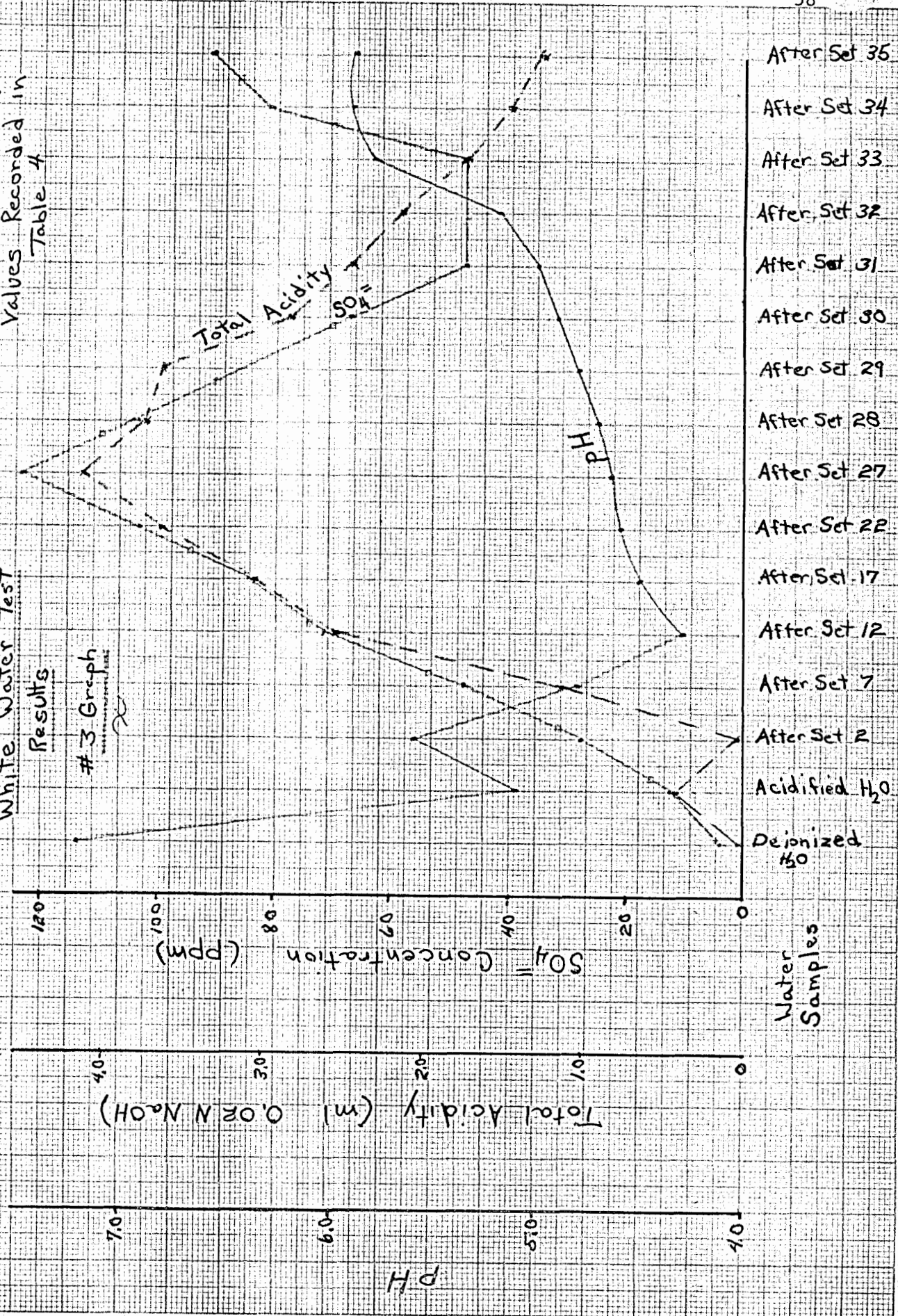
Values Recorded in Table 2

White Water Test
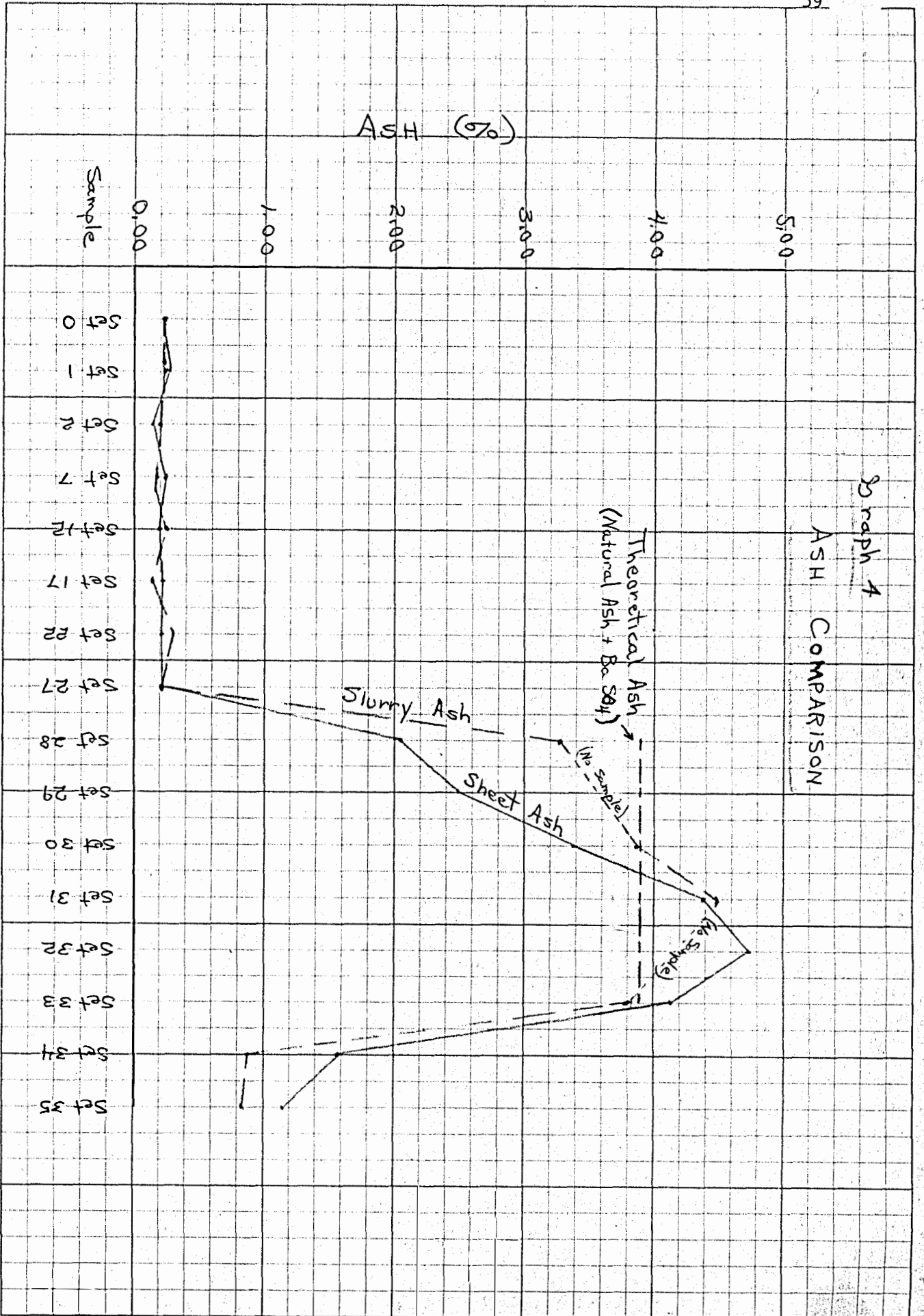Results

#3 Graph

Values Recorded in
Table 4

Total Acidity
SO₄⁼
pH

After Set 35
After Set 34
After Set 33
After Set 32
After Set 31
After Set 30
After Set 29
After Set 28
After Set 27
After Set 22
After Set 17
After Set 12
After Set 7
After Set 2
Acidified H₂O
Deionized H₂O

Water Samples

$SO_4^=$ Concentration (ppm)

Total Acidity (ml) 0.02 N NaOH)

pH

Graph 4
ASH COMPARISON

ASH (%)

Sample

0.00
1.00
2.00
3.00
4.00
5.00

Set 0
Set 1
Set 2
Set 7
Set 12
Set 17
Set 22
Set 27
Set 28
Set 29
Set 30
Set 31
Set 32
Set 33
Set 34
Set 35

Slurry Ash

Sheet Ash

Theoretical Ash
(Natural Ash + Ba SO₄)
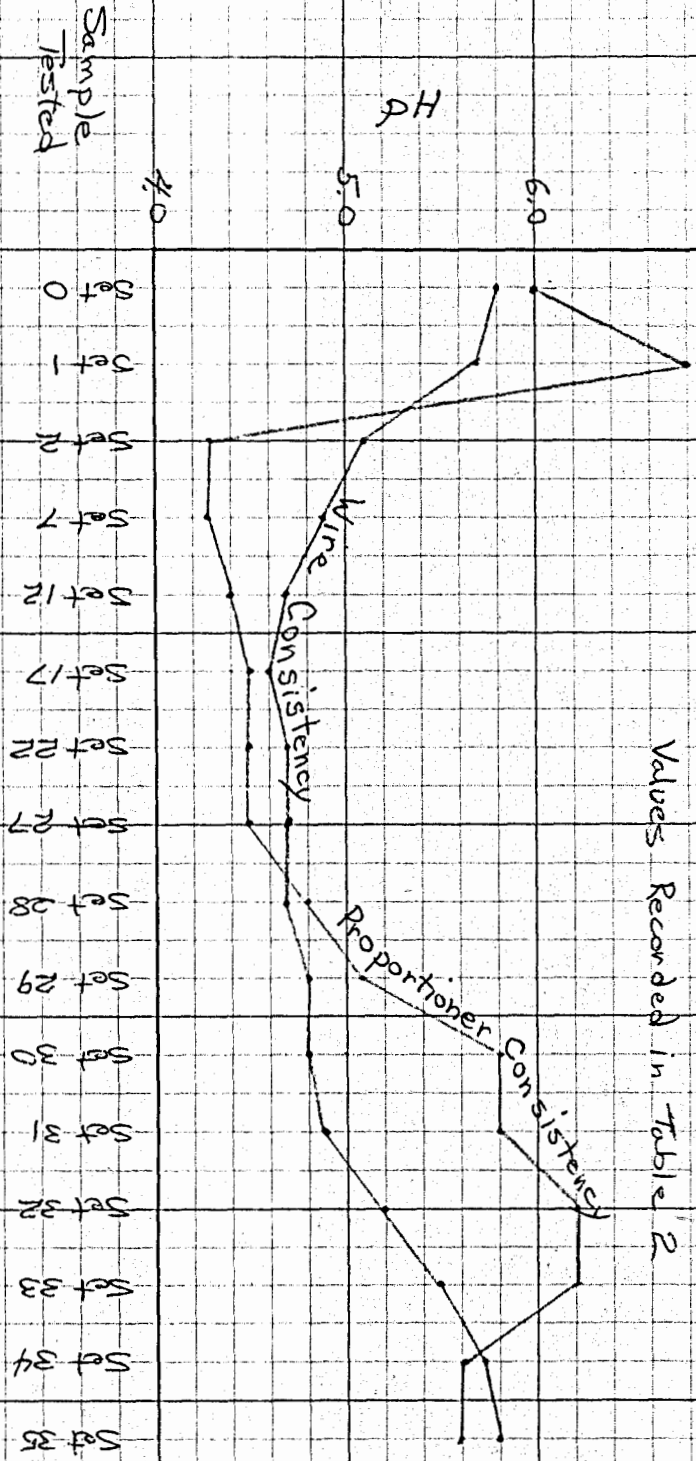
(No Sample)

(No Sample)

5 Squares
to the Inch

Graph 5

pH Comparison at Proportioner and Wire Consistencies

Values Recorded in Table 2

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