DECOLORIZATION OF CAUSTIC WASH LIQUORS FROM

CHLORINE-BLEACHED, SULFATE, WOOD PULP

by

Peter William Ruggieri, Jr.

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APPROVED: APPROVED:

_____   _____
Director of Graduate Studies   Head of Department

_____   _____
Dean of Engineering   Major Professor

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I. INTRODUCTION

Laws have been passed which control the amount of waste material

that can be released into the rivers and streams in this state,

thus restricting industrial stream pollution by chemical industries.

This investigation was concerned with the problem of color abatement

or removal for the pulp and paper industry.

The paper industry uses large quantities of water in its operations

of cooking, washing, and bleaching of the wood fibers and thus produce

large volumes of highly colored waste. Although the wastes have been

treated to reduce the biochemical oxygen demand, the treatments have

had little effect on the color. The color is chiefly caused by

resinous and lignous compounds that are extracted when the cooked and

bleached pulp is washed. The color is objectionable to the eye but does

not affect aquatic life. Although the objections are aesthetic in nature,

the stream is considered polluted by the public, and the pulp and paper

companies have taken steps to reduce the stream pollution through

research in waste treatment.

Various methods of treatment to remove color have been

investigated in the laboratory and the degree of removal compared and

evaluated by determining the light transmittancies of samples with a

spectrophotometer. The treatments were principally chemical in

nature. The use of both crystal aluminum sulfate and of papermakers

alum slurry to coagulate the colloidal particles in the caustic waste

has been suggested. Flocculating aids, synthetic, long chain polymers,

that carry a charge opposite to that of the colloidal particles, should

coalesce the floc. They may be used in very dilute solutions and may be economical. Laboratory tests should serve to evaluate their usefulness in treating this waste. Pilot plant tests of such size that their performance data may be extrapolated to full scale also would be desirable.

The purpose of this investigation was to study the practical application of various treatments of caustic wash liquor from chlorine-bleached, sulfate, wood pulp and to design and evaluate a pilot plant for testing further, the most promising possibility for its decolorization.

II. LITERATURE REVIEW

The literature review for this investigation consists of six parts: (1) pulp manufacturing processes, (2) stream pollution outlook, (3) chemistry of wood with respect to pulping and pulp purification, (4) color, (5) chemical treatment of waste to remove color, and (6) industrial waste treatment and disposal.

Pulp Manufacturing Processes

The following sections contain a general description of the major methods of pulp and paper manufacture in industry: (1) Mechanical process, (2) Semi-chemical process, (3) Sulfite process, (4) Soda process, and (5) Sulfate process. Also included are a discussion of the pulp washing and bleaching processes, waste streams from pulp bleaching, and of production activities at West Virginia Pulp and Paper Company at Covington, Virginia.

Mechanical Process. In the mechanical process the wood [23] log is transformed into the fibrous state without the aid of chemicals. This is done by holding the logs with pressure against the surface of a grinding stone. A stream of water continuously washes away the loosened fibers. The pulp is used to make the lower grade of paper products such as wrapping paper and magazines.

Semi-chemical Process. There are many steps in this process [98] but less chemical treatment is required than found in the three common chemical processes. A sodium sulfite solution is usually used. The

chief products made from this semi-chemical pulp are container board and coarse wrapping paper.

Sulfite Process. The sulfite process [34] is essentially an acid process since an acidic liquor is used to remove the undesirable constituents of the wood.

The sequence of operations in the sulfite process is as follows: "(1) Sulfur dioxide gas is produced by burning either sulfur or pyrites (FeS_2) in air under controlled conditions, (2) The resulting gas is freed from dust and cooled, (3) The gas is absorbed in a tower containing limestone, magnesium carbonate or milk lime. This is done with maximum efficiency, all waste gases being reabsorbed, and the resulting weak liquor is re-fortified with the waste sulfur dioxide evolved from the digesters. The acid liquors are then passed to storage tanks ready for use, (4) The acid and charge of wood are mixed in the digesters, (5) After digestion, the pressure is relieved, and the excess of sulfur dioxide gas evolved at this stage is recovered and reused, (6) The pulp and waste liquors are dropped into a chest below the digester. The liquor is removed through a perforated bottom, and (7) The pulp goes forward for washing, screening, and bleaching."

Soda Process. The soda process [34] is one of two types of alkaline processes for cooking wood pulp. The sulfate, or kraft process, is the other. The important feature of the alkaline process is the recovery and reuse of the digester liquor and washings after digestion. This serves the double purpose of economy and elimination of the trouble of disposing of an objectionable effluent. The function

of removal of the non-fibrous constituents of the wood is common with that of the sulfite process.

(34)
Any type of wood may be converted into pulp by an alkaline process, (spruce is better for sulfite process).

For the soda and sulfate processes, the woods processed and the types of paper for which the pulps are used differ considerably.

The essential difference between the two alkaline processes is (34) that in the soda process the wood is cooked with sodium hydroxide, the residual liquor being evaporated, and the residue burnt which leaves sodium carbonate. When lime is added to a solution of this, sodium hydroxide is regenerated, and this is used in a subsequent digestion. During this operation, some sodium compounds are lost (in washings, or dust from furnace), so only a part of the original alkali added is recovered. Therefore, it is necessary to add a little alkali to each batch so as to maintain the strength for the subsequent digestions, and sodium hydroxide or soda ash is used for this purpose. The latter is added before the lime, so that it is eventually converted into the former.

(74)
Sulfate Process. The sulfate , or kraft process, is the youngest of the three major methods for making chemical pulpwood and was first utilized in this country in 1910. In 1952, the capacity for making kraft pulp was increased to 9.5 million tons and represented 50 per cent of the total woodpulp capacity for all grades.

(74)
Raw materials for kraft pulp and paper mills consist of pulp wood (chiefly resinous), water, sodium sulfate, lime, sulfur, chlorine, hypochlorites, chlorine dioxide, peroxides, sodium hydroxide, starch,

rosin, wax, alum clay, talc, calcium and barium sulfates, titanium

dioxide, zinc sulfide, calcium carbonate, pigments, and dyes. The raw

materials of greatest significance in relation to waste effluents are

the pulp wood, water, and sodium sulfate.

Kraft pulp is made by cooking the debarked and chipped wood in

digesters under steam pressure in a solution known as kraft white

liquor. Sodium hydroxide and sodium sulfate are the essential

ingredients of the white liquor. The spent cooking liquor, dark brown

in color and known as black liquor, is separated from the cooked pulp

by washing, filtering, and pressing operations (74).

The dissolved wood substances and the spent cooking chemicals are

in the black liquor which is processed by evaporation and incineration

so as to recover the chemicals and to utilize the heating value of the

dissolved wood substance contained therein.

Sodium sulfate is added (74) during this recovery process to replace

the small proportion of chemicals lost in the various steps of the

process. After this addition and the incineration of the material, the

smelt is dissolved in water to form green liquor. The chemical

compounds in the green liquor are converted to the desired cooking

chemicals by the addition of lime which forms white liquor and a lime

mud composed chiefly of calcium carbonate. The white liquor is

returned to the cooking operation and the lime mud is calcined to form

calcium oxide which is re-used in converting green liquor to white

liquor.

The cooked pulp which is separated from the spent cooking liquor

is screened (75) and subjected to various refining operations, following

which it may be bleached. Then it is transported to the paper machine where the fibers are formed into products such as paperboard.

In order to produce one ton of kraft pulp (75) two tons of pulpwood are necessary. The pulping operation dissolves the non-fibrous portion of the wood, leaving behind the fiber. The non-fibrous portion of the coniferous type of wood used in kraft pulping amounts to 50 per cent. This non-fibrous portion is roughly 60 per cent lignin, 30 per cent carbohydrates, 7 per cent resins and fats, and the remainder is protein and other minor compounds. During the cooking operation, the reactions in the digester consist essentially of the hydrolysis of the lignin and carbohydrates, resulting in the formation of water soluble salts or an excess of alkali. Fats and resins are saponified and are dissolved or carried in suspensions in the black liquor. Some wood alcohol is formed from the hydrolysis of liquor and is released in the digester relief gases along with recoverable amounts of turpentine and small amounts of dimethyl sulfide, methyl mercaptan, and ketones. Sodium salts of formic, acetic, and lactic acid are formed by the oxidation of the carbohydrates. The black liquor contains in addition to the turpentine, recoverable amounts of the sodium salts of resin and fatty acids which separate upon the concentration and cooling of the black liquor. This material is called crude sulfate soap and after skimming from the black liquor, it is treated with acid to form tall oil.

In an effeciently operated kraft mill, the loss of the dissolved wood substance amounts to less than 57 per cent of the total dissolved wood substances, or about 90 pounds per ton of pulp produced. This loss is found in the kraft mill effluent (75).

Present day water usage is in the range of 20-30,000 gallons of
water per ton of unbleached kraft pulp [75].

The odors produced in the sulfate process [34] are particularly
objectionable. They arise from the organic sulfur compounds produced
by the action of the sulfide on the wood.

Washing. After cooking [34], the pulp is washed in diffusers,
(Large vertical cylindrical tanks of a volume about equal to the
digester). At the top is the inlet, below which is an umbrella or
cone-shaped spreading device which breaks the force of the fall of
the charge. Washing sprays are under the diffuser top. Across the
base are perforations which lead to an outlet to the recovery plant.
The pulp settles on the false bottom and is usually removed through
a hole in the side of the diffuser by high-pressure steam and water
jets from the opposite side of the diffuser. The diffusers are
usually placed in a circle around the digester, so any one may be
connected to at will by the swiveling discharge pipe from the digester.
The washed pulp falls into a common pit.

The washing operations are important and occur several times
during the process of making pulp. Besides the washing after cooking,
there is washing between bleaching stages which is an essential feature
of multi-stage bleaching processes. In the washing after bleaching,
the pulp is diluted by the addition of a considerable quantity of
water (pulp consistency of 1 to 2 per cent) and then concentrating it
again so that water content is reduced to 75 per cent.

Washing removes those substances which degrade the color and
strength of the paper on storage. Acids, or compounds which may

produce acids, subsequently are particularly detrimental to the performance of the paper.

Bleaching. The pulp must be purified to the desired quality. The purification and bleaching of pulp is the second basic step in pulp production. Bleaching (97) may be defined as the destruction or solubilizing of coloring matter to make possible removal of the color. Two principal reactions (24) take place during bleaching: solubilization and removal of color, and changing the colored matter to a colorless form.

Bleaching (106) has developed through the years from batch operations to the present multi-stage operations which consist of chlorination, alkaline extraction, hypochlorite treatment, and in many mills chlorine dioxide treatment. Each stage is followed by a water wash to remove the chemicals used and formed in the previous stage.

The use of chlorine as a delignifying agent is principally a purification process rather than a true bleaching process. Chlorine (96) acts rapidly on lignin chiefly through substitution with the resulting formation of hydrochloric acid. Only a small part of the resulting chlorinated products is water soluble (96) so that the washing stage following the chlorination removes the hydrochloric acid formed and the soluble matter, but still leaves a colored pulp.

The colored chlorinated compounds are soluble in alkaline solutions and the extraction (26) of the chlorinated pulp is carried out with a weak caustic sodium hydroxide solution to remove the chlorinated lignins, natural dyestuffs, and water insoluble organic acids. The chief materials (28) removed by alkali extraction are the chlorinated lignins

of high molecular weight. The effluent from the caustic extraction stage is very dark, appearing almost black in color. This effluent is considered waste and it is this stream that is the subject of this investigation.

The chlorinated pulp (28) that has been extracted with weak caustic still has a dark color due to the presence of residual chlorinated lignin and other colored substances. The function of the hypochlorite treatment is to remove the colored residues in the pulp by oxidation. The hypochlorite stage, which is usually the final stage in the bleaching, may actually consist of two stages. In this event, the first stage is a strong hypochlorite bleach for a short period of time, followed by a weak treatment for a longer period.

In some pulp mills the pulp is given a final treatment with acid to impart special properties to the pulp. Also, some mills wash the pulp with a reducing agent to remove any excess active chlorine.

Recently there has been considerable interest in the use of chlorine dioxide as a commercial bleaching agent. At present, due to its high cost, it is used primarily as the final stage in multi-stage bleaching when it is desirable to produce a sulfate pulp of very high brightness.

Waste Streams from Pulp Bleaching. Two dissimilar wastes are produced: the acid waste from the chlorine and hypochlorite stages which contain the hydrochloric acid formed by chlorination, the excess bleaching agent and water soluble lignin compounds; and the alkaline wash, or caustic extraction waste, which separates the two chlorine additions and is very highly colored. If these waste streams are

mixed, they react to produce a waste (29) substantially neutral and with

a volume of from 30,000 to 60,000 gallons per ton of bleached pulp.

There are about 1,500,000 gallons of the caustic extractions waste per

day.

West Virginia Pulp and Paper Co. Operations at Covington, Virginia.

Operations at Covington are those of a completely integrated pulp and

paper mill (71). The processes involved are: wood handling and storage,

log de-barking, chipping, chemical digestion of chips, pulp washing and

screening, evaporation, and recovery of spent chemicals (black liquor),

mechanical heating of pulp, chemical conditioning and proportioning of

pulps, and papermaking. Six paper machines and three board machines,

with a rated daily capacity of 700 tons, produce board for corrugated

boxes. Other processes produce these by-products and chemicals:

activated carbon, tall oil, caustic soda, and calcium hypochlorite.

Seven waste streams total about 25,000,000 gallons per day.

Biological oxygen demand reductions are similar in activated sludge

pilot plants treating bleached and unbleached wastes. However,

unbleached kraft wastes lose over one-half their color while the

bleaching wastes go through the activated sludge processes almost

unchanged.

Stream Pollution Outlook

One of the most serious problems facing industry today is the

disposal of liquid wastes from the many manufacturing and processing

plants. The problem of water pollution is not a new one but its

importance has been greatly magnified by the huge growth of industry and by population increases and movements. The problem is even worse away from the ocean and where streams are small. Many people do not look beyond the surface of a river before pronouncing it grossly polluted, so practically all objections to color are aesthetic in nature and this makes the problem difficult [78]. Pressure has been brought against industry in an attempt to force a solution to problems that have accumulated in some cases over a long period of time.

What Constitutes Pollution. A substance is a pollutant [2] if it reduces the oxygen content of the receiving water, adds toxic ingredients, tends to cause obnoxious accumulation of decomposing materials, causes floating scums or otherwise makes the water unpleasant to eye or nose, renders the water unsafe for human or animal consumption without expensive treatment, renders the stream incapable of supporting fish life, or in any way renders the stream unsuitable for any of its normal uses.

Aquatic Biology. Like all living things [78], fish need oxygen but they live in an atmosphere where oxygen is measured in almost infinitesimally small quantities. Oxygen is very slightly soluble in water; at 20 $^{\circ}$C only about 75 pounds of it is dissolved in 1,000,000 gallons of water. When the amount of oxygen dissolved in the water is reduced much below 40 per cent of this saturation level [69] by the oxidation of waste material, fish life is endangered. Warm water fish are tolerant of much lower oxygen concentrations [77] than commonly supposed.

The turbidity [63] of a stream has no direct effect upon fish, in
fact, many of the best fishing streams in the world are turbid.
However, turbidy by cutting off some sunlight does reduce the amount
of plant life in a stream.

Biochemical Oxygen Demand. The biochemical oxygen demand is the
amount of oxygen [32] required to oxidize biologically the organic matter
in a waste over a stated period time. It is actually a measure of the
demand of the organic waste on the oxygen resources of the stream.
Chemical oxygen demand, on the other hand, is a measure of the demand of
chemicals in the waste on the available oxygen. The complete depletion of
dissolved oxygen [70] results in anaerobic decomposition, and in by-products
which may have noxious odors.

Reducing agents such as hydrogen sulfide, sulfur dioxide, soluble
sulfite salts, sulfoxylates, and ferrous iron salts resemble organic
pollutants [36] in that they consume oxygen from the stream and so may
cause anaerobic or septic conditions. The standard biochemical oxygen
demand test includes both types of reaction. Since the inorganic
reducing chemicals react rapidly with the oxygen, its loss can be
designated as "immediate oxygen demand" (IOD).

The major constituents of the coffee-colored kraft effluent which
cause pollution and exert a biochemical oxygen demand are the organic
materials composed of wood sugar, hemi-cellulose, and cellulose
degradation products. Lignins and tannins exert little or no
biochemical oxygen demand and they are the chief source of color.
Kraft mill effluents exhibit no toxic or inhibitory quantities.

The Jackson River. The Covington, Virginia, mill of the West
Virginia Pulp and Paper Company is located on the Jackson River, a
highly fluctuating mountain stream. It is the headwaters of the
James River and eventually empties into the Atlantic Ocean [83]. At
certain times of the year the Jackson River reaches a low flow of
40,000,000 gallons per day which approaches the total fresh water
usage of the mill. Due to the low flow and the constantly increasing
mill production, a means had to be found to reduce pollution of the
stream. An activated sludge waste treatment plant was developed and
installed. This plant is discussed in greater detail in another
section of this literature review.

Reduction of Industrial Pollution. "The most effective measure [75]
in the abatement of stream pollution is the prevention of discharge
of pollutants rather than their treatment."

The industry has spent huge sums for savealls, improved chemical
recovery and water reuse systems. This is in addition to the millions
spent for the construction and operation of waste treatment facilities.

Process Equipment Changes. Waste problems [54] can frequently be
solved by radically changing the process. In some cases the cost of
waste treatment over a period of time would justify process changes
that would prevent or reduce the amount of waste. The amount of waste
can usually be reduced at the source; for instance, surface condensers
can be used in place of steam or water jet condensers.

The use of multi-stage, vacuum washers for draining and washing
pulp prevents cooking liquor losses to the sewer [76]. This type of
washing system operates as a closed system with a wash water entering

the system and flowing counter-current to the pulp flow. No wash water is discharged and the concentration of dissolved matter increases to the point where it is economical to evaporate it for the recovery of the spent cooking chemicals.

Another type of equipment [76] that has reduced sewer losses is the foam trap which prevents foam from spilling over and allowing the entrained liquor to find its way to the sewer.

An improvement in the multiple body evaporator has resulted in the practical elimination [76] of black liquor carryover due to foaming and entrainment during the evaporation of black liquor.

"Save-alls" clarify white water and recover fibers for reuse and are located primarily on the paper machine.

Waste Treatment. Industry has had to install expensive water and waste treatment plants in order to fight pollution [2]. The activated sludge process appeared to offer the best method of reducing the oxygen demand of pulp and paper effluents [83]. However, no economical process has yet been found for removing a satisfactory amount of color from the waste streams from the paper mills.

Segregation of Water Streams. The segregation of uncontaminated water from contaminated water is often the simplest and most effective way [81] of reducing the magnitude of a water pollution problem. The size of the treatment facilities may then be greatly reduced.

Water Conservation. With the accelerating growth of industry, industrial wastes are increasing, as is the need for greater supplies of a vital commodity, clean water.

"Water conservation practice has a definite effect upon, and in association with, effluent quality improvement (76). Reuse of water is an important aspect of water conservation, but introduces problems, especially those dealing with the continual build-up of some of its constituents."

"By proper education and policing policies (81), the amount of process water can be greatly reduced." In some cases waste process water which is only slightly contaminated can be reused. Also, after much money has been spent in treating waste water, it is a pity to discharge it all into a stream.

Paper mills practicing strict water conservation may reduce fiber losses significantly, resulting in less load on the stream or treatment facility. Continuing research can probably solve many of the remaining problems.

Public Reaction. Just as people have begun to take care of the wastes from cities (54), industry has had to begin the job of cleaning up its wastes.

An attempt to estimate how much color producing material (31) a paper mill could release into a river without producing an adverse public reaction must be based upon an assumption of how much color in the river would "get by" the public. "The layman often judges the condition of a water sample by its color (63) but color in itself is not necessarily harmful."

Water is supposed to be returned to a stream in the same volume (2) and condition as when it was removed.

(3)
It is becoming common practice   to design the waste treatment
facilities of a plant and have these approved by the governing
authorities before plant construction is begun.

National Council for Stream Improvement. The National Council
for Stream Improvement is a non-profit research and service corporation
organized by the pulp, paper, and paperboard industry for the purpose
of developing solutions to the industry's waste disposal and utilization
problems. The paper industry has taken the initiative in fighting the
(77)
stream pollution problem that is affecting all industries   .

Chemistry of Wood with Respect

to Pulping and Pulp Purification

The reasons for and sources of color in the waste stream include
a study of the chemistry of wood with respect to pulping and pulp
purification. The following sections contain the results of this phase
of the literature and is divided chiefly into (1) Composition of Wood
and (2) Bleaching of Pulp.

Composition of Wood. Wood [93] is a complex material that is
produced in the living tree by synthesis and oxidation-reduction
reactions from carbon dioxide and water. A number of very complex
chemical substances are formed by these reactions which complement
one another and form the living tree. The physical and chemical
methods of the pulping and purification processes remove the nonfibrous
portion of these substances and leave a fibrous pulp which is purified
to the desired degree depending upon its intended use. Wood [21] contains
five principal materials; cellulose, hemicellulose, lignin, mineral
matter and extractives. Cellulose [109] and hemicellulose are called
holocellulose while the mineral matter and extractives may be considered
extraneous materials.

Chemistry of the Holocellulose Fraction. The holocellulose fraction
consists of a complex mixture of long-chain molecules [45] which are
classified into three chemicals groups: the polyuronides, the cellusans,
and cellulose. The polyuronides, which contain one or more uronic
acid groups in addition to many hexose or pentose, are readily attached
by aqueous alkali and pass into solution as sodium salts due to the
presence of the carboxylic acid group. The cellusans are carbohydrates

closely associated with cellulose and believed to be free of uronic
acid groups. Cellulose (94) is the fibrous portion of wood and which
is the object of the pulping process. It forms the principal
constituent of nearly all plant cells. The name cellulose is often
used, however, to denote the fibrous product obtained in pulping
processes. This is not pure cellulose but contains a mixture of
polyanhydroglucoses. While glucose units are the primary building
unit in cellulose, it has been shown that cellulose (101) from coniferous
woods contains appreciable amounts of mannose units and small amounts
of xylose units.

Chemistry of Lignin. (19)

Lignin is one of the major substances in
wood, but relatively little is known of the fundamental chemical and
physical properties of the compound. It is a complex, non-cellulosic,
non-carbohydrate material that cements the fibers together in wood and
which is dissolved along with the xylans in the papermaking process.
It is dissolved away from the cellulose chiefly by the action of sodium
hydroxide. Lignin is a high molecular weight polymer whose exact
molecular weight is unknown, but is considered to be a multiple of 840.
It may constitute as much as 30 per cent of the wood, where the breakdown
for coniferous wood is approximately 63.5 per cent carbon, 6.0 per cent
hydrogen, 15 per cent methoxyl, and the remainder miscellaneous
substances. Some aromatic rings and phenolic groups are apparently
present. The lignin bond of the wood is released by the action of
high pressure steam which activates the lignin so it can be used as a
plastic binder. It may be used as a filler and extender in the

compounding of plastics of the phenolformaldehyde type, and as a raw material for some organic products.

A great amount of work has been carried out in studying the degradation products of lignin. As a result of this work, Brams[10] has shown a structural formula which may be accurate.

In the sulfate pulping process[28], sulfur enters the lignin molecule and forms alkali-soluble thiolignin. Under the relatively mild conditions used in commercial bleaching processes, lignin is converted into water or alkali-soluble products. Several of the reactions of lignin are discussed in the following paragraphs.

<u>Halogenation of Lignin.</u> The reaction of chlorine[11] with lignin is the oldest of the reactions of halogens with lignin and the most important technically because of its use in the bleaching of pulp. A lignin from a commercial kraft liquor chlorinated in a water suspension for 12 hours gave a chlorolignin with 18.6 per cent chlorine. In an attempt[12] to find a use for spent sulfite liquor from a coniferous wood, a liquor of 25 Be' was treated by passing chlorine into it. The liquor consumed 35-40 per cent of its weight of chlorine, and formed hydrochloric acid to such an extent that a 20 per cent acid was obtained which caused the chlorinated ligno-sulfonic acid to separate as an orange-yellow powder.

<u>The Hydrolysis of Lignin.</u> In the soda and sulfate pulping process, lignin[14] is dissolved in the alkaline solution from which it can be obtained in a solid form by acidification. The lignin from a soda cook is called alkali lignin, and from a sulfate cook is called thiolignin. In the sulfate process the material[15] precipitated on

acidification is actually a mixture of alkali lignin and thiolignin.

The chemistry of the process is discussed in the next section and only

hydrolysis of separated lignin will be discussed here.

Treatment of [16] hydrochloric acid spruce lignin with sodium sulfide

gave a clear reddish brown solution. On acidification of the solution,

a light grayish brown thiolignin was precipitated. Acid and couxam

lignins [15] were completely dissolved when subjected to an alkaline

hydrolysis with sodium hydroxide. The lignin was almost quantitatively

recovered from the dark red-brown solution on acidification with

carbon dioxide or mineral acid.

Sulfonation of Lignin. The sulfonation of lignin [13] is technically

one of the most important lignin reactions because it is the basis of

the production of sulfite cellulose. Concentrated and fuming sulfuric

acids completely destroy lignin by splitting off water and causing

carbonization.

Lignosulfonic Acids. These compounds [102] have been reviewed by

Wise. When wood is heated with a solution of sulfurous acid and acid

sulfites, the lignin goes into solution. The solution containing the

lignin, for instance the sulfite waste liquor from pulp mills, has been

the subject of numerous investigations.

The chemistry of the various reactions that take place, whereby the

lignin is rendered soluble in the sulfite cooking liquor, is rather

obscure. Lindsey and Tollens were the first to demonstrate that the

lignin in sulfite waste liquor was present in the form of a calcium salt

of a sulfonic acid (previously suggested by Pedersen). Streeb, working

in Tollen's laboratory, found that the lignosulfonic acids could be

desulfonated by treatment with alkali. Lignosulfonic acids are mixtures (confirmed by Melander et al). Melander precipitated the lignosulfonic acids from sulfite waste liquor with sodium chloride and found that only a portion of the total lignin derivations were thus precipitated such as alpha-ligno-sulfonic acid; however, beta-ligno-sulfonic acid was not precipitated.

This alpha-lignin-sulfonic acid apparently differed materially from the alpha-lignin-sulfonic acid of Klason who used calcium chloride in place of sodium chloride because the excess precipitant could be removed with alcohol.

Of the total ligno-sulfonic acids in the sulfite waste liquor, approximately two-thirds was alpha-acid and one-third beta-acid, which according to Klason, contains an acrylic acid group.

Lignin, according to Klason, combines with four molecules of sulfur dioxide, only two of which are present in the form of the sulfonic acid.

The rate of dissolution of the lignin is directly related to the pH of the cooking liquor. Lignin does not behave like a true unsaturated compound.

(17)

Lignosulfonic acids of a low molecular weight have a relatively high sulfur content. Flourescence is caused by solid lignosulfonic acid in unbleached pulp. Isolated lignosulfonic acid also shows a strong deep violet flourescence.

(103)

Wood Resins. The non-volatile portion of the ether extract from wood contains the resin and fatty acids, fats, phytosterols, waxes, and resins when they are present. They are soluble in

alcohol or alcohol-benzene mixtures and in petroleum ether to a lesser extent.

Resins in wood [22] are objectionable in papermaking because they form pitchy deposits on the paper machine, and tend to cause discoloration of paper on aging. In the sulfate process [22] most of the resin and fatty acids are recovered as tall oil.

Resin acids [103] (oxidation products of the diterpenes) are monobasic and have the empirical formula $C_{20}H_{30}O_2$. They are optically active and give addition compounds similar to the terpenes. Abietic acid and d-Pimaric acid are the best known. Both have two double bonds but some uncertainty exists concerning their location in the molecules. Resins find extensive use in the paper, soap, paint, and varnish industries. The resin acids possess a multitude of melting points [103] : d-Pimaric acid (211, 211-212, 213, 218-219) ^{0}C, l-Pimaric acid (148-150, 150, 150-152) ^{0}C, and l-Abietic acid (156-160, 172-173) ^{0}C.

Tannins. Tannins [22] are soluble in water and usually removed in the pulping liquor. They are complex polyhydric phenols, which precipitate gelatin and alkaloids from solution, are astringent, and give color reactions with iron salts. Tannins are easily oxidized in alkaline solutions. They range in color from light straw to a dark reddish-brown.

Coloring Matters of Wood. All woods [22] contain a small percentage of organic coloring matter which is partially removed in pulping, however, most of this coloring matter is removed when the pulp is bleached. Many of the coloring matters are crystalline substances of known structure, but the constitution of others is largely unknown.

Bleaching of Pulp. The principal [24] colored matter in pulp is
lignin, although other coloring matter may be present. The principal
bleaching and purifying agents used for bleaching pulp are chlorine
and hypochlorite. In the following paragraphs is discussed the
chemistry involved in the use of each of these bleaching agents.

Chlorination. Under suitable conditions [99], chlorine is
capable of reacting with organic compounds in three ways; substitution,
addition, or oxidation. Results [99] indicate that the main reaction
involved in the chlorination of pulp is substitution, and that
oxidation occurs as a side reaction. The thio-lignin residues in
kraft pulp seem to have hydrogen atoms in the phenolic nucleus
capable of replacement by chlorine and after the double bonds in the
molecule are saturated with chlorine, the excess chlorine enters the
lignin molecule, ortho to a methoxyl group. This results in a
simultaneous cleavage of the methoxyl group. The chlorination of
lignin increases the solubility of the molecule in an alkaline solution
but not a great extent the solubility in acidic solutions in water.
The accepted practices in the bleaching of sulfate pulp is to partially
chlorinate the lignin, and remove the chlorolignin by dissolving it in
alkali. Some of the chlorinated residues in sulfate pulp are insoluble
in dilute alkali and are removed by hypochlorite treatment.

Hypochlorite Treatment. Hypochlorite bleaching [25] is mainly an
oxidation process which decolorizes and solubilizes the lignin,
coloring matter, and other impurities in the pulp fibers. Lignin is
subject to both oxidation and chlorination, either of which can occur
in hypochlorite treatment, depending upon the pH. At the high pH valves

normally used in hypochlorite bleaching, the reaction is considered to
be primarily oxidation. Sulfate pulp (26) can not be satisfactorily
bleached with single state hypochlorite treatment.

COLOR

In the following sections will be included a discussion of color
and how it affects this investigation. The topics include theory of
light, factors of structure affecting removal of color, source of color
in pulp and effluents, measurement of color, transmittance and
absorbance of light, and methods of removing color.

Theory of Light. The visible spectrum of radiant energy (18)
when arranged according to wavelength produces to the eye, a series
of color sensations which, as observed in the rainbow or spectroscope,
shade through violet, indigo, blue, green, yellow, orange, and red.

White light (80) (actually a composition of all colors) contains
radiant energy in the form of photons which, although they travel
at the speed of light, may possess various wave lengths or frequency
waves. When radiant waves strike a liquid such as dye water they
are either unaffected by the liquid (liquid appears transparent) or
are altered by the dye waste (liquid appears colored). The chemical
structure of the dye compound which absorbs certain wave lengths is
the determining factor in the final color of the solution. Most
modern theories agree that there are at least two important structural
groups that must be present in a compound in order to develop visible
color. These are discussed in the following paragraphs.

One of the types of groups that contribute to the color is an unsaturated group such as (-N = O), (C = C), (- N = N -_, (C - O), or (C - N -). This is called a chromophore group.

The other compound affecting color is a saturated, salt-forming group[80] such as (- OH), (-N ^H_H), (-N ^H_R), (-N ^R_R) and is called an auxochrome. The oscillation of electrons from the chromophores to the auxochromes is currently believed to be the direct cause of color. The more powerful the auxochrome group in a given compound, the more intense will be the resulting color. "The important fact to remember about auxochromes is that any reduction in their ability to contribute oscillating electrons to the compound will reduce the length of the radiant wave which the compound exhibits at maximum transmission." This means that the resulting color will usually consist of shorter wave lengths and will be less objectionable when discharged to the river.

Intrinsic Factors of Structure Affecting Removal of Color. The intrinsic factors affecting color removal are: "(1) longer chain length of colored compound reduces surface tension and are easily coagulated, (2) concentration of solute in surface film also alters surface tension, (3) number and strength of individual electrical charges on the surface of colored compounds, (4) amphoteric nature of the colored matter, (5) total electric charge of the colored matter (solute), greater charge indicates increased solubility, (6) solubility of colored matter (solute), this is usually a function of the length of the carbon chain, i. e. longer chains contain more non-polar groups rendering it less soluble in water. Temperature also affects the solubility, (7)

the tendency of the colored matter to form ionic micelles, (8) the

isoelectric point of the solute, and (9) the pH of foreign ions,

radicals, or colloids in the medium may affect the changes on the

colloidal micelle or interfere with chemical or biological treatment

of the colored compound." These factors illustrate the complexity of the

problem of the color reduction [79].

Source of Color in Pulp. Freshly made sulfate pulp [26] has a

light-brown, grayish color, but on contact with air is oxidized to

a dark brown color which is difficult to remove. The coloring matter

acts as an indicator since the pulp becomes lighter in color in acid

solution and darker in alkaline solution.

The color [105] of kraft pulp was at one time attributed to the

fact that brown dyes were obtained by roasting organic material in

the presence of sodium sulfide. It was found that coloring materials

extractable from the kraft pulp were lignin degradation products formed

in cooking.

The bleaching of pulp is carried out to remove these coloring

matters. Only a small part of the reaction products of lignin and

chlorine [97] are soluble in water, leaving a dark colored pulp. The

effluent from the chlorination stage is a light, clear brown. The

chlorinated colored compounds are soluble in alkaline solution, and

are removed by extraction [27] with weak caustic solution. The chief

materials [28] removed by alkali extraction are chlorinated lignins of

high molecular weight, natural dyestuffs [27] and water-insoluble organic

acids. The effluent from the caustic extraction is very dark, almost

black, in color. This stream is the subject of this investigation.

The pulp from the alkali extraction still has some brown color, most of which is removed by hypochlorite treatment which oxidizes the coloring matters.

Color in Pulp Mill Effluents. The color bodies in kraft effluents are mainly lignin compounds which are formed through the dissolving action of the cooking and bleaching chemicals used in the manufacturing process. Approximately 95 per cent of these dissolved lignin compounds are recovered and burned in the chemical recovery system of the pulping process. The remainder are found in the mill effluents which are discharged. Kraft effluent color bodies increase in intensity with increasing pH. They become more insoluble at pH values in the acid range.

The nature of the receiving stream[78] has an effect on the apparent color of the effluent, inasmuch as water in deep pools appears much darker than the same water flowing over shoals. This is true not only on account of the "white water" produced by the rapids, but also because in deep pools, mere depth of water is available to absorb the incident light.

There is no relationship[43] between the color of a waste solution and the oxygen demand or the dissolved matter present. Also, there is no relation between the pH and the amount of color present.

Measurement of Color. Rudolfs & Hanlon[64] have described accurate spectrophotometric and filter photometric methods of determining color in industrial waste in terms of the dominant wavelength (which defines the hue or kind of color), luminance (which defines the degree of brightness) and purity (which defines saturation, i. e. pastel, pale, etc).

The procedure is given in the latest edition of the American Public Health Association Standard Methods.

Many instrumental methods of determination of pollution [66] are finding increasing application in pollution problems. Such a method is chromatography, a method of separating substances (especially mixtures of complex closely related organic material) by passage of the sample in a suitable solvent through a vertical column of an absorbent (generally alumina). Another method is absorption spectroscopy, which is a measurement of the optical density of a substance at different wavelengths, generally in the ultra-violet region, by using a spectrophotometer. Other methods are emission spectroscopy, flame photometry, polarography, physical titration methods, and oxidation-reduction potential. The chemical methods are mainly volumetric (titrimetric) and colorimetric.

There are several instruments [66] available for measuring the intensity and quality of colored solutions. These include the spectrophotometer, filterphotometer, and the color comparator such as that made by Hellige. The measurement is made with transmitted light.

High color water has a color exceeding 20 parts per million of platinum [82]. The Technical Association of the Pulp and Paper Industry suggest tolerances of five parts per million for high grade projects and only 15 parts per million for lower grades.

Depth of color [82] is measured by visual comparison with American Public Health Association color standards. The primary standard contains 500 parts per million platinum and 250 parts per million

cobalt and is slated to have a color of 500 parts per million. Other
standards are made by diluting this primary standard.

Measurement of Suspended Solids, Dissolved Solids and Total
Solids. The Gooch crucible method involves filtration by suction of
a known volume of the sample through a specially prepared asbestos mat
in a Gooch crucible, which is then dried at (100 - 105) $^{\circ}$C.

The filtrate from the Gooch crucible can be used for a
determination of dissolved solids or soluble solids by evaporating a
known volume to dryness. This determination includes all suspended
colloidal matter present.

Total solids can be determined by evaporating a known volume of
the well shaken sample to dryness on the water bath and drying it at
(100 - 105) $^{\circ}$C.

Transmittance of Light. To describe color as seen by the eye, it
is probably best to use transmittance[17], since this method of notation
tends to emphasize the observed color. The ratio of the transmitted
light to the incident light is the transmittance, which when multiplied
by 100, is the per cent of light transmitted.

In relatively clear solutions a large per cent change is required
in the concentration of colored material produced. "This is evident
from Beer's Law[31], which states that the negative log of the
transmittancy varies as the concentration of the substance. For a
solution showing a transmittancy of 0.900 (90 per cent) the negative
log of the transmittancy is 0.0458. A solution having only half
the concentration of this solution would therefore have a negative
log of transmittance of 0.0229 and a corresponding transmittance of

0.949 (94.9 per cent)." Also, just as for relatively clear solutions, a large percentage change in concentration is required before any appreciable change in transmittancy is obtained.

A strong dye (or digester liquor) solution[31], and the same solution diluted with an equal volume of water, will appear to the eye to have the same intensity of color. If a sample of highly colored mill waste water allows a transmittance of ten per cent, and if the sample were diluted with an equal volume of colorless water, the new transmittance would be 31.6 per cent; but to the eye the original and diluted samples would appear identically black.

In the receiving stream, the color is a function of the color intensity of the original waste[37] and of the dilution available. However, there are other factors involved: the depth of the water, the light absorbing properties of the stream bottom, the suspended solids in the waste, the nature and hue of the light source, and the angle of observation. "The effect of depth can be calculated on the basis of transmissivity. For example, 90 per cent transmission of light in a 50-millimeter test cell would be $(0.90)^{305/50}$ or only 53 per cent transmittant in a 305-millimeter, or one foot depth." In a stream, light must pass twice through the water depth, instead of once as in the laboratory, therefore, the dark appearance is even more pronounced.

Rudolfs and Hanlon found that light transmittancy properties[85] vary with the type of waste. The variation is due to a difference in chemical structure, hence the chemical structure of wastes is the factor which governs the type of treatment effective for color

reduction. The measurement of transmitted light is useful in determining the effectiveness of color removal by treatment.

Absorbance. The absorbance (1) is the negative logarithm to the base 10 of the transmittance. The absorbance is obtained b, comparison with a standard as its transmittance.

Determination of Color with the Spectrophotometer. The spectrophotometer was used primarily as a research tool by providing a means of measuring and correlating the transmittance of light with other physical and chemical properties.

A spectrophotometer (92) consists of the following parts: a source of light, a device for obtaining relatively monochromatic light, an absorption cell for the sample and the standard (distilled water in our experiments), and a means of measuring the difference of absorption between the sample and the standard.

Color Removal by Various Methods. The methods of color removal mentioned include chlorination, chemical treatment and coagulation, heat treatment under pressure, absorption, light treatment, and biological treatment.

Effect of Waste Concentration. The degree of color reduction was approximately the same regardless of the dilution (89).

Chlorination. Chlorination (87) has been used rather extensively for color removal processes, commonly referred to as bleaching.

When chlorination is in the acid region below pH 3, the color reduction of wastes is practically instantaneous. However, the rate of color reduction obtained at pH 7 is somewhat slower (88).

Chlorination effectively reduces the color (88) of various industrial

wastes, but tests showed that the quantity of color return increased

with increasing color reduction. Results indicated that the color

reduction was a result of chemical substitution and not necessarily

a breakdown of a complex structure (88) .

Experiments were performed to determine the degree of chlorine

loss in open chlorination systems (89) . There was a significant

loss of chlorine from the open system; therefore, there was less color

reduction in the open system. At the point of maximum color reduction

the chlorine loss to the atmosphere was about 35 per cent.

"A color return of from 5 - 15 per cent of the color removed

from an industrial waste by chlorination (89) may be expected within

a 10-day holding period."

The effectiveness of chlorination (89) for industrial waste color

reduction varies with the form of chlorine and the pH of the waste

solution. In general the rate of reaction of chlorine with industrial

wastes increases with decreasing pH. Studies are now being made at

Virginia Polytechnic Institute to determine the effectiveness of

chlorine in removing color from caustic waste.

Chemical Treatment and Coagulation. Chemical treatment (80)

has been used to some degree to remove color from various industrial

wastes. Little attention has been paid to the chemical structure of

the colored compound being treated. The first step is to ascertain the

structure of a given colored compound. Then chemical and physical

methods can be applied on a scientific basis to decrease the

oscillation of electrons within the molecule. This should not be too difficult a task because the textile and paper dye chemists are constantly at work doing just the opposite; that is, increasing the oscillation of electrons to develop brighter, more saturated hues in their dyes.

Various chemical treatments using hydrated lime, alum, ferric chloride, chlorinated copperas, phosphoric acid, waste pickle liquor, and a barium alumina silicate compound have been experimented with and have yielded varying degrees of color removal from kraft effluents[72].

Critical examination of results showed that in all cases the quantity of chemicals needed to achieve the desired degree of color reduction was uneconomical[72]. However, recovery of the color-removal spent chemicals, if done economically, would overcome, to a large degree, the disadvantage of high treatment cost. Moggio concluded that hydrated lime, because of its abundance and low price, offered the greatest possibility for eventual success. Even though hydrated lime dosages are high, it offered the best recovery and reuse possibilities.

Foushee[33] reported that 90 per cent of the color in the paper mill caustic extraction waste could be removed by alum coagulation using 1.5 grams alum per liter of waste at a pH of 6.

Heat Treatment Under Pressure. "When waste sludge is heated under a pressure of about 150 pounds per square inch to a temperature of about 360 °F for 45 minutes[68], its gel structure is completely broken down." This conditioning process is so effective that, after cooling, the sludge can be easily densified by a simple settlement

and then dewatered in filter presses to yield a cake of low moisture content. It is possible that a more dilute waste may also be effectively treated.

Adsorption. Activated carbon (63) is often very effective in reducing or removing the color of a waste but usually large amounts are required. Foushee (33) found that NUCHAR CEE-N activated carbon treatment of caustic extraction waste did not remove a significant amount of color. Chumney (30) evaluated fluorite as an adsorbing medium for the treatment of caustic extraction waste and found that it did remove some of the color, but was uneconomical because of the amount of adsorbent used and the activation treatment involved.

Effect of Light on Certain Wastes. Sunlight (86) is an effective agent for the bleaching of color in natural reservoir water supplies. A study was undertaken to determine the effect of sunlight and ultraviolet rays on color characteristics of industrial waste liquors. "It is believed that the most effective light energy for color reduction originates in the ultraviolet region of sunlight. Greater displacement of outer electrons from molecules with greater energy occur in the ultraviolet region."

For general stream conditions, presence of highly colored waste has little effect on the rate and extent of temperature rise caused by sunlight absorption (86).

Biological Treatment of Wastes. Laboratory studies were made to determine the effects of biological treatment. It was found that the effect of such treatment on the color characteristics of industrial wastes varied with the type of waste (90).

Chemical Treatment of Waste to Remove Color

Studies in flocculation have shown that there is a direct
relation between color and the amount of chemical such as alum
necessary to remove it (43). Very finely divided suspended matter
must be rendered settleable by the addition of coagulants (45). The
combination of flocculation and sedimentation is called chemical
precipitation.

Types of Coagulants. There are many available coagulants on
the market today (39), as shown in Table I, page 37.

"The most widely used coagulant is aluminum sulfate, but ferrous
sulfate and chlorinated copperas are also used (82)." Alum is cheap and
generally available, both in solid form and in solution. Hydrated lime
is also used extensively.

"Alum is marketed in lump, ground, rice, or powdered form and is
shipped in 100 and 200-pound bags, 325 and 400-pound barrels, 100 and
250-pound drums, and in carloads. It is light tan to gray-green in
color, dusty, and astringent (48)." It is only slightly hygroscopic.
It weighs 60 - 75 pounds per cubic foot and contains 17 per cent
aluminum oxide as a minimum. It is best fed as ground rice alum
because the powder is dusty and therefore arches in hoppers. Suitable
handling materials are iron, steel, and concrete for dry alum; and
lead, rubber, duriron, and stainless steel 316 for alum solutions. It
is usually dissolved in water before being added to the waste.

Flocculating Aids. Suspended particles can assist coagulation (41)
by acting as a nuclei for floc formation. Lime, soda ash, and sulfuric

TABLE I

Coagulants Available on the

Market Today

Name	Formula
Aluminum Sulfate (Alum)	$Al_2(SO_4)_3 \cdot 14H_2O$
Ferric Sulfate	$Fe_2(SO_4)_3 \cdot 9H_2O$
Ferric Chloride	$FeCl_3$ and $FeCl_3 \cdot 6H_2O$
Chlorinated Copperas	$FeCl_3$ and $Fe(SO_4)_3$
Ferrous Sulfate (Copperas)	$FeSO_4 \cdot 7H_2O$
Hydrated Lime	$Ca(OH)_2$
Quicklime	CaO
Activated Silica	SiO_2

Haney, P. D.: Principles of Flocculation Related to Water

Treatment, Journal of the Hydraulics Division,

Proceedings of the Amer. Soc. of Civil Eng.

HY_4, **82**, 8-(1036-1) (1956)

acid are aids in the sense that they can be used when necessary for pH

adjustment. Addition of chlorine ahead of the coagulation process has

been reported advantageous.

Polyelectrolytes [41] are a recent development of interest and are

available commercially. They are synthetic organic compounds and it

has been shown [55] that long chain linear polymers act as coagulants.

Some commercial flocculating aids have been especially designed for

rapid flocculation of solids present in an aqueous phase. The use of

these flocculating aids should be studied and evaluated in the

laboratory and the results, to be useful, just as in the case of the

coagulants, must be interpreted in terms of actual plant performance.

Chemical Reactions. When alum is dissolved in water, it ionizes

yielding aluminum ions bearing a high positive charge and negatively

charged sulfate ions [39].

$$Al_2(SO_4)_3 \longrightarrow 2Al^{+++} + 3SO_4^{--}$$

Alum also hydrolyzes readily:

$$Al_2(SO_4)_3 + 6H_2O \longrightarrow 2Al(OH)_3 + 3H_2SO_4$$
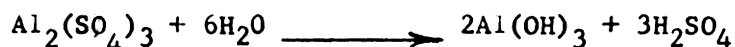
The sulfuric acid formed by this reaction is neutralized when an

alkaline agent is present. Aluminum hydroxide is an amphoteric

substance; therefore it is dissolved by a surplus of either hydrogen

ions or hydroxyl ions:

$$Al(OH)_3 + 3H^+ \longrightarrow Al^{+++} + 3H_2O$$

$$Al(OH)_3 + OH^- \longrightarrow AlO_2^- + 2H_2O$$
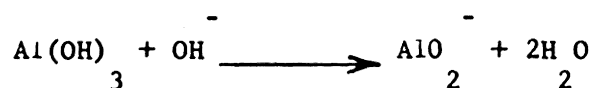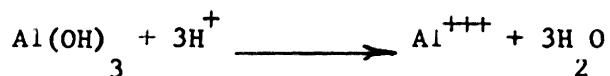
Alum is classified as an acid salt because upon hydrolysis there is

an increase in hydrogen ion concentration resulting in a reduction of

the pH value of the aqueous solution. "Because of its amphoteric

nature, the solubility of alum floc is sensitive to the pH value

of the water and pH adjustments are required to achieve optimum

conditions for precipitation."

The reaction for aluminum sulfate can also be expressed as
follows[47] :

$$Al(SO_4)_2.14H_2O \longrightarrow 2Al^{+++} + 3SO_4^{--} + 14H_2O$$

$$2Al^{+++} + 6OH^- \longrightarrow Al_2O_3.xH_2O$$
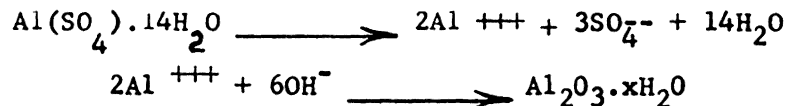
The pH of relative insolubility of the alum floc is 5-7.

Precipitates formed by iron coagulants do not exhibit amphoteric

behaviour, at least not the extent shown by those formed from alum.

Colloidal Particles. Colloidal particles[38] play an important

role in coagulation. Some of the significant characteristics of

colloidal suspensions are large specific surface area, particle size,

high adsorptive capacity, and particle charge.

Surface Area. Colloidal particles have a large specific surface
area[40]. "If water contains 200 parts per million of a material

colloidally dispersed as sperical particles of 1.0 millimicron

diameter, and has a specific gravity of 2.5, then each 1,000

gallons of water would contain 6×10^{20} particles and their surface

area would be approximately 45 acres."

Particle Size. Colloidal particles[40] are arbitrarily considered

to be those falling in the diameter range of 1.0 to somewhat less than

500 millimicrons. Colloidal dispersions consist of a homogeneous medium

such as water and particles dispersed therein. "In general, colloidal

particles are not microscopically resolvable nor can they be readily separated from water by means of filtration." There is a "continuous transition" from suspensions through colloids and on to so-called true solutions. The smaller the particle the greater the total surface area and the greater is the adsorptive capacity.

(40)

Particle Charge. "Colloidal particles normally carry a charge and the stability of many colloids is explained by the fact that the particles carry like charges thus repelling each other and continuing the dispersion." Ions possessing a charge opposite to those borne by the colloidal particles (38) tend to precipitate the colloid.

When the ions causing the charge (46) on colloids are acidic or basic ions, a change in the pH toward neutralization will promote coagulation. Increasing the concentration of the negative ions in the waste will aid coagulation of the positively charged aluminum oxide colloids. The effectiveness of the ions increases with the number of their charges. Sulfate ions are therefore better than chloride ions; in fact, they are 100 times more effective. Aluminum ion is roughly 500 times more effective than the sodium ion for precipitating a negatively charged colloidal particle. "The greater the concentration of dissolved mineral salts (40) (ionic strength), the more readily precipitation occurs."

Mechanism of Coagulation. The coagulant (41) furnishes trivalent aluminum or ferric ions with a high plus charge capable of neutralizing the negative charge on colloidal particles of color and turbidity. If the coagulation reaction occurs below pH 7, the result of the initial action of the coagulant is the formation of positively charged particles

of color. Then the flocculation phase involves further adsorption, charge neutralization, and finally agglomeration of the micro-flocs into larger and larger particles.

With regard to flocculating aids, apparently the most effective polyanionic polymers (polyelectrolytes) contain a mixture of both ionic and unionized hydrophilic groups [55]. These groups are probably adsorbed on the particle surface, and the ionized groups keep the polymer in an extended position; this leads to particle bridging and coagulation.

The Floc-forming Process. The raw waste [82] enters the mixing chamber of the floc-former where it is rapidly and well mixed with the coagulating chemicals. The treated water then flows through successive floc-former chambers, each of which is fitted with agitators which are controlled to give a slow and gently rolling mix. The coagulated waste then flows to a baffled settling basin or tank. The bulk of the floc is discharged through a sludge-removal system after settling to the bottom. Filters or centrifuges perform the dewatering of the sludge prior to incineration and chemical recovery.

Important factors in the coagulation process are pH, mixing, temperature, and time-concentration.

pH Control. The pH of water solutions affects "(1) the solubility of precipitates formed by aluminum and iron, (2) the time required for floc formation, and (3) the charge on the colloidal particles [41]."

Therefore, pH control is important. According to Garner [67], the

optimum formation of floc when waste water is coagulated with alum occurs

between pH 6.3 and 6.5. Other workers have found it around pH 5.

Mixing. There are "rapid" or "flash" mixers for the few seconds of

rapid mixing when the coagulating chemical is first added to the raw

waste. The coagulant must be evenly distributed throughout the waste to

be treated. Once the floc growth (42) has begun, the rate of stirring

should be controlled with a "slow" mixer so as not to break up the floc

that has formed. Opportunity for coalescence is greatly enhanced by

slow mixing. The amount of alum or ferric salts (5) required for

coagulation of paper mill waste is 0.2 to 0.4 pound per 1,000 gallons.

Iron salts produce a heavier floc than alum does and settle more

rapidly.

For practical operating control there is no substitute for trial

determination of coagulant dosage conducted with laboratory stirring

equipment.

Temperature. The principal effect of temperature is its influence

on the rate of floc formation. Generally, the lower the temperature,

the longer the time required to produce good flocculation (41).

Time-Concentration. "A high concentration (41) of coagulant produces

results in less time than a low concentration."

Sedimentation. Flocculent suspensions (44) are composed of particles

that form larger and larger masses, or flocs, as they settle because

the particles stick together when faster moving solids catch up with

slower moving ones; this is true in substantially quiescent tanks.

"Opportunity for particles to come together is best when their

concentration is high, difference in settling velocities of the

individual particles is great, and the surface area is large. Vertical,
upward flow [45], in a tank may be favorable because the treated waste

rises through the settling and suspended flocs as if it were pushing its

way through a filter." To obtain larger floc growth does not imply

improvement in its settling velocity [44] because the entrainment of water

and the consequent reduction in the specific weight of the floc cut down

its settling velocity at the same time. Water offers viscous resistance

to the settling of small, light particles (Stoke's Law) and eddying

resistance (Newton's Law) to that of heavy ones.

Sludge. The volume of sludge by chemical precipitation is large [49]

because "(1) greater amounts of solids are removed, (2) the precipitants

themselves form part of the sludge, and (3) the water content of the

sludge is high." Wet sludge [50] will flow by gravity in open or closed

conduits and can be pumped over short or long distances. Sludge paste

should be transported on belt conveyors because it tends to cake and

ball in screw conveyors [50]. If the moisture in the sludge is to be

reduced to less than 10 per cent, as required for commercial fertilizer,

heat must be applied [52].

Cost of Chemicals. The type of chemical chosen should produce the

desired result with the least amount added and with the least overall

cost. Polymeric coagulants (polyelectrolytes) are more expensive than

the commonly used coagulants, but the amounts required are quite small.

It would be advantageous if any industry near the waste treatment

plant turned out wastes containing chemicals useful as coagulants [55].

Industrial Waste Treatment and Disposal

Relatively few successful full-scale waste treatment plants have been constructed for the abatement of industrial pollution. Much has been accomplished in reducing biochemical oxygen demand but no economical method has been devised for the removal of color from paper mill waste streams although there are some promising processes under investigation. Activated sludge treatment, a discussion of color removal equipment, the dewatering of sludge, and the development of a low cost treatment plant will be included in the following sections.

Activated Sludge Treatment Plant. The West Virginia Pulp and Paper Company installed a $2,000,000 nutrient fed activated sludge waste disposal plant which started operation in May, 1955[83]. "The mountainous terrain at Covington, Virginia, precluded the possibility of lagooning the wastes and diminished the attractiveness of trickling filters as a means of pollution abatement."

Plant Design. Its maximum capacity is 24 million gallons per day with a design capacity of 16 million gallons per day, about two-thirds of the total waste flow from the mill. This flow[83] includes all the wastes from the woodyard to about halfway through the bleaching process. Most of the remaining wastes from the mill are high-volume, low biochemical oxygen demand effluents for which this type of treatment would be superfluous. There is a primary settling tank, 100 feet in diameter, having a side-water depth of 12 feet and a theoretical retention time of two hours. This clarifier treats about two-thirds of the total flow while the remaining one-third, low in suspended

solids concentration, is by-passed into a mixing chamber. The mixing chamber collects the total influent after solids removal. From here there is an equal split of flow to two combination aeration and settling units operating in parallel. These units provide a circular secondary clarifier surrounded by an annular shaped aeration chamber. The clarifiers are 175 feet in diameter, while the aeration chambers around the units are 25.5 feet in width and 15 feet deep, providing a theoretical three-hour retention. The inner settlers have a 2-1/2-hour detention period. The effluent from the final clarifier goes directly to the river and the settled activated sludge is pumped back to the mixing chamber. There are storage facilities for the activated sludge which is converted into a by-product, activated carbon.

The nitrogen and phosphorus nutrients are added in the form of 30 per cent aqueous ammonia and 75 per cent phosphoric acid solution.

Instrumentation for the plant is quite complete and virtually every operation is controlled from one central control panel.

Achievement. The plant (83) treats about 70 per cent of the mill waste, and removes 75 to 80 per cent of the biochemical oxygen demand. In suspended solids removal, the plant has an efficiency of 85 to 90 per cent. The waste which enters the primary clarifier is a very dark grey in color while the bleaching wastes are an intense red brown. Their combination yields a dark grey-black color which undergoes little or no reduction during passage through the treatment plant. The color cannot be filtered out and is so intense that it cannot even be measured properly.

Research for the improvement of the process is being carried out in the development of means to remove the color from the effluent. Sixty per cent of the total color is contributed from the caustic extraction stage of bleaching [83], but is only ten per cent of the total volume of the plant. Therefore, all effort is being concentrated upon developing a method of removing this color. A research fellowship has been granted Virginia Polytechnic Institute to perform basic research on the problem. Foushee [33] evaluated the use of NUCHAR activated carbon and aluminum sulfate as agents for removing a significant amount of color from the caustic extraction waste. He found the carbon did not remove an appreciable amount of color but alum coagulation would decrease the color content approximately 90 per cent [33]. He filtered the sludge from the alum coagulation of the waste through a sand bed and also through a pre-coated rotary vacuum filter.

Color Removal Equipment. Color removal equipment usually consists of chemical feeders, mixing, coagulating, and settling units, and filters or centrifuges.

Feeders. Either wet or dry feeders may be used and the controllers may be either constant rate or proportionating [82]. Constant rate controls are used if water flow (waste flow) is fairly steady, but when the waste flow is variable, proportionating controls are used to feed chemicals in proportion to the flow rate of the waste. The equipment must resist the corrosive action of the chemicals [57]. It is becoming common practice to feed the chemical in ahead of the mixing chamber but it can also be introduced near the mixer.

Alum Rate Regulator. To regulate the alum solution flow rate, an
orifice type flow meter controller (84) is mounted in the waste inlet line.
"The linear electric control (proportional to waste flow rate) from this
meter is transmitted to a thymotrol panel. This panel automatically
varies the speed of the controlled volume alum pump in direct response
to the flow meter controller signal."

Mixing. The rapid mixing of coagulant and sewage can be
accomplished by the use of motor-driven vertical or inclined shafts
submerged in the waste (58), to which one or more impellers or paddles
are attached.

Flocculators. The flocculator must allow enough detention time
for complete coagulation with the formation of large, tough floc (82).
One of the simplest types of flocculators (58) consists of one or more
horizontal shafts, which are placed longitudinally in the tank beneath
the surface of the waste. Attached to each shaft is a series of
paddles, which rotate slowly and impart a circulatory motion to the
waste.
Another type (58) provides for a reverse current which carries a
portion of the floc back toward the inlet of the tank to serve as
nuclei for floc formation.

Paddle blades decrease in width toward the outer end of the tank
so that mixing gradually decreases (58). Mixing can be further reduced
by lowering the speed of the paddles. Some types of equipment handle
both the mixing and the flocculating in the same unit.

Settling Tanks. Their purpose is to settle out the bulk of the
floc so to ease filter or centrifuge load.

A sedimentation tank[56] should be designed so that the velocity of the flocculated waste entering the tank is rapidly reduced. In all parts of the tank the velocity should be nearly the same.

Imhoff[53] states that the most important inlet consideration is that the velocity be started off in a horizontal direction. At the inlet, a perforated or slotted baffle which comprises a diffusion wall is also recommended at the outlet end of the basin. Density currents are less prominent in deep tanks than in shallow ones. With too little inlet energy, the tank is liable to have severe shortcircuiting and large dead zones. "In tank design, the settling velocity[45] must be greater than the tank depth divided by the detention period, or the settling particles will not reach the tank bottom in the time allowed for sedimentation."

The factors[56] encountered in the design of the settling tank are: "(1) the dimensions of the tank; depth, ratio of length to width and depth, and surface area, (2) the shape of the tank, (3) the sludge removal system, (4) the baffles, (5) the inlets and outlets, (6) the velocity of flow, (7) the detention period, (8) the specific gravity and viscosity of the liquid waste, and (9) the solid content of the waste; concentration of solids, coalescence of solids, shape of the solids, and their size."

Two or more settling tanks should be provided so one is available when the other is being cleaned or repaired.

Sludge Pumps. Pumps are usually necessary to remove the settled sludge[6] from sedimentation tanks. The sludge deposited should be removed continuously in an amount equal to its deposition. The plunger

type of pump with adjustable stroke offers the greatest advantage in
control. These pumps are equipped with electric time-clock controls,
set to start and stop the pump at given intervals, run it for a short
period, and then let it rest for another period.

(7)

The centrifugal pump with open impellers is recommended for
pumping the untreated waste and effluents.

(59)

Dewatering of Sludge. The chief reason for dewatering sludge
is to reduce the quantity of material that has to be disposed of.

(73)

However, in some of the more promising processes for color removal ,
dewatering has been the major obstacle. Several methods of reducing the
moisture content of the sludge are discussed in the following sections.

(61)

Factors Affecting Sludge Filtration. The factors to be
considered include: "(1) the type of sludge, (2) its physical and
chemical characteristics, (3) the amount and kind of coagulant, (4)
the amount of cake produced, (5) the moisture in the cake, and (6)
the character of the filtrate."

(60)

Vacuum Filtration. A popular vacuum filter is the Oliver filter
consisting of a partially submerged horizontal drum, supported in a steel
tank. The wet sludge is fed into the filter tank through a pipe
connection at the bottom of the tank. As the drum rotates, suction
is applied to successive compartments immersed in the sludge. Water
is drawn through the filter cloth while the adhering cake is freed from
the revolving drum by a scraper. Vacuum filters require considerable
accessory equipment. Precoats (filter-aid) on the revolving drum
enhance filtration.

Centrifuging. Technological progress has made centrifuges available that can handle sludge dewatering problems. Bird [9] manufacturers a continuous centrifuge that can be fed slurries containing as little as three per cent solids or very thick flows with ease and efficiency. The capacities of the centrifuges are available in the range of 400 or more gallons per hour.

Sharples manufactures a centrifuge [91], PY-14 "Super-D-Canter" which applies high centrifugal force for separation in combination with an internal screw conveyor for continuous removal of solids. There is also continuous discharge of clarified liquor. Capacities in the range of 2,000 gallons per hour are available.

Freezing and Thawing. An entirely new principle in sludge dewatering consists of alternate freezing and thawing [68]. The thawed sludges can be readily filtered giving sludge cakes which are porous and friable, and which have a high solids content.

Heat Driers. Various heat dryers [68] have been used for conversion of wet sludge from centrifuges and sludge cake from filters into a dry product which can be subsequently incinerated or used as a fertilizer.

According to combustion engineers, at 70 per cent moisture content the waste solids from paper mill wastes are burnable [91].

Flash drying of feed [4], the most modern method, is especially satisfactory when fresh sludge is mixed with a sufficient quantity of previously dried sludge to reduce the moisture content [52] of the incoming sludge to about 50 per cent. The temperature of the drying gases is usually about 1,000 $^\circ$F and the exhaust gases leave at about 250 $^\circ$F. Countercurrent flow conserves heat and also part of the

required heat may be obtained from waste heat from an adjoining
incinerator⁽⁴⁾. The dust carried out by the gases is collected in
cyclones.

Incinerators. Heat drying must precede incineration⁽⁵²⁾.
Some supplementary fuel may be required for chemically precipitated
sludge. Incineration is one of the best methods of disposal of
sludge, but for it to be economical, as much water as possible must be
removed from the sludge. The operation of various types of incinerators
is described in the literature⁽⁶²⁾.

Development of a Low-Cost Plant. The factors⁽⁸⁾ concerning the
development of a low cost of operation are listed as follows: "(1)
initial cost of the plant; cost of necessary equipment and apparatus,
cost of installation of equipment, cost of excavation (if necessary),
cost of preparing ground at site (pilings), cost of special design work,
concrete, electric connections (wiring, controls), cost of land, cost
of covering tanks (if necessary), (2) cost of operation of the plant;
cost of electric power required daily, cost of chemicals, cost of
maintenance of equipment, cost of labor, cost of repairs and supplies,
(3) fixed charges; interest on investment in plant, and
amortization for plant obsolescence." All of the above factors should
be taken into consideration for each promising treatment process found
for decolorization of the waste. This method provides for rapid
evaluation of the process and will insure that at least the most
economical treatment will be used.

III. Experimental

The experimental section of this thesis contains the purpose of the investigation, plan of investigation, lists of materials and apparatus, experimental procedure, data, and results obtained during the investigation.

Purpose of Investigation

The purpose of this investigation was to study the practical application of various treatments of caustic wash liquor from chlorine-bleached, sulfate, wood pulp, and to design and evaluate a pilot plant for testing further, the most promising possibility.for its decolorization.

Plan of Investigation

The plan of investigation consisted of three phases, the first being a literature review of pulp manufacturing processes, wood chemistry, color, stream pollution, methods of chemical treatment of waste, and chemical waste treatment plants; the second was a bench scale study of coagulants and flocculating aids and their effect on the caustic waste; and the third was the design and evaluation of a waste treatment plant for decolorization of the caustic waste.

Literature Review. A study was made of the source and composition of the waste, and of past work that was done here and by others elsewhere. In order to gain a deeper insight into the problem, a review of both color and of stream pollution was

made. Types of chemical and other treatments were reviewed with
emphasis put on coagulation. Finally, the literature was
scanned so to become familiar with waste treatment plants such
as the one installed by the West Virginia Pulp and Paper Company
at Covington, Virginia, the types of equipment necessary, and
the essential factors for determining the feasibility of a
process.

Preliminary Studies. Tests were performed to determine
whether or not the coagulation of the caustic waste with alum
would be enhanced by the addition of flocculating agents. The
following commercial flocculating aids were evaluated: Separan,
Guartec, Burtonite, Good-rite K-720S, Good-rite K-721S, Orzan P,
and Lytron X-886.

The data for settling rates, volume of sludge, rate of
filtration of sludge, effect of varying pH, transmittance of the
supernatant liquors, and the amount of dry solids both before
and after ashing were collected. Solutions of chemically pure
aluminum sulfate and the papermakers alum solution, hereafter
called alum slurry, containing finely divided clay were used with
the flocculating aids to determine their relative effectiveness
as a coagulant. Alum treatment, with and without flocculating
aids, was compared with chlorine treatment, concentrated acid
treatment, ferrous sulfate coagulation, and modifications of
these procedures.

Large Scale Tests. After studying and correlating the data
from the preliminary tests, a series of tests were performed

that were 16 times larger in magnitude than the first tests.
From this information, and after a thorough consideration of
the literature, a pilot plant for decolorization of the caustic
waste was designed and evaluated by comparison with other
processes.

Materials

The materials used in the experiments were as follows:

Acid, Sulfuric. Reagent, A. C. S. Standard, Lot No. 6137
CP, 96.5 per cent. Obtained from J. T. Baker Co., Phillipsburg,
N. J. Used in dilute form to adjust the pH of the caustic
extraction waste and in concentrated form to treat the waste.

Air, Compressed. Available at 15 pounds per square inch,
gage. Used to exert pressure on the feed into the Sharples
centrifuge.

Aluminum Sulfate. $Al_2(SO_4)_3 \cdot 18H_2O$ crystals, CP, Catalog
No. A-613, Lot No. 511104. Manufactured and distributed by the
Fisher Scientific Co., Silver Spring, Md. Used as a coagulant
to precipitate solids and decolorize the caustic extraction waste.

Aluminum Sulfate Slurry. An aqueous solution of 18 weight
per cent $Al_2(SO_4)_3$ containing fine clay particles and traces of
other dissolved impurities. Obtained from West Virginia Pulp
and Paper Co., Covington, Va. Used as a coagulant to precipitate
solids and decolorize the caustic extraction waste.

Buffer Solution. Type 3581, concentrated pH 7, to be

diluted 25 fold. Obtained from Beckman Division of Beckman

Instruments, Inc., Fullerton, Calif. Used to standardize the

pH meter.

Burtonite. Water-soluble vegetable colloid, polyelectrolyte,

No. 78. Obtained from The Burtonite Co., Nutley 10, N. J. Used

as a flocculating agent in the treatment of the caustic waste.

Calcium Hydroxide. Reagent grade. Obtained from J. T.

Baker Co., Phillipsburg, N. J. Used to raise the pH of the

treated waste after the addition of alum.

Ether. Anhydrous, A. C. S. Standard, Lot No. 6436.

Obtained from J. T. Baker Chemical Co., Phillipsburg, N. J. Used

to partially dissolve crystals obtained from treatment of caustic

extraction waste with concentrated sulfuric acid.

Filter Paper. Whatman No. 1, 32.0 centimeters, chemically

prepared. Distributed by the Fisher Scientific Co., Silver Spring,

Md. Used to filter the liquor from the sludge obtained from the

treatment of the caustic waste.

Foil, Aluminum. Reynolds Wrap, pure aluminum foil.

Manufactured and distributed by the Reynolds Metals Co.,

Louisville, Ky. Used as a cover for the settling basin.

Good-rite K-720S. Water soluble synthetic resin,

polyelectrolyte. Obtained from the B. F. Goodrich Co., 3135

Euclid Avenue, Cleveland, Ohio. Used as a flocculating agent

in the treatment of the caustic waste.

Good-rite K-721S. Water-soluble synthetic resin, polyelectrolyte. Obtained from the B. F. Goodrich Co., 3135 Euclid Avenue, Cleveland, Ohio. Used as a flocculating agent in the treatment of the caustic waste.

Guartec. Vegetable colloid, polyelectrolyte. Obtained from General Mills, Inc., Special Commodities Division, 400 Second Avenue South, Minneapolis 1, Minn. Used as a flocculating agent in the treatment of caustic waste.

Lytron X-886. Water soluble calcium salt, polyelectrolyte. Obtained from Monsanto Chemical Co., Plastics Division, Springfield, Mass. Used as a flocculating agent in the treatment of caustic waste.

Orzan P. Sixty per cent lignin sulfonic acids, precipitated from dilute solutions by the addition of alum. Obtained from the Crown Zellerbach Corp., Chemical Products Division, Camas, Washington. Used as a flocculating agent in the treatment of caustic waste.

Potassium Fluoride. Purified, anhydrous, code 2091, Lot No. 6360. Obtained from General Chemical Division, Allied Chemical and Dye Corp., New York, N. Y. Used in quantitative analysis of sludge for alum determination.

Separan 2610. Synthetic water-soluble polymer, polyelectrolyte. Lot No. 427. Obtained from the Dow Chemical Co., Midland, Mich. Used as a flocculating agent in the treatment of caustic waste.

Sodium Carbonate. Anhydrous, A. C. S. Standard Lot No. 4295. Obtained from J. T. Baker, Chemical Co., Phillipsburg, N. J. A ten per cent weight solution was used to raise the pH of highly acidified waste.

Sodium Hydroxide. A. C. S. Standard, Lot No. 9127. Obtained from J. T. Baker Chemical Co., Phillipsburg, N. J. Used to neutralize strongly acidic waste solutions and in treating acid solutions containing aluminum ions.

Sulfate, Ferrous. Reagent grade. Obtained from J. T. Baker Co., Phillipsburg, N. J. Used as a coagulant to precipitate solids and decolorize the caustic waste.

Waste, Caustic Extraction. See Table IV, page 72. Received from the West Virginia Pulp and Paper Co. Used in all waste treatment tests and is the waste which is to be decolorized.

Waste, Hydrochloric Acid. See Table IV, page 72. Received from the West Virginia Pulp and Paper Co. Used to lower the pH of the caustic waste.

Water, Distilled. Distilled in a Barnstead still, equipped with an electric heater and a tin condenser. Obtained from Fisher Scientific Co., Silver Spring, Md. Used in making all chemical solutions and in final washing of glassware.

Water, Tap. Used in trial runs of the Sharples super centrifuge.

Apparatus

The apparatus used in the experiments was as follows:

Agitator. Six positions, six paddles, ac-dc variable speed motor, 115 v. Obtained from Fisher Scientific Co., Silver Spring, Md. Used to agitate treated caustic waste samples.

Balance, Analytical. "Chainomatic," capacity 200 grams, one-milligram graduations with vernier for tenth mg. Manufactured by Seederer-Kohlbusch, Inc., Jersey City, N. J. Used to weigh samples.

Centrifuge, Sharples Super. Laboratory size, type T-41-23, Serial No. 381A312, semi-continuous. Manufactured by Sharples Specialty Co., 23rd and Westmoreland Streets, Philadelphia, Pa. Used to dewater the sludge from the settling tank.

Crucible, Gooch. Coors porcelain, without covers, perforated bottoms for filtering, size No. 2. Obtained from Fisher Scientific Co., Silver Spring, Md. Used with an asbestos mat to filter treated waste under vacuum.

Funnel, Sintered Glass. Coarse and medium. Obtained from Fisher Scientific Co., Silver Spring, Md. Used to filter samples of treated waste with the aid of an air aspirator.

Glassware, Pyrex. Assorted: beakers, burettes, erlenmeyer flasks, funnels, graduated cylinders, condenser, pipettes, round reaction flasks, stirrers, and weighing dishes. Obtained from Fisher Scientific Co., Silver Spring, Md. Used in the waste treatment experiments.

Heater, Electric. Plate type, No. ROPH7066, 120 v. Manufactured by Edwin L. Wiegand Co., Pittsburgh, Pa. Used to heat samples of caustic waste.

Mixing and Settling Tank. Twenty-liter capacity, pyrex glass beaker, 11-1/2 in. diam., 11-1/2 in. high, 3/16 in. thick walls. Obtained from Fisher Scientific Co., Silver Spring, Md. Used to mix and settle the alum treated waste.

Oven, Electric Utility. Model No. CV-8, serial No. 8-270, 110 v, ac, 5 amp. Obtained from Model Electric Laboratories, Chicago, Ill. Used to dry apparatus, samples, and chemicals.

Furnace, Electric. Type FD 204C, serial No. 34928, 110 v, 30.9 amp. Manufactured by Hoskin Mfg. Co., Detroit, Mich. Obtained from Fisher Scientific Co., Silver Spring, Md. Used to reduce samples of treated waste to ash.

pH Meter, Beckman. Glass electrode, model H-2, serial No. 87327, 0-14 pH units, 0.1 graduations. Obtained from Fisher Scientific Co., Silver Spring, Md. Used to measure pH of waste samples before, during, and after treatment.

Spectrophotometer. Model B, serial No. 70554, transmittance range from 0-100 per cent, sensitivity adjustments from 1-4, wave length adjustable from 310-1,020 mu, slit opening variable from 0.0-1.5. Obtained from Fisher Scientific Co., Silver Spring, Md. Used to measure the transmittance of treated waste samples.

Stirrer. Magnetic, variable speed type, 100 v, ac, 50 cy. Obtained from Laboratories, Inc., Chicago, Ill. Used to agitate caustic waste samples during addition of sulfuric acid and alum.

Thermometer. Laboratory, mercury in glass; range, -10 to 400 $^{\circ}$C, subdivisions, 1 $^{\circ}$C. Obtained from Fisher Scientific Co., Silver Spring, Md. Used to measure the temperature of the waste during various phases of treatment.

Method of Procedure

The method of procedure for carrying out this investigation is given in the following sections which include the flocculation of the alum treated waste, the preparation of the flocculating aid solutions, the measurement of sludge, filtration of sludge, large scale tests, centrifuging of the sludge, spectrophometric analysis, determination of per cent solids, treatment of caustic waste with concentrated sulfuric acid, and quantitative analysis for alum in centrifuge bowl scrapings.

General Procedure. A series of tests were planned to obtain data concerning the effect of various commercial flocculating aids when used with alum on each of the following: the transmittance of the supernatant liquor, the rate of sludge settling, and rate of filtration. In other tests, for comparison, alum alone was used. Stock sulfuric acid of 0.5 N strength was used to adjust the pH of the caustic waste. However, in several tests, waste hydrochloric acid from the chlorination bleach stage was used in place of the C. P. sulfuric acid solution. Both a C. P. alum solution and papermakers' alum slurry from West Virginia Pulp and Paper Company, in Covington, Virginia, were used as coagulants. A series of tests showed the alum slurry to be more effective of the two.

The transmittances of the test samples were obtained both before and after treatment using a spectrophotometer. The height of the sludge was recorded at fixed time intervals so that the rate of sludge settling could be determined. After the supernatant liquor was decanted, the various sludges were filtered so that the effect of the flocculating aids on the rate of filtration of the alum treated waste could be determined.

The general procedure in treating the waste was to first adjust the pH of the waste to the desired value, then to add the flocculating aid while agitating at a rate of 75 revolutions per minute. Then, the desired amount of alum was added and the agitation continued at the same speed for another minute; after which the rate of mixing was decreased to 20-25 revolutions per minute and continued for 15 minutes. The stirrers were then stopped and the sludge allowed to settle.

Preparation of 0.5 N Sulfuric Acid. To 986.2 milliliters of distilled water was added 13.8 milliliters of concentrated sulfuric acid. (96.5 weight per cent, specific gravity of 1.84). This solution was prepared and stored in a one-liter volumetric flask and used as a 0.5 N stock solution to acidify the waste.

Preparation of Alum Slurry Solution from Alum Slurry as Received. A ten weight per cent alum solution was prepared by adding 400 milliliters of distilled water to 500 milliliters of alum slurry as received from West Virginia Pulp and Paper Company. This diluted solution was used chiefly in the flocculating aid tests. In the other tests, the alum slurry was used as recieved.

Preparation of Burtonite Solution. A 0.1 weight per cent solution of Burtonite was prepared by adding one gram of Burtonite to 999 milliliters of water. This mixture was stirred at 110 revolutions per minute for 25 minutes. One milliliter of this solution added to 1000 milliliters of caustic waste represent one part per million.

Preparation of Good-rite Solution. A 0.01 weight per cent solution of Good-rite K-720S was prepared by adding 0.05 gram of the Good-rite to 500 milliliters of distilled water. This mixture was stirred at 110 revolutions per minute for 25-30 minutes. The solution of Good-rite K-721S was prepared in the same way. Ten milliliters of these solutions added to 1000 milliliters of waste represent one part per million.

Preparation of Guartec Solution. A 0.1 weight per cent solution of Guartec was prepared by adding 500 milligrams of Guartec to 500 milliliters of distilled water. This mixture was stirred for 25-30 minutes at 110 revolutions per minute. One milliliter of this solution added to 1000 milliliters of waste represents one part per million.

Preparation of Lytron X-886 Solution. A 0.01 weight per cent solution of Lytron X-886 was prepared by adding 0.05 gram of the Lytron to 499 milliliters of distilled water. This mixture was stirred at 50 revolutions per minute for one hour. Ten milliliters of this solution added to 1000 milliliters of waste represents one part per million.

Preparation of Orzan P Solution. A 0.005 weight per cent solution of Orzan P was prepared by adding 0.05 grams of Orzan P to 999.9 grams of distilled water very slowly and stirred at 50 revolutions per minute for 45 minutes. Twenty milliliters of this solution added to 1000 milliliters of waste represent one part per million.

A 0.01 weight per cent solution of Orzan P was prepared by adding 0.50 gram of Orzan P to 499.9 milliliters of distilled water which was heated first to 60 $^\circ$C. This mixture was stirred at 50 revolutions per minute for 30 minutes. Ten milliliters of this solution added to 1000 milliliters of waste represent one part per million.

Preparation of Separan Solution. A 0.001 weight per cent solution of Separan was prepared by adding 0.005 gram of Separan to 500 milliliters of distilled water. This mixture was stirred at 110 revolutions per minute for two hours. One hundred milliliters of this solution added to 1000 milliliters of waste represent one part per million.

Spectrophotometric Analysis. A Beckman spectrophotometer was used for measuring and comparing the color content of the treated waste samples. The color content was expressed as per cent transmittance, relative to 100 per cent transmittance for distilled water. The transmittance of the waste was obtained both before and after treatment. A standard operating procedure [1] was followed in all determinations of transmittance. Preliminary studies revealed that a wavelength of 580 millimicrons provided a satisfactory operating range.

Properties and Composition of the Caustic Waste, Acid Waste, and the Aluminum Sulfate Slurry. The light transmittance of the waste samples was determined by using a spectrophotometer and their pH was obtained with a pH meter. The density, per cent dry solids and per cent non-volatile solids of the acid waste and alum slurry were obtained by standard operating procedures. The caustic waste was titrated with the acid waste to determine how much acid waste was required to lower its pH.

Treatment of Caustic Waste with Concentrated Acids. To 100 grams of caustic waste was added one milliliter of concentrated sulfuric acid. The mixture was stirred and the particles of precipitate allowed to coagulate and settle. The resulting mixture was filtered under vacuum through a pre-ignited, pre-weighed Gooch asbestos lined crucible. The crucible and sample were dried at 120 ^{o}C and weighed and then ignited in an electric oven at 700 ^{o}C and the crucible reweighed. The per cent dry solids and non-volatile solids were determined.

Also, ten liters of caustic waste were treated with 100 milliliters of concentrated sulfuric acid. A portion of the dried solids from this batch were purified by dissolving them and then re-precipitating the solids. The dried solids were dissolved with 1.0 N sodium hydroxide and heated to 98 ^{o}C. The solids were re-precipitated by acidification with both dilute and concentrated sulfuric acid. The sludge was filtered, washed, and dried, and the per cent recoverery of solids determined.

The waste was also treated with other acids. These included nitric acid, hydrochloric acid, and phosphoric acid. In most cases 100

milliliters of waste was treated. Sludge settling data were collected and the transmittances of the supernatant liquors obtained.

Measurement of Sludge. Both the height of the sludge and the height of the supernatant liquor and the sludge were measured with a scale. The measurements were made at least three times within 24 hours and in many tests were made each 15 minutes during the first hour. The measurements were recorded and calculations made so that the sludge volume was given in milliliters.

Filtration of Sludge. As much supernatant liquor as possible was siphoned from each sample, taking care not to disturb the sludge. The sludge was then stirred so that it was well mixed with the remaining liquor. The mixture was then poured carefully onto a No. 1, thirty-two-centimeter filter paper on a glass funnel. The volume of collected filtrate was observed and recorded at designated times.

Large Scale Tests. Sixteen liters of caustic waste were acidified with 0.5 N sulfuric acid in a 20-liter glass tank. The desired amount of alum slurry was then added and the mixture agitated for one minute at 75 revolutions per minute, then mixed for 15 minutes at 15-20 revolutions per minute. The particles were allowed to settle and the rate of settling was determined by frequent measurements. After the settling was complete, the supernatant liquor was siphoned off and the volume of liquor and sludge measured and recorded. The solids content of both the liquor and the sludge was determined and part of the sludge centrifuged.

Centrifuging the Sludge. The sludge obtained from the coagulation of the caustic waste with alum slurry was fed from a calibrated feed

tank to the feed nozzle at the bottom of the Sharples super centrifuge
by the combination of gravity flow and five to ten pounds per square
inch, gage, of air pressure. The centrifuge bowl was eight inches high
and 1-3/4 inches in diameter. The hold-up of the bowl, using ring dam
No. 5 C, was about 175 milliliters when in motion. When operating
correctly the sludge was dewatered, packing the inner wall of the bowl
with wet solids and yielding a clear effluent through the two nozzles.
During the several tests, by varying the steam pressure from 25 to 40
pounds per square inch, gage, the speed of the centrifuge bowl was
varied from 3000 to 7000 revolutions per minute. The average rate of feed
was about 75 milliliters per minute. Occasionally, the feed line plugged
but was cleared by increasing the air pressure. The average time for a
test was about 15 minutes.

During the tests there was some leakage from the bottom of the
bowl. Also, when the test was completed and the centrifuge bowl had come
to rest, all of the hold-up drained out. All of the streams; the feed,
effluent (both clear and cloudy), leakage, drainage, and scrapings from
the bowl were sampled and their weight or volume recorded. The solids
content of the samples was determined.

The data obtained from centrifuging the sludge and the analyses of
the samples for solids and per cent aluminum sulfate recovery was
pertinent in the design of the treatment plant.

Analysis of Samples for Solids Content. Samples of treated waste
and of streams entering and leaving the centrifuge were analyzed for
total solids, insoluble solids, and non-volatile solids. Standard weighing,
drying, and igniting procedures were followed in all tests.

Quantitative Analysis for Aluminum Sulfate in Scrapings from the
Centrifuge Bowl. A sample of about five grams of bowl scrapings was
weighed accurately on an analytical balance. The sample was placed in a
round bottom flask and 25.0 grams of distilled water added. Then
5.514 grams of concentrated sulfuric acid was added. The flask was
fitted with a reflux condenser and heated to boiling and allowed to
remain at the boiling point for one hour. The mixture was then allowed
to cool at room temperature and filtered. The filtrate was diluted to
100 milliliters with the wash water that passed through the filter
paper. Then, 100 milliliters was divided into four equal parts using
a 25-milliliter pipette. Two of the aliquots were titrated with
standardized 0.9940 N sodium hydroxide as they were. One gram of
potassium fluoride was dissolved in each of the other two aliquots and
then these were titrated in the same way. A potassium fluoride blank
was also titrated. The difference in volume of sodium hydroxide
solution of known normality represented an equivalent amount of aluminum
sulfate. The purpose of the potassium fluoride was to tie up the
aluminum sulfate ions so they would not be titrated.

Data and Results

The following section contains the data and results obtained from the investigation of various treatments of caustic wash liquor from chlorine-bleached, sulfate, wood pulp.

Flocculating Aids. The data for the tests using Separan are shown in Table II, and graphically in Figures 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, and 12.

The data for the tests using Burtonite, Good-rite K-720S, Good-rite K-721S, Guartec, Lytron X-886, and Orzan P are shown in Table III, and is shown graphically in Figures 13, 14, 15, 16, 17, 18, and 19.

Coagulation with C. P. Alum and Alum Slurry. The data for the tests using C. P. alum and alum slurry are shown in Tables II and III, and shown graphically in Figures 20, 21, 22, and 23.

Properties and Composition of the Caustic Waste, Chlorination Stage Acid Waste, and the Aluminum Sulfate Slurry. The data showing the properties and composition of the caustic waste, acid waste, and the aluminum sulfate slurry are shown in Tables IV and V.

Data for pH Titration of Caustic Extraction Waste Streams with Hydrochloric Acid Waste. The data obtained from the titration of the caustic waste with the acidic waste from the chlorination bleach stage are shown in Table VI.

Quantities of Chemical Added in Large Scale Coagulation of Caustic Waste. The data representing the amounts of chemicals added in the treatment of the caustic waste are shown in Table X.

Results of Centrifuge Tests. The data for the tests in which the sludge resulting from alum coagulation of the waste are shown in Table XI.

Determination of Per Cent Solids in Streams Entering and Leaving the Centrifuge. The data for the determination of per cent total solids, insoluble solids, and non-volatile solids of the various streams entering and leaving the centrifuge are shown in Table XII.

Quantitative Analysis to Determine the Per Cent Alum Recovery after Centrifuging. The data for the tests to determine the recovery of alum are shown in Table XIII.

TABLE II

Experimental Conditions and Results From Treatment of Caustic"

Wash Liquors with Alum and Separan

Sample & Test No.	pH of Waste	pH After Adding Acid	pH After Adding Alum	Acid Added GM/L	Alum Added GM/L	Separan Added PPM	Temperature °C	Total Vol. Ml.	Time Hr.	Sludge Vol. Ml.	Sludge %	Time Hr.	Sludge Vol. Ml.	Sludge %	Time Hr.	Sludge Vol. Ml.	Sludge %	Volume Decanted Ml.	1 min. Ml.	2 min. Ml.	4 min. Ml.	10 min. Ml.	12 min. Ml.	20 min. Ml.	Before Adding Alum %	After Settling %	Remarks
																			30.0	49.5	75.2	121.0	126.0		10.8	30.0	pH was adjusted
IV	10.40	6.00	4.10	0.893	1.49	0.015	30.0	1052.8	0.5	510	48.5	6.00	319	30.3	23.00	288	27.4	711	15.0	29.0	51.0	90.0	93.0		11.3	80.0	to 4.00-4.30.
V	10.40	6.00	4.07	0.878	1.50	0.030	30.4	1053.8	0.5	447	42.4	5.67	271	25.7	22.50	246	23.4	680	17.0	31.0	55.0	99.0	104.0		9.5	79.2	For tests IV
VI	10.40	6.00	4.05	0.920	1.50	0.045	31.8	1057.0	0.5	536	50.8	5.33	316	29.9	22.33	284	26.9	652	30.0	48.0	72.0	113.8	126.0		10.5	79.8	through XIII after
VII	10.40	6.00	4.10	0.925	1.50	0.060	31.8	1058.6	0.5	474	44.8	4.90	291	27.5	22.00	243	23.0	712	37.5	58.0	83.0	126.5	138.0		10.9	78.0	addition of alum and
VIII	10.40	6.00	4.10	0.913	1.50	0.120	28.5	1064.1	0.5	359	33.7	5.50	210	19.7	19.00	186	17.5	786	19.0	34.0	54.0	90.0	102.0		10.8	78.0	before addition of
IX	10.40	6.05	4.10	0.907	1.50	0.240	30.0	1076.0	0.5	350	32.5	4.80	226	21.0	18.50	200	18.6	806	21.0	36.0	65.0	108.0	120.0		10.8	75.0	Separan.
X	10.40	6.00	4.12	0.957	1.50	0.000	28.6	1054.0	0.5	407	38.6	4.20	229	21.7	17.75	204	19.3	710	30.0	49.0	74.0	118.0	127.0	155.0	10.8	80.0	
XI	10.40	6.00	4.30	0.898	1.50	0.480	29.0	1099.6	0.5	360	32.7	3.50	282	25.6	22.00	240	21.8	810	25.0	43.0	62.0	96.0	104.0	133.0	10.8	81.0	Amount of Separan added
XII	10.40	5.95	4.30	0.903	1.50	0.960	29.0	1147.8	0.5	337	29.4	3.16	275	24.0	21.67	230	20.0	885	26.0	44.0	70.0	114.0	125.0	161.0	10.9	84.0	ed was varied at pH of
XIII	10.40	5.80	4.30	0.878	1.50	2.000	30.0	1250.8	0.5	333	26.6	2.84	269	21.5	21.33	238	19.0	935	13.0	22.0	33.5	52.0		74.0	8.0	7.0	5.80 for I-C & II-C
I-C	10.40		5.80		1.50	0.480	28.5	1063.0	0.5	381	35.8	8.00	349	32.8	24.00	285	26.8	690	13.0	22.0	33.5	52.3		77.8	8.0	8.0 cloudy	and at pH 5.73 for I-D
II-C	10.40		5.80		1.50	0.960	29.0	1111.0	0.5	458	41.2	8.00	380	34.2	24.00	289	26.0	734							9.0		through IV-D.
I-D	10.10		5.70		1.50	0.000	25.4	1015.0	0.5	599	58.0	7.50	306	30.1	18.00	294	29.0								8.0		
II-D	10.20		5.73		1.50	0.120	25.8	1027.0	0.5	513	50.0	7.16	332	32.4	17.67	317	30.8								8.0		0.5 N H₂SO₄ added to
III-D	10.18		5.73		1.50	0.240	26.0	1039.0	0.5	418	40.3	6.84	263	25.3	17.33	239	23.0		18.0	28.0	42.0		76.0	97.5	88.0		Tests I-D through IV-D
IV-D	10.20		5.73		1.50	0.480	26.4	1063.0	0.5	525	49.4	6.50	334	31.4	17.00	302	28.4	550									to bring pH to 4.00-4.70
I-D′		4.70		0.140			28.0	1020.7	0.5	574	56.2	12.50	348	34.1	22.50	336	32.9		19.0	33.0	50.0		89.5	114.5	85.0	92.0	after alum and Separan
II-D′		4.50		0.169			28.0	1033.0	0.5	602	58.1	12.33	370	35.8	22.16	355	34.3	482							92.0	92.0	had been added.
III-D′		4.35		0.230			28.6	1048.4	0.5	404	38.5	12.09	323	30.8	21.91	307	29.3		19.0	33.0	50.0					10.0	Amount of alum used in
IV-D′		4.03		0.340			28.4	1075.4	0.5	407	37.8	11.84	347	32.3	21.67	331	29.8	580	18.0	29.0	44.5		81.0	103.5	9.0	10.0	Tests I-A through V-A
I-A	10.30	6.00	5.45	0.918	0.375	0.015	32.0	1042.7	0.5	no sludge		5.80	no sludge		18.50	no sludge									9.4	44.0	and tests I-K through
II-A	10.32	6.00	4.50	0.946	0.750	0.015	32.0	1047.6	0.5	280	26.7	5.67	268	25.6	18.33	195	18.6								10.0	77.0	IV-K was varied.
III-A	10.30	6.00	4.13	0.938	1.500	0.015	31.0	1054.8	0.5	415	39.3	5.67	264	25.0	18.00	227	21.5								9.5	70.0	
IV-A	10.30	6.00	4.00	0.953	3.000	0.015	32.2	1079.4	0.5	421	39.0	5.67	240	22.2	17.75	236	21.9								9.5	72.0	
V-A	10.28	6.00	3.90	0.957	6.000	0.015	31.8	1100.5	0.5	412	38.4	5.25	263	23.9	17.30	249	22.6								9.8	cloudy	
I-K	10.10	6.00	4.50	0.844	0.750	0.480	23.2	1089.9	0.5	211	19.3	12.00	189	17.3	24.20	133	12.2								9.8	84.0	
II-K	10.10	6.00	4.15	0.818	1.500	0.480	23.0	1096.4	0.5	374	34.1	11.67	265	24.2	23.80	248	22.6								10.0	73.0	
III-K	10.10	6.00	4.00	0.848	3.000	0.480	22.6	1112.6	0.5	325	29.2	11.33	278	25.0	23.50	262	23.6								10.2	cloudy	Amount of alum and the
IV-K	10.10	6.00	3.80	0.829	6.000	0.480	22.2	1141.8	0.5	398	34.8	11.00	286	25.0	23.20	270	23.6								10.2	86.0	pH varied for tests
I-B	10.40	7.88	6.00	0.543	0.750	0.015	29.7	1031.1	0.5	98	9.5	5.67	85	8.3	18.00	85	8.3	585	22.0	40.0	65.0	111.0			9.8	92.0	I-B through IV-B.
II-B	10.40	8.00	4.75	0.526	1.500	0.015	29.7	1032.0	0.5	535	51.8	5.33	304	29.4	18.00	280	27.1	545	18.0	33.0	51.0	91.0				86.0	
III-B	10.40		4.50		3.000	0.015	29.8	1031.5	0.5	516	50.0	5.00	381	36.9	18.00	356	34.5	605	14.0	27.0	45.0	80.0			9.8	84.0	pH was varied for tests
IV-B	10.40		4.30		6.000	0.015	29.6	1061.5	0.5	388	36.5	4.75	325	30.6	24.67	288	27.1	630	24.0	42.0	65.0		121.0	150.0	8.0	88.0	I-E through III-E, I-G
I-E	10.30	7.90	4.75	0.486	1.500	0.480	27.5	1082.8	0.5	516	47.6	6.16	290	26.8	24.33	220	20.2	715	17.0	28.5	45.0		84.0	105.0	9.0	82.0	through III-G, I-H
II-E	10.30	7.90	4.50	0.626	1.500	0.480	28.0	1088.1	0.5	427	39.2	5.84	256	23.5	24.00	198	34.8	740	21.0	35.0	54.0		96.5	124.5	10.0	93.0	through III-H, and I-J
III-E	10.30	6.00	4.25	0.915	1.500	0.480	28.5	1100.3	0.5	334	30.4	5.54	222	20.2	24.00	272	25.8								7.0		through III-J.
I-G	10.10	8.00	4.80	0.427	1.500	0.480	29.5	1080.4	0.5	524	48.5	11.25	376	34.8	23.25										9.0	89.0	
II-G	10.10	7.00	4.55	0.493	1.500	0.480	30.0	1084.1	0.5	518	47.7	11.00	405	37.3	23.00	292	26.9								10.0	84.0	
III-G	10.10	6.00	4.28	0.868	1.500	0.480	30.5	1098.9	0.5	392	35.7	10.50	314	28.6	22.50	235	21.4								7.0	91.0	
I-H	10.30	8.00	4.35	305.0a	1.500	0.480	27.0	1368.0	0.5	628	45.9	4.75	339	24.8	23.80	282	20.6								9.0	91.0	
II-H	10.30	7.00	4.25	416.0a	1.500	0.480	26.8	1479.0	0.5	614	41.5	4.33	316	21.4	23.33	298	20.1								12.0	88.0	
III-H	10.30	6.00	4.00	662.0a	1.500	0.480	27.1	1725.0	0.5	475	27.5	4.00	287	16.6	23.00	238	13.8								8.0	cloudy	
I-J	10.10	7.90	5.30	350.0a	15.00b	0.480	27.0	1413.0	0.5	149	10.5	5.00	109	7.7	19.20	109	7.7								10.0	cloudy	
II-J	10.10	7.00	5.00	450.0a	15.00b	0.480	27.0	1513.0	0.5	260	17.2	4.80	185	12.2	18.80	173	11.4								11.0	80.0	
III-J	10.10	6.00	4.25	700.0a	15.00b	0.480	26.8	1763.0	0.5	395	22.4	4.50	234	13.3	18.50	210	11.8										

(a) Acid received from Chlorination stage of pulp process used. (pH of 1.9 at 25°C)

Amount in column is in milliliters.

(b) Alum "mud" used. 18% $Al_2(SO_4)_3$. 500 milliliters of this Alum diluted with 400
milliliters of H_2O. Amount in column in milliliters.

FIGURE I EFFECT OF AMOUNT OF SEPARAN

ON VOLUME OF SETTLED SLUDGE

AT PH OF 4.05- 4.30
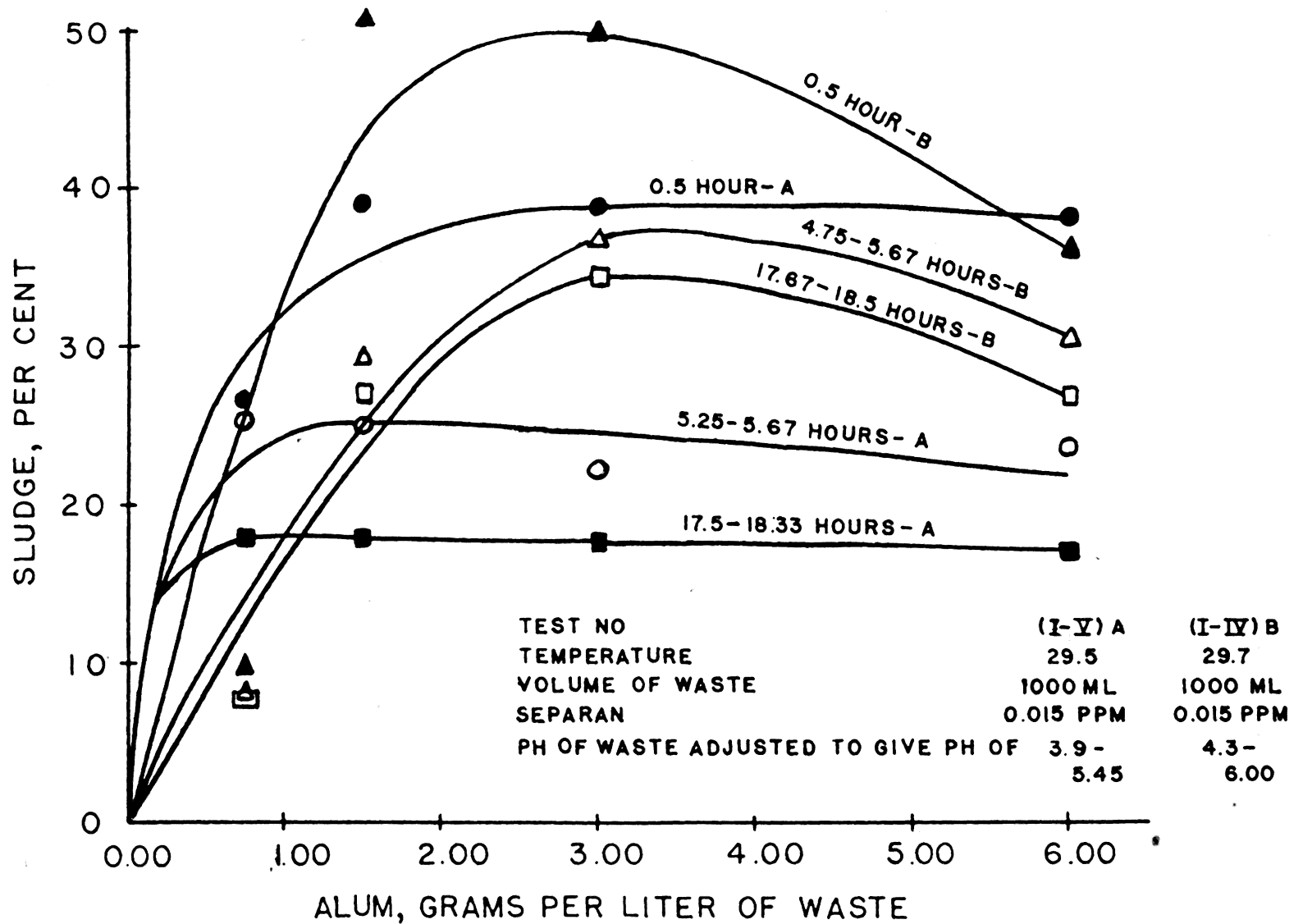
FIGURE 2 EFFECT OF AMOUNT OF ALUM
ON VOLUME OF SLUDGE
USING 0.015 PPM SEPARAN

Chart labels:
- 0.5 HOUR -B
- 0.5 HOUR- A
- 4.75- 5.67 HOURS-B
- 17.67- 18.5 HOURS- B
- 5.25- 5.67 HOURS - A
- 17.5- 18.33 HOURS - A

Y-axis: SLUDGE, PER CENT
X-axis: ALUM, GRAMS PER LITER OF WASTE

TEST NO	(I–V) A	(I–IV) B
TEMPERATURE	29.5	29.7
VOLUME OF WASTE	1000 ML	1000 ML
SEPARAN	0.015 PPM	0.015 PPM
PH OF WASTE ADJUSTED TO GIVE PH OF	3.9 – 5.45	4.3 – 6.00

TESTS (I-IV)D AND (I-II)C
TEMPERATURE - 27° C
VOLUME OF WASTE - 1000 ML
ALUM- 1,5 GM/LITER
PH OF WASTE ADJUSTED TO
GIVE FINAL PH OF 5.7-5.82

SEPARAN, PARTS PER MILLION

FIGURE 3 EFFECT OF AMOUNT OF SEPARAN
ON VOLUME OF SETTLED SLUDGE
AT PH OF 5.7- 5.82
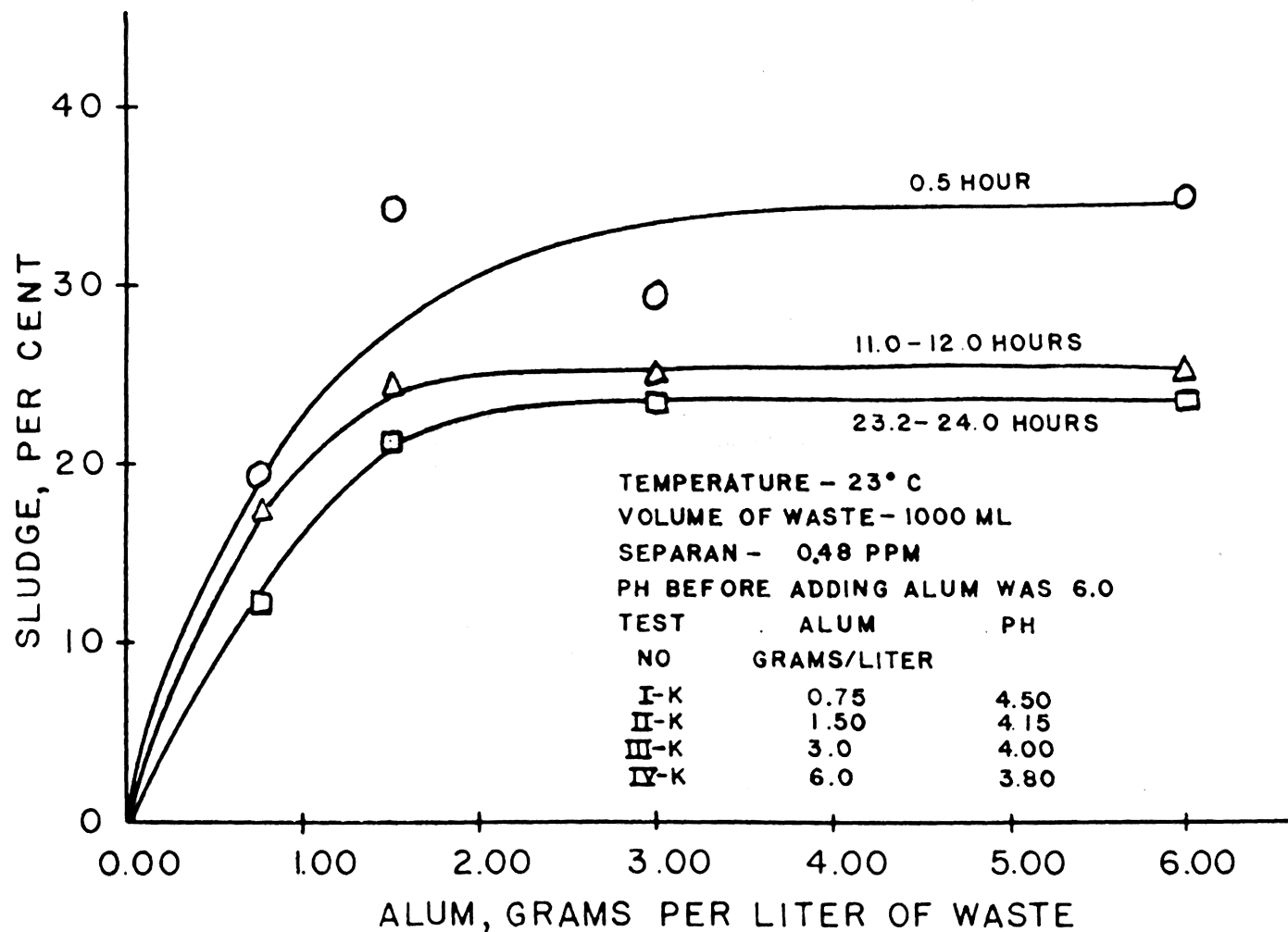
FIGURE 4 EFFECT OF AMOUNT OF ALUM

ON VOLUME OF SLUDGE

USING 0.5 PPM SEPARAN
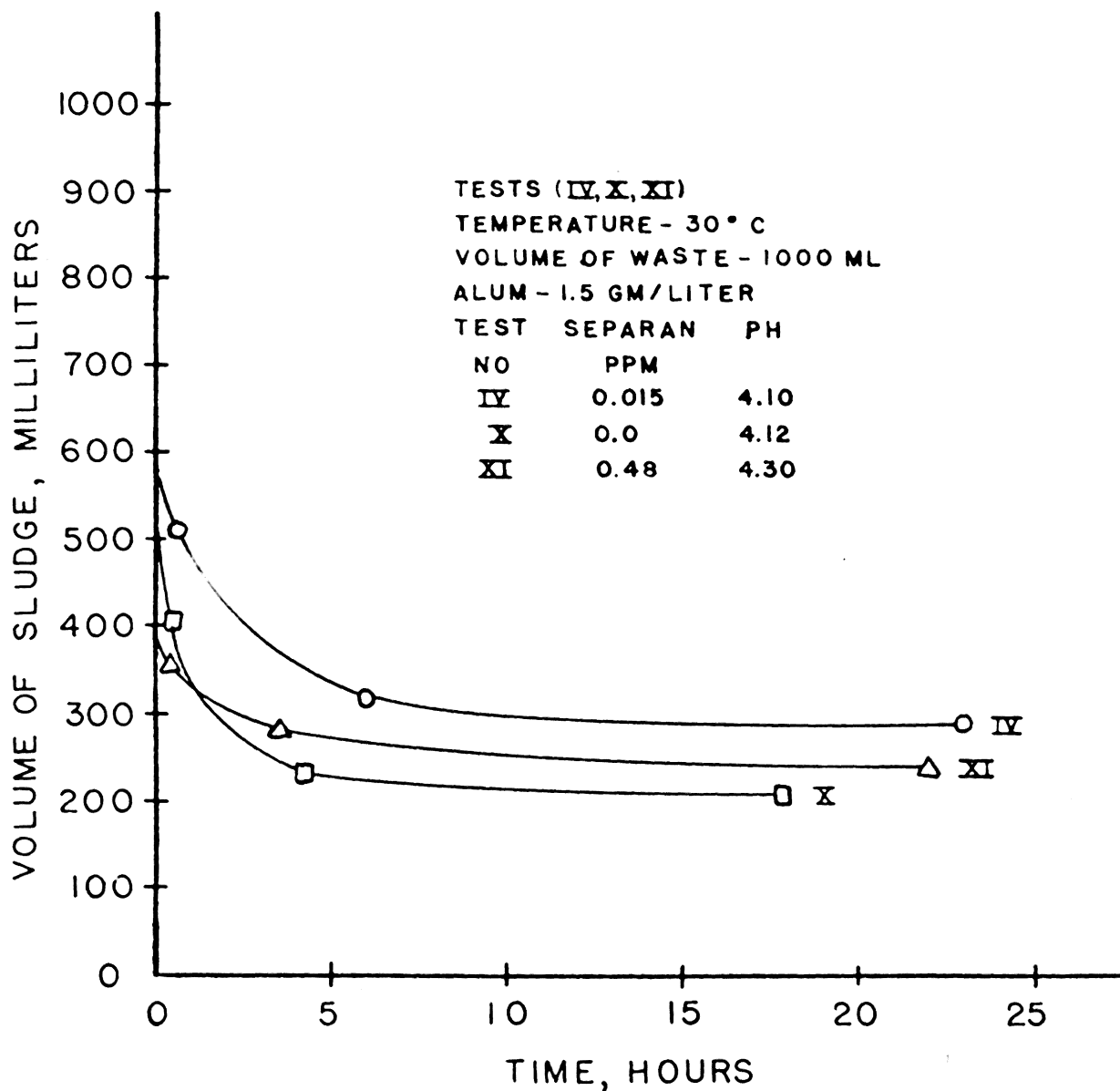
FIGURE 5 EFFECT OF SEPARAN ON
SETTLING OF SLUDGE
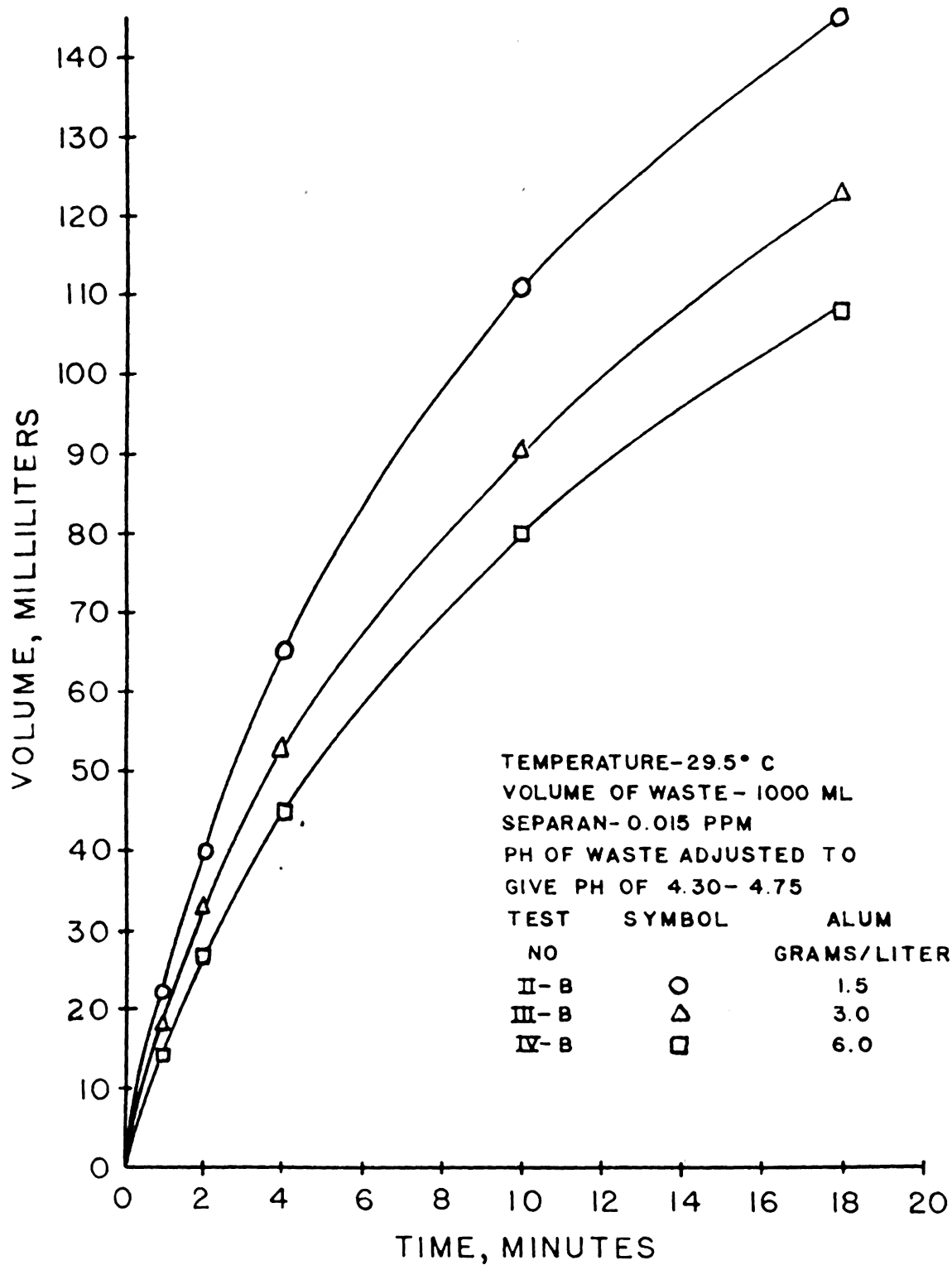
FIGURE 6 EFFECT OF VARYING AMOUNT OF ALUM
ON RATES OF FILTRATION
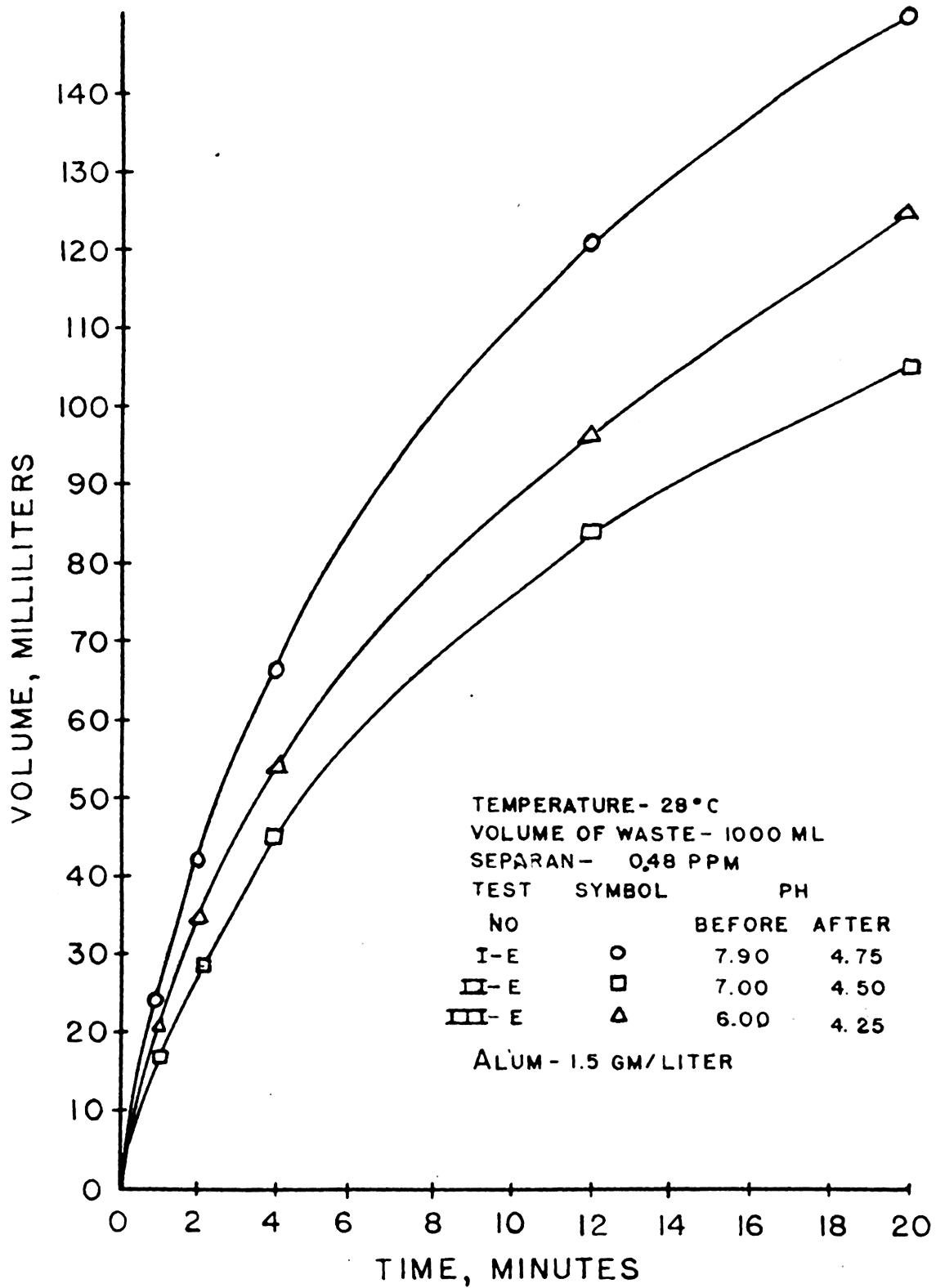
FIGURE 7 EFFECT OF VARYING PH ON RATES OF FILTRATION

TESTS (IV - XIII)
TEMPERATURE - 30° C
VOLUME OF WASTE - 1000 ML
ALUM - (C. P.) 1.5 GM/LITER
PH OF WASTE ADJUSTED TO
GIVE PH OF 4.05 - 4.30
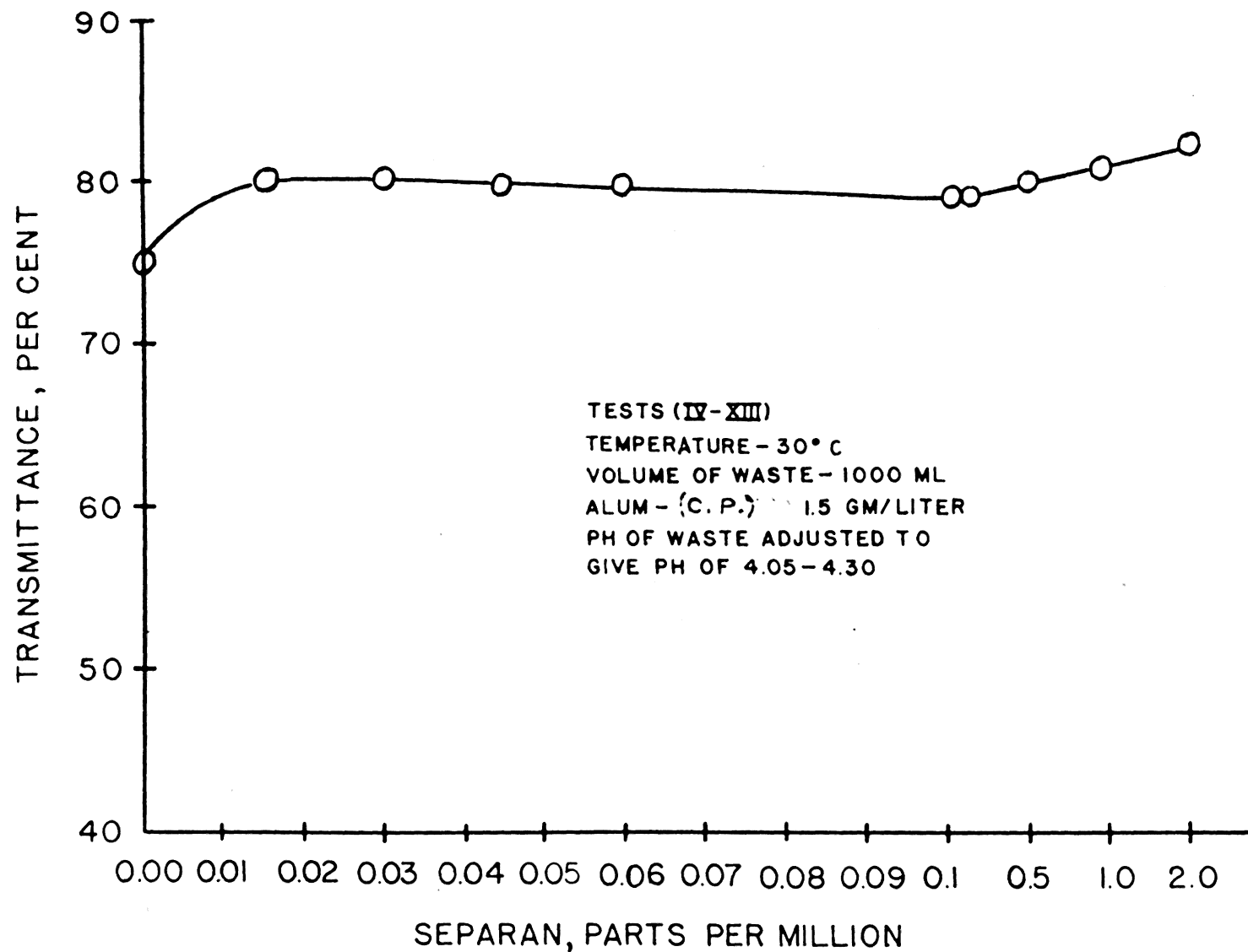
FIGURE 8 EFFECT OF AMOUNT OF SEPARAN ON THE TRANSMITTANCE
OF THE SUPERNATENT LIQUOR

TESTS (I-V) A
TEMPERATURE - 31° C
VOLUME OF WASTE - 1000 ML
SEPARAN- 0.015 PPM
PH OF WASTE ADJUSTED TO
GIVE PH OF 3.9- 5.45
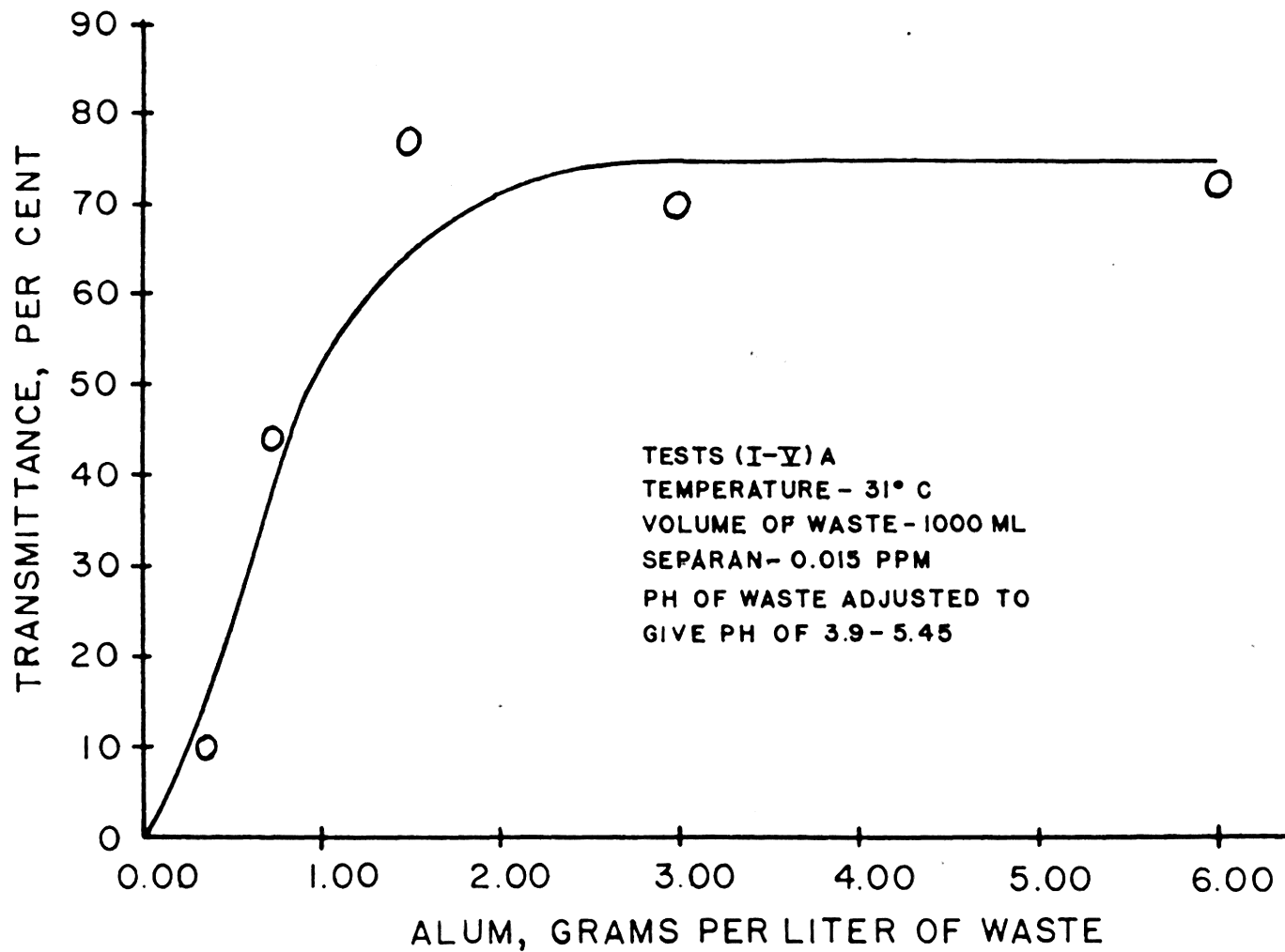
FIGURE 9 EFFECT OF AMOUNT OF ALUM ON THE TRANSMITTANCE
OF THE SUPERNATENT LIQUOR
AT PH OF 3.9-5.45

TESTS (I- IV)B
TEMPERATURE - 29.7 °C
VOLUME OF WASTE - 1000 ML
SEPARAN - 0.015 PPM
PH OF WASTE ADJUSTED TO
GIVE PH OF 4.30 - 6.00
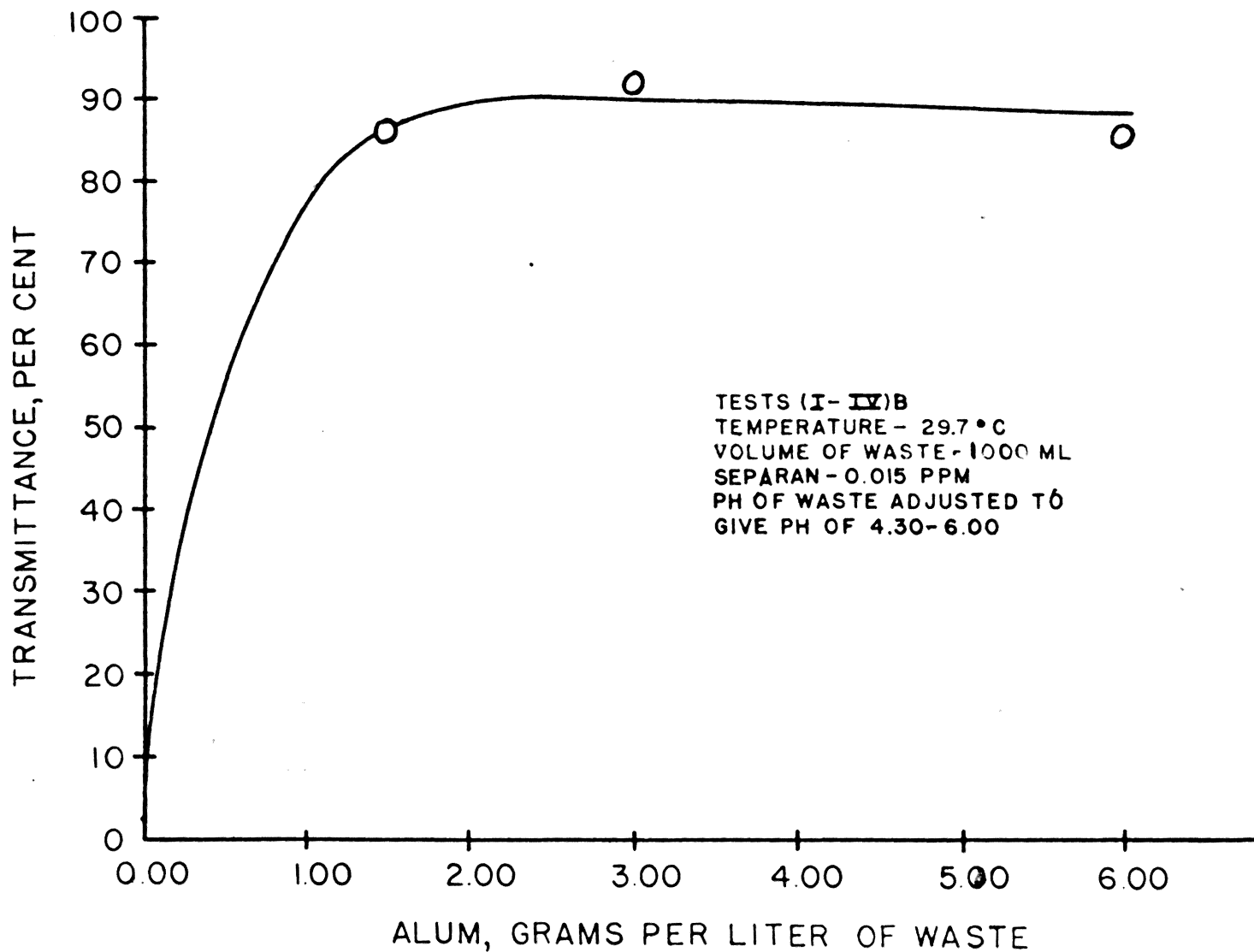
FIGURE 10 EFFECT OF AMOUNT OF ALUM ON THE TRANSMITTANCE

OF THE SUPERNATENT LIQUOR

AT PH OF 4.30 - 6.00

TESTS (I-Ⅲ)H
TEMPERATURE - 27° C
VOLUME OF WASTE - 1000 ML
ALUM (C. P) - 1.5 GM/LITER
SEPARAN - 0.48 PPM
PH OF WASTE ADJUSTED TO
GIVE FINAL PH OF 4.00 - 4.35
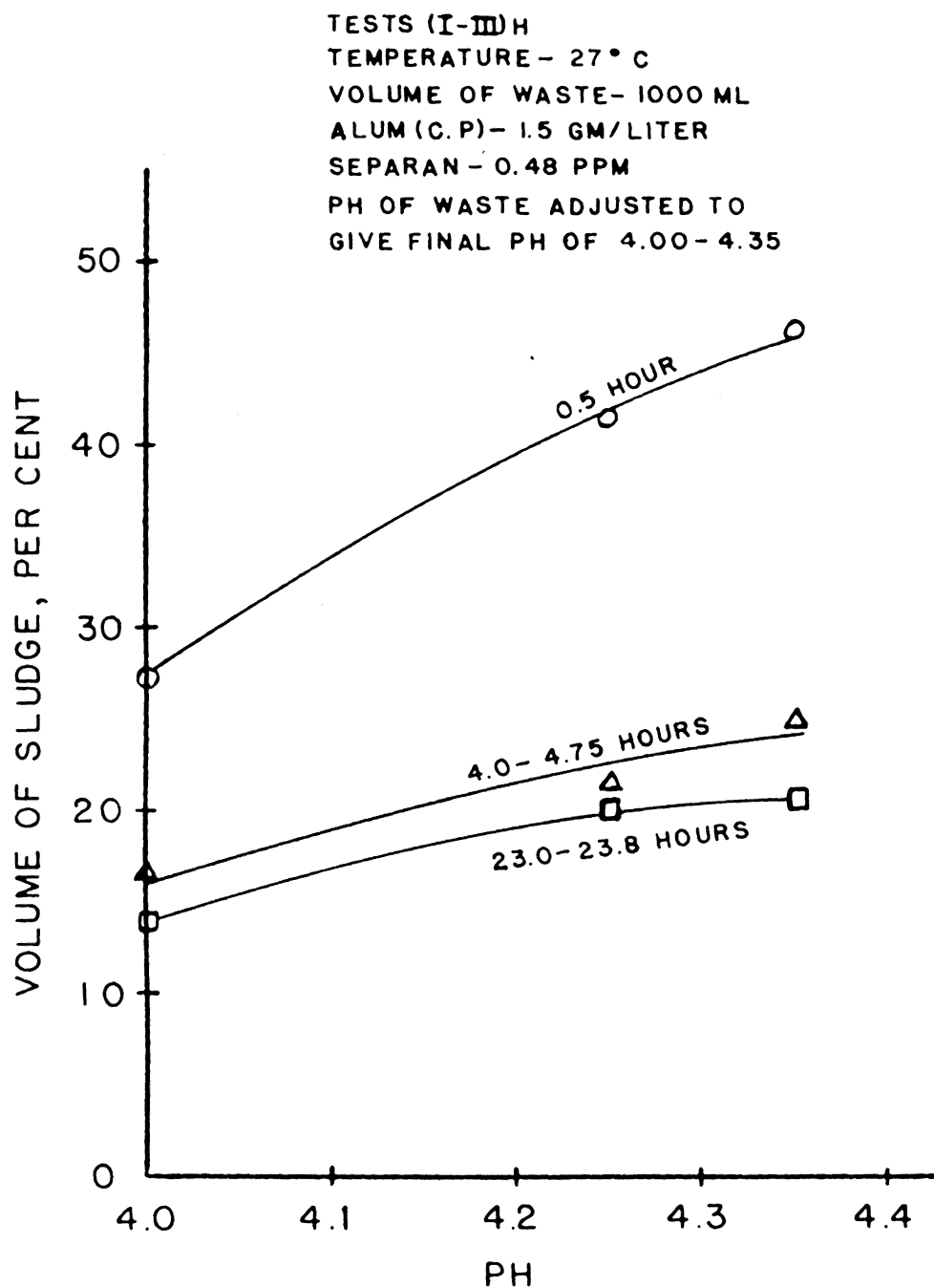
FIGURE 11 EFFECT OF PH ON VOLUME OF SLUDGE
USING WASTE ACID FROM CHLORINE
BLEACH AND C. P. STOCK ALUM

TESTS (I-III) J
TEMPERATURE — 27°C
VOLUME OF WASTE — 1000 ML
ALUM SLURRY — 1.5 — 1.55 GM/LITER
SEPARAN — 0.48 PPM
PH OF WASTE ADJUSTED TO
GIVE FINAL PH OF 4.25 — 5.30

0.5 HOUR

4.5 — 5.0 HOURS

18.5 — 19.2 HOURS

FIGURE 12 EFFECT OF PH ON VOLUME OF SLUDGE
USING WASTE ACID AND ALUM SLURRY

TABLE III.

Experimental Conditions and Results from Various Treatments

of Caustic Liquor to Remove Color

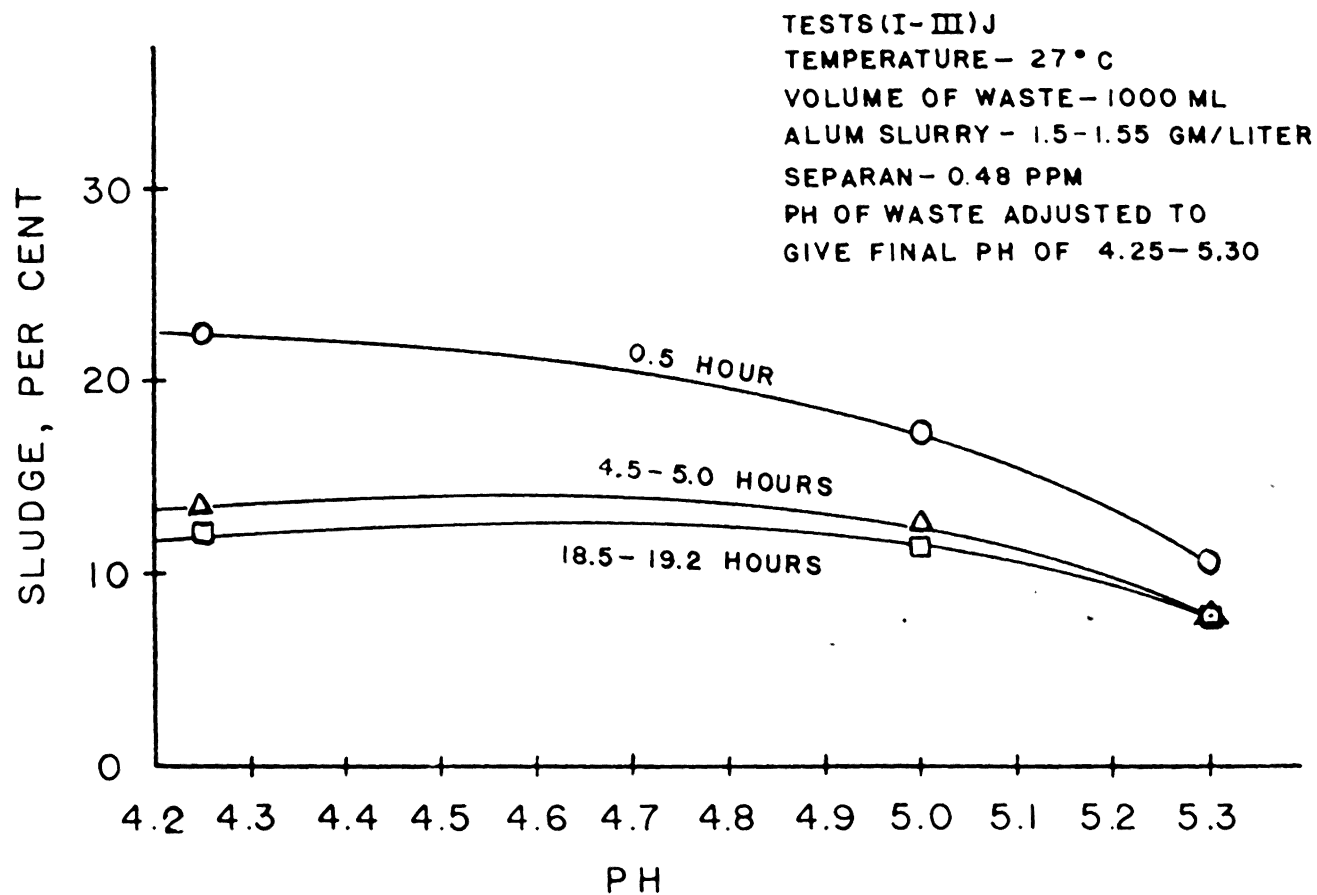| Book 817 Test No.	Page No.	pH of Waste[a]	pH After Adding 0.5 N Sulfuric Acid	pH After Adding C.P. Alum or Alum Slurry	Acid Added Gm/L[b]	Alum Added Gm/L	Flocculating Agent or Cl₂ Added ppm	Temp. When chemicals added °C	Total Volume Ml	0.25 Hr Vol Ml	0.25 Hr %	0.50 Hr Vol Ml	0.50 Hr %	Time Hr	Vol Ml	%	Time Hr	Vol Ml	%	Vol Decanted Ml	Filtrate 1 Min Ml	2 Min Ml	4 Min Ml	10 Min Ml	12 Min Ml	20 Min Ml	Transm. Before %	Transm. After %	Remarks
							C.P. Alum — Burtonite																						
I-F	89	10.20	10.20	5.60	0.00	1.51	5.00	28.3	1020.1	-----	---	381	37.4	7	214	21.0	19	202	19.8								5.0	Cloudy	No acid added to waste.
II-F	89	10.20	6.00	4.30	0.90	1.51	5.00	26.2	1056.7	-----	---	337	31.9	7	196	18.6	19	186	17.6	780	22.0	36.0	55.5	-----	100.5	127.0	10.0	80.0	Alum added before B. in I, II-F
III-F	89	10.20	7.00	4.70	0.54	1.50	5.00	26.5	1042.0	-----	---	495	47.5	7	259	24.8	19	247	23.6	715	19.0	33.5	54.0	-----	103.0	129.5	9.0	90.0	Burtonite added before alum
IV-F	89	10.20	8.00	4.80	0.46	1.50	5.00	26.4	1038.8	-----	---	495	47.7	7	247	23.8	19	235	22.7	715	23.0	41.0	62.0	-----	102.0	121.0	8.0	92.0	in III-F, IV-F, and V-F.
V-F	89	10.20	6.00	4.35	0.87	1.50	5.00	26.0	1055.3	-----	---	465	44.1	7	214	20.2	19	191	18.1	760	24.0	43.0	66.0	-----	126.0	137.0	10.0	82.0	
							C.P. Alum — Guartec																						
I-L	109	9.60	9.00	4.60	0.21	1.50	5.00	30.4	1028.3	-----	---	557	54.2	5	335	32.6	18	301	29.3	---							7.0	97.0	Transmittances after treatment
II-L	109	9.65	7.00	4.35	0.43	1.50	5.00	30.7	1037.7	-----	---	531	51.1	5	305	29.4	18	262	25.3								9.0	96.0	were good, but results nearly
III-L	109	9.65	6.00	4.03	0.74	1.50	5.00	32.1	1050.0	-----	---	423	40.3	5	266	25.3	18	247	23.5								10.0	90.0	as good were obtained in
IV-L	109	10.00	8.00	4.45	0.37	1.50	5.00	32.2	1035.0	-----	---	537	51.7	5	297	28.7	18	290	28.0								7.6	91.0	tests II-M to V-M using only chemically pure alum.
							C.P. Alum																						
I-M	111	10.00	10.00	5.20	0.00	1.50	----	28.0	1015.0	-----	---	690	67.8	9	327	32.2	21	314	30.9	---							7.0	Cloudy	The pH was adjusted to 10, 9,
II-M	111	9.95	9.00	4.50	0.27	1.50	----	28.0	1026.1	-----	---	635	61.9	9	306	29.7	21	293	28.2	680	23.0	39.5	64.5	118.0	129.0	163.0	7.0	93.0	8, 7, and 6 with 0.5 N H₂SO₄
III-M	111	9.95	8.00	4.30	0.46	1.50	----	27.7	1033.7	-----	---	603	58.4	9	283	27.4	21	271	25.9	670	25.5	44.5	75.0	133.0	147.5	185.0	9.0	87.0	and 1.5 grams of C.P. alum
IV-M	111	9.95	8.00	4.35	0.37	1.50	----	27.5	1030.0	-----	---	614	59.5	9	294	28.2	21	282	27.4	700	14.0	22.5	38.0	81.0	87.0	115.0	8.0	95.0	added per liter of waste.
V-M	111	9.95	6.00	4.00	0.74	1.50	----	27.3	1045.0	-----	---	590	56.5	9	236	22.6	21	224	21.4	744	14.0	23.5	39.0	77.0	82.5	110.0	10.0	90.0	
							Alum Slurry																						
I-N	113	9.90	9.00	5.60	0.26	1.76	----	26.9	1025.7	-----	---	111	10.8	5	95	9.2	17	95	9.2	---							7.0	Cloudy	The pH was again adjusted to
II-N	113	9.90	7.00	5.10	0.29	1.76	----	26.7	1032.9	-----	---	228	22.0	5	182	17.7	17	167	16.1	---							9.0	Cloudy	9, 8, 7, and 6 with 0.5 N H₂SO₄
III-N	113	10.00	8.00	4.20	0.38	2.94	----	26.6	1040.4	-----	---	528	50.6	5	311	29.8	17	296	28.4	740	23.0	40.0	63.0	115.0	124.0	157.0	8.0	91.0	but then alum slurry was added
IV-N	113	10.00	6.00	4.30	0.78	1.76	----	26.5	1046.6	-----	---	378	36.1	5	231	22.1	17	219	20.9	810	17.0	29.0	48.0	84.0	91.0	114.0	10.0	85.0	instead of C.P. alum.
							C.P. Alum — Good-rite K-720S																						
I-O	121	9.50	8.00	4.20	0.28	1.50	0.50	29.9	1031.3	-----	---	635	61.6	5	349	34.8	24	318	30.8	632	26.0	45.0	73.0	126.0	138.0	177.0	9.0	96.0	The pH was adjusted to 8, 7,
II-O	121	9.50	7.00	4.10	0.39	1.50	0.50	29.9	1035.8	-----	---	640	61.8	5	366	35.3	24	318	30.7	672	24.0	42.0	69.0	119.0	130.0	167.0	9.0	96.0	and 6 with 0.5 N H₂SO₄, then
III-O	121	9.65	6.00	4.05	0.62	1.50	0.50	29.9	1045.5	-----	---	476	45.5	5	296	28.4	24	265	25.4	712	11.0	20.5	37.0	78.0	89.0	126.0	10.0	90.0	0.5 ppm of Good-rite K-720S
I-O'	139	10.30	(2) 4.30	(1) 5.50	0.30	1.20	0.50	29.6	1034.0	-----	---	235	23.2	-	---	----	-	---	----								9.0	Cloudy	was added. In tests (I-III)O',
II-O'	139	10.30	(2) 4.30	(1) 6.00	0.47	1.00	0.50	29.2	1036.0	-----	---	190	18.6	-	---	----		---	----								9.0	Cloudy	varying amounts of alum were
III-O'	139	10.30	(2) 4.30	(1) 6.70	0.64	0.80	0.50	29.3	1039.0	-----	---	170	16.4	-	---	----											9.0	Cloudy	added before the acid and the
I-O''	141	10.30	9.20	4.55	0.30	1.50	0.50	29.4	1029.2	-----	---	604	58.6	1	380	36.8											9.2	Cloudy	Good-rite. In test I-O'' the acid was added first.
							C.P. Alum — Good-rite K-721S																						
I-P	125	9.40	7.00	4.20	0.36	1.51	0.50	30.9	1034.6	-----	---	616	59.0	5	321	31.0	24	284	27.3	672	16.0	29.0	50.0	94.0	104.0	136.0	9.8	94.0	These tests were similar to
II-P	125	9.50	6.00	4.40	0.30	1.50	0.50	31.0	1032.4	-----	---	640	61.9	5	321	31.0	24	295	28.5	640	20.0	37.0	62.0	113.0	125.0	161.0	9.4	96.0	(I-III) O except that Good-rite
III-P	125	9.50	6.00	4.00	0.62	1.50	0.50	31.0	1045.4	-----	---	486	46.5	5	276	26.4	24	243	23.1	700	19.0	33.0	56.0	101.0	112.0	148.0	10.0	92.0	K-721S was used.
							Alum Slurry																						
I-R	129	9.50	8.00	4.10	0.29	1.70	----	29.0	1041.7	-----	---	538	50.6	16	270	25.9	18	258	24.4	714	8.0	14.0	24.0	51.5	59.5	87.0	9.2	94.0	These tests determined the
II-R	129	9.50	7.80	5.20	0.32	0.83	----	29.0	1027.9	-----	---	121	11.8	16	97	9.4	18	97	9.4		Cloudy						8.4	Cloudy	effect of varying the amount
III-R	129	9.55	8.00	6.30	0.30	0.44	----	29.1	1020.4	-----	---	No perceptible sludge									Cloudy						---	Cloudy	of alum slurry on transmittance and settling rates of the waste.
							Alum Slurry — 5% Ca(OH)₂																						
I-S	135	8.90	-----	4.90 / 4.90 (Ca(OH)₂ 0.00)		2.16	----	29.0	1012.0	-----	---	254	25.3	1	266	26.5	2	237	23.6	No Filtration Tests							10.0	Cloudy	After adding alum slurry, 5 per
II-S	135	9.00	-----	4.80 / 6.00 (Ca(OH)₂ 0.50)		2.25	----	29.0	1022.0	-----	---	285	37.6	1	326	31.8	2	278	27.1								10.0	Cloudy	cent Ca(OH)₂ was added to raise
III-S	135	9.00	-----	5.00 / 7.00 (Ca(OH)₂ 0.80)		2.16	----	28.8	1028.0	-----	---	448	43.6	1	384	37.8	2	308	29.9								10.0	Cloudy	the pH to 5, 6, 7, and 8.
IV-S	135	9.00	-----	5.00 / 8.00 (Ca(OH)₂ 1.18)		2.16	----	28.5	1035.5	-----	---	542	52.4	1	486	47.0	2	349	33.7								10.0	Cloudy	
							Waste Heated — 5% Ca(OH)₂																						
I-Q	137	8.80	-----	4.70 / 4.70 (Ca(OH)₂ 0.00)		2.16	----	48-52	1012.0	-----	---	234	23.3	1	223	22.2	10	198	19.7	No Filtration Tests							10.1	Cloudy	The transmittances and settling
II-Q	137	8.80	-----	4.70 / 6.10 (Ca(OH)₂ 0.55)		2.16	----	48-52	1023.0	-----	---	238	23.5	1	214	21.1	10	203	20.0								10.1	Cloudy	rates were determined using
III-Q	137	8.80	-----	4.70 / 7.10 (Ca(OH)₂ 1.00)		2.16	----	48-52	1032.0	-----	---	216	21.1	1	204	19.9	10	180	17.5								10.1	Cloudy	alum slurry and adjusting pH
IV-Q	137	8.80	-----	4.50 / 8.00 (Ca(OH)₂ 1.40)		2.34	----	48-52	1040.0	-----	---	251	24.1	1	226	21.7	10	188	18.1								10.1	Cloudy	with 5 per cent Ca(OH)₂ at higher temperatures (48-52)°C.
							Alum Slurry — Orzan-P																						
1[c]	193	10.00	8.90	6.90	0.29	1.50	0.50	27.8	1030.4	-----	---	Cloudy															10.2	Cloudy	The pH was varied and 0.5 ppm
2	193	10.00	8.00	6.35	0.38	1.50	0.50	27.8	1034.0	-----	---	Cloudy															10.2	Cloudy	of flocculating agent, Orzan
3	193	10.00	7.10	5.35	0.56	1.50	0.50	27.8	1041.0	-----	---	371	36.0	2	246	23.6	19	220	21.1								10.2	78.0	P, was used.
4	195	10.00	9.00	6.70	0.29	1.50	1.00	27.7	1043.0	-----	---	Cloudy															10.2	Cloudy	Tests repeated using 1.0 ppm
5	195	10.00	8.00	6.05	0.37	1.50	1.00	27.7	1043.5	-----	---	Cloudy															10.2	Cloudy	of Orzan P.
6	195	10.00	7.10	5.20	0.59	1.50	1.00	27.7	1052.5	-----	---	357	33.9	1	293	27.6	18	222	21.1								10.2	86.0	
1-a	199	10.00	9.00	6.80	0.28	1.50	0.50	30.6	1024.8	-----	---	Cloudy															10.3	Cloudy	The pH was varied and 0.5 ppm
2-a	199	10.00	8.00	6.80	0.38	1.50	0.50	30.6	1028.8	-----	---	Cloudy															10.3	Cloudy	of Orzan P solution that was
3-a	199	10.00	7.00	5.05	0.71	1.50	0.50	30.6	1042.3	-----	---	393	37.7	6	208	20.0	24	208	20.0								10.3	83.0	heated was added.
1-b	201	10.00	9.00	6.65	0.21	1.50	----	29.2	1016.2	-----	---	Cloudy															10.3	Cloudy	The pH was varied and only
2-b	201	10.00	7.00	5.00	0.41	1.50	----	29.2	1024.8	-----	---	421	41.1	-	---	----	21	208	20.0								10.3	Cloudy	alum slurry then added.
1-c	203	10.00	7.00	4.90	0.43	1.50	1.00	29.2	1035.0	-----	---	335	32.6	-	---	----	21	188	17.9								10.3	Cloudy	Added 1.0 ppm Orzan at pH 7.
2-e	209	10.00	5.95	4.08	0.82	1.50	1.00	29.2	1051.9	-----	---	380	35.2	-	---	----	20	224	21.6								10.1	84.0	Added 1.0 ppm Orzan at pH 6.
2-f	211	10.00	6.00	4.50	0.81	1.13	1.00	31.8	1049.4	-----	---	257	24.5	-	---	----	19	182	17.3								10.1	Cloudy	Test 2-e repeated using less alum.
							Alum Slurry — Lytron X-866																						
1-d	205	10.00	7.00	4.95	0.41	1.50	0.50	29.0	1032.2	-----	---	407	39.6	-	---	----	1.5	233	22.6								10.3	Cloudy	The pH of waste was varied and
2-d	205	10.00	8.00	5.85	0.31	1.50	0.50	29.0	1026.0	-----	---	Cloudy															10.3	Cloudy	0.5 ppm of Lytron X-866 added.
3-d	207	10.00	7.00	4.90	0.42	1.50	1.00	29.0	1035.3	-----	---	293	28.3	-	---	----	6	200	19.6								10.3	Cloudy	The pH of waste was varied and
4-d	207	10.00	7.95	5.75	0.30	1.50	1.00	29.0	1030.5	-----	---	194	18.8	-	---	----	6	140	13.7								10.3	Cloudy	1.0 ppm of Lytron X-866 added.
3-e	209	10.00	6.00	4.00	0.81	1.50	1.00	29.0	1051.5	-----	---	390	37.0	-	---	----	20	239	22.6								10.1	85.0	Added 1.0 ppm Lytron X-886 at pH 6.
3-f	211	10.00	6.00	4.45	0.81	1.13	1.00	31.8	1049.4	-----	---	277	26.4	-	---	----	19	182	17.3								10.1	Cloudy	Test 3-e repeated using less alum.
1-e	209	10.00	6.00	4.00	0.82	1.50	----	32.0	1041.9	-----	---	367	35.2	-	---	----	20	224	21.6								10.1	83.0	Only alum slurry added at pH 6.
1-f	211	10.00	6.00	4.50	0.82	1.13	----	31.8	1039.6	-----	---	284	27.3	-	---	----	19	196	18.9								10.1	Cloudy	Test 1-e repeated using less alum.
							Alum Slurry																						
1-f'	229	9.5	(1) 6.00 (3) 4.00	(2) 5.00	1.04	1.00	----	26.4	1047.1	Cloudy																	3.0	Cloudy	Test 1-f repeated; 1.00 grams alum added then more acid to complete lowering of pH.
							8.8% FeSO₄																						
1-A	219	9.50	9.00	7.40	0.15	1.5	----	25.0	1008.0	Cloudy																	3.0	Cloudy	10 per cent FeSO₄ was added
2-B	219	9.50	8.00	7.10	0.25	1.5	----	25.0	1012.0	Cloudy																	3.0	Cloudy	to the waste at pH of 9, 8, 7,
3-C	219	9.50	7.00	6.80	0.37	1.0	----	25.0	1017.0	Cloudy																	3.0	Cloudy	and 6.
4-D	219	9.50	6.00	6.00	0.81	1.0	----	25.0	1035.0	Cloudy																	3.0	Cloudy	
							Chlorination Waste Liquor[e] / Alum Slurry cc/l																						
B	232	9.50	6.00	3.85	775	2.54	----	25.0	1787.0	No Settling Tests																	3.0	Cloudy	Chlorination stage waste was
B-I	235	9.50	6.55	6.15	475	0.63	----	25.0	1478.0	No Perceptible Sludge																	3.0	Cloudy	used to lower the pH of the
B-II	235	9.50	6.55	5.80	475	1.06	----	25.0	1480.0	No Perceptible Sludge																	3.0	Cloudy	caustic waste, then varying
B-III	235	9.50	6.60	5.35	475	1.48	----	25.0	1482.0	No Perceptible Sludge																	3.0	Cloudy	amounts of alum slurry (0.63-
B-IV	235	9.50	6.55	4.85	475	1.90	----	25.0	1484.0	595	40.0	430	29.0	0.75	365	24.5	1	325	22.0								3.0	80.0	2.54 grams per liter of waste)
B-V	235	9.50	6.50	5.10	475	1.69	----	25.0	1483.0	Cloudy																	3.0	Cloudy	were added.
							0.5 N H₂SO₄ / Alum Slurry																						
C-I	241	9.25	6.10	4.75	0.90	1.48	----	25.0	1043.9	282	27.0	240	23.0	1	214	20.5	4	160	15.3								3.0	13.5	0.5 N H₂SO₂ was used in place
C-II	241	9.25	6.05	4.35	0.90	1.90	----	24.5	1045.8	522	50.0	407	39.0	1	329	31.5	4	282	27.0								3.0	84.5	of the chlorination stage waste
C-III	241	9.25	5.75	4.40	1.02	1.27	----	24.5	1047.7	408	39.0	314	30.0	1	262	25.0	4	183	17.5								3.0	44.5	and tests B(I-V) repeated, varying
C-IV	241	9.30	5.75	4.20	1.03	1.69	----	25.0	1050.0	484	46.0	315	30.0	1	262	25.0	4	210	20.0								3.0	69.5	pH twice; adding alum over a range
C-V	241	9.30	5.50	4.20	1.10	1.27	----	24.5	1051.0	316	30.0	242	23.0	1	189	18.0	4	161	15.3								3.0	37.0	of 1.27-1.90 grams per liter.
							Conc. HCl, Cl₂ / Alum Slurry / Chlorine																						
E-1	253	9.50	5.45-2.60	2.45	5 cc	1.39	400 cc	24.2	1011.6	203	20.0	162	16.0	0.75	122	12.0	1	122	12.0								3.0	33.0	These tests were performed to
E-2	253	9.50	5.00-5.40	3.95	----	1.39	400 cc	24.1	1006.6	302	30.0	232	23.0	0.75	211	21.0	1	122	12.0								3.0	87.0	discover the alum requirements
E-3	253	9.50	9.50-5.60	4.50	----	1.39	350 cc	24.1	1006.6	267	26.5	232	23.0	0.75	232	23.0	1	232	23.0								3.0	82.0	of the caustic waste if it were
E-4	253	9.50	9.50-6.90	5.70	----	1.39	300 cc	24.0	1006.6	Cloudy																	3.0		first chlorinated.
							10% Na₂CO₃ Added																						
E-1a	257	2.45-3.4	3.40	5.5	----	1.30	----	25.0	1033.3	Cloudy																	33.0	65-70	10 per cent Na₂CO₃ was added to results of test E-1 to clear it.
							0.5 N H₂SO₄ / Alum Slurry																						
F	255	9.10	6.00	4.50	0.95	1.39	----	25.0	1045.6	---	---	309	29.6	-	---	----	final	230	22.0								3.0	85.0	1.4 grams of alum was added slowly over a 3-minute period.
							Waste Heated																						
D-1	248	9.10	6.10	4.65	0.80	1.18	----	41-51	1038.2	Cloudy																	3.0	Cloudy	The waste was first heated to
D-2	248	9.10	6.10	4.50	0.80	1.29	----	40-51	1038.7	Cloudy																	3.0	Cloudy	50°C, acidified with 0.5 N H₂SO₄
D-3	248	9.10	6.10	4.00	0.90	1.48	----	36-50	1044.2	449	43.0	282	27.0	0.75	219	21.0	final	157	15.0								3.0	82.0	and treated with 1.18-1.48 grams
G-1	259	9.10	6.00	4.50	0.96	1.29	----	79-90	1045.4	Cloudy																	3.0	Cloudy	alum. In tests G(1-4), the waste
G-2	259	9.10	6.00	4.35	0.94	1.39	----	77-90	1044.8	481	46.1	402	38.5	-	---	----	final	162	15.5								3.0	80.0	was first acidified to a pH of 6
G-3	259	9.10	6.00	4.20	0.96	1.48	----	79-90	1046.0	523	50.0	232	31.0	-	---	----	final	162	15.5								3.0	80.0	then heated to 90°C, then the
G-4	261	8.85	6.00	4.50	0.91	1.35	----	70-90	1043.4	Cloudy																	3.0	55-60	amount of alum added varied from 1.29-1.48 grams per liter.
							Centrifuge Tests																						
I	145	10.30	6.50	4.10	0.62	3.16	----	25.5	16645.0	Settling Data not Recorded																	10.2	88.0	These tests involved treatment
II	173	9.40	6.55	4.15	0.72	3.32	----	26.0	16721.0	Settling Data not Recorded																	10.0	85.0	of 16 liters of caustic waste
III	223	9.60	6.50	4.15	0.54	3.10	----	27.0	16585.0	13800	83.3	10400	62.9	2	5550	33.4	6	3720	22.4								3.0	89.0	with 0.5 N H₂SO₄ and alum slurry
IV	278	8.20	5.90	4.60	0.92	1.41	----	24.5	16707.0	---	---	8860	53.0	2	4810	28.8	5	3760	22.5								3.0	85.0	to produce large quantities of sludge for centrifuging.

[a] One liter of caustic extraction waste was treated in all tests, with the exception of I-IV, where 16 liters were treated.

[b] The 0.5 N H₂SO₄ contains 0.0245 grams of acid per milliliter.

[c] pH values of tests 1-6, 1-a, 2-a, and 3-a are correct with plus or minus 0.1.

[d] Orzan P solution was heated before adding.

[e] Acid from chlorination stage of pulp bleaching process used. Its pH was 1.90 at 25.0°C. The amount used is given as cc per liter of waste.

TESTS (I–IV)L
TEMPERATURE – 31.5°C
VOLUME OF WASTE – 1000 ML
GUARTEC – 5.0 PPM
ALUM (C. P.) – 1.5 GM/LITER
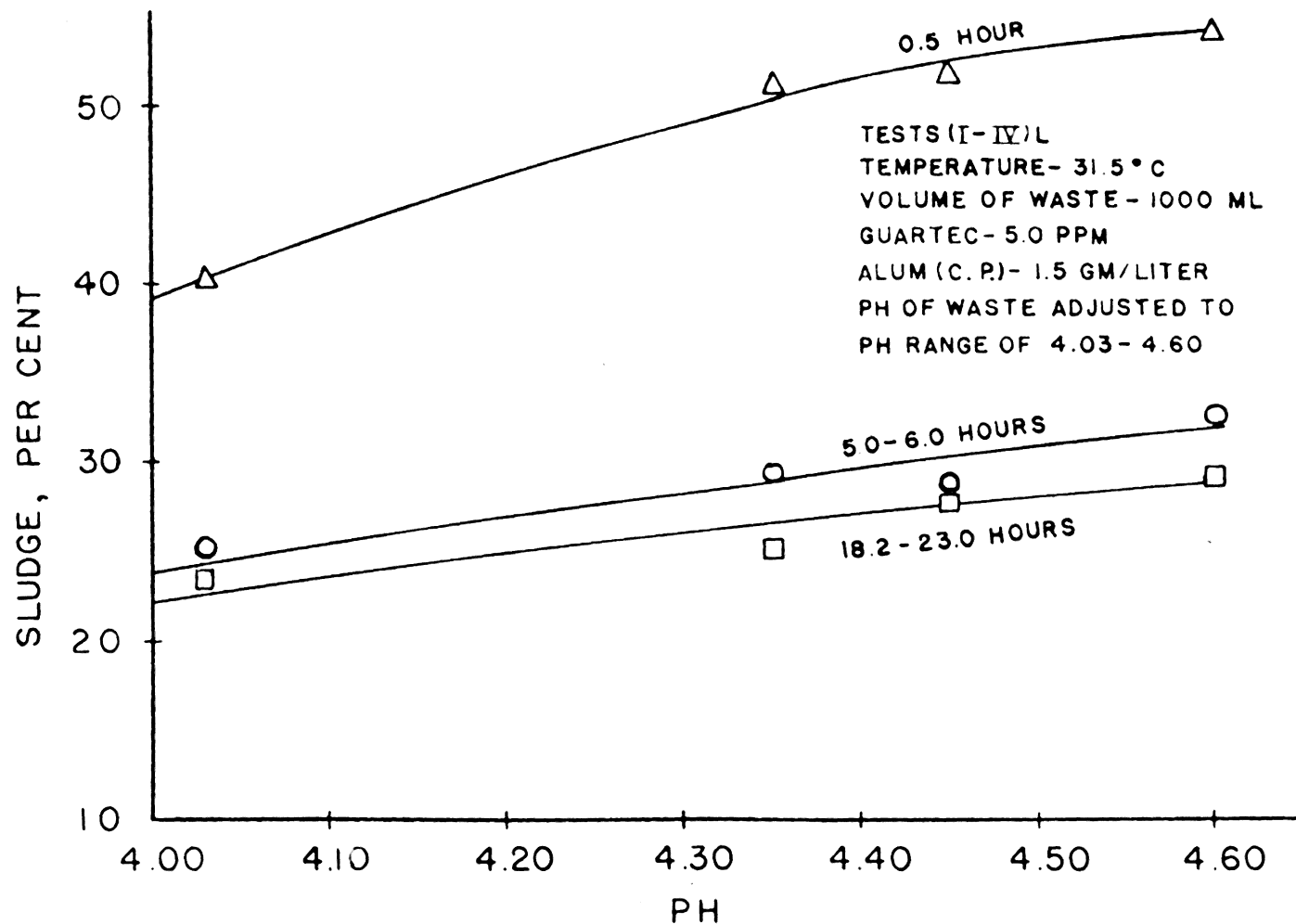PH OF WASTE ADJUSTED TO
PH RANGE OF 4.03 – 4.60

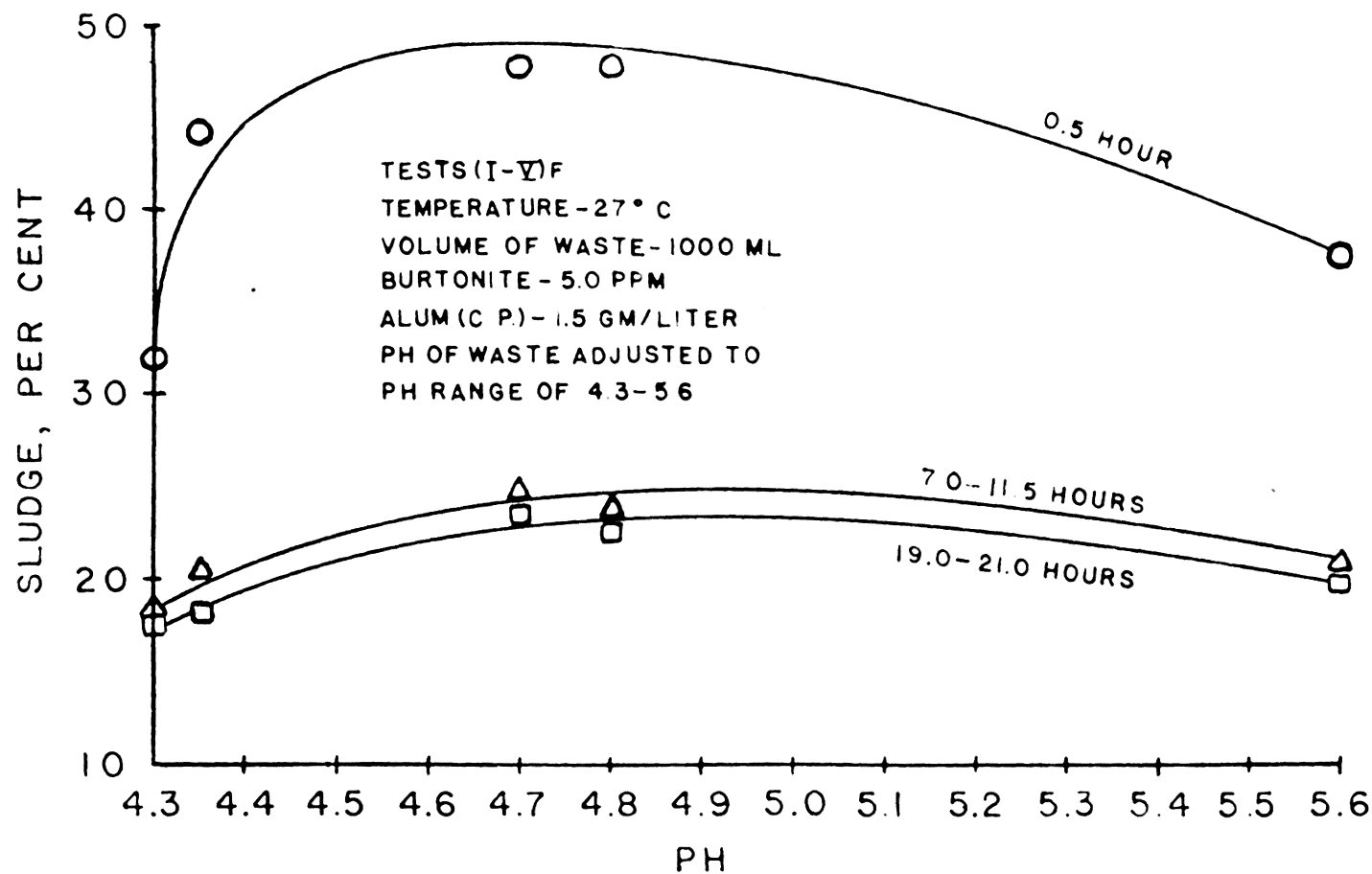FIGURE 13 EFFECT OF VARYING PH USING GUARTEC
ON VOLUME OF SETTLED SLUDGE

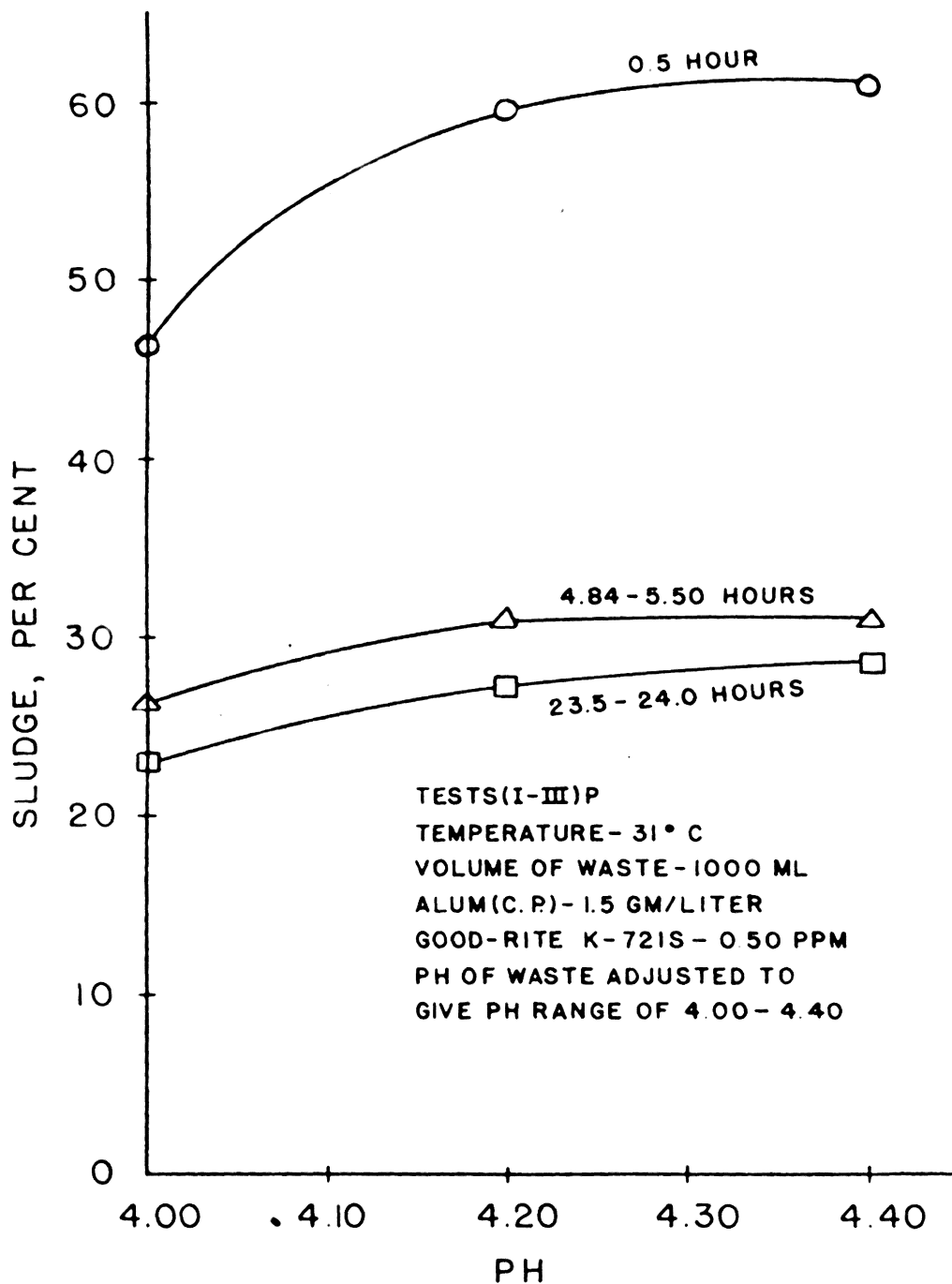FIGURE 14 EFFECT OF VARYING PH USING BURTONITE

ON VOLUME OF SETTLED SLUDGE

FIGURE 15 EFFECT OF VARYING PH USING
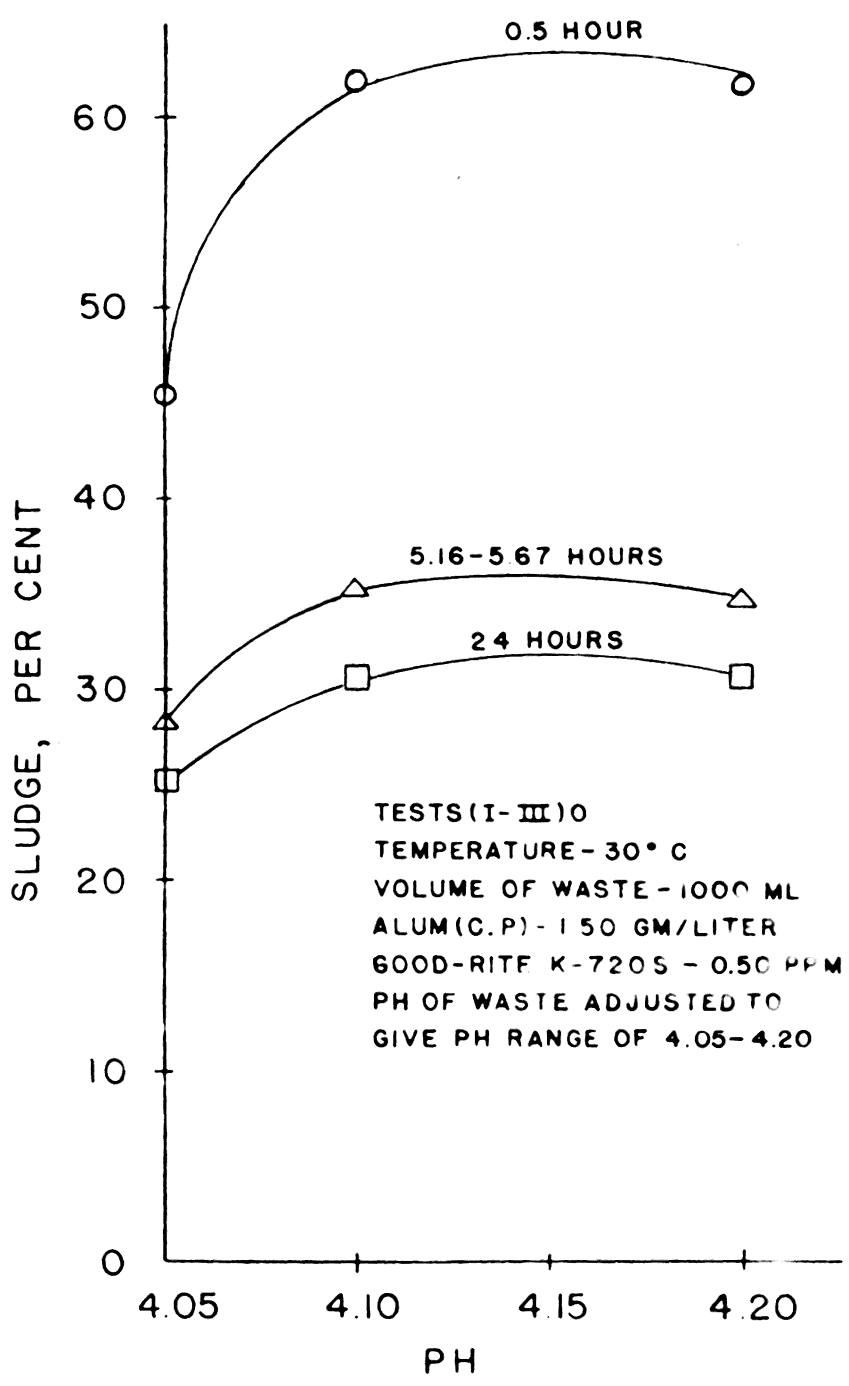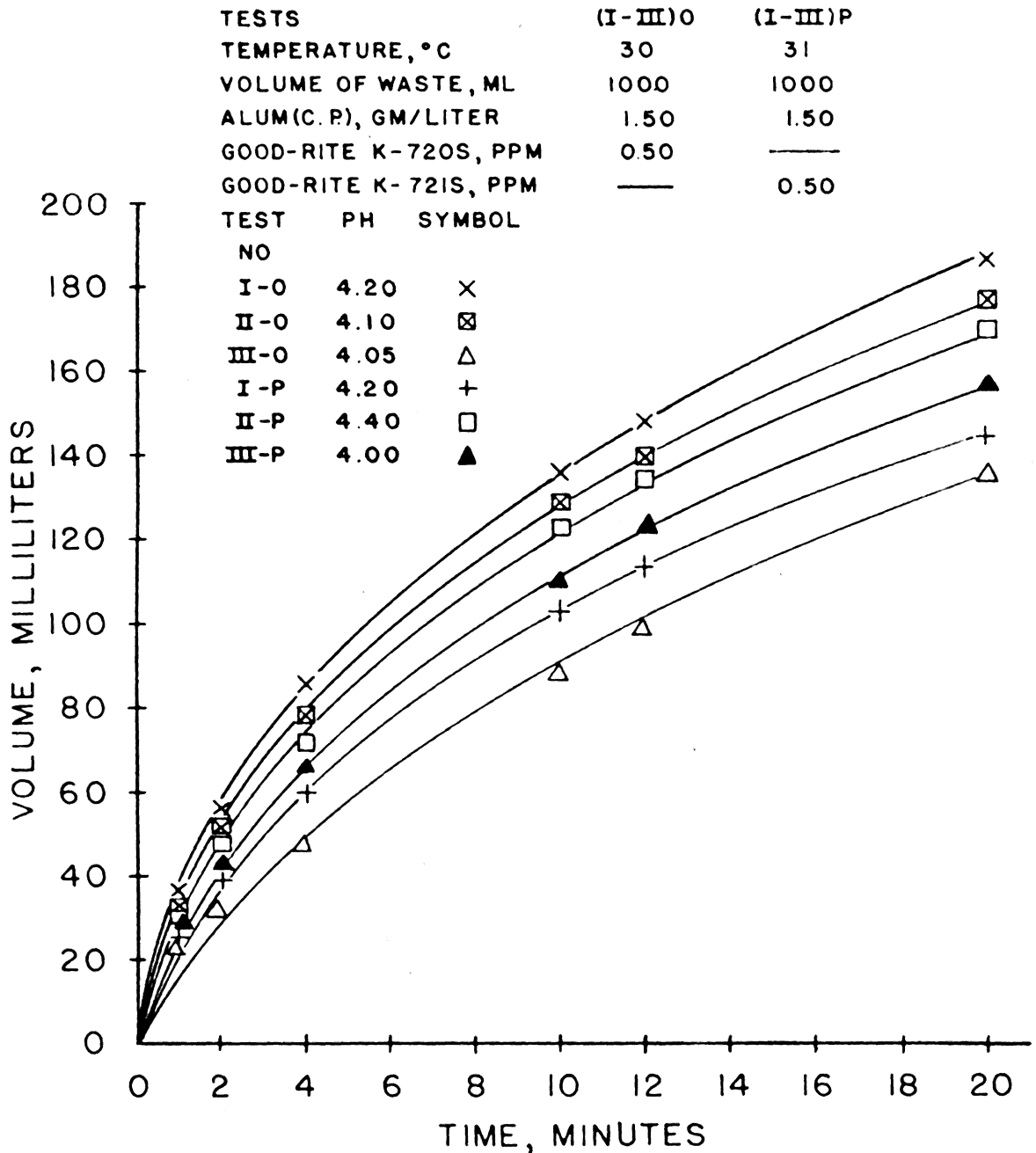GOOD-RITE K-721S ON VOLUME
OF SETTLED SLUDGE

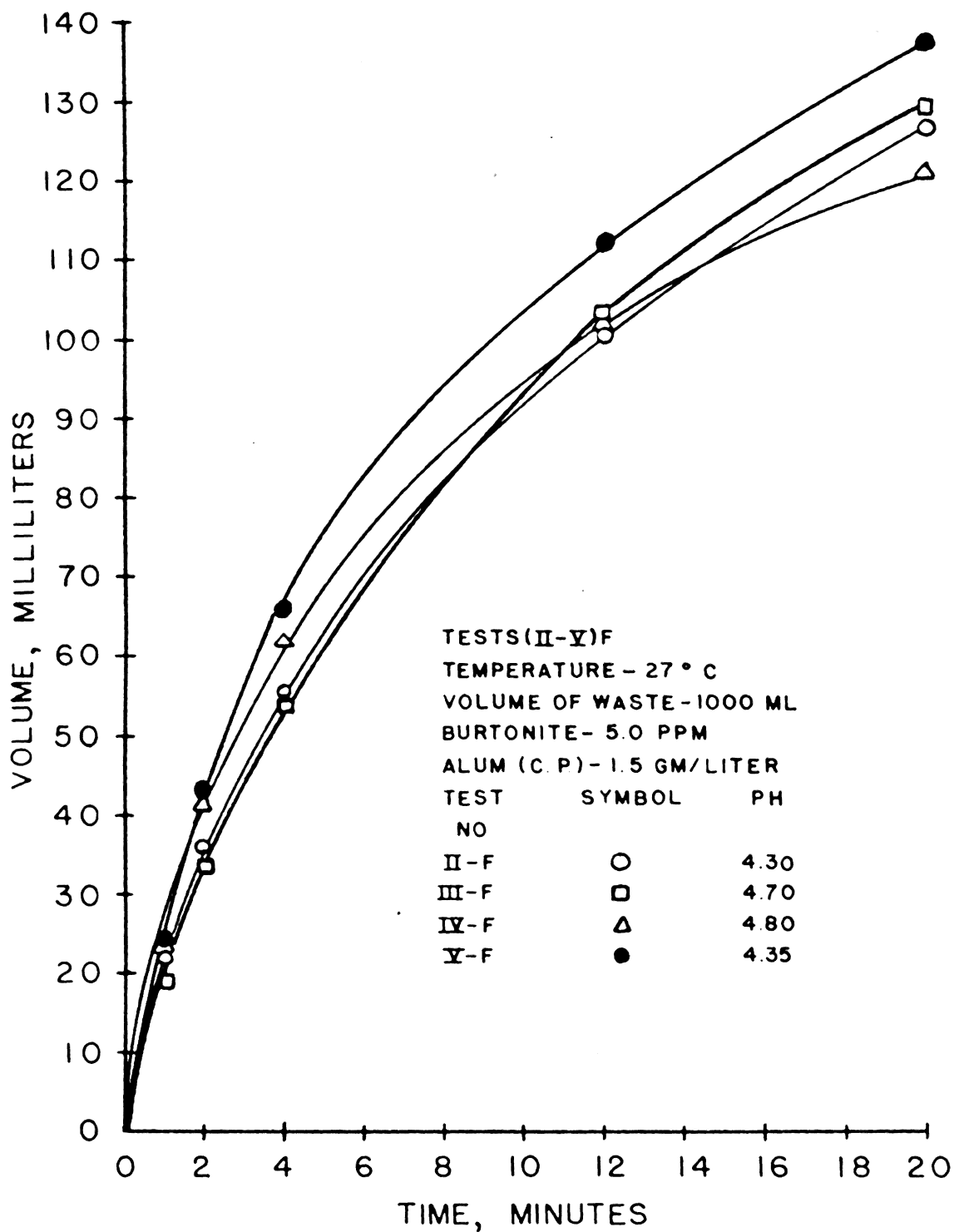FIGURE 16 EFFECT OF VARYING PH USING
GOOD-RITE K-720S ON VOLUME
OF SETTLED SLUDGE

FIGURE 17 EFFECT OF VARYING PH USING
GOOD-RITE K-720S AND K-721S ON
RATES OF FILTRATION

FIGURE 18 EFFECT OF VARYING PH USING BURTONITE
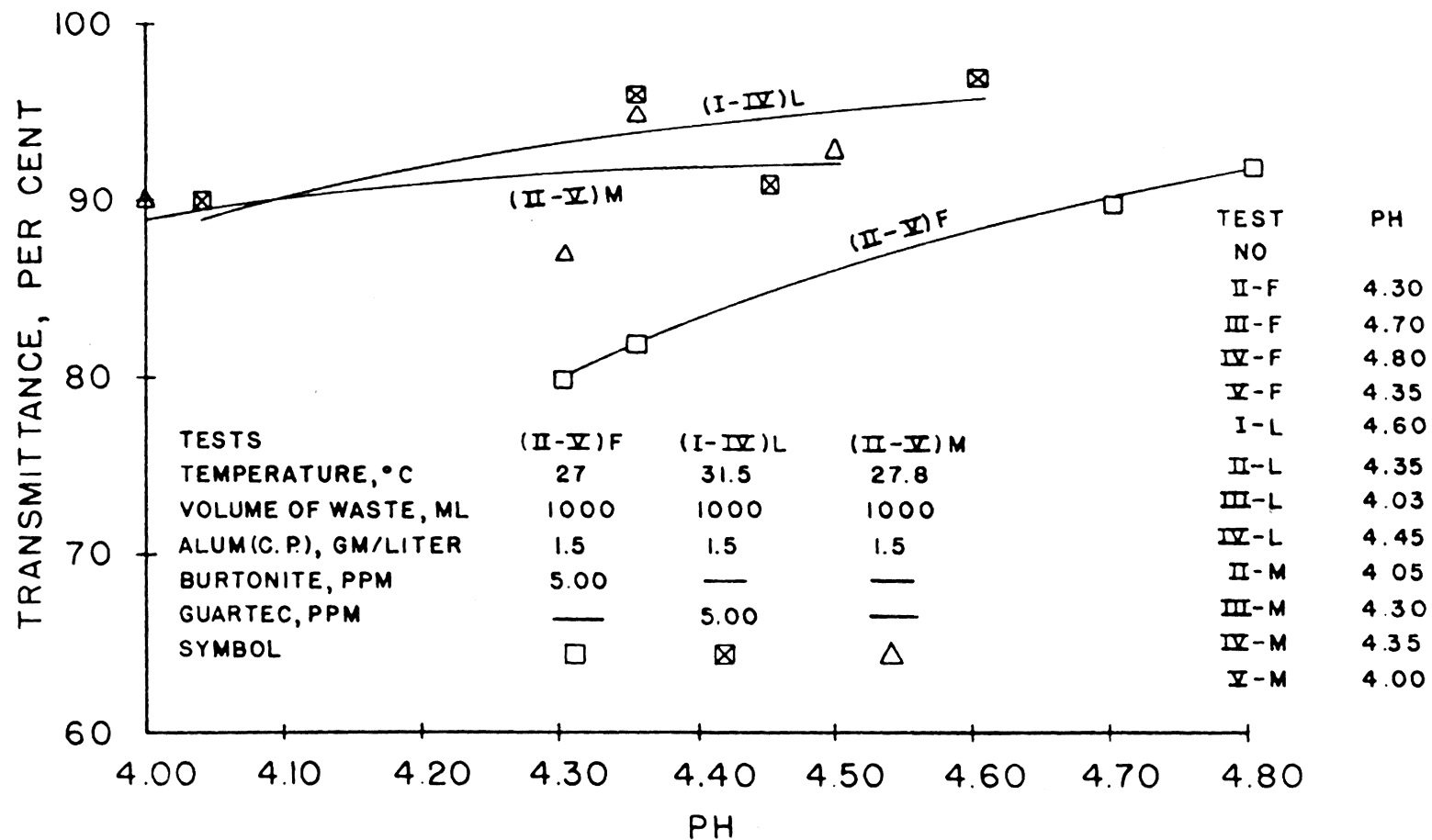ON RATES OF FILTRATION

The following appears within the figure:

TESTS(II-V)F
TEMPERATURE – 27°C
VOLUME OF WASTE – 1000 ML
BURTONITE – 5.0 PPM
ALUM (C.P) – 1.5 GM/LITER

TEST NO	SYMBOL	PH
II-F	○	4.30
III-F	□	4.70
IV-F	△	4.80
V-F	●	4.35

Axis labels: VOLUME, MILLILITERS (vertical), TIME, MINUTES (horizontal)

FIGURE 19 EFFECT OF VARYING PH ON TRANSMITTANCE OF SUPERNATANT
LIQUOR USING BURTONITE, GUARTEC, AND STOCK ALUM (C.P.)
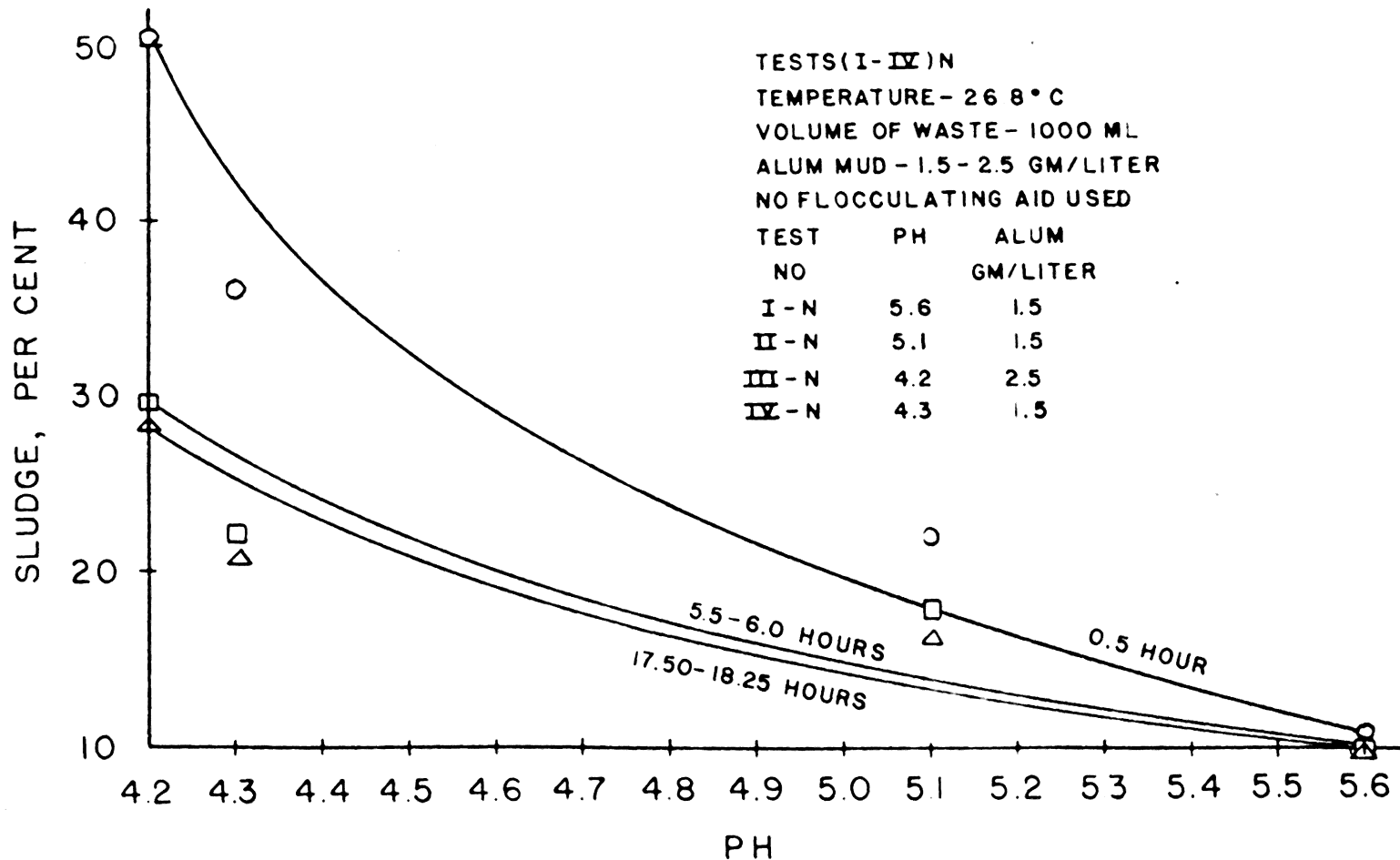
FIGURE 20 EFFECT OF VARYING PH USING ALUM SLURRY ON VOLUME OF SETTLED SLUDGE
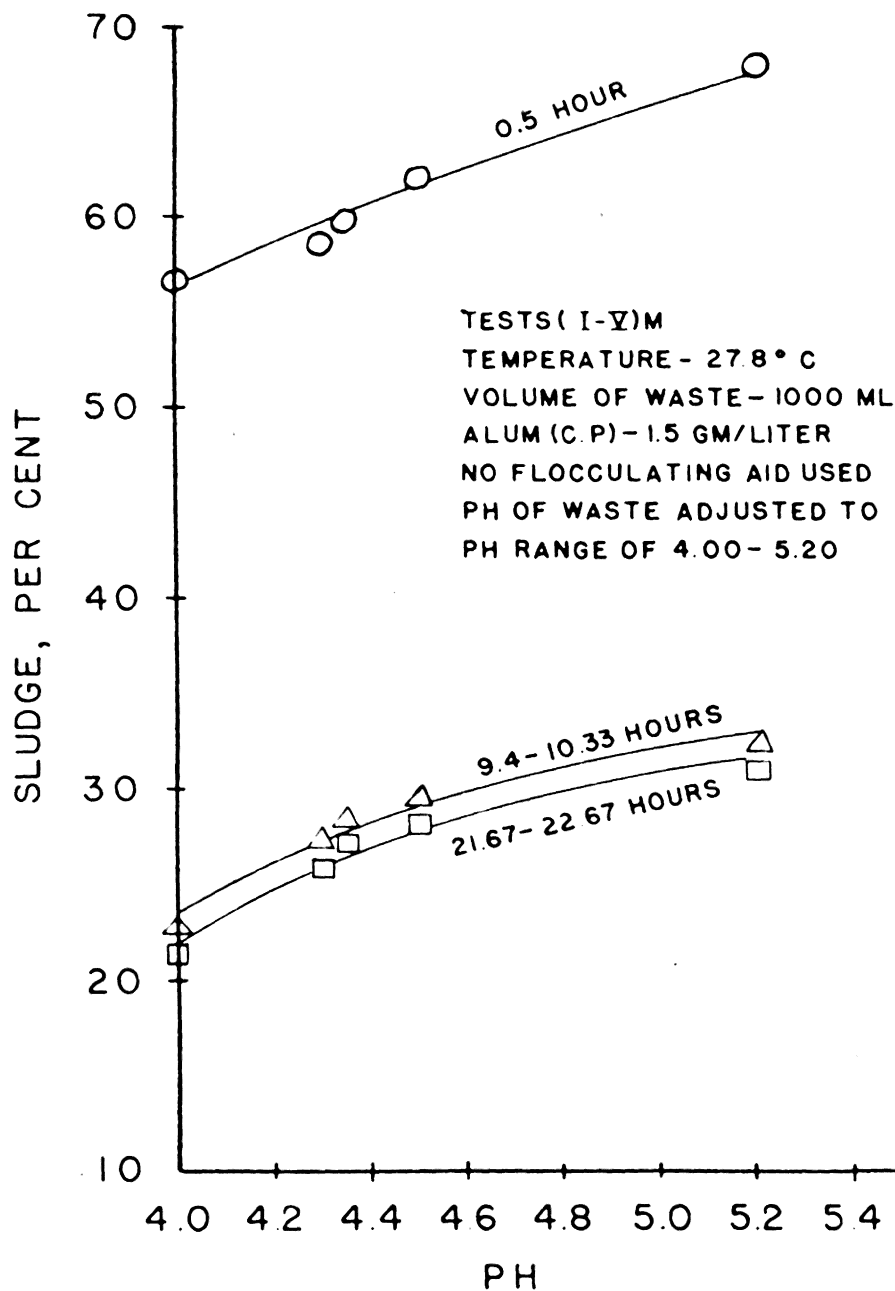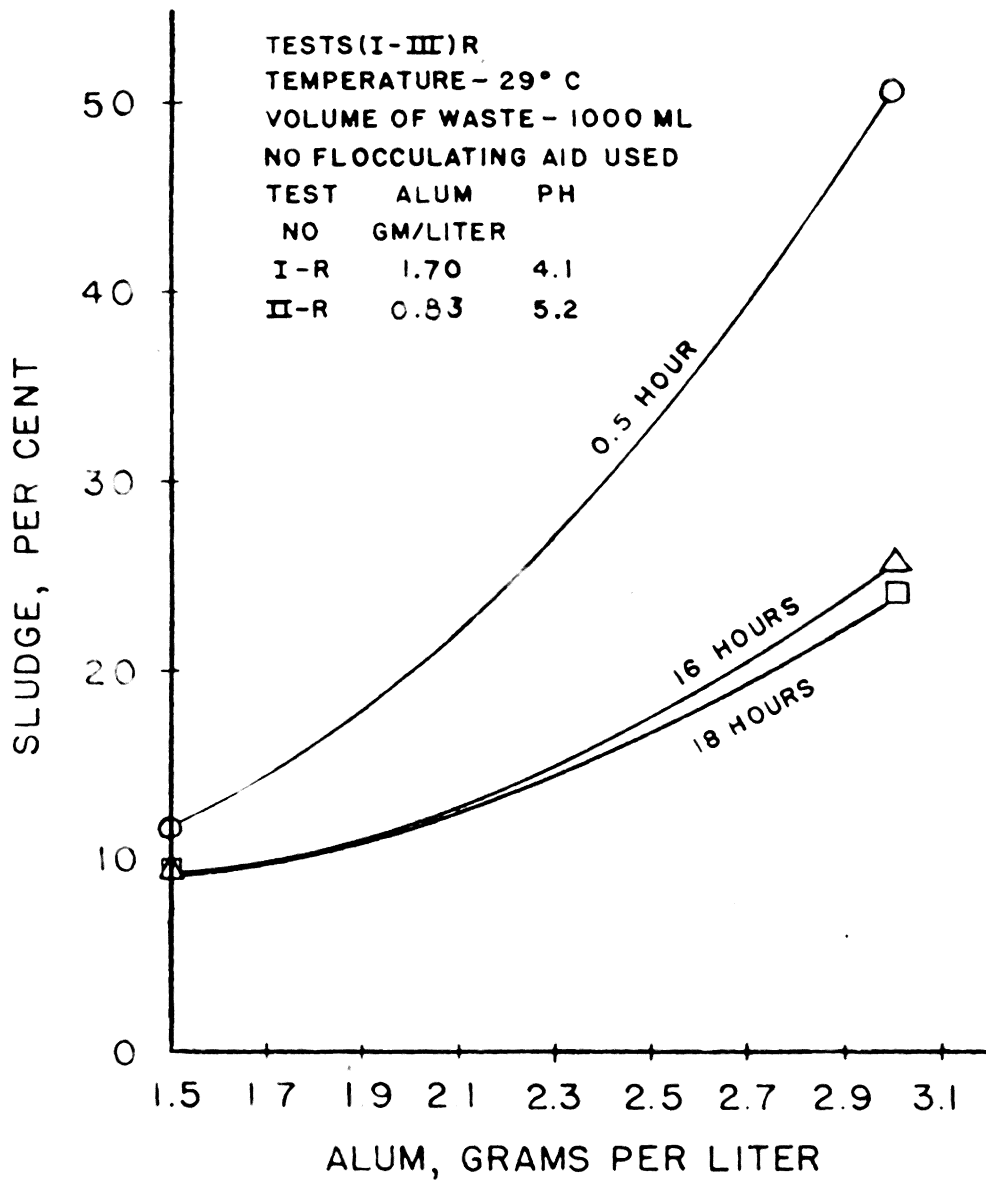
TESTS(I-Ⅴ)M
TEMPERATURE - 27.8° C
VOLUME OF WASTE - 1000 ML
ALUM (C.P) - 1.5 GM/LITER
NO FLOCCULATING AID USED
PH OF WASTE ADJUSTED TO
PH RANGE OF 4.00 - 5.20

FIGURE 21 EFFECT OF VARYING PH USING
C.P. STOCK ALUM ON VOLUME OF
SETTLED SLUDGE

FIGURE 22 EFFECT OF VARYING THE AMOUNT OF
ALUM SLURRY AND PH ON VOLUME
OF SETTLED SLUDGE

TESTS	(II-V)M	(III-IV)N	I-R
TEMPERATURE, °C	27.8	26.8	29
VOLUME OF WASTE, ML	1000	1000	1000
ALUM(C. P.), GM/LITER	1.5	—	—
ALUM SLUDGE, GM/LITER	—	1.50-2.50	3.00
NO FLOCCULATING AID USED			

TEST NO	PH	SYMBOL
II-M	4.50	+
III-M	4.30	⊠
IV-M	4.35	⧋
V-M	4.00	×
III-N	4.20	▲
IV-N	4.30	□
I-R	4.10	△
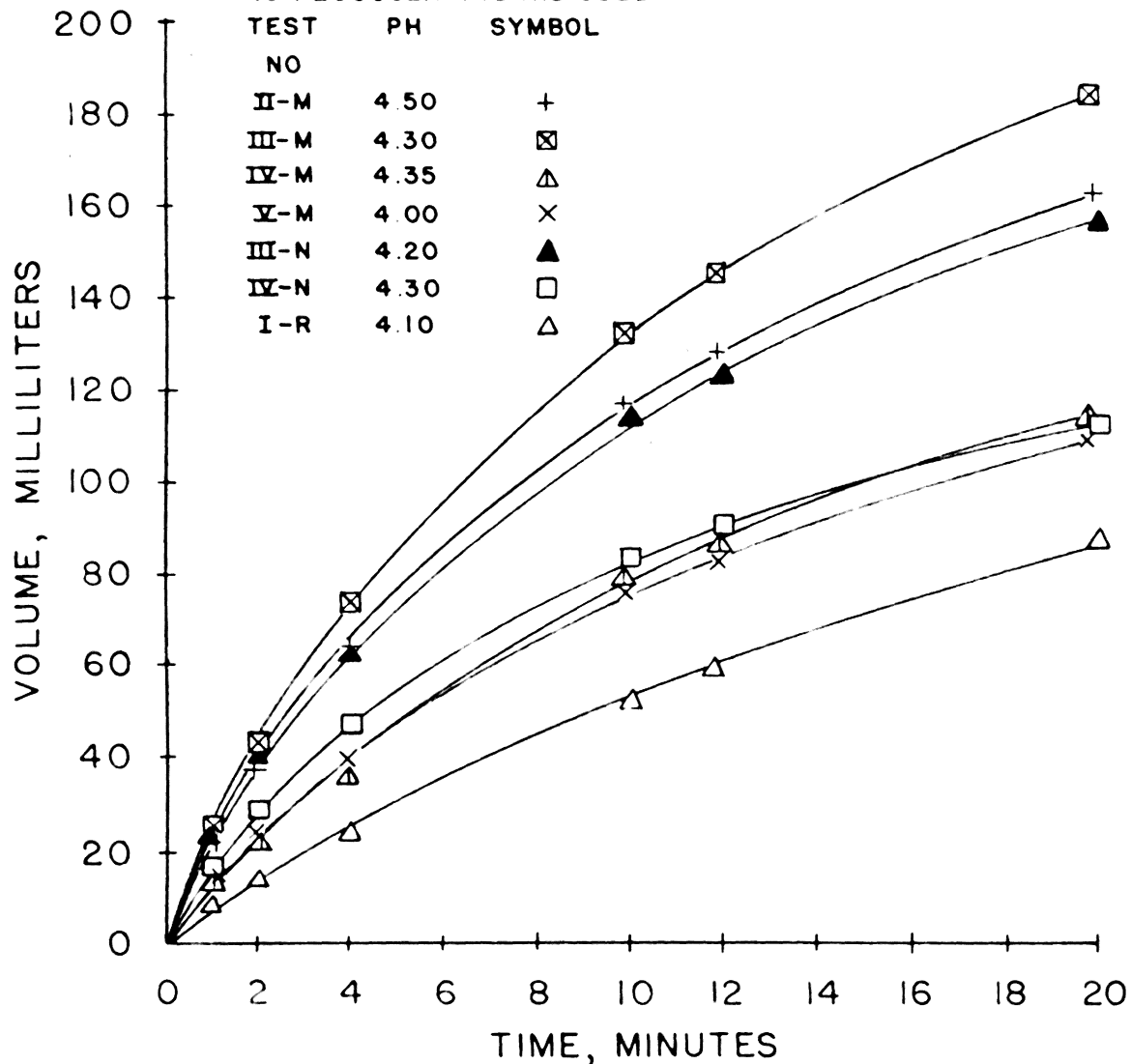
FIGURE 23 EFFECT OF VARYING PH USING C.P.
ALUM AND ALUM SLURRY ON RATES
OF FILTRATION

TABLE IV.

Properties and Composition of the Caustic and

Hydrochloric Acid Waste Streams from
a
the Pulp Bleaching Process

	Caustic Waste	Acid Waste
Light transmittance, %	10	12
pH	10.3	1.9
Density, g/ml	0.998	----
Dry solids, %	0.495	----
Non-volatile solids, %	0.001	----

a
  As received from West Virginia Pulp and Paper Company.
  The hydrochloric acid waste stream results from washing the
  sulfate, pine pulp after it has been treated with chlorine
  in the first stage of the pulp bleaching process.

  The caustic extraction waste results from washing the
  chlorine-bleached, sulfate, pine pulp after caustic (sodium
  hydroxide) treatment in the second stage of the pulp
  bleaching process.

TABLE V.

Properties and Composition of the [a]
Aluminum Sulfate Slurry

Density, g/ml	1.174
Aluminum sulfate - $Al_2(SO_4)_3$, %	18.0
Aluminum oxide (equivalent), %	4.35
Dry solids (residue at 120 °C), %	22.2
Water (volatile at 120 °C), %	77.8
Clay residue (by difference), %	4.2

[a]
 As received from West Virginia Pulp and Paper Company,
who produce it for use in the papermaking process.

TABLE VI

Data for pH Titration of Caustic Extraction Waste Stream

with Hydrochloric Acid Waste from the

Chlorination Bleach Stage

Volume of Acid Added[a] ml	pH	Volume of Acid Added ml	pH
0	10.10	52	7.09
1	10.06	54	6.99
2	10.02	56	6.90
3	10.00	60	6.75
4	9.97	65	6.60
5	9.94	70	6.48
7	9.90	75	6.35
10	9.80	80	6.30
15	9.68	85	6.20
20	9.51	90	6.10
22	9.45	95	6.00
25	9.34	100	5.86
30	9.10	105	5.70
32	8.98	110	5.51
34	8.81	115	5.32
36	8.62	120	5.10
38	8.40	125	4.90
40	8.13	130	4.70
42	7.85	135	4.51
44	7.63	140	4.35
46	7.48	145	4.20
48	7.33	150	4.07
50	7.22		

[a] The volume of caustic waste treated was one liter.

TABLE VII

The Treatment of Caustic Extraction Waste with

Concentrated Sulfuric Acid

Sample	Test No.			
	A-1	A-2	A-3	B
Weight of waste sample gm	100.0	100.0	100.0	10000.0
Volume of conc. H_2SO4, ml	1.0	1.0	1.0	100.0
Weight of conc. H_2SO4, gm	1.84	1.84	1.84	184.0
Weight of solids, gm				
after drying at 120 ^{o}C	0.082	0.083	0.080	8.65
after igniting at 700 ^{o}C	0.001	0.000	0.001	----
Dry solids, % at 120 ^{o}C	0.082	0.083	0.080	0.0865
Non-volatile % at 700 ^{o}C	0.001	0.000	0.001	----

TABLE VIII

Purification of Dried Sludge Obtained from Sulfuric

Acid Treatment of Caustic Waste

Weight of dried solids from Test B, gm	1.0055
Volume of 1-N NaOH added, ml	25.00
pH of resulting mixture,	12.40
Temperature after heating, ^{o}C	98.0
Volume of 0.5-N H_2SO_4 added, ml	52.0
Temperature after cooling, ^{o}C	24.0
pH of resulting mixture,	3.70
Volume of concentrated H_2SO_4 added, ml	5.00
Final pH of treated sample,	0.60
Weight of filtered, washed, dried solids, gm	0.304
Recovered solids, %	30.23

The known properties of the purified dry solids obtained from the concentrated sulfuric acid treatment of the caustic waste are as follows:

    (1)   Melting point greater than 345 ^{o}C,

    (2)   Insoluble in ether,

    (3)   Insoluble in acid solution,

    (4)   Insoluble in water,

    (5)   Soluble in alkali,

    (6)   After ignition, the per cent non-volatile solids is

           negligible.

TABLE IX

Effect of Acid on Waste from Alkali Wash of Chlorine-Bleached Kraft Pulp

Acid Used	Volume of Acid ml.	Volume of Waste ml.	Other Chemicals Used	Time, Minutes — Settling (ml. of Waste Containing Sludge)											pH	Liquor Transmittance %
				10 ml.	15 ml.	20 ml.	30 ml.	40 ml.	50 ml.	60 ml.	70 ml.	90 ml.	120 ml.	1440 ml.		
HNO3	1	100	None	70-95 0-37	—	70-90 0-30	70-85 0-30	30	28	26	24	—	—	12	1.1	64
H2SO4	2	100	None	85-100 0-55	90-100 0-30	90-100 0-28	—	25	23	—	21	20	19	12	0.60	78
H2SO4	1	100	None	80	71	42-60 0-35	35	30	27	25	23	—	—	12	0.95	66
H2SO4	1	100	1 ml. of 0.001 % Separan	90	—	57	40	35	31	29	—	—	—	14	0.95	67
H2SO4	1	100	0.0905 gm. powdered Zinc	80	40	32	20	17	15	14	—	—	—	10	1.0	73
H2SO4	0.5	100	None	35	—	25	22	20	18	17	—	—	—	12	1.35	51
H2SO4	0.4	100	None	80	70	(d)	(d)	(d)	(d)	(d)	(d)	(d)	(d)	10	1.30	49
H2SO4	0.3	100	None	(a)	(b)	(d)	(d)	(d)	(d)	(d)	(d)	(d)	(d)	7	1.50	17
H2SO4	0.2	100	None	100	—	(c)	(c)	(c)	(c),(d)	(c),(d)	(c),(d)	(c),(d)	(c),(d)	2	1.70	8
H2SO4	0.1	100	None	100	—	—	—	—	—	—	—	—	—	—	2.30	13
H2SO4	0.05	100	None	100	—	—	—	—	—	—	—	—	—	—	3.90	4
H2SO4	0.01	100	None	100	—n	—	—	—	—	—	—	—	—	—	7.50	2
HCl	1	100	None	—	74	62	40	31	28	25	24	—	—	12	1.25	56
H3PO4(e)	1	100	None	7	—	—	—	—	—	—	—	—	—	7	1.90	11
H3PO4(e)	1	50	None	no coagulation										2	1.60	19
H3PO4(e)	1	25	None	coagulation but no settling			8							25	1.3	58

(a) Coagulation could be observed.

(b) No settling took place.

(c) Coagulation observed.

(d) Majority of particles contained in volume given but some still suspended.

(e) Color changed to clear dark red but only slight precipitate was formed.

TABLE X

Quantities of Chemicals Added in Large Scale

Coagulation of Caustic Waste[a]

Sample	Test No.			
	I.	II.	III.	IV.
Book 817, page No.	145	173	223	278
Volume of waste treated, l	16	16	16	16
Volume of 0.5-N sulfuric acid added, ml	405	471	350	600
Volume of alum slurry added, ml	240	250	235	107

[a]See also Table III.

TABLE XI.

Results of Centrifuging the Sludge Obtained from

Coagulation of Caustic Waste with Alum Slurry

	I-A	I-B	III-A	IV-A
Book 817, page No.	148	158	265	280
Volume of sludge, ml	1000	1000	1000	2620
pH of sludge,	4.10	4.15	4.15	4.60
Steam pressure, lb/sq in., g	25	30	40	35
Centrifuge speed, rpm	3000	7000	7000	4000
Average feed rate, ml/min	75	50	100	90
Volume of effluent				
Clear: upper nozzle, ml	65	--	25	55
lower nozzle, ml	250	--	41	
Total: upper nozzle, ml	167	155	25	300
lower nozzle, ml	455	143	41	
Unused feed sludge, ml	35	250	255	1000
Leakage from bowl, ml	63	192	420	1100
Drainage from bowl, ml	150	184	190	175
Weight of scrapings, gm	35	25	59	65

a
  The data concerning the production of the sludge used in the above
  tests can be obtained from Table III, page 83, tests I, III, and
  IV. The same sludge was used in centrifuge tests I-A and I-B.

TABLE XII

Per Cent Total Solids, Insoluble Solids, and Non-volatile
Solids in the Various Streams Entering and
Leaving the Sharples Centrifuge

Total Solids:				Streams		
Dry, %	Feed	Leak-age	Drain-age	Upper Nozzle	Lower Nozzle	Scrap-ings
Test No. I-B	1.26	----	1.27	0.509	0.491	5.75
III-A	2.62	1.82	0.75	0.520	0.570	18.40
IV-A	1.70	1.098	0.75	0.450 [a] 0.650	0.450 0.650	12.90
Insoluble, %						
Test No. I-B	1.02	----	0.991	0.173	0.202	5.52
III-A	----	----	-----	0.000	0.020	----
IV-A	----	----	-----	-----	-----	----
Non-Volatile[b], %						
Test No. I-B	----	----	-----	-----	-----	----
III-A	1.44	----	-----	0.410	-----	9.23
IV-A	0.96	0.47	-----	------	-----	5.60

a
 The clear effluent from the upper and lower nozzles contained 0.45%
dry solids; the cloudy effluent from the two nozzles contained 0.65%
dry solids.

b
 The total dry solids determination was made at a temperature of
120 $^{\circ}$C while the non-volatile determinations were made at a temperature
of (700-1000) $^{\circ}$C.

TABLE XIII

Determination of Alum Recovery by Digestion of

Scrapings from the Centrifuge Bowl Using

Concentrated Sulfuric Acid

Sample	Test No.	
	III-A	IV-A
Weight of scrapings, gm	5.007	5.339
Weight of distilled water added, gm	30.00	25.00
Weight of concentrated sulfuric acid added, gm	5.514	5.514
Heating period, min	60	60
Volume of diluted filtrate, ml	100.0	100.00
Titration: using 0.9940-N NaOH		
Average volume of base used for aliquots no. 1, 2; ml	24.85	25.00
Weight of potassium fluoride added to aliquots no. 3, 4; gm	1.000	1.000
Average volume of base used for aliquots no. 3, 4; ml	22.50	23.75
Difference in volume of 0.9940 N NaOH, ml	2.35	1.25
Volume of base to neutralize a 1.0 gm KF blank, ml	1.05	0.005
Total volume of 0.9440 N NaOH used to back titrate aliquot, ml	2.40	1.30

Sample Calculations

In the following sections are the sample calculations employed in this investigation.

Aluminum Sulfate in Treated Waste. The following are calculations for the amount of alum in the slurry used in treating one liter of waste:

$$R = \frac{D\ A\ X}{WV}$$

where: D = density of alum slurry, grams per milliliter

A = concentration of aluminum sulfate, per cent

X = volume of alum slurry, milliliters

V = volume of caustic waste, liters

W = density of caustic waste, grams per milliliter

R = grams alum per liter of waste.

Using data from pages 72, 96, and 101,

$$\frac{(1.174)\ (0.18)\ (107.0)}{(0.998)\ (16.0)} = 1.415 \text{ grams alum per liter waste.}$$

Material Balance about the Settling Tank. The following section

contains the material balance about the settling tank:

W + A + DY = S + E + L

where: W = weight of caustic waste, grams

A = weight of 0.5 N sulfuric acid, grams

Y = volume of alum slurry, milliliters

D = density of alum slurry, grams per milliliter

S = weight of settled sludge, grams

E = weight of supernatant liquor, grams, and

L = loss, grams.

Using data from pages 83, 96, and 101,

16,000 + 600 + (1.174) (107.0) = 2620 + 14,080 + L

L = 26 grams.

Material Balance about the Centrifuge. The following is the
material balance about the centrifuge:

$$F = E + L_1 + D + S + U + L_2$$

where: F = weight of feed sludge from settling tank, grams

L_1 = weight of effluent, grams

L_1 = weight of bowl leakage, grams

D = weight of bowl drainage, grams

S = weight of bowl scrapings, grams

U = weight of unused feed, grams and

L_2 = loss, grams.

Using data from page 102,

$$2,620 = 275 + 1,000 + 175 + 65 + 1,100 + L_2$$

$$L_2 = 5 \text{ grams.}$$

Determination of Amount of Alum in Feed per Gram of Dry Solids.

The following is the determination of the amount of alum in the settled
sludge per gram of dry solids:

$$\frac{B\ C\ M}{V\ M_1\ X_1} = W_2$$

where: B = volume of caustic waste, liters

C = ratio, grams of alum per liter of waste

M = molecular weight of aluminum oxide, grams per gram-mol

M_1 = molecular weight of aluminum sulfate, grams per gram-mol

V = total weight of settled sludge, grams

X_1 = dry solids in feed sludge, grams per 100 grams, and

W_2 = grams of aluminum oxide per gram of dry solids.

Using data from pages 83, 101, 103, and 105,

$$\frac{(16.0)\ (1.415)\ (102)}{(2620)\ (342)\ (0.017)} = W_2$$

W_2 = 0.152 grams aluminum oxide per gram dry solids.

Determination of Amount of Alum in Scrapings from the Centrifuge
Bowl. The following is the calculations for the determination of the
amount of alum in the scrapings per gram of dry solids:

$$\frac{K\,N\,M\,A\,M'}{P\,1,000\,S\,M\,X} = W_1$$

where: K = volume of 0.994 N sodium hydroxide, milliliters

N = normality of sodium hydroxide solution, equivalents
per liter

M = molecular weight of aluminum sulfate, grams per gram-mol

A = number of aliquot samples containing aluminum sulfate

M' = molecular weight of aluminum oxide, grams per gram-mol

P = stoichiometric number of mols of sodium hydroxide

S = weight of sample of scrapings, grams

X = dry solids in scrapings, grams per 100 grams sample, and

W_1 = ratio, grams of aluminum oxide per gram of dry solids.

Using data from pages 103 and 104,

$$\frac{(1.30)\ (0.994)\ (342)\ (4)\ (102)}{(6)\ (1,000)\ (5.339)\ (342)\ (0.129)} = W_1$$

W_1 = 0.127 grams aluminum oxide per gram dry solids.

Determination of Per Cent Aluminum Sulfate Recovery. The following section contains the calculations for the amount of aluminum sulfate recovered;

$$\frac{W_1}{W_2} = R$$

where: W_1 = ratio, grams of aluminum oxide per gram of dry solids in feed sludge

W_2 = ratio, grams of aluminum oxide, per gram of dry solids in centrifuge scrapings

R = aluminum oxide recovery or the equivalent of aluminum, per cent.

Using data from pages 108 and 109,

$$\frac{0.127}{0.152} \times 100 = 83.7 \text{ per cent.}$$

Heat Balance about Rotary Calciner. The following section is the heat balance about the rotary calciner based on a million gallons of waste per day:

$$W H + Q = W_1 C_1 \Delta T + W_1 \lambda_1 + (W_2 C_2 + W C_3 + W_4 C_4) \Delta T$$

where: W = weight of lignous matter, pounds

H = heat of combustion, btu per pound

Q = heat to be added as fuel, btu

W_1 = weight of water in sludge, pounds

W_2 = weight of clay in sludge, pounds

W_4 = weight of aluminum oxide in sludge, pounds

C_1 = specific heat of water, btu per pound per degree Fahrenheit

C_2 = specific heat of clay, btu per pound per degree Fahrenheit

C_3 = specific heat of lignous matter, btu per pound per degree Fahrenheit

C_4 = specific heat of aluminum oxide, btu per pound per degree Fahrenheit

ΔT = difference in temperature between sludge in and solids out, degrees Fahrenheit

λ = latent heat of steam at one atmosphere, btu per pound.

Using data from pages 124 and 128,

$$(10,680) (8,000) + Q = (109,900) (1.0) (112)$$

$$+ (109,900) (970) + (2700) (0.22) (112)$$

$$+ (10,680) (0.3) (112) + (2,900) (0.18) (112)$$

Q = 34,243,100 btu added per million gallons of waste.

Determination of Quantity of Natural Gas Required as Fuel for the

Dryer and Incinerator.   The following section contains the determination

of the volume of natural gas required on a basis of a million gallons of

waste per day.:

$$\frac{Q}{H\,E} = V$$

where: Q = heat to be added by fuel, btu

H = lower heating value of natural gas,
btu per cubic foot

E = burner efficiency, per cent, and

V = volume of gas, cubic feet .

Using data from page 111,

$$V = \frac{34,243,000}{(1050)\,(0.50)} = 65,250 \text{ cubic feet}.$$

Determination of Quantity of Concentrated Sulfuric Acid Required per Day to Regenerate Spent Alum. The following section contains the determination of the quantity of concentrated sulfuric acid required per million gallons of waste to regenerate aluminum sulfate from the aluminum oxide:

$$\frac{A\ N\ M}{M_1} = W$$

where: A = weight of aluminum oxide, pounds

M_1 = molecular weight of aluminum oxide, pounds per pound-mol

N = number of pound-mols of sulfuric acid required to react with one mol of aluminum oxide

M = molecular weight of sulfuric acid, pounds per pound-mol

W = weight of sulfuric acid required, pounds.

Using data from page 124,

$$W = \frac{(2900)\ (3)\ (98)}{(102)}$$

W = 8,350 pounds.

IV. DISCUSSION

The following section contains a discussion of the results obtained
from this investigation, recommendations for future study, and the
limitations imposed upon this experimentation.

Discussion of Results

This section contains a discussion of the results which includes
the effects of various addition agents and treatments on the caustic
waste and a discussion concerning the proposed treatment plant for
color removal.

Effect of Various Addition Agents on the Caustic Waste. From
previous work it was found that 1.50 grams of alum per liter of the
waste caustic wash liquor caused significant removal of color and
yielded a supernatant liquor with a light transmittance of 85 to 90
per cent. Flocculating aids were recommended for study and evaluation
to determine their value as a supplement for alum treatment.

Several commercial flocculating aids were tried with the alum
treated waste, and the settling rates, the volume of sludge, filtration
rates of the sludge, and transmittance of the supernatant liquor were
measured, using both chemically pure alum and papermakers alum slurry.

Effect on Settling. Separan did not improve the rate of settling
of the sludge appreciably in the pH range from 4.05 to 4.30 or from
5.70 to 5.82 (Figures 1, 3, 5 on pages 71, 73, and 75). The effect of
varying the amount of chemically pure alum with Separan on the volume

of sludge is shown by tests that were run at pH's in the range from
3.9 to 5.45, 3.80 to 4.50 and 4.30 to 6.00 (Figures 2 and 4 on pages
72 and 74). The least volume of sludge (17 per cent), was obtained
using 0.015 parts per million of Separan at an initial pH of
3.9 to 5.45. Tests were also performed with no flocculating aid
using chemically pure alum and alum slurry (Table III, page 83 and
Figures 21 and 22, pages 92 and 93). The comparison of the results
of these tests showed that alum slurry alone produced a volume of
sludge comparable to that formed by chemically pure alum alone or
any combination of alum and Separan. Other flocculating aids were
tried and appeared to exert their maximum effect at pH values
specific for each.

Guartec did not decrease the amount of sludge formed (Figure 13,
page 84). The effect of Burtonite, Good-rite K-720S, and Good-rite
K-721S on the volume of sludge was determined (Figures 14, 15, and
16 on pages 84, 85, and 86). Only Burtonite produced results that
were comparable with alum slurry and there was no appreciable
improvement over the use of alum slurry alone.

Lytron X-886 and Orzan-P produced no appreciable improvement in
settling rates or decrease in the volume of sludge formed (Table III,
page 83).

The effect of pH on the volume of sludge formed using both
chemically pure alum and alum slurry and using waste acid from the
chlorination stage of the pulp bleaching process for neutralizing
was determined (Figures 11 and 12, on pages 81 and 82). Larger volumes
of sludge were formed because the chlorination stage waste was used

but use of alum slurry resulted in a smaller volume of sludge than was obtained when chemically pure alum was used. These test proved that alum slurry, when added to the waste (1.50 grams of alum per liter of waste) at a pH of about 6.0, yielded a sludge volume comparable to or less than any tests using chemically pure alum or flocculating aids. The mud in the alum slurry apparently improves the rate of settling and decreases the final volume of the sludge.

Effect on Filtration of Sludge. Separan does not affect the rate of filtration of the sludge appreciably (Tests IV - XIII, Table III, page 83). Apparently, as the amount of alum is increased the rate of filtration decreases. Again, this is probably due to the increased amount of clay present.

Filtration rates when Separan was added were highest at a pH of 4.75 (Figure 7, page 77). The rate of filtration obtained using Good-rite K721S at a pH of 4.2 was better than that obtained using Separan at 4.75 (Figure 17, page 88). The highest rate obtained when using Burtonite at a pH of 4.3 (Figure 18, page 89) was lower than that obtained using Good-rite K721S. The use of chemically pure alum yielded a higher filtration rate at a pH of 4.30 than when alum slurry was used (Figure 23, page 94). The reason for the lower rates when the alum slurry was used is apparently caused by the clogging effect of the clay solids. Therefore, although the use of alum slurry is advantageous with respect to settling of sludge, its use results in slower filtration rates.

Effect on Clarification. The addition of Separan to waste treated with chemically pure alum does not appreciably increase the transmittance (Figure 18, page 78). Apparently Separan fails to coalesce the colloidal particles that escape being settled by the hydrated aluminum oxide floc. The alum treatment yielded higher transmittances in the pH range 4.30 - 6.00 (Figures 9 and 10, pages 79 and 80). The addition of 1.50 grams of alum slurry produced a transmittance of 8.5 per cent, comparable to that obtained using chemically pure alum. After approximately 2.25 grams of alum have been added to a liter of waste, the addition of more alum fails to increase the transmittance past 90 per cent.

Burtonite, at a pH of 4.8, produced a supernatant of 90 per cent transmittance (Figure 19, page 90). However, the transmittance decreased as the pH was decreased. Guartec produced the same transmittance at lower values of pH and maintained it over the pH range 4.00 to 4.80.

Good-rite K-720S and K-721S produced supernatant of consistently higher clarity than other treatments over the range of pH from 4.10 to 4.40 (Table III, page 83). The transmittance of the supernatant was not appreciably improved by using either Orzan P or Lytron S-886 (Table III, page 83).

Summary of Results with Flocculating Agents. In summary, the flocculating agents used in this investigation failed to increase appreciably the rate of settling of alum treated waste or to decrease the volume of sludge.

Also, the filtration rates of the sludge were not appreciably improved by their use. Several of the flocculating aids such as Burtonite and Good-rite improved the transmittance from five to ten per cent, but all of them failed completely to supplement the required alum dosage.

Summary of Conditions Concerning Alum Coagulation. The use of alum slurry alone to coagulate the waste produced a sludge volume comparable or less than any formed by chemically pure alum alone or by any combination of alum and flocculant.

The use of alum slurry to coagulate the caustic waste after acidification with acid waste produced a smaller volume of sludge (five to ten per cent) than that obtained when chemically pure alum was used.

The use of chemically pure alum produced sludge that filtered at appreciably faster rates than sludge formed using alum slurry.

Neither chemically pure alum or alum slurry appear to possess a decided advantage over the other with respect to the light transmittance of the supernatant liquor.

Effect of Acid Treatment on the Waste. Various concentrated acids (sulfuric, nitric, phosphoric, and hydrochloric) were used to coagulate the waste. Sulfuric acid produced the best transmittance of any of the acids. However, the transmittance was only 78 per cent (Table VI, page 97). The addition of a flocculating aid caused a decrease of eleven per cent in transmittance of the supernatant liquor (Table IX, page 100). No solids in the ignited sludge from sulfuric acid treatment were less than 0.001 per cent non-volatile. Therefore, the sludge is

nearly 100 per cent volatile. After alum treatment, the sludge contained nearly 1.0 per cent non-volatile solids after ignition. Comparison of these tests shows that the residue contains a negligible amount of organic matter. The remainder must be all aluminum oxide and clay.

Purification of the dry solids obtained from the sulfuric acid treatment of the waste indicate that a material similar or related to rosin acids is being separated.

Effect of Ferrous Sulfate on Waste. A freshly made, 8.8 per cent solution of ferrous sulfate added to the waste at various acidities produced unsatisfactory results, since the supernatant liquor was colored and cloudy. In these tests, the pH of one-liter waste samples was adjusted to 6, 7, 8, and 9, and 1.00 and 1.50 grams of ferrous sulfate were added (Table III, page 83).

Effect of Initially Chlorinating the Waste. Tests were performed to discover what the alum requirements of the waste would be if it were first chlorinated. Transmittances of 87 and 82 per cent were obtained and settling rates were increased by the chlorine treatment (Table III, page 83). However, 350 to 400 cubic centimeters of chlorine gas were used and 1.39 grams of alum per liter of waste were still required. In test E-1, hydrochloric acid was used to acidify the caustic waste to a pH of 5.45 before the addition of the chlorine. The chlorine further reduced the pH to 2.60 at which pH the alum was ineffective. This proves that the alum cannot be added at low pH values and satisfactory coagulation obtained. Such

initial chlorine treatment before alum addition appears quite uneconomical.

Various Modifications of Waste Treatment. In the following paragraphs, the effects of order of addition of the chemicals to the waste, heating the waste, retarding the rate of addition of the alum slurry, and using waste hydrochloric acid in place of 0.5 N sulfuric acid are discussed.

The effect of reversing the order of addition of alum and Burtonite had no effect on the transmittance and almost negligible effect on settling and filtration rates (Tests (1-V) F, Table III, page 83). When varied amounts of alum were added before the acid or Good-rite K-720S, cloudy mixtures were produced. It appears that the order in which the chemicals are added does not affect the sludge volume, settling rates, filtration rates, or transmittance.

The effects of temperature of the waste before treatment was studied (Table III, page 83). The waste was heated to about 50 °C and the transmittance and settling rates determined, using varied amounts of alum slurry and adding 5.0 weight per cent calcium hydroxide to raise the pH after alum treatment hoping to reduce the amount of alum required. The settled liquor was cloudy. Tests (I - IV) were performed at room temperature and again the use of calcium hydroxide failed to produce a clear supernatant liquor.

The waste was heated to 50 °C, acidified to a pH of about 6.0 with 0.5 N sulfuric acid, and treated with 1.18 to 1.48 grams of alum (Tests (I - III) Table III, page 83). A transmittance of 82 per cent was obtained but this was no better than when the waste was not heated.

When the waste was heated to 90 ^{o}C, (Test (I - IV) G), a transmittance of 80 per cent was obtained. These resulted in a significant reduction in the amount of alum (from 1.48 to 1.39 grams per liter) required. However, if the waste is not discharged hot, it may not be practical to heat the waste to this temperature. Another significant fact is that there was a substantial increase in settling rates and a decrease in the sludge volume after heating. This may follow from the fact that the heated floc particles were larger than when the waste was not heated.

Tests were performed to determine whether or not the rate of addition of the alum to the waste affected the degree of color removal (Test F in Table III, page 83). When the alum slurry was added dropwise to the acidified waste, a transmittance of 85 per cent was obtained. The alum particles in the slurry came into more thorough contact with the colloidal waste particles. The reduction in alum requirement, as a result of the slow rate of addition, amounted to 0.98 gram per liter of waste. The same degree of reduction of alum resulted from heating the waste to 90 ^{o}C.

A large scale test was performed in which the alum slurry (1.395 grams of alum per liter instead of 1.48) was added slowly. The floc formed uniformly and grew into large particles throughout the coagulated waste and attempted to settle although swept up again by the slowly revolving paddle. The transmittance of the supernatant liquor was 85 per cent. This shows that 1.395 grams of alum per liter of waste is effective in removing a satisfactory amount of the color when the alum is added slowly and continuously. This slow rate of addition would

require a hold-up time of several minutes to insure optimum contact time
between the alum and waste particles. The longer the hold-up period,
the lesser the degree of agitation should be, or the newly-formed floc
would be destroyed before it could increase in size. The final choice
of what detention time is required must be determined by larger scale
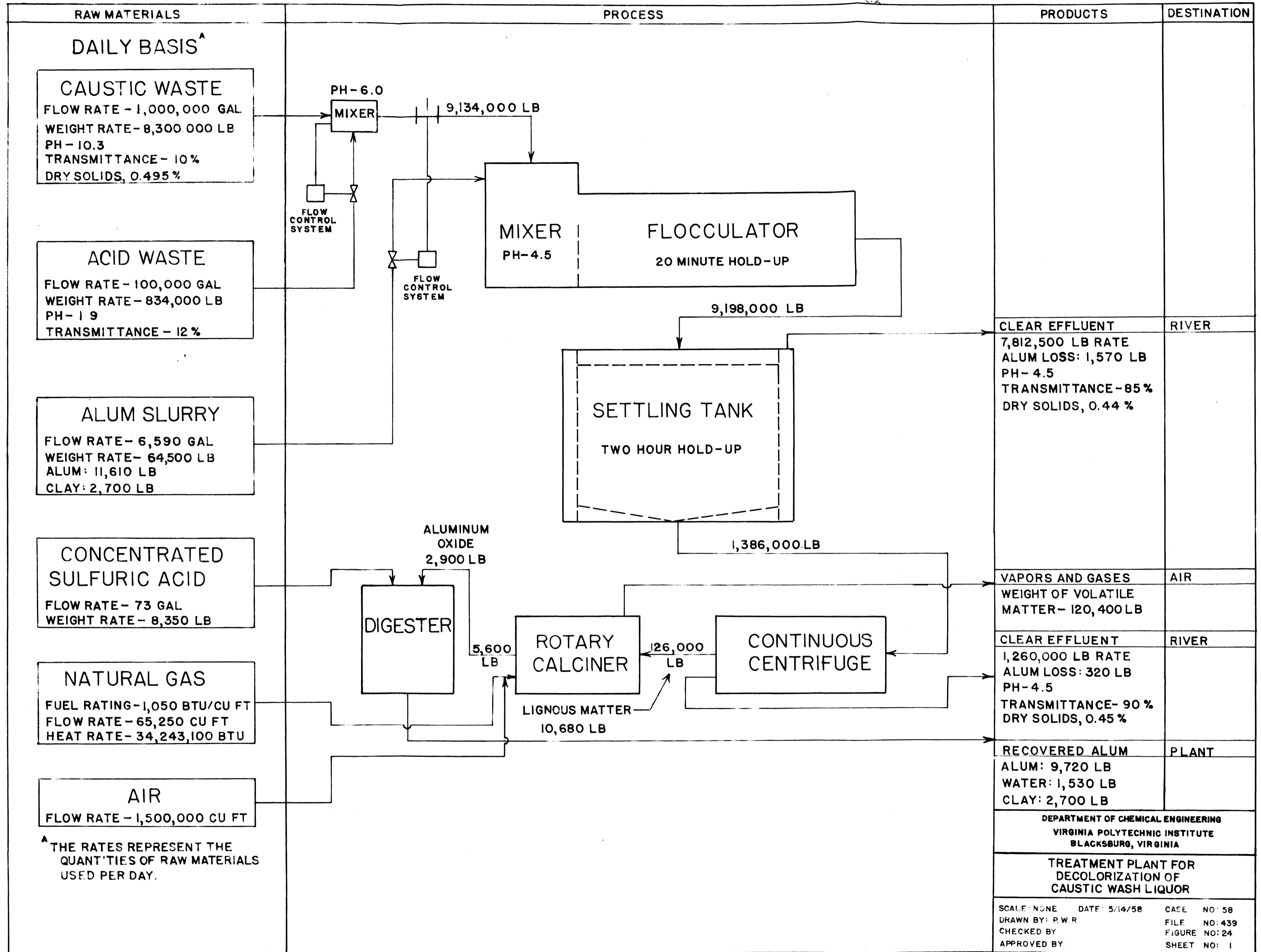experiments.

To make the color removal as economical as possible, waste
hydrochloric acid from the bleaching process was substituted for 0.5 N
sulfuric acid, was used to reduce the pH of the caustic waste before
adding the alum slurry. It has been shown that alum is most effective
when added to waste that has been acidified to a pH of 6.0 (Table III,
page 83). By titration, it was found that 95 milliliters of acid waste
will lower the pH of one liter of caustic waste from 10.10 to 6.00
(Table VIII, page 99). The comparison of Figures 22 and 23, pages 93
and 94, indicates that the volume of the sludge will be five to ten
per cent greater when using the acid waste. The addition of the acid
waste to the caustic waste also introduced some colored particles. This
dilution effect would account for reduction in transmittance from 85 to
80 per cent using the same amount of alum per liter of caustic waste.
This test was performed before the effect of adding the alum at a
slower rate was known. Therefore, a treatment consisting of using
the combined waste and adding about 1.415 grams of alum per liter at
the slower rate and mixing it well, should produce a satisfactory
transmittance.

The Treatment Plant for Color Removal. For decolorization of the
caustic waste, the choice of equipment was based on the results of the

laboratory tests. A flow sheet showing materials, quantities, process equipment, streams, products, and their destination was prepared (Figure 24, page 124). Calculations involving the approximate size of the equipment were based on: (1) 1,000,000 gallons of caustic waste per day, (2) pH adjusted to 6.0 with 100,000 gallons of chlorination acid waste per day, (3) coagulation with 6,600 gallons of alum slurry per day, (4) a two - three-minute hold-up for mixing, (5) a twenty-minute hold-up for flocculation, (6) a two-hour hold-up for settling, (7) 25 per cent of waste volume, as sludge, centrifuged per hour and, (8) a reduction of volatile matter in the calciner from 87 per cent to zero.

The caustic waste, as received, had a dry solids content of 0.495 per cent. So, on the basis of 1,000,000 gallons, or 8,300,000 pounds, all but 42,500 pounds were water. Thus, the magnitude of the dewatering problem is easily recognized. The acid waste, added to reach a pH of 6.0, contains very few solids, being quite similar in that respect to the caustic waste. Therefore, the amount of water to be removed in the dewatering processes is increased by about 100,000 gallons by addition of acid waste. In this proposed process, the water is removed by the following methods: ordinary evaporation to the atmosphere, as effluent from the settling tank and centrifuges, and that driven off from the sludge in the rotary calciner. Therefore, two of the chief factors in the economics of the process are the volume of sludge that settles out in the settling tank and the amount of moisture in the sludge from the centrifuge. The more compact the sludge is, the

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RAW MATERIALS	PROCESS	PRODUCTS	DESTINATION

DAILY BASIS [A]

CAUSTIC WASTE
FLOW RATE – 1,000,000 GAL
WEIGHT RATE – 8,300,000 LB
PH – 10.3
TRANSMITTANCE – 10 %
DRY SOLIDS, 0.495 %

ACID WASTE
FLOW RATE – 100,000 GAL
WEIGHT RATE – 834,000 LB
PH – 1 9
TRANSMITTANCE – 12 %

ALUM SLURRY
FLOW RATE – 6,590 GAL
WEIGHT RATE – 64,500 LB
ALUM: 11,610 LB
CLAY: 2,700 LB

**CONCENTRATED
SULFURIC ACID**
FLOW RATE – 73 GAL
WEIGHT RATE – 8,350 LB

NATURAL GAS
FUEL RATING – 1,050 BTU/CU FT
FLOW RATE – 65,250 CU FT
HEAT RATE – 34,243,100 BTU

AIR
FLOW RATE – 1,500,000 CU FT

[A] THE RATES REPRESENT THE
QUANTITIES OF RAW MATERIALS
USED PER DAY.

PH – 6.0
MIXER

FLOW CONTROL SYSTEM

FLOW CONTROL SYSTEM

9,134,000 LB

MIXER
PH – 4.5

FLOCCULATOR
20 MINUTE HOLD-UP

9,198,000 LB

SETTLING TANK
TWO HOUR HOLD-UP

1,386,000 LB

ALUMINUM OXIDE
2,900 LB

DIGESTER

5,600 LB

**ROTARY
CALCINER**

126,000 LB

**CONTINUOUS
CENTRIFUGE**

LIGNOUS MATTER
10,680 LB

CLEAR EFFLUENT
7,812,500 LB RATE
ALUM LOSS: 1,570 LB
PH – 4.5
TRANSMITTANCE – 85 %
DRY SOLIDS, 0.44 %

RIVER

VAPORS AND GASES
WEIGHT OF VOLATILE
MATTER – 120,400 LB

AIR

CLEAR EFFLUENT
1,260,000 LB RATE
ALUM LOSS: 320 LB
PH – 4.5
TRANSMITTANCE – 90 %
DRY SOLIDS, 0.45 %

RIVER

RECOVERED ALUM
ALUM: 9,720 LB
WATER: 1,530 LB
CLAY: 2,700 LB

PLANT

DEPARTMENT OF CHEMICAL ENGINEERING
VIRGINIA POLYTECHNIC INSTITUTE
BLACKSBURG, VIRGINIA

TREATMENT PLANT FOR
DECOLORIZATION OF
CAUSTIC WASH LIQUOR

SCALE: NONE DATE: 5/14/58	CASE NO: 58
DRAWN BY: P.W.R	FILE NO: 439
CHECKED BY	FIGURE NO: 24
APPROVED BY	SHEET NO: 1

higher is its solids content; and, therefore, a greater quantity of a clearer supernatant liquor is discharged. The same is true of the centrifuged sludge. The more compact it is, the less water there is entering the calciner. Less fuel would then be required to evaporate the water in the sludge.

Returning to the next step in the proposed process, the pH of the waste is lowered to 4.5 by the addition of alum slurry in a rapid mixer. Papermakers alum slurry was chosen as the coagulant for this process because: (1) the clarification, settling rates, and volume of sludge obtained using it were comparable with or better than that obtained with chemically pure aluminum sulfate, and (2) because it is already being produced nearby. Therefore, there is an abundant and cheap supply available where the waste will be treated.

Some of the alum would be lost in the several effluents, probably because of the slight solubility of aluminum compounds. Flocculating aids apparently failed to precipitate the very small particles and thus were of no help in improving the decolorization of the waste.

The purpose of the mixer is to bring the waste particles, which are colloidal in size, into contact with the hydrated aluminum oxide nuclei. After consideration of the colloidal properties of the waste and flocculent, and the amount of waste to be treated, it appears that a rapid mixer of 3,000 gallons capacity with a hold-up period of about three minutes is necessary. The length of the hold-up period would depend on the rate of floc formation and results from further large scale studies. Flocculation occurs after the introduction of the highly charged aluminum ions into the waste mixture containing the very small

particles. Since the coagulation reaction occurs below pH 7, positively charged particles are formed. Then the flocculation phase involves further adsorption, charge neutralization, and finally coalesence of the micro-flocs into larger and larger particles.

The flocculator is the next step after rapidly mixing the waste and alum, and it should have a hold-up period of twenty minutes or a capacity of 18,000 gallons. This length of residence time should allow sufficient contact during the much slower mixing and promote optimum particle growth.

The transfer from the flocculator to the settling tank should be as gentle as possible so to minimize the breaking-up of the floc that has formed. In the proposed process, a 100,000-gallon tank would be necessary to handle the flow of waste and furnish a two-hour hold-up period, required as shown by experimental settling tests. Another tank of the same size would serve as a spare when the other was being cleaned. It is desirable to reduce the bulk of the floc so as to decrease the amount of dewatering required by centrifuging and calcining. The clear effluent having a transmittance of 85 per cent could be reused or discharged into the river. The volume of sludge resulting from chemical precipitation is large since the coagulant (alum in this process) forms part of the sludge.

In the proposed process, 6,950 gallons of sludge would be discharged per hour from the settling tanks and pumped to centrifuges. Two continuous centrifuges, with a five-minute hold-up period each, would be required to handle the sludge. To dewater this sludge various methods were considered before the choice of centrifuging was made.

After reviewing the literature concerning chiefly the methods of vacuum filtration and centrifuging and the results of Foushee's vacuum filtration tests [33], and after studying the results of the centrifuge tests (Table XI, page 102), it was decided that the continuous centrifuge offered the most advantages. Continuous centrifuges continually produce both a concentrated sludge and a clear effluent. The Sharples centrifuge used in this investigation produced an effluent with transmittances up to 90 per cent. The same centrifuge yielded scrapings containing 12.9 and 18.4 per cent dry solids for different feed sludges. The reason for the large difference in the amount of solids is that different amounts of alum slurry were added to the waste when it was coagulated. This also means that a different amount of clay was present in each sludge. A modern, continuous centrifuge should produce a sludge containing less water and more solids than the centrifuge used in this investigation.

It is proposed that after the sludge is centrifuged, that the concentrated sludge be dried and burned in a rotary calciner. In the proposed process, 635 gallons of sludge would be fed to a rotary calciner per hour. A combination of drier and incinerator such as a rotary calciner, appears more economical. The fuel value of the combustible material in the sludge would be significant and help support combusion. However, as shown by the heat balance on page 111, and by the calculations on page 112, an additional amount of fuel (62,250 cubic feet of natural per day) would be required. The heating

values for the combustible (probably lignous) material in the sludge and for the natural gas were obtained from the literature [70, 105].

The values for the specific heats of the clay, alum, and combustible material in the sludge were estimated [70]. The calculations for the amount of gas required were based on a calciner efficiency of only 50 per cent and 12.9 per cent dry solids in the sludge. A rough estimate [70] indicates that about 1,500,000 cubic feet of air per day would be necessary to support combustion of the sludge and natural gas and still furnish a 20 per cent excess of oxygen. The calciner would discharge 5,600 pounds of ash per day and the economics of the proposed process would depend upon the amount of alum recovered.

The procedure used in digesting the ash with sulfuric acid to regenerate the alum is found on page 67. Sample calculations on pages 110 and 112, show that 8,350 pounds of 96.5 weight per cent sulfuric acid are required to recover 83.7 per cent of the alum. This would result i in a recovery of almost 9,700 pounds of alum per day, while nearly 1,890 pounds of the alum would be lost in the several effluents. It was assumed that none of the insoluble clays present in the alum slurry was lost in the process. The ash residue, consisting essentially of aluminum oxide and clay, could be sent directly to the plant where the papermakers alum slurry is made. The cost of the raw materials are considred in the following paragraphs.

Cost of Raw Materials. The pH of the caustic waste can be lowered by the addition of another waste produced by the pulp bleaching process. The alum slurry used for coagulation is cheap and available in abundant

quantities; also, a large proportion, at least 83.7 per cent, of the alum is recoverable.

The quantity of concentrated sulfuric acid required per day to regenerate the alum is relatively small.

Natural gas is cheap and abundant, but the large amount required (65,250 cubic feet per million gallons of waste per day) could be decreased by reducing the moisture content in the sludge to be burned and by calcining with greater than 50 per cent efficiency.

Equipment Costs. The equipment cost is the major economic factor. Hold-up tanks for the caustic waste, acid waste, alum slurry, and concentrated sulfuric acid would probably all be necessary. An agitator would be necessary to mix the caustic and acid waste streams where they converge early in the process. A controller would be necessary to regulate the addition of acid waste if the caustic waste rate should change. An orifice and flow controller would be necessary to regulate the amount of alum slurry if the acidic waste rate were to change. The major prices of equipment for the process include a mixer, flocculator, two settling tanks (only one used at a time), two centrifuges (used simultaneously), a rotary calciner of sufficient size to handle 635 gallons of wet sludge per hour, and a digester, unless the ash is sent directly to the paper makers alum slurry plant.

Recommendations

On the basis of the information obtained during this investigation, the following recommendations are made.

Large Pilot Plant Tests. The largest amount of caustic waste acidified and then coagulated with alum slurry was 16 liters. The results of the tests with respect to the transmittance of the supernatant liquor, settling rates, volume of sludge and centrifuging of the sludge were encouraging. Therefore, larger tests should be performed using a Dorr thickener. The resulting sludge should be concentrated in a borrowed or rented Bird or Sharples continuous centrifuge.

High-Pressure Steam Treatment of Caustic Waste. A study should be made of the effect of steam at pressures in the range of 500 to 1,000 pounds per square inch, gage, on the color of the caustic waste.

Heat Treatment of Sludge under Pressure. The treatment of sludge under high pressure and temperature completely breaks down the gel structure, so that after cooling, the sludge can be easily settled and dewatered. Sludge produced by coagulation of the caustic waste should be pressure treated at higher temperatures to evaluate the effect of the above treatment.

Decolorization with Clay. Further experiments on decolorizing with clay, which has been previously reported by Chumney,[29] should be performed. The revitalizing of the clay by burning off the absorbed color material should be evaluated.

LIMITATIONS

The limitations under which this investigation was made were as follows.

Pressure. All tests were conducted under atmospheric pressure.

Temperature. The majority of the waste treatment tests were performed at room temperature which varied from 25 to about 30 ^{o}C. Some of the tests were performed using waste that had been heated to 50 ^{o}C and 90 ^{o}C.

Quantities of Caustic Waste Treated. One liter of waste was treated in two-liter beakers in most of the tests. In four larger scale tests, 16 liters of waste were treated in 20-liter containers.

Waste Used. The pH of the caustic waste was 10.3 and its transmittance was ten per cent as received.

The pH of the hydrochloric acid waste from the bleaching process was 1.9 and its transmittance was 12 per cent as received.

Agitation. After acidification and alum treatment of the caustic waste, the stirring rates were 75 revolutions per minute for one minute followed by 15 minutes of stirring at 20 - 25 revolutions per minute.

Centrifuging. A laboratory size Sharples super centrifuge was used to concentrate the sludge from the settling tank. The hold-up of the centrifuge bowl was about 175 milliliters when revolving 4,000 to 7,000 revolutions per minute. Sludge feed rates above 100 milliliters per minute resulted in a cloudy effluent. The average feed rate was 75 milliliters per minute.

Calculations used to design a waste color removal plant were based on 1,000,000 gallons of caustic waste per day of the concentration and transmittance of the samples used in this investigation.

V. CONCLUSIONS

On the basis of the experiments performed with the purpose of studying the application of various treatments for decolorizing caustic wash liquor, the following conclusions were drawn.

1. The caustic extraction waste resulting from washing the chlorine-bleached, sulfate, pine pulp after caustic treatment has a ten per cent transmittance and a pH of 10.3. It can be decolorized to yield a transmittance of 85 to 90 per cent, by acidification to a pH of 6.0 with waste hydrochloric acid from the chlorination stage of the bleaching process and by the controlled rate of addition of 1.415 grams of alum per liter of caustic waste, mixing for one minute at 75 revolutions per minute and then at 10 - 25 revolutions per minute for 15 minutes.

2. Flocculating aids do not appreciably increase the rate of settling, volume of the sludge, rate of filtration of the sludge, or the transmittance of the supernatant liquor from alum treatment of the caustic waste.

3. Alum slurry improves the rate of settling and is as effective as chemically pure alum in decolorization of the caustic waste.

4. Use of dilute waste hydrochloric acid from the chlorination stage of the bleaching process can be used for acidification of the caustic waste but results in an increased volume of liquor treated and of settled sludge.

5. The most noticable effect of treating the waste at temperatures of 50 and 90 ^{o}C was to increase the settling rate of the sludge and decrease the volume of the sludge by ten per cent.

6. Further study of the process for decolorizing the waste caustic wash liquor from chlorine-bleached, sulfate, pine pulp on a larger scale appears to be warranted from the results obtained.

VI. SUMMARY

Previous investigation at Virginia Polytechnic Institute proved that a significant amount of color could be removed from the caustic by coagulation with aluminum sulfate. It was recommended that commercial flocculating aids be used with alum to determine their value as a supplement for alum treatment. Therefore, it was the purpose of this investigation to study the practical application of various treatments of caustic wash liquor from chlorine-bleached sulfate, pine pulp, and to design and evaluate a pilot plant for testing further the most promising possibility for its decolorization.

Preliminary tests were performed to obtain data for settling rates of the alum coagulated waste, volume of sludge, rate of filtration of sludge, effect of varying pH, transmittance of the supernatant liquor, and amounts of dry solids before and after ashing. The coagulating properties of C. P. Aluminum sulfate and papermakers alum slurry were compared both with and without flocculating aids. Laboratory tests showed that other methods of treating the waste, such as chlorination of the waste before the addition of the alum, coagulation with various concentrated acids, and coagulation with ferrous sulfate, were of no advantage over plain alum treatment. The tests also showed that the flocculating aids failed to decrease the quantity of alum required or to appreciably increase the transmittance of the resulting effluent. These tests proved that waste acid from the chlorination stage of the pulp bleaching process could be used to lower the pH of

the caustic waste to the desired level of 6.0 at which pH the addition of alum afforded the most effective coagulation.

Sixteen-liter tests were performed to produce larger quantities of sludge for dewatering by means of centrifugation. As a result of these dewatering tests, a plant was designed to produce an effluent whose light transmittance would be 85 per cent when treating 1,000,000 gallons of caustic waste per day. The pH of the highly colored waste (light transmittance of ten per cent) would be adjusted to 6.0 by the addition of 100,000 gallons of the acid waste and then coagulated with 6,600 gallons of alum slurry (18 per cent aluminum sulfate). Treatment of the dried sludge would recover 83.5 per cent of the alum being used.

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VIII. <u>ACKNOWLEDGEMENTS</u>

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