ALUM TREATMENT OF CAUSTIC WASH FROM

CHLORINE BLEACHED KRAFT PULP

by

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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>II. LITERATURE REVIEW</td>
<td>3</td>
</tr>
<tr>
<td>Source and Composition of Waste</td>
<td>4</td>
</tr>
<tr>
<td>Previous Work Done at Virginia Polytechnic Institute</td>
<td>8</td>
</tr>
<tr>
<td>Chlorination of Waste</td>
<td>8</td>
</tr>
<tr>
<td>The Evaluation of Florite as an Adsorbing Medium</td>
<td>9</td>
</tr>
<tr>
<td>Treatment Using Activated Carbon and Aluminum Sulfate</td>
<td>10</td>
</tr>
<tr>
<td>Decolorization Using Various Coagulants and Flocculating Aids</td>
<td>15</td>
</tr>
<tr>
<td>III. EXPERIMENTAL</td>
<td>18</td>
</tr>
<tr>
<td>Purpose of Investigation</td>
<td>18</td>
</tr>
<tr>
<td>Plan of Investigation</td>
<td>18</td>
</tr>
<tr>
<td>Literature Review</td>
<td>18</td>
</tr>
<tr>
<td>Pilot Plant Tests</td>
<td>19</td>
</tr>
<tr>
<td>Apparatus</td>
<td>21</td>
</tr>
<tr>
<td>Materials</td>
<td>29</td>
</tr>
<tr>
<td>Method of Procedure</td>
<td>31</td>
</tr>
<tr>
<td>General Procedure</td>
<td>31</td>
</tr>
<tr>
<td>Dewatering</td>
<td>35</td>
</tr>
<tr>
<td>Spectrophotometric Analysis</td>
<td>36</td>
</tr>
<tr>
<td>Analysis of Samples for Solids Content</td>
<td>36</td>
</tr>
<tr>
<td>Quantitative Analysis for Aluminum Sulfate in the Alum Slurry</td>
<td>37</td>
</tr>
<tr>
<td>Dilution Tests</td>
<td>39</td>
</tr>
<tr>
<td>Data and Results</td>
<td>40</td>
</tr>
<tr>
<td>Pilot Plant Tests</td>
<td>40</td>
</tr>
<tr>
<td>Dewatering Tests</td>
<td>40</td>
</tr>
<tr>
<td>Dilution of Treated Waste with Distilled Water</td>
<td>40</td>
</tr>
<tr>
<td>Properties and Composition of the Aluminum Sulfate Slurry</td>
<td>40</td>
</tr>
<tr>
<td>Sample Calculations</td>
<td>46</td>
</tr>
<tr>
<td>Mass Flow Rates</td>
<td>46</td>
</tr>
<tr>
<td>IV. DISCUSSION</td>
<td>47</td>
</tr>
<tr>
<td>Discussion of Results</td>
<td>47</td>
</tr>
<tr>
<td>General Considerations</td>
<td>47</td>
</tr>
<tr>
<td>Fluctuations</td>
<td>48</td>
</tr>
<tr>
<td>Foaming</td>
<td>50</td>
</tr>
<tr>
<td>Settling</td>
<td>51</td>
</tr>
<tr>
<td>Dewatering Tests</td>
<td>54</td>
</tr>
<tr>
<td>Dilution Test</td>
<td>57</td>
</tr>
</tbody>
</table>
Material Balance ........................................ 58
Light Transmittance ................................... 59
Recommendations ....................................... 60
Limitations ............................................. 61
V. CONCLUSIONS ........................................ 63
VI. SUMMARY ........................................... 65
VII. BIBLIOGRAPHY ...................................... 69
VIII. ACKNOWLEDGMENTS ............................... 71
IX. VITA .................................................. 72
LIST OF TABLES

<table>
<thead>
<tr>
<th>TABLE</th>
<th>I.</th>
<th>Chronological Account of Pilot Plant Tests Made for Alum Treatment of the Caustic Wash Waste Stream</th>
<th>41</th>
</tr>
</thead>
<tbody>
<tr>
<td>TABLE</td>
<td>II.</td>
<td>Calculated Results of Pilot Plant Tests on Color Removal from Caustic Wash of Chlorine Bleached Sulfate Pulp</td>
<td>42</td>
</tr>
<tr>
<td>TABLE</td>
<td>III.</td>
<td>Results of Merco Model 9 Centrifugal Separator Test</td>
<td>43</td>
</tr>
<tr>
<td>TABLE</td>
<td>IV.</td>
<td>Effect of Dilution on Transmittance for Treated Caustic Wash Waste</td>
<td>44</td>
</tr>
<tr>
<td>TABLE</td>
<td>V.</td>
<td>Properties and Composition of the Aluminum Sulfate Slurry</td>
<td>45</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 1.</td>
<td>Merco Model 9 Centrifugal Separator</td>
<td>22</td>
</tr>
<tr>
<td>Figure 2.</td>
<td>Dorr Thickener</td>
<td>23</td>
</tr>
<tr>
<td>Figure 3.</td>
<td>Alum Mixing Tank</td>
<td>27</td>
</tr>
<tr>
<td>Figure 4.</td>
<td>Flocculating Tank</td>
<td>28</td>
</tr>
<tr>
<td>Figure 5.</td>
<td>Schematic Diagram of Equipment Used in the Alum Treatment of Caustic Waste</td>
<td>32</td>
</tr>
</tbody>
</table>
I. INTRODUCTION

Stream pollution is one of the evils born of the industrial age which requires no small amount of consideration and investigation for its elimination. State and federal authorities as well as public opinion have spurred industrial organizations into action to control the amount of waste dumped into rivers and streams. The impetus for this action has been furnished by the passage of restrictive laws which attempt to stipulate that water taken from a stream or river should be returned to the stream or river from which it was taken in the same or better condition than it was when first used.

The pulp and paper industry has been faced with a unique waste disposal problem in which the color of the waste as well as the toxicity is a pollution factor which must be contended with. The color that appears in pulp mill waste streams is caused by extracted resins and lignin products that are washed out of cooked and bleached pulp.

Commercial flocculating agents have been investigated as a means of removing the color from
the pulp waste streams. These flocculating agents do not remove all of the color, but the light transmittance of the waste is greatly increased by their use. Preliminary studies made at Virginia Polytechnic Institute, Blacksburg, Virginia, have indicated that treating the waste with acid to reduce the pH of the waste from approximately 9.5 to 6.0, and then treating the waste with aluminum sulfate, or alum slurry (18 per cent aluminum sulfate), will produce an effluent whose light transmittance will be approximately 85 per cent.

The purpose of this investigation was to continue the color reduction study of alum treatment of caustic wash from chlorine bleached kraft pulp, to determine if a double tray Dorr thickener could be used to settle the coagulated waste, and to determine if a centrifugal separator could be used to dewater the sludge from the Dorr underflow.
II. LITERATURE REVIEW

The literature review for this study consists of a study of the published information on the source and composition of the caustic wash waste from chlorine bleached kraft pulp, previous work done at Virginia Polytechnic Institute on the same waste, and a review of recent published methods of treatment to decrease the color of this waste. This investigation is a continuation of the investigation carried out by Mr. P. W. Ruggieri at Virginia Polytechnic Institute, Blacksburg, Virginia. Ruggieri's work was performed on bench scale with a variety of coagulants while this investigation is on a pilot plant scale, using aluminum sulfate as coagulant. This literature review covers only those phases of waste treatment that have evolved recently. For a presentation of background information, the reader is referred to Mr. Ruggieri's thesis.
Source and Composition of Waste

The following paragraphs briefly describe the source and composition of the wastes from the kraft pulping process.

The alkaline processes provide a minimum of waste in the production of paper, since the digester liquor and washings after digestion are recovered and neutralized. This serves the double purpose of economy and elimination of the difficulty of disposing of an objectionable effluent (3).

During the pulping process, after the charge is blown from the digesters, it is washed several times (4). This wash water is mixed with the spent cooking liquor from the digesters, the black liquor, in order to recover the alkali used in the process. An account of recovery operations has been given in the literature (4,11,12,13). There is some loss of chemical in the waste gases from the recovery furnace operation. These losses amount to 80 to 150 pounds of sodium sulfate per ton of pulp produced.

Another source of waste in the sulfate process occurs in the clarification of the green liquor. The solid material from the recovery furnace is mixed with
a solution of "dissolving liquor" from the causticizing plant. As the chemical dissolves, the liquor becomes green in color. The color is imparted by the iron compounds. The insoluble impurities are settled with the assistance of slaked lime and other coagulating agents\(^{(4,12)}\). The sludge is further treated to recover chemicals. The "white liquor" is now ready to be used in the digesters again. The dregs from the clarifier are washed, and the solids remaining are disposed as waste.

Cellulose is chemically degraded by excessive bleaching\(^{(4)}\); therefore, bleaching conditions must be such as to hold this degradation to a bare minimum.

Chlorine compounds, either direct chlorine or hypochlorite, are generally used to bleach chemical wood pulps\(^{(4)}\). Free chlorine is used as a delignifying agent, acting on the lignin by a substitution reaction which forms hydrochloric acid. The washing stage following chlorination is effective in removing the hydrochloric acid formed, but the remaining chlorinated products are insoluble in water. It is these products which leave a colored pulp.

The water insoluble chlorinated lignins, natural dyestuff, water insoluble organic acids, and other
compounds which color the pulp, are soluble in alkaline solutions. The removal of these colored compounds is carried out by extraction with a weak alkaline solution; caustic soda has been found to be the most effective\(^4\). The chief materials removed by alkali extraction are the chlorinated lignins of high molecular weight. The waste stream from the caustic extraction stage is very dark in color, almost black, and it is this stream which is the subject of this investigation.

All of the colored substances are not removed by the alkaline extraction and the chlorinated and extracted pulp still has a dark color. The function of hypochlorite in multi-stage bleaching is to remove or oxidize the colored residues remaining in the pulp. The amount of hypochlorite needed in the final stage depends upon the degree of previous chlorination and caustic extraction. The hypochlorite treatment of sulfate pulp may be split into two stages\(^4\). The first stage is of short duration and employs a relatively strong hypochlorite. The final stage is carried out for a longer period of time with a small amount of hypochlorite of a low density.
The pulp and paper industry produces two distinct types of waste. They are (1) waste products from pulp mills, and (2) waste products from paper mills. Each process has its own particular treatment problems.

The pulp mill waste products are in the liquors from the digesters, pulp preparation (i.e., sawing logs, debarking, reduction of chips in preparation for cooking, knot removing machines), and pulp thickeners.

The paper mill wastes are produced as the pulp is being combined with other materials such as loaders or fillers. These materials are usually clay, talc, gypsum, precipitated calcium sulfate, or barium sulfate. The waste products come from beaters, regulating and mixing boxes where the fillers are added, and from the actual paper machines.

The digester liquors contain excess chemicals and intercellular substances which have been extracted from the raw wood in the digester.

A typical analyses of pulp and paper mill wastes show that in the sulfate process 64,000 gallons of waste per ton of product are produced and the biological oxygen demand is 123 parts per million. In the miscellaneous paper mill wastes with no bleach there are 39,000 gallons
of waste per ton of product. The biological oxygen demand of this waste is 19 parts per million, and the suspended solids are 452 parts per million. The miscellaneous waste from a paper mill using a bleach process amounts to 47,000 gallons of waste per ton of product, of which the biological oxygen demand is 24 parts per million, and the suspended solids are 66 parts per million.

Mercaptans, which have a very obnoxious odor and are toxic to fish life in concentrations of more than 1.0 part per million, are components of the sulfate process wastes.

**Previous Work Done at Virginia Polytechnic Institute**

The following paragraphs briefly describe previous work conducted at Virginia Polytechnic Institute on removal of color from the caustic wash of chlorine bleached kraft pulp.

**Chlorination of Waste.** Hart\(^{(8)}\) chlorinated caustic wash (acidified with 38 per cent hydrochloric acid) as received from the pulp mill with humidified chlorine gas. He reported that the addition of acid to the waste prior to chlorination reduced the amount of chlorine needed to
achieve a desirable light transmittance of 70 per cent. The maximum chlorine utilization was 400 milliliters at one atmosphere and 25 °C added to 250 milliliters of the caustic wash waste. Reduction of the pH of the waste to values less than 1.0 prior to chlorination made the color removal, from the waste, permanent, while chlorination of the waste at pH values greater than 1.0 removed the color from the waste, but the color returned over a period of a week. Addition of sodium hydroxide to the waste chlorinated at a pH of approximately 0.7, did not reverse the reaction or cause the color of the waste to return. But, when sodium hydroxide was added to samples chlorinated at a pH of 2.0 or greater the color returned very rapidly. The cost of raw materials used in this color removing process was calculated to be $92.84 per ton of paper produced which was obviously uneconomical.

The Evaluation of Florite as an Adsorbing Medium. Chumney(5) conducted an investigation to evaluate a commercial adsorbant, florite, as an adsorbing medium for the removal of color from the waste caustic extraction stream of a bleached kraft process. He used a glass column approximately one inch in diameter,
between 12 and 18 inches high, with an overhead feed tank, and a sampling tap at the bottom of the column. The column was packed with florite obtained from the Floridim Company, Tallahassee, Florida.

Chumney (5) allowed the waste to flow down through the column and collected the treated waste in 100 milliliter lots at the bottom. When the light transmittance of the collected waste became less than 50 per cent, he stopped the operation to wash and reactivate the florite. The florite was regenerated by pouring 50 milliliters of three weight per cent ammonia solution through the column. The florite was then reactivated with a solution of three weight per cent of sulfuric acid.

The results of Chumney's work indicated that florite would remove the color from the caustic extraction stream of a kraft paper process. Furthermore, if the caustic extraction feed is neutralized, 45 per cent more waste can be decolorized to a transmittance of above 80 per cent than if the waste had been used as received from the pulp mill.

Treatment Using Activated Carbon and Aluminum Sulfate. Foushee (7) conducted an investigation to
determine the possibility of using either activated carbon or aluminum sulfate for removing a significant amount of color from the caustic waste stream from bleaching of a kraft pulp.

Color removal tests were performed on the caustic extraction waste utilizing NUCHAR CEE-N activated carbon. He treated 100-milliliter samples of waste with varying amounts of carbon. Six samples were treated with 0.1 gram of activated carbon and stirred for 1, 3, 5, 10, 15, and 30 minutes, respectively. The samples were then filtered through Number 4 Whatman filter paper, and the transmittance of the filtrate was determined. This procedure was repeated using 0.3 gram of carbon per 100 milliliters of waste. All tests were made at a temperature of 25 °C, and pH values of waste ranging from 3.0 to 11.4. Foushee concluded that under these conditions NUCHAR CEE-N activated carbon will not remove a significant amount of color from the caustic extraction waste.

In tests using aluminum sulfate as a color removing agent, Foushee first diluted the caustic wash waste with distilled water prior to the addition of alum. This was done in order to obtain more accurate transmittance
readings on the spectrophotometer. The samples were diluted in the ratio of one volume of waste to two volumes of distilled water and were treated with alum in amounts varying from 0.2 gram to 0.5 gram per liter of diluted waste. The pH of the waste was lowered to approximately 6.0 using 20 per cent sulfuric acid prior to the addition of the alum. The alum was added to the waste by pipeting from an alum solution containing 0.1 gram of aluminum sulfate per milliliter of solution. After addition of the alum, the treated samples were agitated for five minutes at 75 revolutions per minute, and then for 25 minutes at 45 revolutions per minute. The decrease in the color of the samples was determined by measuring the transmittance of settled samples before and after treatment.

After completion of the alum treatment tests on diluted waste samples, the same procedure was repeated using undiluted caustic wash waste.

Using alum as a color removing agent, Foushee concluded that 90 per cent of the color present in the caustic wash waste can be removed by alum coagulation using 1.5 grams of alum per liter of waste at a pH value of 6.0, at 25 °C and stirring time of five minutes at
75 revolutions per minute and 25 minutes at 45 revolutions per minute.

The undiluted waste produced a large volume of sludge when coagulated with alum, and this presented another phase of the investigation, the determination of the settling and filtering characteristics of the sludge.

Two types of filtration experiments were made on the settled sludge from the alum treated caustic wash waste. One operation entailed the use of a sand bed in a Buchner funnel. After 1000 milliliters of the treated waste had settled, the supernatant liquid was removed which left approximately 350 milliliters of sludge. The sludge was fed on the sand bed of approximately 11 square inches. The sludge was allowed to filter through under a gravity head. Foushee reported that sand filtration of the sludge from alum coagulated waste does not appear to have significant value as a means of liquid-solid separation. A throughput of 320 milliliters in 90 minutes is equivalent to a filtering rate of approximately 0.74 gallon per square foot per hour.

Another type of filtration process which Foushee used in his experiments was carried out in two phases. In the first phase the sand bed was replaced by a
0.75 inch bed of filter aid, and the sludge was filtered under a vacuum of 21 inches of mercury. The second phase of vacuum filtration utilized a rotary drum filter at a vacuum of 21 inches of mercury and a filter area of 3.4 square feet. The filter was operated according to FEINC filter operating instructions (6).

Two sludge samples were filtered through a 0.5 inch precoat of filter aid. The drum speed was 0.896 revolution per minute. The volume of the first sludge sample was nine gallons, and was filtered for 15 minutes. The volume of the second sludge sample was 20 gallons and it was filtered for 35 minutes.

The vacuum filtration produced erratic filtration rate data. However, Foushee reported filter rates of 0.176 and 0.168 gallon per square foot per minute for the two sludge samples filtered.

At the conclusion of his tests, Foushee recommended that a centrifuge be investigated as a means of concentrating the sludge formed by coagulation. Foushee also recommended that coagulating or flocculation aid, such as Separan produced by the Dow Chemical Company, be evaluated to determine their value as supplements or replacements for alum.
Decolorization Using Various Coagulants and Flocculating Aids. Ruggieri (10) conducted an investigation to study the practical application of various treatments of caustic wash liquor from the kraft process, and to design and evaluate a pilot plant for testing the most promising possibility for its decolorization.

Ruggieri based his investigation of the results of Foushee's (7) work which showed that a significant amount of color could be removed from the caustic wash waste by coagulation with aluminum sulfate. To determine settling rates, 1000 milliliter samples of undiluted waste were treated with 1.5 grams of alum at a pH of 6.0. After stirring, the sludge was permitted to settle for 30 minutes, the volume occupied by the sludge being recorded at five minute intervals.

Ruggieri used the following flocculating agents in conjunction with alum to determine if coagulation of the caustic waste would be improved by their use: Separan, Guartec, Burtonite, Good-rite K-720S, Good-rite K-721S, Orzan P, and Lytron X-886. The 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
treatment were recorded. Solutions of chemically pure
aluminum sulfate and paper makers alum solutions were
used with the flocculating aids. Alum treatment, with
and without flocculating aids, was compared with
chlorine treatment, concentrated acid treatment, and
ferrous sulfate coagulation.

Sixteen-liter tests were made to produce large
quantities of sludge for dewatering tests by means of
centrifugation. A Sharples centrifuge with a bowl eight
inches high and 1-3/4 inches in diameter was used in
these dewatering tests. The hold-up of the bowl, using
ring dam Number 5C, was about 175 milliliters when in
motion. The speed of the centrifuge bowl was varied
from 3000 to 7000 revolutions per minute. The average
feed rate was approximately 75 milliliters per minute.
During these tests the sludge was dewatered, packing the
inner wall of the bowl with wet solids and yielding a
clear effluent through the nozzles.

The Sharples centrifuge used in this investigation
produced an effluent with transmittances up to 90 per
cent. The bowl scrapings contained 12.9 and 18.4 per
cent dry solids for different feed sludges.
The results of tests using flocculating aids indicated that they failed to decrease the quantity of alum required or to appreciably increase settling rate of the solid or the transmittance of the resulting effluent. Waste hydrochloric acid from the chlorination stage of the pulp bleaching process was shown to be suitable for lowering the pH of the caustic wash from 10.3 to approximately 6.0. The use of dilute waste hydrochloric acid from the bleaching waste for acidification increases the volume of liquor to be treated.

Also, Ruggieri showed that the caustic wash waste could be decolorized with paper makers alum to produce a clear effluent with a transmittance of 85 to 90 per cent, and that the paper makers alum is just as effective as chemically pure alum as a decolorizer. Treating the waste at temperatures of 50 °C and 90 °C increased the settling rate of the sludge and decreased the volume of sludge by 10 per cent.
III. EXPERIMENTAL

In this section is contained information relating to laboratory methods, procedure, data obtained, materials, apparatus, and calculated results.

Purpose of Investigation

The purpose of this investigation was to continue the color reduction study of alum treatment of caustic wash from chlorine bleached kraft pulp, to determine if a double tray Dorr thickener could be used to settle the coagulated waste, and to determine if a centrifugal separator could be used to dewater the sludge from the Dorr underflow.

Plan of Investigation

The general plan of this investigation consisted of a literature review, assembly of a pilot plant, operation of the pilot plant, and evaluation of the process.

Literature Review. A literature review was made of the source and composition of the caustic wash waste,
of previous work done at Virginia Polytechnic Institute on the same waste, and of waste treatment processes for pulp and paper mills.

**Pilot Plant Tests.** Sedimentation tests were performed using a 350-gallon, double tray, Dorr thickener. On the basis of laboratory experiments the capacity of this thickener was estimated at 700 gallons per hour. At least a five or six hour run should be made, which would require about 4000 to 5000 gallons of caustic wash liquor. This liquor was received by tank truck which acted as supply tank. The liquor was pumped and metered to a 50-gallon mixer where hydrochloric acid was added to bring the pH to 6.0.

The neutralized waste flowed to another 50-gallon mixer where paper makers alum was added at a rate varying from one gallon per 36 gallons of waste to one gallon per 53 gallons of waste. This mixture was agitated rapidly with a portable mixer for 0.5 to 2.0 minutes. The effluent from the mixer flowed to a 110-gallon tank, where with slow agitation, floc was formed. The suspension flowed to the Dorr thickener at a rate varying up to 300 gallons per hour to determine the settling capacity.
The clear effluent was tested for color, total solids, and alum content. The thickened sludge was pumped to a storage tank, sampled for analysis, and retained for feed to the experimental centrifuge.

**Dewatering.** Various suppliers were contacted to determine the types and sizes of continuous dewatering equipment (centrifuges, decanters) available and the terms for loan or rent.

From 5000 gallons of caustic waste, about 1000 gallons of thickened sludge were available for dewatering tests. Capacity, product analysis, cycle time, and equipment behavior were evaluated. In cooperation with the supplier, data was to be accumulated to permit estimation of size and cost of a full scale unit.

**Dilution Tests.** To determine the effect of disposal of the effluent into a stream on the color of the stream, the treated waste was diluted with distilled water in ratios varying from 1:1 to 1:20, and the transmittance measured after each addition of distilled water.

**Evaluation.** The data secured was analyzed and the proposed process evaluated for possible economic use.
Apparatus

The apparatus used in this investigation was as follows.


**Centrifugal Separator.** Pilot plant size, Merco, model 9, continuous, serial No 42-257. Manufactured by the Dorr-Oliver Corporation, Stamford, Conn. Used to dewater the sludge from the overflow of the Dorr thickener (Figure 1).

**Crucible, Gooch.** Coors porcelain, without covers, perforated bottoms for filtering, size 2. Obtained from Fisher Scientific Co., Silver Spring, Md. Used with an asbestos mat to filter treated waste under vacuum.

**Dorr Thickener.** Double tray, 30 inches in diameter, 32 inches high. Manufactured by the Dorr-Oliver Corporation, Stamford, Conn. Used to thicken the sludge from the flocculated waste (Figure 2).
Figure 1. Merco Model 9 Centrifugal Separator
FIGURE I. MERCO MODEL 9 CENTRIFUGAL SEPARATOR
DING OLIVER CORPORATION, STAMFORD, CONNECTICUT


Oven, Electric Utility. Model 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.


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.

Used in acid mixing tank to mix hydrochloric acid with incoming caustic wash waste feed.

**Mixer.** Lightnin, serial No 38533, model C-3. Manufactured by Mixing Equipment Co., Rochester, N. Y. Used in alum mixing tank to mix acidified waste with the alum slurry.

**Pump.** Centrifugal, capacity 15 gallons per minute, 3550 rpm, serial No 197032. Manufactured by the Byron Jackson Co., Los Angeles, Calif. Used to pump caustic waste from tank truck to acid mixing tank.

**Pump.** Sigmamotor, model T-6. Maximum capacity 30 gallons per hour through 1/2 inch tube; minimum capacity 5 milliliters per minute through 3/16 inch tube. Obtained from Sigmamotor, Inc., Middleport, N. Y. Used to pump alum to alum mixing tank.

**Spectrophotometer.** Model B, serial No 70554, transmittance range from 0-100 per cent, sensitivity adjustments from 1-4, wave length adjustable from 310-1020 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.
**Tank, Flocculating.** Capacity 110 gallons, wooden. Obtained from Hauser-Stander Tank Co., Cincinnati, Ohio. Used as a container to allow growth of flocculated particles (Figure 3).

**Tank, Mixing.** Capacity 20 gallons, metal, constructed from two lubrication grease containers, volume 3.9 cubic feet, 44 inches high, 14 inches in diameter. Used to mix alum and acidified waste (Figure 4).

**Tank, Mixing.** Capacity 55 gallons, metal, constructed from a standard steel shipping drum. Used to mix hydrochloric acid and raw caustic wash waste.

**Tank, Settling.** Capacity 890 gallons, wooden. Obtained from Hauser-Stander Tank Co., Cincinnati, Ohio. Used as a storage tank for underflow from Dorr thickener, and as a feed tank to the centrifugal separator.
FIGURE 3. FLOCCULATING TANK
FIGURE 4. ALUM MIXING TANK
Materials

The following materials were used in this investigation.

**Acid, Hydrochloric.** ACS specification, lot No 9011A, specific gravity 1.185-1.192, assay 36.5-38.0 per cent. Obtained from J. T. Baker Chemical Co., Phillipsburg, N. J. Used to acidify the caustic wash waste.

**Aluminum Sulfate Slurry.** An aqueous solution of 18 weight per cent $\text{Al}_2(\text{SO}_4)_3$ 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 7.0, to be diluted 25 fold. Obtained from Beckman Division of Beckman Instruments, Inc., Fullerton, Calif. Used to standardize the pH meter.

**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 aluminum in alum slurry.
Standard Sodium Hydroxide Solution. Normality 0.5120.
Prepared from ACS standard, lot No 9127. Standardized
with potassium acid phthalate. Obtained from J. T. Baker
Chemical Co., Phillipsburg, N. J. Used in titrations
determining per cent of Al₂O₃ in alum slurry.

Waste, Caustic Extraction. Density 0.998 gram per
milliliter, pH 10.3, light transmittance 3.0 per cent,
dry solids 0.495 per cent, nonvolatile solids 0.001 per
cent. Received from the West Virginia Pulp and Paper
Co., Covington, Va. Used in all waste treatment tests
and was the waste which was decolorized.
Method of Procedure

The method of procedure for carrying out this investigation is given in the following sections which include the alum treatment of the caustic wash of chlorine bleached kraft pulp for the removal of color, spectrophotometric analysis, determination of per cent solids, and quantitative analysis for alum in the alum slurry used.

General Procedure. A series of pilot plant tests were planned to obtain data concerning the effect of the amount of alum added to the caustic waste on the rate of settling of the sludge obtained. The light transmittance of the waste solution was measured to fully determine the effect of the alum treatment on the waste.

The waste was delivered to the pilot plant by a tank truck which served as a storage tank for the duration of each test. The waste was pumped to the acid mixing tank 5, Figure 5, by a centrifugal pump 1. The rate at which the waste entered the system was measured by the rotameter 4. The feed rate of the caustic wash was an important factor in the overall operation of the pilot plant for this was the rate which determined the
FIGURE 5. SCHEMATIC DIAGRAM OF EQUIPMENT USED IN THE ALUM TREATMENT OF CAUSTIC WASTE
hold-up time in the alum mixing tank, the flocculating tank, and the Dorr thickener.

Concentrated hydrochloric acid (37 to 38 per cent) from the storage tank 10, was added at a rate to maintain a pH of 5.5 to 6.0 in the acid mixing tank. The neutralized waste solution was then piped to the alum mixing tank 6, where it was subjected to fast agitation while the alum was added to the mixture. The hold-up time in this tank was two minutes for a feed rate of five gallons per minute. A standpipe was installed in the tank, and the height of the standpipe determined the hold-up time. For example, with a feed flow rate of five gallons per minute and a standpipe approximately 7 inches tall, the hold-up time was two minutes. A change in either the feed rate or the height of the standpipe would alter this hold-up time, i.e., a feed rate of five gallons per minute and a standpipe 14 inches tall would give a hold-up time of four minutes, or a feed rate of 10 gallons per minute and a standpipe seven inches tall would give a hold-up time of only one minute. The hold-up time in the alum mixing tank was critical because with the violent agitation, the floc would be broken up if the hold-up time was too long; and when the
solution reached the Dorr thickener, a very unsatisfactory separation would result.

The alum was added to the mixture at various rates so that a study could be made of the settling character of alum sludge and of the light transmittance of the treated waste. The feed rate of the alum was controlled through the use of a variable speed Sigmamotor slurry pump 2, and a constant head storage tank 2, which contained the alum slurry.

The alum treated waste flowed from the alum mixing tank to the flocculating tank 7, where the mixture was subjected to slow agitation and a hold-up time of 20 minutes at a five gallon per minute flow rate. Here again the hold-up time was dependent on the feed rate. The standpipe in the flocculating tank was 31 inches tall and the tank itself was 32 inches tall by 32 inches in diameter, so that a limitation existed in that the hold-up time could not be increased for any given feed rate but could only be decreased. The treated solution from the flocculating tank was piped to the Dorr thickener 8, where separation of the solid particles in the solution was obtained. The underflow from the Dorr thickener flowed to the receiving tank 2, for further use. The
overflow from the Dorr thickener was emptied into the sewer. Samples of waste were taken, periodically, from the system at the sampling taps 11, for analysis.

**Dewatering.** The Dorr underflow in the receiving tank 2, was transferred by the centrifugal pump 12, to the continuous centrifugal separator 13. The centrifugal separator used for these tests was a Model 9, Merco centrifugal separator obtained from Dorr-Oliver Corporation, Stamford, Connecticut. The amount of feed supplied to the centrifugal was controlled by valve 15. Initially, valve 16 was closed and valve 14 opened. The feed flow was regulated by opening or closing valve 15, and measured by collecting in a weighed bucket under valve 14. When the desired flow rate was obtained, valve 14 was closed and simultaneously valve 16 was opened. It was necessary to know the centrifugal feed rate so that a material balance could be made around the centrifugal. Samples of the underflow from the separator were taken for analysis. The separator overflow was sampled. Both flows were discharged to the sewer.

Two sizes of nozzles were used in the separator. When the separator was operated at 1610 revolutions per
minute, a nozzle of 0.097 inch in diameter was used. Operating at 2300 revolutions per minute, a nozzle of 0.053 inch in diameter was used.

Spectrophotometric Analysis. A model B, Beckman spectrophotometer was used for measuring and comparing the light transmittance of the treated waste samples. This was expressed 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 was followed in all determinations of transmittance. Preliminary studies revealed that a wavelength of 580 millimicrons provided a satisfactory operating range.

Analysis of Samples for Solids Content. Samples of the raw waste, of the treated waste, and of the streams entering and leaving the Dorr thickener were analyzed for total solids, insoluble solids, and nonvolatile solids. To determine the total solids, a ten milliliter sample was weighed and then placed in an oven where it was dried at 110 °C for 24 hours. The dried sample was weighed and the per cent of total solids was calculated from the difference in weight of the wet sample and the dry sample. To determine the nonvolatile
solids, the dried sample used in determining the total solids in its crucible was placed in an oven and heated to 500 °C for 24 hours. The crucible and sample were cooled and reweighed, and the weight of the residue represented the nonvolatile solids in the sample. The nonvolatile solids as per cent of total solids was calculated from the weight of the total solids and the weight of the nonvolatile solids.

In determining the insoluble solids, ten milliliters of the waste was filtered through a dried, tared Gooch crucible containing an asbestos mat. The solids and crucible were dried in an oven at 105 °C for 24 hours and then weighed. The difference in the weight of the crucible and the mat before and after the filtration of the waste was the amount of insoluble solids.

Quantitative Analysis for Aluminum Sulfate in the Alum Slurry. Samples of 25 grams of the aluminum sulfate slurry were diluted to 100 milliliters and thoroughly agitated. A 25 milliliter aliquot of this sample was titrated with standardized 0.5120 normal sodium hydroxide to a phenolphthalein end point. The volume of sodium hydroxide used in this titration was called A. One
gram of potassium fluoride was added to a 25 milliliter aliquot of the diluted aluminum sulfate slurry and this was titrated with 0.5120 normal sodium hydroxide solution to a phenolphthalein end point. The volume of sodium hydroxide used in this titration was called B. The difference between volume A and volume B was the net volume of 0.5120 normal sodium hydroxide equivalent to the amount of aluminum sulfate in the aliquot. The purpose of the potassium fluoride was to tie up the aluminum sulfate ions so they would not be titrated.
The per cent aluminum sulfate (Al₂(SO₄)₃) in the liquor analyzed was calculated from the analytical results as follows:

\[
\% \text{Al}_2(SO_4)_3 = \frac{(C)(342)(0.5120)(4)(100)}{(6)(1000)(25)}
\]

where:

- \( C \) = net milliliters of 0.5120 normal alkali required for the titrations
- 342 = molecular weight of aluminum sulfate
- 6 = number of equivalents in aluminum sulfate
- 0.5120 = normality of alkali used for titration
- 4 = number of aliquots of sample
- 1000 = milliliters per liter
- 25 = weight of sample, grams
- 100 = conversion to percentage.

**Dilution Tests.** To determine the effect of disposal of the effluent into a stream on the color of the stream, ten milliliters of treated waste with a light transmittance of 80 per cent were diluted with distilled water in ratios varying from 1:1 to 1:20, and the transmittance measured after each addition of distilled water.
Data and Results

The data and results of this investigation are contained in this section.

Pilot Plant Tests. The chronological data taken during the pilot plant tests made on the alum treatment of caustic wash from chlorine bleached kraft pulp using various amounts of alum and varying raw feed flow rates are shown in Table I. The amount of solids in the Dorr thickener overflow and underflow, the ratio of raw feed to alum and raw feed to hydrochloric acid was calculated from the results shown in Table I and are summarized in Table II.

Dewatering Tests. The results of dewatering the underflow from the Dorr thickener using a Merco Model 9 centrifugal separator are presented in Table III.

Dilution of Treated Waste with Distilled Water. The effect on the light transmittance of the overflow diluted with distilled water, is presented in Table IV.

Properties and Composition of the Aluminum Sulfate Slurry. Table V shows the physical properties and composition of the alum used in the pilot plant tests conducted during this investigation.
TABLE I

Chronological Account of Pilot Plant Tests
Made for Alum Treatment of the
Caustic Wash Waste Stream
### TABLE 1

<table>
<thead>
<tr>
<th>Time</th>
<th>Raw Feed</th>
<th>Alum</th>
<th>ML</th>
<th>Durr Top</th>
<th>Durr Bottom</th>
<th>Total Solids</th>
<th>Insoluble Solids</th>
<th>Haemovit Solids</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>gal/min</td>
<td>gal/min</td>
<td>gal/min</td>
<td>gal/min</td>
<td>gal/min</td>
<td>$%$</td>
<td>$%$</td>
<td>$%$</td>
</tr>
<tr>
<td>Test No 1, July 8, 1958</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9:05 AM</td>
<td>10.0</td>
<td>0.082</td>
<td>0.014</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>9:15</td>
<td>10.0</td>
<td>0.082</td>
<td>0.014</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>9:25</td>
<td>10.0</td>
<td>0.082</td>
<td>0.014</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>9:35</td>
<td>10.0</td>
<td>0.082</td>
<td>0.014</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>9:45</td>
<td>10.0</td>
<td>0.082</td>
<td>0.014</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>9:55</td>
<td>10.0</td>
<td>0.082</td>
<td>0.014</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Test No 2, August 2, 1958

| Time     | Raw Feed | Alum | ML | Durr Top | Durr Bottom | Total Solids | Insoluble Solids | Haemovit Solids |
|----------|----------|------|----|---------|-------------|---------------|                 |                 |
| 9:05 AM  | 10.0     | 0.000 | -  | -       | -          | -             | -               | -               |
| 9:15     | 10.0     | 0.000 | -  | -       | -          | -             | -               | -               |
| 9:25     | 10.0     | 0.000 | -  | -       | -          | -             | -               | -               |
| 9:35     | 10.0     | 0.000 | -  | -       | -          | -             | -               | -               |
| 9:45     | 10.0     | 0.000 | -  | -       | -          | -             | -               | -               |
| 9:55     | 10.0     | 0.000 | -  | -       | -          | -             | -               | -               |

Test No 3, October 8, 1958

| Time     | Raw Feed | Alum | ML | Durr Top | Durr Bottom | Total Solids | Insoluble Solids | Haemovit Solids |
|----------|----------|------|----|---------|-------------|---------------|                 |                 |
| 9:05 AM  | 10.0     | 0.076 | 0.009 | -       | -          | -             | -               | -               |
| 9:15     | 10.0     | 0.076 | 0.009 | -       | -          | -             | -               | -               |
| 9:25     | 10.0     | 0.076 | 0.009 | -       | -          | -             | -               | -               |
| 9:35     | 10.0     | 0.076 | 0.009 | -       | -          | -             | -               | -               |
| 9:45     | 10.0     | 0.076 | 0.009 | -       | -          | -             | -               | -               |
| 9:55     | 10.0     | 0.076 | 0.009 | -       | -          | -             | -               | -               |

**Notes:**

1. Specific gravity of raw feed approximately 1.00.
2. Specific gravity of alum slurry approximately 1.15.
### TABLE II

**Calculated Results of Pilot Plant Tests on Color Removal from Caustic Wash of Chlorine Bleached Kraft Pulp**

Ratio of Dorr overflow to underflow was approximately 4:1 for all experiments
Density raw feed was 8.33 pounds per gallon at 70 °F
Density of alum slurry was 9.83 pounds per gallon at 70 °F
Density of hydrochloric acid was 9.9 pounds per gallon at 70 °F

<table>
<thead>
<tr>
<th>Test Date</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
</tr>
</thead>
<tbody>
<tr>
<td>Date of test</td>
<td>7-8-58</td>
<td>8-1-58</td>
<td>8-6-58</td>
<td>8-6-58</td>
<td>8-5-58</td>
<td>10-8-58</td>
<td>10-8-58</td>
</tr>
<tr>
<td>Time of test</td>
<td>10:15 am-11:30 am</td>
<td>9:00 am-11:40 am</td>
<td>2:30 pm-4:30 pm</td>
<td>8:30 pm-10:10 pm</td>
<td>2:30 pm-3:30 pm</td>
<td>9:00 am-2:30 pm</td>
<td>2:30 pm-9:00 pm</td>
</tr>
<tr>
<td>Raw waste feed flow rate, pounds per hour</td>
<td>2137</td>
<td>2472</td>
<td>1999</td>
<td>1999</td>
<td>2499</td>
<td>2780</td>
<td>1720</td>
</tr>
<tr>
<td>Alum slurry flow rate, pounds per hour</td>
<td>25.3</td>
<td>40.8</td>
<td>32.0</td>
<td>46.8</td>
<td>60.0</td>
<td>44.0</td>
<td>49.0</td>
</tr>
<tr>
<td>Acid flow rate, pounds per hour</td>
<td>4.7</td>
<td>5.7</td>
<td>5.1</td>
<td>4.1</td>
<td>5.2</td>
<td>5.4</td>
<td>5.6</td>
</tr>
<tr>
<td>Total feed rate to Dorr thickener (raw waste + alum + acid), pounds per hour</td>
<td>2167</td>
<td>2552</td>
<td>2041</td>
<td>2050</td>
<td>2264</td>
<td>2629</td>
<td>1804</td>
</tr>
<tr>
<td>Total solids in feed to Dorr thickener, pounds per hour</td>
<td>-</td>
<td>24.0</td>
<td>14.4</td>
<td>33.3</td>
<td>33.4</td>
<td>33.4</td>
<td>33.4</td>
</tr>
<tr>
<td>Total solids in overflow from Dorr thickener, pounds per hour</td>
<td>12.9</td>
<td>17.0</td>
<td>11.4</td>
<td>37.2</td>
<td>33.3</td>
<td>33.3</td>
<td>33.3</td>
</tr>
<tr>
<td>Total solids in underflow from Dorr thickener, pounds per hour</td>
<td>5.5</td>
<td>5.7</td>
<td>8.1</td>
<td>9.2</td>
<td>9.8</td>
<td>5.6</td>
<td>8.0</td>
</tr>
<tr>
<td>Nonvolatile solids in feed to Dorr thickener, pounds per hour</td>
<td>-</td>
<td>13.3</td>
<td>10.0</td>
<td>11.2</td>
<td>8.1</td>
<td>9.1</td>
<td>9.1</td>
</tr>
<tr>
<td>Nonvolatile solids in overflow from Dorr thickener, pounds per hour</td>
<td>-</td>
<td>7.0</td>
<td>6.1</td>
<td>10.2</td>
<td>8.0</td>
<td>6.0</td>
<td>9.8</td>
</tr>
<tr>
<td>Nonvolatile solids in underflow from Dorr thickener, pounds per hour</td>
<td>-</td>
<td>3.2</td>
<td>3.2</td>
<td>4.8</td>
<td>2.0</td>
<td>4.0</td>
<td></td>
</tr>
<tr>
<td>Insoluble solids in feed to Dorr thickener, pounds per hour</td>
<td>-</td>
<td>7.7</td>
<td>6.4</td>
<td>7.8</td>
<td>9.5</td>
<td>5.1</td>
<td>6.5</td>
</tr>
<tr>
<td>Insoluble solids in overflow from Dorr thickener, pounds per hour</td>
<td>-</td>
<td>2.0</td>
<td>0.8</td>
<td>0.5</td>
<td>2.8</td>
<td>1.0</td>
<td>4.0</td>
</tr>
<tr>
<td>Insoluble solids in underflow from Dorr thickener, pounds per hour</td>
<td>-</td>
<td>3.1</td>
<td>5.9</td>
<td>4.4</td>
<td>6.2</td>
<td>3.5</td>
<td>4.0</td>
</tr>
<tr>
<td>Light transmittance of Dorr overflow, per cent</td>
<td>69</td>
<td>80</td>
<td>58</td>
<td>66</td>
<td>72</td>
<td>66</td>
<td>75</td>
</tr>
<tr>
<td>Test</td>
<td>Flow Rates</td>
<td>Amount of Insoluble Solids</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>------</td>
<td>------------</td>
<td>---------------------------</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Overflow</td>
<td>Underflow</td>
<td>Overflow</td>
<td>Underflow</td>
<td>Overflow</td>
<td>Underflow</td>
<td></td>
</tr>
<tr>
<td></td>
<td>lb/min</td>
<td>lb/min</td>
<td>%</td>
<td>%</td>
<td>lb/hr</td>
<td>lb/hr</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>32.0</td>
<td>14.0</td>
<td>0.41</td>
<td>1.02</td>
<td>7.0</td>
<td>8.6</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>19.5</td>
<td>7.5</td>
<td>0.43</td>
<td>1.29</td>
<td>5.1</td>
<td>5.8</td>
<td></td>
</tr>
<tr>
<td>Using nozzle No 40, bowl speed 1610 rpm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>48.0</td>
<td>16.0</td>
<td>0.99</td>
<td>2.35</td>
<td>2.9</td>
<td>2.3</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>48.9</td>
<td>16.0</td>
<td>0.85</td>
<td>2.19</td>
<td>2.5</td>
<td>2.1</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>14.0</td>
<td>44.0(1)</td>
<td>0.06</td>
<td>0.14</td>
<td>0.51</td>
<td>0.37</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>20.0</td>
<td>20.0(1)</td>
<td>0.02</td>
<td>0.01</td>
<td>0.24</td>
<td>0.12</td>
<td></td>
</tr>
<tr>
<td>Using nozzle No 53, bowl speed 2300 rpm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(1) The results of these tests are not valid due to the fact that clarified liquor was being pumped from the storage tank to the centrifugal separator.
### TABLE IV

**Effect of Dilution on Transmittance for Treated Caustic Wash Waste**

<table>
<thead>
<tr>
<th>Dilution Ratio</th>
<th>Transmittance</th>
</tr>
</thead>
<tbody>
<tr>
<td>ml water/ml waste</td>
<td>%</td>
</tr>
<tr>
<td>0</td>
<td>81.0</td>
</tr>
<tr>
<td>1</td>
<td>81.0</td>
</tr>
<tr>
<td>2</td>
<td>90.0</td>
</tr>
<tr>
<td>4</td>
<td>92.0</td>
</tr>
<tr>
<td>6</td>
<td>92.0</td>
</tr>
<tr>
<td>8</td>
<td>92.5</td>
</tr>
<tr>
<td>10</td>
<td>93.0</td>
</tr>
<tr>
<td>20</td>
<td>94.0</td>
</tr>
</tbody>
</table>
TABLE V

Properties and Composition of the Aluminum Sulfate Slurry

<table>
<thead>
<tr>
<th></th>
<th>Drum Number(1)</th>
<th>VPI(2)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>1.147</td>
<td>1.147</td>
</tr>
<tr>
<td>pH</td>
<td>3.0</td>
<td>3.3</td>
</tr>
<tr>
<td>Per cent Al₂O₃</td>
<td>4.7</td>
<td>4.85</td>
</tr>
<tr>
<td>Per cent insoluble solids</td>
<td>6.7</td>
<td>4.6</td>
</tr>
</tbody>
</table>

(1) As received from West Virginia Pulp and Paper Company, who produce it for use in the paper making process.

(2) This solution of alum was made at Virginia Polytechnic Institute using technical grade alum. The solution contained approximately 18 weight per cent alum. It was used for part of Experiment 3.
Sample Calculations

An example of the calculation that was employed is given in this section.

**Mass Flow Rates.** The mass flow rates for total, insoluble solids, and nonvolatile solids, as shown in Table II, page 42, were calculated by multiplying the volume flow rate of the solutions in the various streams to the Dorr thickener, by the per cent of solids in the particular stream. To calculate the pounds of insoluble solids in the feed stream to the Dorr thickener the following calculation was made from data shown in Table I, page 41:

\[ K = (R_v)(t)(d)(W_i) \]

where:

- \( K \) = insoluble solids in feed stream, lb/hr
- \( R_v \) = rate of feed to Dorr thickener, gal/min
- \( t \) = conversion factor from minutes to hours
- \( d \) = density of feed solution, lb/gal
- \( W_i \) = insoluble solids, weight fraction

\[ K = (5)(60)(8.33)(0.003) = 7.7. \]
IV. DISCUSSION

The following sections contain an examination of the results obtained in this investigation, the recommendations for further study of the problem, and the limitations imposed upon the experiment.

Discussion of Results

The results of the pilot plant tests and dewatering experiments are discussed in the following paragraphs.

General Considerations. During the first pilot plant test, test A, the conditions were not changed according to a time table as was done in tests B to G, but were changed according to visual observations made during the test. These observations included the amount of sludge in the overflow and underflow of the Dorr thickener, and the color of the Dorr overflow, whether dark or light, clear or murky. The reason the conditions were changed according to visual observation was primarily due to the mechanical functions of the equipment. In other words, the first test constituted a starting-up operation. The performance of the equipment had to be observed during an actual operation before improvements could be made.
Fluctuations. The first test, A, Table I, page 41, performed in the series pointed up the mechanical fallacies which existed in the equipment more than giving any conclusive results. However, the defects which came to light in test A enabled the remaining tests to be made with relatively little mechanical trouble; and, therefore, made the results of the other tests more valid.

In the first pilot plant tests all of the pipe lines from the various tanks were connected to the bottom of the tanks. After the predetermined liquid level in each tank had been reached, the incoming flow rate was adjusted to the same value as the outgoing flow rate to keep the liquid level in the tank constant. This method proved to be very unsatisfactory in establishing steady state conditions throughout the system. It was not possible to adjust all of the flow rates of the incoming feed lines so that they would exactly equal the outgoing flow rates. Because of this inequality in the flow rates, the incoming flow rate had to be changed to prevent the tanks from overflowing or from draining completely. The result of the constant changing of the incoming flow rate was fluctuations throughout the
system. Visual observations, made during this time, indicated that the sludge in the Dorr overflow, after settling, was approximately half the volume of sludge found in the underflow. It is believed that the excessive amount of sludge found in the Dorr overflow was a direct result of the fluctuations in the system.

To eliminate the unsteady flow rate throughout the system, standpipes were installed in the acid mixing tank, the alum mixing tank, and the flocculating tank. These standpipes served two purposes. They gave a constant flow rate throughout the system, and they provided a means of establishing a desired hold-up time in the respective tanks. The height of the standpipe in the acid mixing tank was not critical because the purpose of this tank was only to provide a container to mix the hydrochloric acid and the raw caustic waste. However, the height of the standpipe in the alum mixing tank, and the height of the standpipe in the flocculating tank was critical because, in these two tanks, hold-up time was an important factor. Figure 4, page 28, shows the alum mixing tank with a 4-inch standpipe 7 inches in height. The hold-up time for the mixture in this tank was two minutes.
A 4-inch pipe was used as a standpipe because it offered less slug-flow of fluid and thereby reduced the fluctuations to greater extent than a smaller pipe had done. A vent pipe was added to release any entrained air that might be carried into the pipe line to the floc tank.

Figure 3, page 27, shows the flocculating tank with a 2-inch standpipe 31 inches in height. The hold-up time for the mixture in this tank was 20 minutes.

This arrangement of standpipes completely eliminated fluctuations in the flow of the waste to the Dorr thickener.

Foaming. When the alum was added to the acidified caustic waste, a thick foam formed. The foam when wet was light tan in color, and felt like and had the consistency of "aerosol" shaving soap. The foam probably resulted from a reaction involving the release of carbon dioxide from the raw waste by reaction of the acid alum with the waste. Foam accumulated in the floc tank to a height which varied from 3 to 12 inches and subsequently overflowed. The foam was an additional factor which contributed to the fluctuations in the system.
Settling. Table I, page 41, and Table II, page 42, present the data and results of all the tests made in this investigation. Because the Dorr thickener settles only insoluble solids, these solids are all that are discussed. There was no data for the insoluble solids obtained from test A, because it was a visual operation; and by observing the amount of sludge in the Dorr overflow, it could be determined whether or not the Dorr thickener was functioning properly.

The feed rate for tests B and E was 2555 pounds per hour. In test B the insoluble solids were thickened so that the concentration in the underflow was 6.5 times that in the overflow. The proportion of insoluble solids was one part in the overflow and 7.3 parts in the underflow, in test E.

The concentrations in the overflow resulting from tests B and E are too high for good operation of a Dorr thickener.

The feed rate for tests C and D was 2045 pounds per hour. In test C the insoluble solids were concentrated in the proportion of one part in the overflow and 27 parts in the underflow. The insoluble solids concentration for test D was one part in the overflow and 34 parts in the underflow.
The concentrations resulting from tests C and D showed a definite improvement in the settling characteristics of the Dorr thickener.

The only change that was made in the operating conditions for tests C and D that was different from the operating conditions of tests B and E was the reduction in the feed flow rate to the Dorr thickener. The better settling values obtained in tests C and D were attributed to the 500-pound per hour reduction in the feed flow rate.

In test F the Dorr feed rate was 2429 pounds per hour. The insoluble solids were concentrated in the ratio of one part in the Dorr overflow and 14 parts in the Dorr underflow. In this test the only change made in the operating conditions was to increase the Dorr feed flow rate approximately 384 pounds per hour above the Dorr feed flow rate for tests C and D. The effect of the increase in the Dorr feed flow rate manifests itself when the concentrations of insoluble solids in the Dorr overflow and underflow were compared. In tests C and D for a lower feed rate the underflow to overflow concentration rates of insoluble solids were increased by 16 parts or approximately doubled from
what it was in test E. The feed flow rate for test E was 116 pounds per hour less than the feed flow rate for tests B and E. The increase in the insoluble solids concentration ratio of underflow to overflow was approximately eight parts or double the concentration ratio obtained in tests B and E. The results of these five tests indicate that the maximum feed flow rate for the Dorr thickener used in this investigation, using the alum treated caustic waste slurry, is four gallons per minute or 1999 pounds per hour.

The feed flow rate for test G was 1804 pounds per hour. However, the results obtained from this test were very poor when compared with the five previous tests which had higher feed rates. The concentration of insoluble solids in the Dorr thickener was one part in the overflow and four parts in the underflow. During this test the operation had to be stopped twice. The feed tank on the truck was divided into three compartments, and the operation had to be stopped when a changeover was made from an empty compartment to a full compartment. Another factor which probably contributed to the results obtained in test G was the alum that was used. The paper makers alum which had been used in
previous tests was not available at the start of test Q. Instead, an 18 per cent alum solution made from technical grade alum was made up in the laboratory and this solution was used for about one half of the duration of the test. Paper makers alum was used for the remainder of the test.

Dewatering Tests. The original plans were to use a Bird continuous horizontal solid-bowl centrifuge with a spiral scraper to separate the water from the solids in the Dorr underflow. The solids were to be treated to recover the alum used in the process. A representative of the Bird Machine Company studied the sludge produced in this process and suggested that a Merco continuous centrifugal separator be used instead of the Bird machine because the specific gravity of the slimy sludge and the liquor was essentially the same value, and the Bird continuous centrifugal filter is limited to separations of coarse, nonfriable crystals.

The Merco centrifuge was rented from the Dorr-Oliver Corporation, Stamford, Connecticut, and shipped to the Chemical Engineering Department from Oakland, California.
The Merco centrifugal separator is a disc-bowl type of continuous centrifuge. Figure 1, page 22, shows three views of the Merco centrifugal separator. When used as a clarifier, the feed slurry enters the top of the rotating bowl. As the slurry flows down into the bowl, the liquid travels inward and upward while the solid particles are thrown outward and collect in the bowl. In order to remove the separated solids continuously, the solids with a small amount of liquid are discharged continuously as a slurry into a discharge cover through radial nozzles in the periphery of the bowl. In order to control the density of the discharged sludge, part or all of the sludge may be recirculated.

Table III, page 43, presents the results of the dewatering tests made in this investigation, using a Merco Model 9 centrifugal separator. During tests 1 and 2, nozzle No 40 was used. The diameter of this nozzle opening was 0.097 inch and the bowl traveled at a speed of 1610 revolutions per minute. Only the flow rates of the overflow and underflow were varied during these tests. Also, during tests 1 and 2 the feed solution in the storage tank was continuously agitated.
In test 1 the ratio of overflow to underflow was 2.3. The amount of insoluble solids in the overflow was 7.9 pounds per hour and in the underflow 8.6 pounds per hour. In test 2 the ratio of overflow to underflow was 2.6. The amount of insoluble solids in the overflow was 5.1 pounds per hour and in the underflow 5.8 pounds per hour. In both of these tests the centrifuge only succeeded in dividing the insoluble solids in the feed proportionally in the overflow and underflow, with some slight concentration in the underflow.

In tests 3 and 4 the ratio of overflow to underflow was three. The diameter of the nozzle was 0.053 inch and the bowl traveled at a speed of 2300 revolutions per minute. During tests 3 through 6, the feed slurry in the storage tank was not agitated because of mechanical difficulties, and also the tests were made approximately 24 hours after tests 1 and 2. This is significant because the solids had time to settle in the storage tank; as a consequence, there was a greater concentration of solids in the feed slurry to the centrifuge for tests 3 and 4 than there was for tests 1 and 2. The overflow in tests 3 and 4 contained approximately 2.7 pounds of insoluble solids per hour, and the underflow contained
approximately 2.6 pounds of insoluble solids per hour. Even with the greater concentration of solids in the feed slurry, the centrifuge only succeeded in dividing the insoluble solids proportionally in the overflow and underflow as was noted for tests 1 and 2.

The feed solution for tests 5 and 6 was the clear supernatant liquid from the storage tank, and this accounts for the small amount of insoluble solids found in the overflow and underflow. The results of these two tests do not show an appreciable increase in the solids concentration in the underflow.

The results from the dewatering tests indicate that this Merco centrifugal separator is not satisfactory for dewatering this sludge. This is because of the physical nature of the sludge in the solution. There is a negligible difference in the specific gravities of the sludge and the liquid. The sludge is more of a slime than a solid precipitate.

No alum analysis was made on the sludge from the centrifugal separator because of the unsatisfactory results obtained from the dewatering tests.

**Dilution Test.** A ten-milliliter sample of Dorr overflow which had a light transmittance of 80 per cent
was diluted with distilled water to determine the effect of adding the overflow from the thickener to a river or stream as a means of disposing the treated waste. The results are presented in Table IV, page 44. Diluting the waste tenfold increased the light transmittance approximately 12 per cent.

**Material Balance.** Total solids material balances made on tests B through G indicate discrepancies in the amount of total solids entering the Dorr thickener and the amount of total solids leaving the Dorr thickener. The results from test B indicate that 5.5 per cent of the total solids in the feed to the Dorr thickener remained in the Dorr thickener; from test C, 3.5 per cent remained; from test E, 12 per cent remained. The results from test D indicate that 50.5 per cent more total solids were discharged from the Dorr thickener than originally came in with the feed; for test E, 61 per cent more total solids were discharged; for test G, 15.5 per cent more total solids were discharged.

The discrepancies listed above can be attributed to sampling technique. Grab samples rather than composite samples were taken for each test. If composite samples had been taken, a large number of containers would have
been required to hold the sample, and these containers were not available. When the operating conditions were changed at the beginning of each test, the process was allowed to continue for two hours before any samples were taken. It was thought that two hours would be sufficient time for the process to reach a state of equilibrium. Obviously, a composite sample taken during the first stages of the test would have little value; and after a state of equilibrium had been reached grab samples would furnish the necessary information.

Apparently, when the samples were taken for tests 2, E, F, and G a state of equilibrium had not been attained in the system, or there were fluctuations in the composition of the streams.

**Light Transmittance.** The light transmittance of filtered samples of the Dorr overflow was measured. Transmittances ranging from 58 per cent to 80 per cent were obtained from the tests. These transmittances were not as good as were expected from Ruggieri's\(^{(10)}\) results. Preliminary investigations indicated that desirable light transmittance could be obtained from the process used in this investigation, and the purpose of this investigation did not concern this phase of the process.
Recommendations

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

Dewatering Tests. Tests should be made on various filter aids which could be added to the sludge in the Dorr underflow to increase the specific gravity of the solids. The increase in specific gravity might facilitate the removal of liquid from the sludge in a centrifugal separator.

Centrifugal Separators. If filter aids are not used on the sludge from the Dorr underflow, the Merco centrifugal separator and the Bird continuous separator are eliminated as means of separating the sludge from the liquor of the Dorr underflow. Preliminary tests have indicated that the Sharples Super centrifuge can be used to clarify the sludge obtained in the process. This is a batch process. It is recommended that further tests be made with a Sharples centrifuge to study processes for dewatering the sludge obtained in this process.
Limitations

The scope of work accomplished in this investigation is bounded by the following limitations.

Waste Used. The waste treated for color removal was the caustic wash from chlorine bleached, pine, sulfate digested pulp.

Temperature. All tests were made at a temperature of approximately 130 °F.

Quantities of Caustic Waste Treated. Approximately 5000 gallons of caustic wash waste were treated for each test.

pH. The pH of the waste as received was 10.3. Concentrated, C.P. 38 per cent hydrochloric acid was used to reduce the pH of the waste from 10.3 to approximately 6.0. All tests were made with the pH of the waste reduced to approximately 6.0.

Settling. A double tray Dorr thickener with a volume capacity of approximately 332 gallons was used to settle the treated waste.

Centrifuging. Only a Merco Model 9 centrifugal separator was tested to separate the sludge from the liquor.
Coagulating Agent. The coagulating agent used in the tests was an 18 per cent aluminum sulfate slurry more commonly known as "paper makers alum."

Flow Rates. The caustic waste flow rate was limited to 5.0, 4.0, and 3.5 gallons per minute for the tests in the Dorr thickener and to 27 to 65 pounds per minute for the tests using the Merco Model 9 centrifuge.
V. CONCLUSIONS

The alum treatment of the caustic wash from chlorine bleached kraft pulp using paper makers alum at a temperature of approximately 130 °F, reducing the pH of the caustic wash from 10.3 to 6.0 with 38 per cent concentrated hydrochloric acid before adding alum, settling the treated waste in a 332 gallon double tray Dorr thickener, and dewatering the Dorr underflow with a Merco Model 9 continuous centrifugal separator led to the following conclusions.

1. The Dorr thickener used in this investigation concentrated the sludge formed in the waste solution in the ratio of one part in the overflow and 30 to 35 parts in the underflow when the feed rate to the Dorr thickener was four gallons per minute.

2. A feed rate of five gallons per minute, to the Dorr thickener, produced a concentration ratio of one part in the overflow and eight parts in the underflow.

3. The highest feed rate for this particular waste slurry which would produce satisfactory settling in this Dorr thickener was four gallons per minute.
4. The light transmittance of the filtered caustic waste as received was 2.5 per cent and was increased to 80 per cent when one pound of alum slurry was added to 53.4 pounds of caustic wash from chlorine bleached kraft pulp at a pH of 6.0.

5. One pound of concentrated 38 per cent hydrochloric acid will reduce the pH of approximately 450 pounds of caustic wash waste from 10.3 to 6.0.

6. The Merco Model 9 centrifugal separator concentrated the sludge from the Dorr underflow to only a small extent and this machine was not suitable for dewatering this sludge.
VI. SUMMARY

The purpose of this investigation was to continue the color reduction study of alum treatment of caustic wash from chlorine bleached kraft pulp, to determine if a double tray Dorr thickener could be used to settle the coagulated waste, and to determine if a centrifugal separator could be used to dewater the sludge from the Dorr underflow.

Three experiments were made during this investigation. Each experiment used approximately 5000 gallons of caustic wash from chlorine bleached kraft pulp. The first experiment was a starting-up operation and provided a means for eliminating mechanical difficulties from the equipment used. The results of the first test were not very conclusive. The second experiment was divided into four different tests. During these tests the raw feed flow rate was varied from 2000 to 2500 pounds per hour while the alum slurry flow rate was varied from 39 pounds per hour to 60 pounds per hour. The hydrochloric acid flow rate was five pounds per hour. The third experiment was composed of two tests. The raw feed flow rate varied
from 1750 pounds per hour to 2380 pounds per hour, and the alum slurry flow rate was varied from 44 pounds per hour to 49 pounds per hour. The hydrochloric acid flow rate remained about 5.4 pounds per hour.

The raw caustic wash waste was pumped from a tank truck to a mixing tank where it was mixed with 38 percent hydrochloric acid to reduce the pH of the waste from 10.3 to approximately 6.0. The acidified waste went from the acid mixing tank to an alum mixing tank. In the alum mixing tank aluminum sulfate slurry was added to the acidified waste mixture. The solution was agitated in this tank for approximately two minutes and then flowed to a flocculating tank. The hold-up time in the flocculating tank was approximately 20 minutes, and the solution was subjected to slow agitation while it was in this tank.

The treated solution was sent from the flocculating tank to a Dorr thickener, which had a volume of approximately 332 gallons, where the coagulated solids were concentrated. The percent of insoluble solids in the underflow varied from 0.65 to 1.35. The supernatant liquor from the Dorr thickener overflowed to the drain. The concentrated solids from the Dorr thickener were
pumped to a storage tank which served as a feed tank for the centrifugal separator tests. A Merco continuous centrifugal separator was used for dewatering. Approximately one half of the solids in the feed stream to the Merco centrifuge was found in the Merco overflow while the other half was found in the Merco underflow; therefore, the Merco centrifugal separator was deemed unsatisfactory.

The Dorr thickener used in this investigation concentrated the sludge formed in the waste solution in the ratio of one part in the overflow and 30 to 35 parts in the underflow when the feed rate to the Dorr thickener was four gallons per minute.

A feed rate of five gallons per minute, to the Dorr thickener, produced a concentration ratio of one part in the overflow and eight parts in the underflow.

The highest feed rate for this particular waste slurry which would produce satisfactory settling in this Dorr thickener was four gallons per minute.

The light transmittance of the filtered caustic waste as received was 2.5 per cent and was increased to 80 per cent when one pound of alum slurry was added
to 53.4 pounds of caustic wash from chlorine bleached kraft pulp at a pH of 6.0.

One pound of concentrated 38 per cent hydrochloric acid will reduce the pH of approximately 450 pounds of caustic wash waste from 10.3 to 6.0.

The Merco Model 9 centrifugal separator concentrated the sludge from the Dorr underflow to only a small extent and this machine was not suitable for dewatering this sludge.
VII. BIBLIOGRAPHY


6. FEINCO Filter Instructions and Parts List, Filtration Engineers, Inc., Newark, N. J.


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ABSTRACT

ALUM TREATMENT OF CAUSTIC WASH FROM
CHLORINE BLEACHED KRAFT PULP

by

Richard C. Hart

The purpose of this investigation was to continue the color reduction study of alum treatment of caustic wash from chlorine bleached kraft pulp, to determine if a double tray Dorr thickener could be used to settle the coagulated waste, and to determine if a centrifugal separator could be used to dewater the sludge from the Dorr underflow.

Approximately 5000 gallons of caustic wash from chlorine bleached kraft pulp was used for each phase of this investigation. The raw waste feed flow rate was varied from 1750 pounds per hour to 2499 pounds per hour. The alum slurry flow rate was varied from 39 pounds per hour to 60 pounds per hour. The hydrochloric acid flow rate remained constant at approximately five pounds per hour.

The raw waste was acidified with 38 per cent hydrochloric acid to a pH of 6.0, and treated with alum
sulfate slurry to coagulate the solids in the waste. The coagulated solids were concentrated in a double tray Dorr thickener. The per cent of insoluble solids in the Dorr underflow varied from 0.65 to 1.35. The concentrated solids were fed to a Merco centrifugal separator where the insoluble solids were concentrated in approximately equal proportions in the Merco overflow and underflow.