

TREATMENT OF THE CAUSTIC EXTRACTION WASTE
STREAM OF A SULFATE PULP PROCESS

by

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I. INTRODUCTION

One of the major problems confronting the pulp industry today is the disposal of waste materials. Increased demand from state and federal authorities and public opinion is forcing the industry to eliminate any pollution for which it is responsible.

The pulp industry utilizes great quantities of water in such operations as cooking, washing, and bleaching of the wood fibers. The water is usually obtained from a large stream and directed back into the stream after use. The waste effluents from the mills consume a large amount of oxygen from the water and discolor the stream. Treatments of the wastes have been and are being studied to reduce the oxygen demand.

Unfortunately, most of the waste treatment methods being used today have no effect on the color of the mill effluents. Approximately 90 per cent of the color appearing in pulp mill waste streams is caused by lignin and lignin compounds produced largely by the bleaching of the pulp. Although this color has no detrimental effects on the water or the aquatic

life of the stream, the general public regards it as unsightly pollution.

The purpose of this investigation was to determine the possibility of using either NUCHAR activated carbon or aluminum sulfate for removing a significant amount of color from the caustic extraction waste stream of the West Virginia Pulp and Paper Mill in Covington, Virginia.

II. LITERATURE REVIEW

In order to recall for the reader the pulp manufacturing methods and the waste treatment problems confronting the industry, the literature review for this investigation has been divided into four main sections: (1) methods of pulp manufacturing, (2) types and treatment of sulfate pulp wastes, (3) caustic extraction waste stream, and (4) measuring of color in liquids.

Methods of Pulp Manufacturing

The following sections contain an outline of the major methods of pulp manufacture employed in industry: (1) kraft or sulfate process, (2) soda process, (3) sulfite process, and (4) semichemical process. Special emphasis will be given the sulfate process since the waste with which this investigation is concerned is obtained during the caustic extraction of the sulfate pulp.

Sulfate or Kraft Process. As early as 1938 more pulp was made by the sulfate process than was made by the soda and sulfite processes combined⁽³³⁾. A

distinction should be made between the sulfate and kraft processes. Sutermeister⁽³³⁾ states that the sulfate is any cooking process in which the loss of alkali is made up by adding sodium sulfate, while kraft is that subdivision of the sulfate process in which the pulp is intentionally undercooked in order to produce very strong fibers. The major steps in the production of sulfate pulp and the characteristics of the resulting product will be described in the succeeding sections.

Raw Material. The sulfate process has been adapted to practically all wood species⁽²¹⁾, but presently it is applied chiefly to resinous wood such as pine and fir⁽³³⁾. Sawmill wastes, turpentine butts, veneer cores, and even extracted chips have been used, but because of high cost of harvesting and collection these sources have doubtful economic value.

Wood Preparation. In preparing wood for use in the sulfate process, the logs are first debarked and then subjected to a chipping operation. The chipping operation is accomplished by passing the logs diagonally against the face of

a rapidly revolving disk from which project a number of knives. The number of knives varies from four to twelve, and it is suggested that the more knives present, the more uniform the chips will be⁽³³⁾.

After the primary chipping operation, the wood is screened into three grades: (1) very fine material, (2) good chips, and (3) slivers and coarse pieces. The fine material is considered waste, but is often utilized as boiler fuel. The coarse pieces and slivers are usually recycled to the chipper then rescreened⁽³³⁾.

Digestion. Digestion is the treatment of the wood chips in a pressure vessel called a digester. The digestion period lasts from eight to ten hours at a pressure and temperature of approximately 115 pounds per square inch and 344 °F, respectively⁽¹⁴⁾. A cooking liquor is used which is composed mainly of sodium hydroxide and sodium sulfide. The chief constituent of the liquor is sodium hydroxide having a sulfidity generally in the range of 20 to 30 per cent⁽²²⁾.

The purpose of the cooking is to dissolve the fiber bonding materials of the wood by means of the alkaline liquor, thus leaving the pulp as a fibrous residue. The chemical reactions which take place during the operation are indefinite, but involve the hydrolysis of the lignins to alcohols and acids. The hydrolysis also produces mercaptans and sulfides which are partly responsible for the offensive odor of sulfate mills⁽³²⁾.

Subsequent to the cooking operation, the pulp is separated from the residual cooking solution, called black liquor, which contains the spent reagent and about half of the wood material. The black liquor is then concentrated in evaporators to generate steam and to recover the cooking chemicals for reuse in the process. After removal of the black liquor, the pulp is screened to remove any uncooked wood and knots, and sent to filters and thickeners where a large amount of water is removed. The thickened pulp is next subjected to the bleaching operation.

Bleaching. There are basically two methods of bleaching sulfate pulps: a single-stage, or batch process, in which calcium hypochlorite is employed as the bleaching agent, and a multi-stage process which involves treatment of the pulp with free chlorine, alkaline extraction usually with caustic soda, and a final bleach with calcium hypochlorite^(12,32) and/or chlorine dioxide.

Single-stage bleaching with hypochlorite is one of the oldest bleaching processes utilized today in pulp manufacture. In this process, prepared hypochlorite liquor is added to the pulp under controlled conditions and allowed to react until the desired degree of whiteness is obtained. Hypochlorite is predominately an oxidation reaction which decolorizes and solubilizes the lignin, natural dyes, and other impurities in the fibers⁽¹¹⁾.

The advantages offered by continuous multi-stage bleaching have made it a more economical method than batch bleaching for processing sulfate pulp. No time is lost in filling and

emptying reaction vessels, less retention space, and less equipment are needed per ton of pulp, and production schedules proceed more evenly⁽²²⁾.

Multistage bleaching is a method of purifying pulp whereby the purifying and bleaching chemicals are added in stages, separated by intermediate washing stages in which the reaction products are removed⁽¹²⁾. Multistage bleaching consists basically of three stages: chlorination, alkaline extraction, and hypochlorite bleach. In the first stage, chlorine is added directly to the pulp in chlorination towers under controlled pH conditions. The chlorine reacts with the lignin forming fairly colorless soluble substituted compounds⁽¹²⁾. Some of these chlorine compounds are water soluble and are removed by a water wash after chlorination. The remaining lignin compounds are sent along with the pulp to the second, or alkaline extraction, stage. The remaining chlorinated lignin products dissolve readily in a weak caustic solution; therefore, after a thorough washing with water, the pulp is subjected to an alkaline extraction⁽²³⁾. By

removing these substances with an alkaline solution, less hypochlorite is required in the third stage, and a pulp of high color quality is obtained⁽¹²⁾.

Soda Process. In recent years, a chlorine dioxide stage has been added to the bleaching process⁽⁸⁾. The soda process is one of the two principal alkaline processes⁽⁷⁾, the other being the previously discussed sulfate process.

A pure soda process utilizes a cooking liquor which contains no sulfide⁽⁷⁾, and this characteristic is the major difference between a pure soda process and the sulfate process. However, now most soda mills use a sodium hydroxide cooking liquor containing about five per cent sulfide⁽⁷⁾.

Sulfite Process. The sulfite process is essentially an acid process, using a cooking liquor called acid which is a solution of calcium, or mixed calcium-magnesium, containing an excess of sulfurous acid^(6,21). The cooking liquor is produced at the mill by burning sulfur to sulfur dioxide and reacting the gas with some form of lime to produce a cooking acid of the desired composition and strength⁽⁶⁾.

Using spruce, hemlock, and fir as raw materials in this process, a paper of high bursting strength, fairly high tearing strength, and good sheet-forming properties is produced⁽⁶⁾.

Semichemical Process. Semichemical pulping is a multistage process requiring less vigorous chemical treatment to pulp the wood. The most satisfactory agent for semichemical pulping is a solution of sodium sulfite⁽³³⁾.

One advantage of semichemical pulping is its particular application to hardwoods which are converted to container board and strong coarse wrapping paper⁽¹⁰⁾.

Mechanical Process. The mechanical process is a method for disintegrating wood into a fibrous state without the use of chemicals⁽⁹⁾. The separation of the fibers is accomplished by holding the logs with pressure against the surface of a grinding stone⁽⁹⁾. As the fibers are produced, a stream of water carries the pulp away. The sludge is then classified by screening before being made into such products as wrapping, catalogue, magazine, and tablet papers^(9,24).

Types and Treatment of Sulfate

Pulping Wastes

The waste from a sulfate pulping process can be conveniently catalogued into three streams: (1) wood preparation, (2) wood digestion, and (3) pulp bleaching wastes. The following sections contain a brief description of these effluents and a summary of the commonly used treatment methods.

Wood Preparation Waste. Before the actual pulping process can begin, the logs must be debarked and chipped. During these operations the wood is washed with water sprays, and the resulting waste contains mainly bark with some wood slivers, knots, and a very small quantity of dissolved solids⁽²⁹⁾. Generally, the bark is screened, pressed free of water, and burned in the mill boilers^(14,29). The water from the screens is either discharged into the stream or used in other parts of the mill. The waste contains no significant color, and has little, if any, polluting effect⁽¹⁵⁾.

Digestion Waste. The liquors from the digesters are the most important wastes occurring in the pulping process⁽²⁾. The recovery of the chemicals from these

liquors is usually essential for the economical operation of the mill^(14,29). According to Grant⁽¹⁷⁾, these digestion liquors contain the reaction products of the digestion operation, namely, alkaline soluble lignins, carbohydrates, resins, and fats. Also present in the liquor are varying amounts of sodium hydroxide, sodium sulfide, and sodium hydrosulfide which are recovered for reuse in the process^(2,14,29).

The digestion liquor is treated in a two stage recovery process involving evaporation and incineration⁽²⁹⁾. Evaporation, usually accomplished in four effects, concentrates the liquor and produces a large amount of steam for use throughout the pulping process. After evaporation, the liquor is fed into a furnace where the remaining water is driven off in the form of steam, and the solid matter is ignited. Here the organic constituents are burned to carbon dioxide while the sodium compounds react with the gas to form sodium carbonate. The furnace residue is then causticized to recover the sodium as sodium hydroxide.

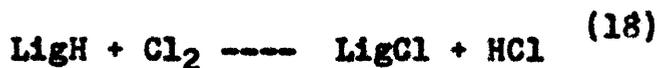
Bleaching Wastes. In the bleaching of sulfate pulp, the total chlorine is usually added in two stages^(18,35). The first, or chlorination stage,

is followed by a water wash and an alkaline wash. The second, or hypochlorite stage, is succeeded by a water wash. The water wash following the first stage is mainly to remove the hydrochloric acid formed by chlorination, and the resulting acid waste is often utilized in the waste treatment for neutralization purposes. A water wash after the hypochlorite stage removes the excess bleaching agent and any water soluble lignin compounds which may still be in the pulp. This waste is generally treated as part of the overall mill waste. The alkaline wash, or caustic extraction waste, separates the two chlorine additions, and the liquor from this operation is the effluent with which this investigation is concerned.

Caustic Extraction Waste Stream

With increased emphasis on stream pollution abatement in the past few years, the significance of color in the kraft mill effluents has greatly increased. The major portion of this color is contributed by the alkaline washing step of the bleaching process. Since the substances which impart the color to the stream exert little or no biochemical oxygen demand, methods for their removal did not until recently enter into the waste treatment problems^(3,27). The following sections contain a summary of the limited amount of literature available concerning the color properties of this stream and the possible methods of color removal.

Color in the Caustic Extraction Waste Stream. In the initial stage of the bleaching process, the pulp is treated with elemental chlorine. The principal reaction which occurs is the substitution reaction of the chlorine with the lignin molecule. The following equation illustrates this reaction with "Lig" representing the unaffected part of the lignin molecule.



After the chlorination is completed, the pulp is washed with water to remove the acid formed in the reaction. Only a small fraction of the chlorinated lignin compounds are soluble in water, but the reaction products are extremely soluble in a weak alkaline solution⁽²³⁾. Therefore, the pulp is caustic extracted or washed after chlorination to remove these lignin compounds which contribute nearly all of the color present in this waste stream.

Removal of Color from Caustic Extraction Waste Stream. Many industrial methods of color removal involve adsorption or coagulation. It is believed that the caustic extraction waste stream can be decolorized by the use of one or both of these processes. In the succeeding sections are presented brief theoretical considerations of adsorption and coagulation, and any available evidence of their utilization for color removal in the pulp industry.

Adsorption by Activated Carbon. Activated carbon and other finely divided powders exhibit the property of removing dyestuffs and similar coloring matter from solution^(26,31). This color removing property is an aspect of the

adsorption phenomenon. It has been suggested that the function of the adsorbent surface may be explained in two ways⁽¹⁶⁾. First, the surface may be regarded as acting in the same manner as in the adsorption of gases, that is, by the mechanisms of molecular attraction or chemical forces. Second, the surface may be regarded as a means for providing a large interfacial area at which the solute may accumulate and lower the existing interfacial tension.

Regardless of which mechanism occurs in adsorption of substances from solution, it is certain that the process depends mainly on the available surface of the adsorbent; and a definite equilibrium is reached in a short time depending on the concentration of the solution and the quantity of adsorbent present⁽¹⁶⁾.

Adsorption was utilized by Chumney⁽¹³⁾ in his investigation of florite as an agent for removing color from the caustic extraction waste stream.

Coagulation. Coagulation of the color in a liquid waste is accomplished by adding to the

liquid a salt, such as the sulfate of aluminum or iron, which hydrolyzes forming the flocculent hydroxide⁽⁴⁾.

The rate and degree of coagulation are controlled by two factors, the probability of adhesion and the probability of collision⁽²⁵⁾. The probability of adhesion is increased by chemical dosing. The object here is to add chemicals to adjust the pH to an optimum value for coagulation, and also provide enveloping films which serve as bonds holding the particles intact after formation. Most industrial applications of coagulation take advantage of the enveloping film effect by using aluminum or iron salts as coagulation reagents. When using aluminum sulfate as the reagent, best results have been obtained between waste pH values of five and six⁽¹⁹⁾.

After chemical treatment of the waste the probability of adhesion is adjusted, and the probability of collision is the controlling factor influencing the rate of coagulation. Usually, a change or two in the direction of flow will permit

enough shear to obtain coagulation in a relatively short time⁽²⁵⁾.

The coagulation process can be employed not only to remove suspended matter from liquids but also to remove dissolved substances from solution^(20,27).

Measuring of Color in Liquids

Two methods widely employed in water and waste treatment processes for measuring of color in liquids are comparison of waste samples with platinum-cobalt color standards⁽¹⁾, and measurement of waste color content in terms of transmittance by means of a spectrophotometer⁽³⁰⁾.

The first method involves the visual matching of waste sample color with the color of prepared solutions of platinum-cobalt standard. The color content of the waste is expressed as 5, 10, 15, etc., corresponding to prepared standard numbers⁽³⁶⁾.

The use of a spectrophotometer involves the measurement of the light transmittance through a standard cell of waste, and the color of the liquid is expressed as per cent transmittance relative to 100 per cent transmittance for an equal cell of distilled water⁽³⁰⁾.

III. EXPERIMENTAL

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

Purpose of Investigation

The purpose of this investigation was to determine the possibility of using either activated carbon or aluminum sulfate for removing a significant amount of color from the caustic extraction waste stream of the West Virginia Pulp and Paper Mill in Covington, Virginia.

Plan of Experimentation

The plan of experimentation for this investigation was divided into two phases, the first being a review of the related literature, and the second being the experimental tests and collection of data.

Literature Review. A review of the available literature concerning various pulping methods, and the characteristics and treatment of the caustic extraction waste stream was conducted to provide a background for this investigation. Methods of measuring the color content of liquids were also reviewed.

Experimental Tests. Color removal tests were performed on the caustic extraction waste utilizing activated carbon and aluminum sulfate as removal agents. Variations in pH of waste at time of treatment and concentration of decolorizing agents were considered. The settling and filtering characteristics of the sludge from the aluminum sulfate treatment were also studied.

Materials

Presented in the following section are the materials used in this color removal investigation.

Acid, Sulfuric. Reagent, CP, 95.5-96.5 per cent, lot No 11014, code 1180. Obtained from the General Chemical Division, Allied Chemical and Dye Corp., New York, N. Y. Used to adjust pH of caustic extraction waste.

Aluminum Sulfate. Crystals, CP, lot No 511104, catalog No A-613. Obtained from the General Chemical Division, Allied Chemical and Dye Corp., New York, N. Y. Used as decolorizing agent.

Aluminum Sulfate "Mud". Solution of aluminum sulfate containing suspended clay. Obtained from West Virginia Pulp and Paper Co., Covington, Virginia. Used as decolorizing agent.

Carbon, Activated. NUCAR CEB-N. Obtained from West Virginia Pulp and Paper Co., Covington, Virginia. Used as decolorizing agent.

Filter Aid, Celite. Obtained from Johns-Manville Corp., New York, N. Y. Used as filter medium in the filtration of the sludge obtained from aluminum sulfate treatment.

Potassium Fluoride. Crystal, lot No F211J, code No 2104. Obtained from the General Chemical Division, Allied Chemical and Dye Corp., New York, N. Y. Used in the chemical analysis of the aluminum sulfate "mud".

Potassium Hydroxide. Pellets, lot No G024A, code No 2118. Obtained from the General Chemical Division, Allied Chemical and Dye Corp., New York, N. Y. Used in the chemical analysis of the aluminum sulfate "mud".

Sand. Mesh, 30/60. Obtained from the Department of Chemical Engineering, Virginia Polytechnic Institute, Blacksburg, Virginia. Used as filter medium in the filtration of the sludge obtained from the aluminum sulfate treatment.

Waste, Caustic Extraction. Obtained from West Virginia Pulp and Paper Co., Covington, Virginia.

Water, Distilled. Obtained from the Department of Chemical Engineering, Virginia Polytechnic Institute, Blacksburg, Virginia. Used for dilution and in chemical analysis.

Apparatus

The apparatus listed below was employed in the experimental portion of this investigation.

Agitator. Six positions, 115 v, ac-dc variable speed motor. Obtained from Fisher Scientific Co., Pittsburgh, Pa. Used to agitate treated caustic waste samples.

Filter, Rotary Vacuum. Serial No SO-209, 12" x 12" drum. Obtained from Filtration Engineers, Inc., Newark, N. J. Used to filter sludge from aluminum sulfate treatment.

Glassware. Assorted, pyrex. Obtained from Fisher Scientific Co., Silver Spring, Md. Used in testing color removal agents.

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.

Spectrophotometer. Model B, serial No 70554, transmittance range 0-100 per cent. Obtained from Fisher Scientific Co., Silver Spring, Md. Used to measure transmittance of waste samples.

Timer. Electric, Precision, "Time-It", graduated in 0.1 second, 115 v, 60 cy, 5 w. Obtained from Precision Scientific Co., Chicago, Ill. Used for timing tests.

Experimental Procedure

The experimental procedure that was followed during this investigation is presented below under the headings of chemical analysis, spectrophotometric analysis, activated carbon treatment, and aluminum sulfate, or alum, coagulation.

Chemical Analysis. The caustic extraction waste was analyzed for total solids, ash, and volatile solids. These determinations were made using procedures presented by Pierce and Haenisch⁽²⁸⁾. A pH titration curve of the waste was made using a pH meter and a known acid solution. From this curve, the alkalinity and normality of the waste were determined.

Spectrophotometric Analysis. A spectrophotometer was selected for measuring the color content of the waste samples. The color content was expressed as per cent transmittance, relative to 100 per cent

transmittance for distilled water. As preliminary studies, the effects of varying wavelength, waste concentration, and pH on the transmittance of the waste were determined.

Effect of Wavelength on Transmittance. A three milliliter sample of untreated waste was placed in the spectrophotometer. The wavelength of the incident light was varied from 0 to 1000 millimicrons in increments of 25 millimicrons, and the corresponding values of transmittance were recorded. From these data, a curve of wavelength versus transmittance was prepared.

Effect of Waste Dilution on Transmittance. Ten samples of untreated waste were diluted with distilled water to concentrations ranging from 25 to 100 per cent waste by volume. The corresponding values of transmittance were recorded, and a curve of dilution versus transmittance was constructed from the resulting data.

Activated Carbon Treatment. The color removal effect of activated carbon, NUCHAR CEE-N, was determined by treating 100-milliliter samples of waste with varying amounts of carbon. Six samples were

each 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 No 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 waste.

Alum Coagulation. The coagulation of the caustic extraction waste with aluminum sulfate, or alum, was first performed on samples diluted with distilled water in order to obtain accurate transmittance readings on the spectrophotometer. Test samples composed of one volume waste and two volumes distilled water were treated with alum in amounts varying from 0.2 gram to 0.5 gram per liter diluted waste. Before treatment, the pH of the samples was lowered to 6 using approximately 20 per cent sulfuric acid. The alum was added to the waste by means of a pipet from an alum solution containing 0.1 gram $\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O}$ per milliliter of solution. Immediately after addition of the alum, the samples were agitated for 5 minutes at 75 revolutions per minute, and then for 25 minutes at 45 revolutions per minute. Decrease in color content

of the samples was determined by measuring the transmittance of the samples before and after treatment.

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

Alum coagulation of the undiluted waste results in a large volume of sludge. The procedures followed in an attempt to determine the settling and filtering characteristics of the sludge are presented in the following sections.

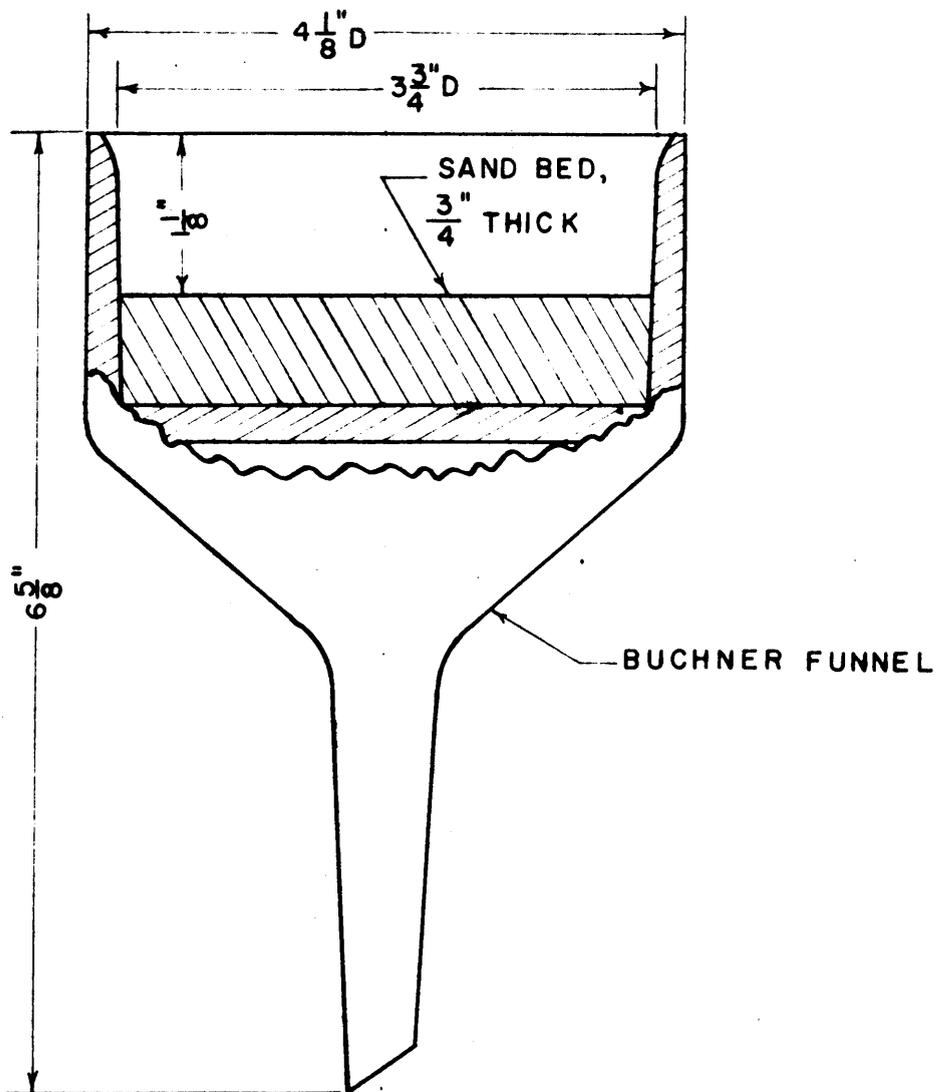
Settling Rate. Two 1000 milliliter samples of undiluted waste were treated with 1.5 grams of alum as previously described. The sludge was permitted to settle for 30 minutes, and the volume occupied by the sludge was recorded at five minute intervals. From these data a plot of volume settled versus time of settling was constructed.

Sand Bed Filtration. A 1000 milliliter sample of waste was treated with alum. After settling for 30 minutes, the supernatant liquid was removed leaving approximately 350 milliliters of sludge. The sludge was then fed onto

a bed of sand in a Buchner funnel, as shown in Figure 1, page 30, and allowed to trickle through under a gravity head. The volume of filtrate at various time intervals was recorded, and plotted as time of filtration versus volume of filtrate.

Vacuum Filtration. Vacuum filtration of the alum coagulated sludge was carried out in two phases. In the first phase, the sand in the sand bed filtration procedure 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 volume of filtrate was recorded at various time intervals and plotted as time of filtration versus volume of filtrate.

The second phase of vacuum filtration was performed utilizing a rotary drum filter under a vacuum of 21 inches of mercury. The filter was operated according to the FEINC filter operating instructions⁽¹⁵⁾. Two sludge samples of 9 and 20 gallons were filtered at a drum speed of 0.896 revolution per minute through a 0.5-inch precoat of filter aid. The times of filtration for the two samples were 15 and 35 minutes, respectively.



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SAND BED FILTER

SCALE: $\frac{3}{4}$ " = 1"	DATE	CASE NO: 57
DRAWN BY: B.R.F.	6-25-57	FILE NO: 599
CHECKED BY: B.R.F.	6-25-57	FIGURE NO: 1
APPROVED BY: <i>F.C.O.</i>	6-20-57	SHEET NO: 1 of 1

At the rate of filtration obtained, calculations were made to determine the filtering area needed to handle 1.5 million gallons of waste per day.

Data and Results

Presented in the following sections are the data and results obtained during the experimental phase of this investigation.

pH Titration. The data obtained from the pH titration of the caustic extraction waste are presented in Table I, page 35, and shown graphically in Figure 2, page 36. From the pH titration curve, the alkalinity and normality of the waste were calculated to be 0.082 per cent and 0.021 normal, respectively, both expressed as sodium hydroxide.

Determination of Wavelength Effect on Transmittance. The data showing the effect of varying wavelength on transmittance of the caustic extraction waste are given in Table II, page 37, and presented graphically in Figure 3, page 38.

Effect of Transmittance of Diluting the Caustic Extraction Waste. Table III, page 39, shows the various degrees to which the caustic waste was diluted and the resulting values of transmittance. These data are presented as a curve of transmittance versus waste concentration curve in Figure 4, page 40.

Effect of pH on Transmittance of Waste. The transmittance of the caustic extraction waste at pH values between 3.0 and 11.4 are contained in Table IV, page 41. The graphical presentation of these data are shown in Figure 5, page 42.

Activated Carbon Treatment of Caustic Extraction Waste. Shown in Table V, page 43, are the various tests made on the caustic extraction waste using NUCHAR activated carbon. Variables of waste pH, carbon dosage, and stirring time were studied.

Data of Alum Coagulation of Diluted Caustic Extraction Waste. The effect of varying the alum dosage, at constant pH, on the transmittance of diluted caustic extraction waste is given by the data in Table VI, page 44. These data are also shown graphically in Figure 6, page 45.

Effect of Varying pH on Waste Transmittance and Sludge Settling Time During Alum Coagulation. Table VII, page 46, shows the data and results obtained from tests conducted to determine the effect of varying the waste pH value, at constant alum dosage, on the transmittance and sludge settling time of the caustic extraction waste.

Sand Filtration of Sludge from Alum Coagulation.

Table VII, page 47, contains filtration time readings and corresponding values of filtrate volume for the sand bed filtration of sludge from the alum coagulation of caustic extraction waste. A graphical presentation of these data are shown in Figure 7, page 48.

Filtration of Sludge Through Filter Aid Bed.

The data obtained from filtration of alum coagulated sludge through a filter aid bed are presented in Table IX, page 49. These data are not presented graphically because of the inability to reproduce the filtration results to a greater degree of accuracy.

Rotary Drum Vacuum Filtration of Sludge from Alum Coagulation of Caustic Extraction Waste. The data obtained from the vacuum drum filtration of two alum coagulated waste samples are presented in Table X, page 50. All of the second sample was filtered because difficulty was encountered in separation of the sludge from the supernatant liquid.

TABLE I

Data and Results of pH Titration of
Caustic Extraction Waste Stream

pH of Sample ^a	Volume of Acid Added ^b
pH	ml
0	11.40
5	10.97
10	10.23
15	9.47
17	8.95
18	8.34
19	7.58
20	7.14
22	6.70
25	6.25
30	5.45
35	4.33
40	3.58
45	2.96
50	2.54

^a Sample volume, 50 milliliters.

^b Normality of acid, 0.05.

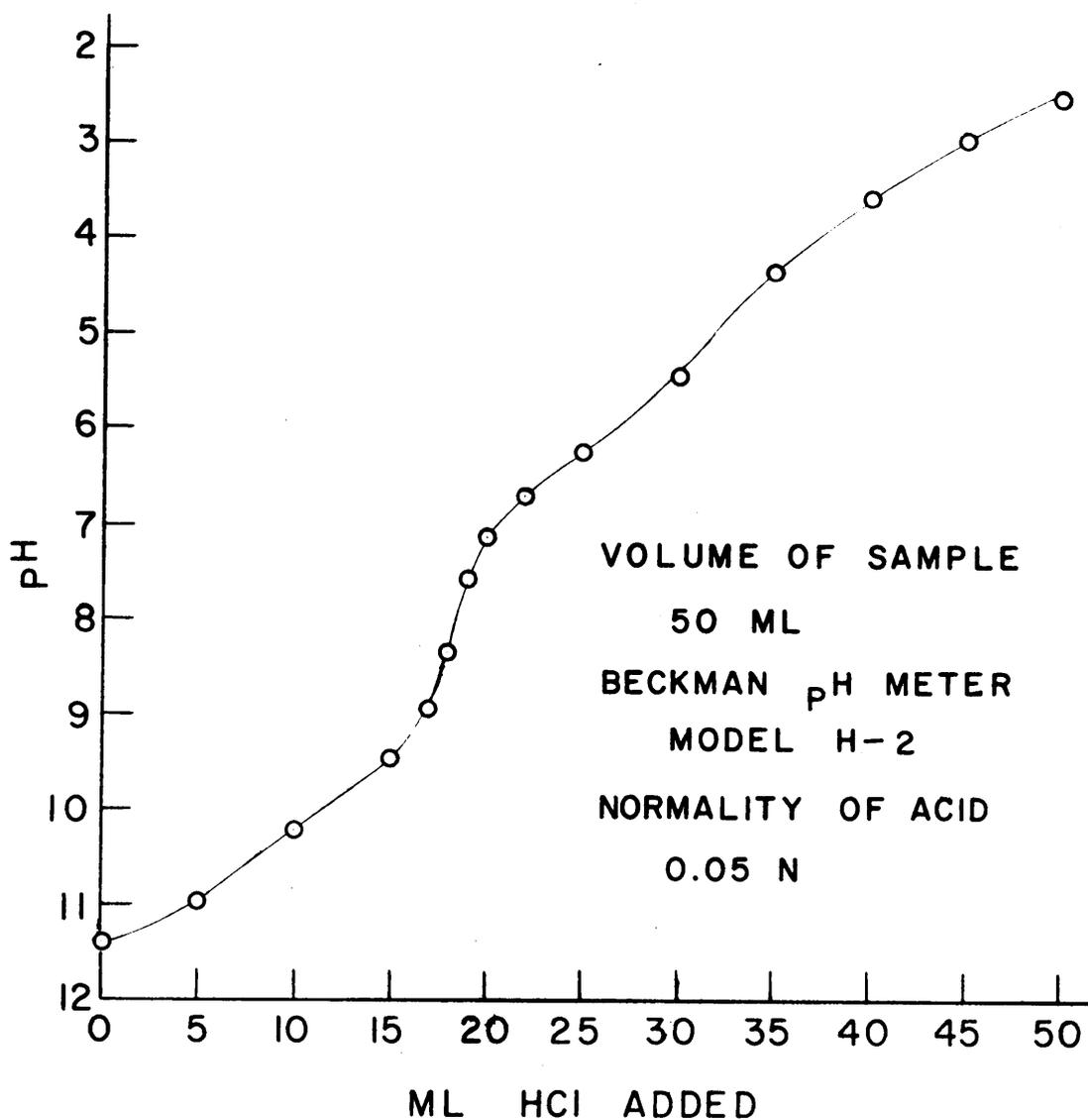


FIGURE 2. pH TITRATION CURVE FOR
CAUSTIC EXTRACTION WASTE STREAM

TABLE II

Data Showing Effect of Transmittance on
Wavelength of Caustic Extraction
Waste Stream

<u>Wavelength</u>	<u>Transmittance</u>
<u>mu</u>	<u>%</u>
550	1.0
575	3.5
600	11.0
625	20.0
650	29.0
675	38.0
700	48.0
725	56.5
750	63.5
775	69.5
800	75.6
825	77.8
850	82.0
875	84.5
900	86.6
925	89.0
950	89.5
975	92.0
1000	92.0

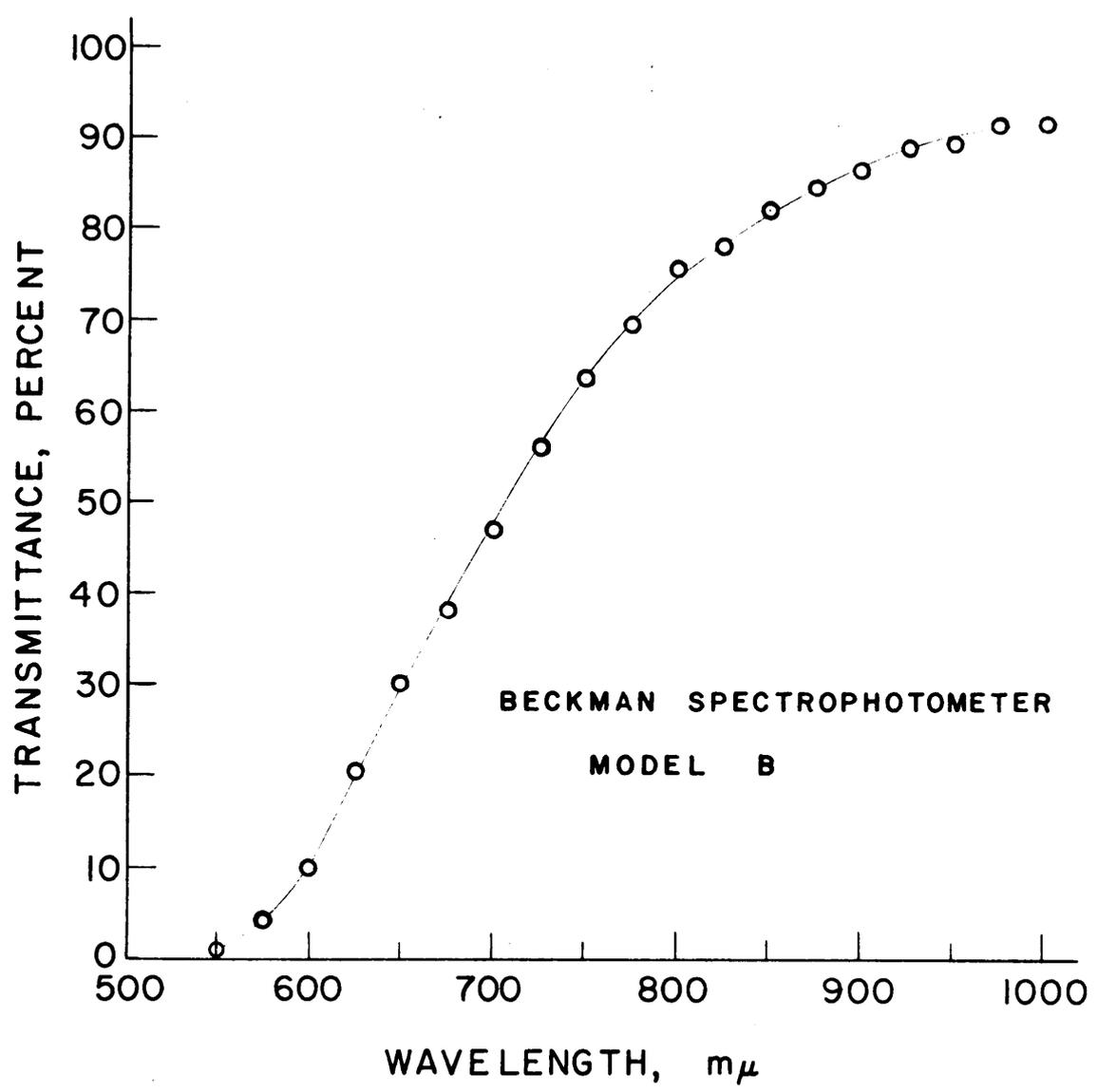


FIGURE 3. RELATION BETWEEN TRANSMITTANCE
AND WAVELENGTH FOR CAUSTIC
EXTRACTION WASTE
STREAM

TABLE III

Effect of Dilution on Transmittance for
Caustic Extraction Waste Stream

Dilution Ratio	Concentration of Waste	Transmittance
<u>ml water</u> <u>ml waste</u>	%	%
0	100.0	7.0
1	50.0	28.5
2	33.3	40.0
3	25.0	50.0
4	20.0	58.0
5	16.7	63.2
8	11.1	75.0
12	7.7	82.0
20	4.8	88.2
30	3.2	92.5
40	2.5	94.0
50	1.96	96.0
65	1.51	97.0
80	1.23	98.0
100	0.99	99.0

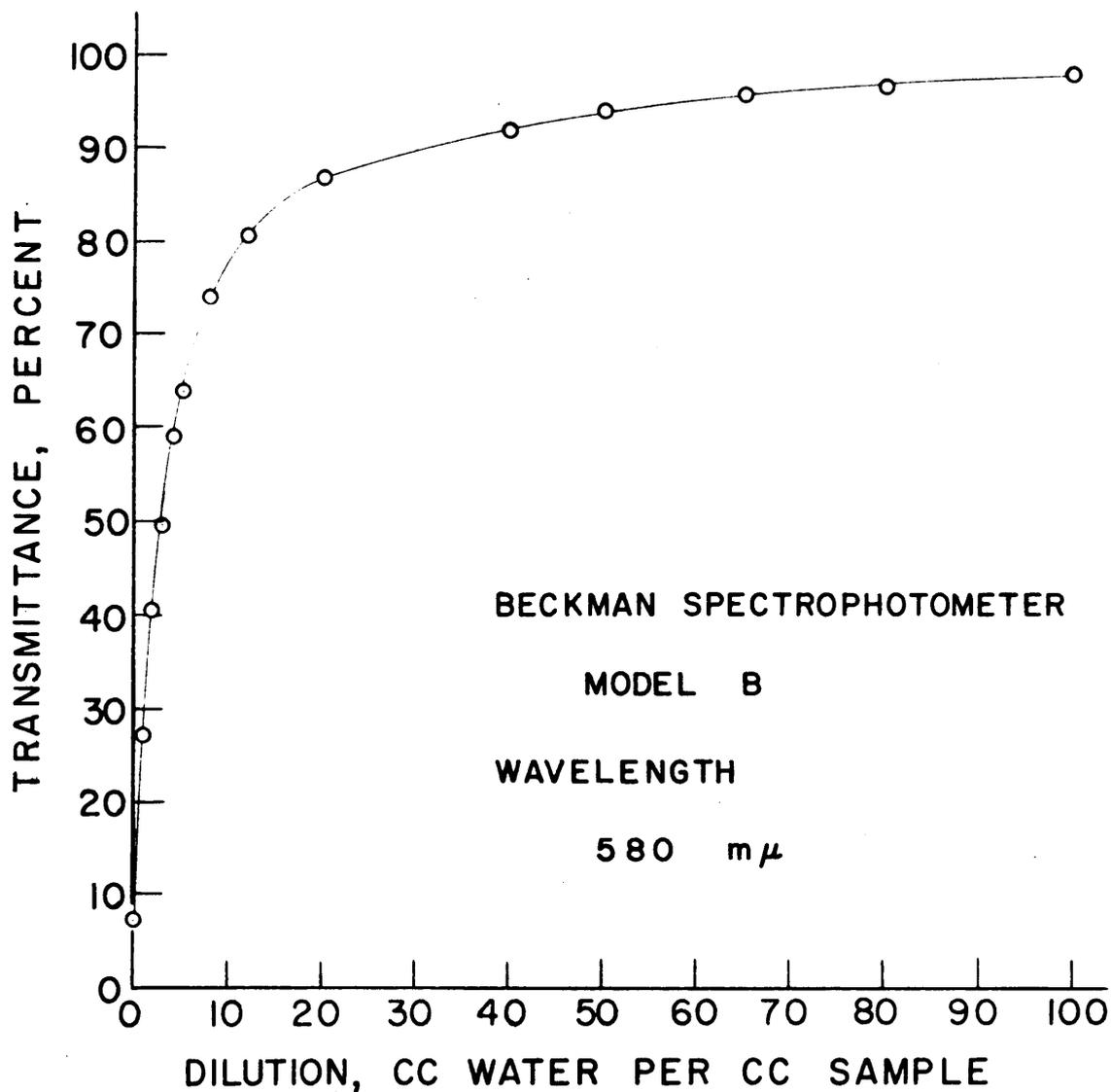


FIGURE 4. RELATION BETWEEN DILUTION AND TRANSMITTANCE FOR CAUSTIC EXTRACTION WASTE STREAM

TABLE IV

Data Showing Effect of pH on Transmittance
of Caustic Extraction Waste Stream

pH ^a of Sample ^b	Transmittance
pH	%
11.4	11.7
9.0	14.9
7.0	19.3
5.0	25.0
4.0	28.4
3.0	31.0

^a Sample pH lowered using approximately 10 per cent hydrochloric acid.

^b Sample volume, 500 milliliters.

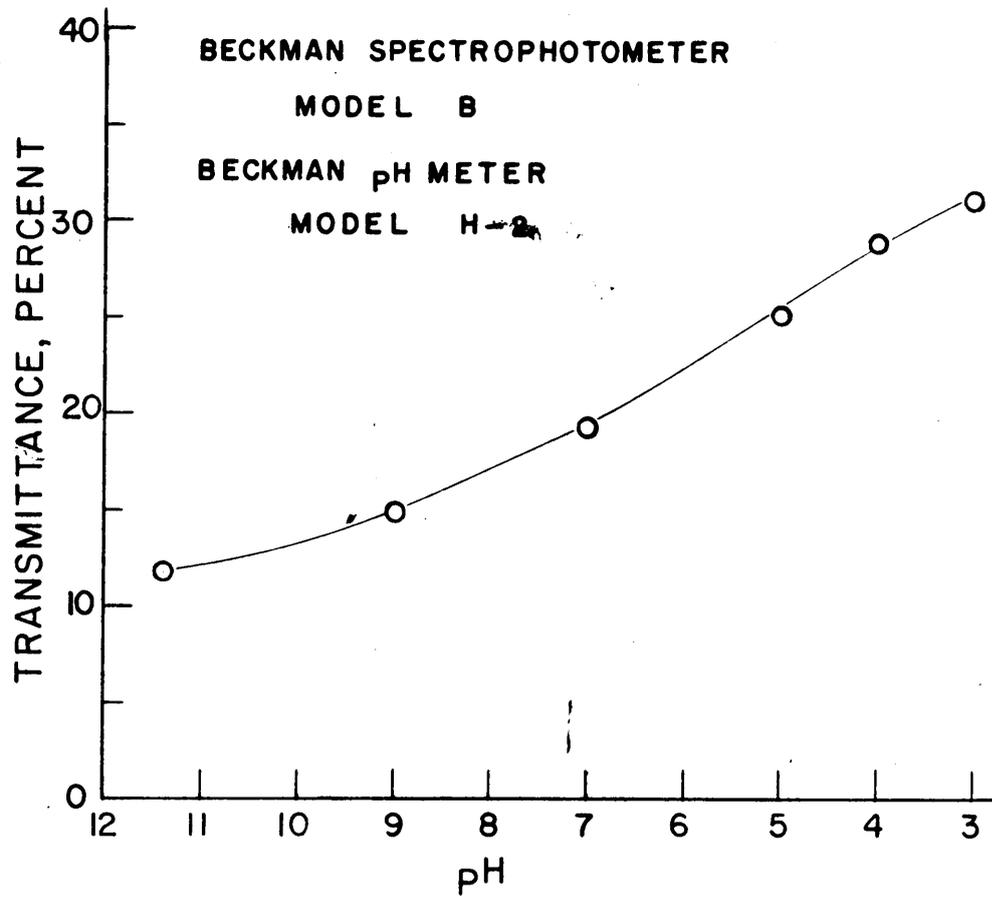


FIGURE 5. RELATION BETWEEN TRANSMITTANCE AND pH FOR CAUSTIC EXTRACTION WASTE STREAM

TABLE V

Data and Results of Activated Carbon Treatment
of Caustic Extraction Waste Stream

Sample ^a No	pH	Carbon ^b Dosage gm	Stirring Time min	Transmittance	
				Before Treatment %	After Treatment %
1	11.0	0.1	1	6.2	7.9
2	11.0	0.1	3	6.2	8.2
3	11.0	0.1	5	6.2	7.9
4	11.0	0.1	10	6.2	6.7
5	11.0	0.1	15	6.2	6.7
6	11.0	0.1	30	6.2	6.2
7	11.0	0.3	1	6.2	8.5
8	11.0	0.3	3	6.2	8.6
9	11.0	0.3	5	6.2	8.6
10	11.0	0.3	10	6.2	8.1
11	11.0	0.3	15	6.2	7.5
12	11.0	0.3	30	6.2	6.4
13	8.0	0.3	10	9.2	10.6
14	7.0	0.3	10	10.4	8.9
15	6.0	0.3	10	13.9	11.9
16	3.0	0.3	10	23.4	20.0

^a Sample volume, 100 milliliters.

^b NUCHAR CEE-N.

TABLE VI

Data and Results of Alum Coagulation of
Diluted Caustic Extraction Waste

Sample ^a	Alum Dosage	pH of Sample	Transmittance	
			Before Treatment	After Treatment
No	gm/l	pH	%	%
1	0.2	6	36	30
2	0.2	6	39.5	34
3	0.3	6	36	73
4	0.3	6	36	23
5	0.4	6	37.5	92
6	0.4	6	35	90
7	0.5	6	39.5	91
8	0.5	6	39.5	86

^a Sample volume, 2000 milliliters containing one volume waste and two volumes distilled water.

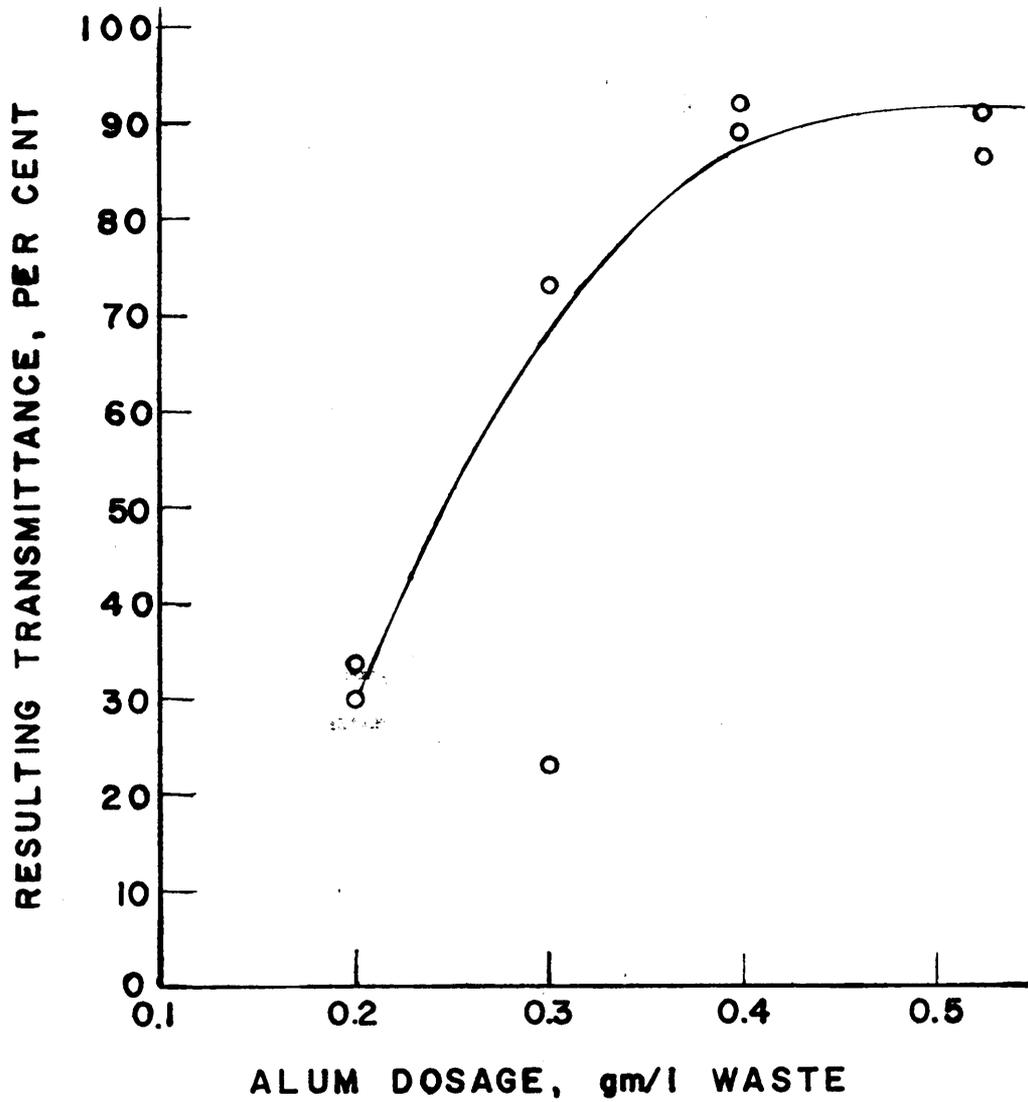


FIGURE 6. EFFECT OF ALUM D DOSAGE ON
TRANSMITTANCE OF CAUSTIC EXTRACTION
WASTE STREAM

TABLE VII

Data Showing Effect of Varying pH and Temperature
on Alum Coagulation of Caustic Extraction Waste

Sample ^a No	Treatment Tempera- ture °C	pH of Sample	Alum Dosage gm/l	Transmittance ^b		Sludge ^c Volume ml
				Before Treat- ment %	After Treat- ment %	
1	25	6	1.5	14	89	300
2	25	6	1.5	14	88	300
3	25	6	1.5	12	74	300
4	25	6	1.5	12	74	300
5	25	8	1.5	4.5	82	400
6	25	8	1.5	4.5	83	400
7	25	9	1.5	4.5	85	600
8	25	9	1.5	4.5	85	600
9	25	10	1.5	3.9	80	850
10	25	10	1.5	3.9	76	850
11	60	6	1.5	3	81	500
12	60	6	1.5	3	83	500
13	61	6	1.5	3	90	500
14	62	6	1.5	3	92	500

^a Sample volume, 1000 milliliters.

^b Transmittance measured at wavelength of 580 millimicrons.

^c After settling 30 minutes.

TABLE VIII

Data Obtained from Sand Filtration^a
of Alum Coagulated Caustic
Extraction Waste^b

Filtration Time	Filtrate Volume
min	ml
0	0
1	30
2	40
4	50
6	60
8	78
10	88
12	100
18	127
24	150
30	170
40	205
50	240
60	265
70	290
80	310
90	320

^a Bed area, 11 square inches.

^b Sludge volume, 350 milliliters.

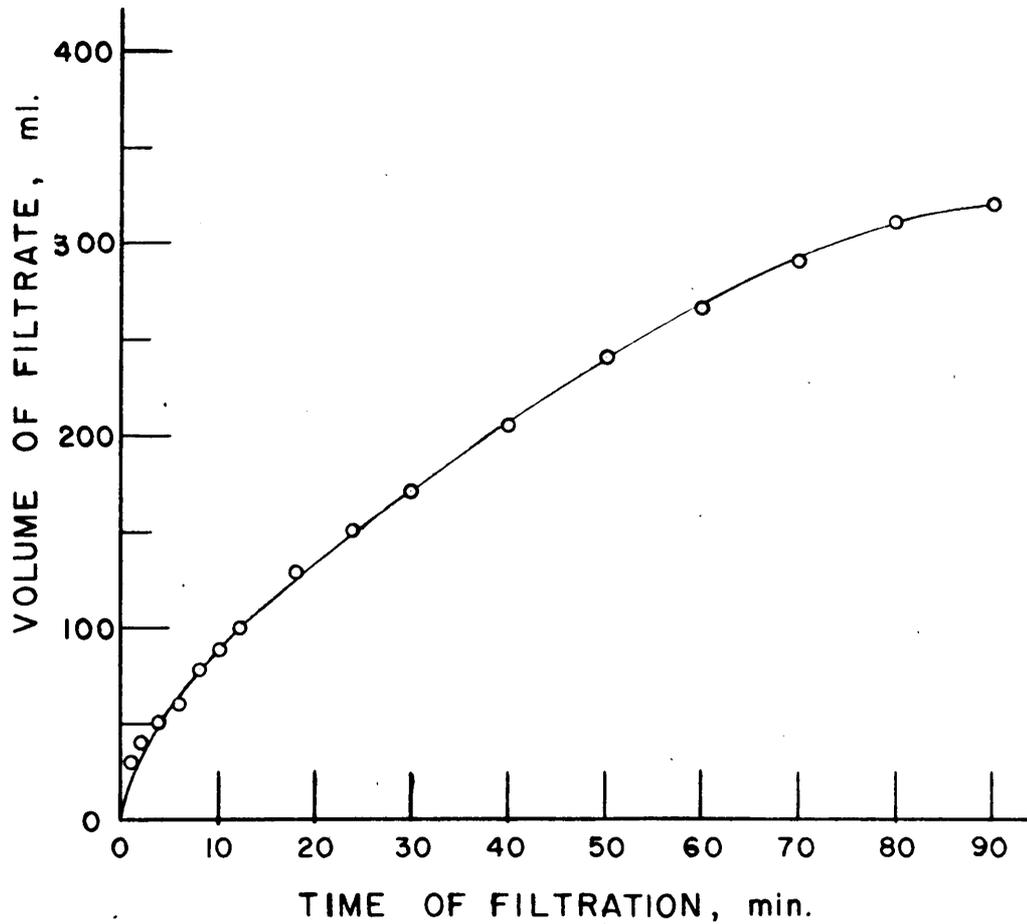


FIGURE 7. RELATION BETWEEN TIME OF FILTRATION AND VOLUME FILTERED FOR SAND FILTRATION

TABLE IX

Data for Vacuum^a Filtration of Alum
Coagulated Caustic Extraction
Waste Through Filter Aid^b

Sample ^c Number					
1		2		3	
Time	Volume	Time	Volume	Time	Volume
min	ml	min	ml	min	ml
0	0	0	0	0	0
1	80	0.18	50	0.33	50
2	150	0.36	100	0.55	100
4	275	0.56	150	0.86	150
6.5	400	0.76	200	1.21	200
		1.0	250	1.86	250
		1.34	300	2.20	300
		1.69	550	3.75	400
		2.12	400	5.17	500
				8.50	600
				11.33	700
				13.50	800

^a Vacuum, 22 inches Hg.

^b Area of bed, 11 square inches; depth of bed, 0.75 inch.

^c Sample volumes before settling: No 1, 1000 milliliters; No 2, 1000 milliliters; No 3, 2000 milliliters.

TABLE X

Data Obtained from Filtration of Alum
Coagulated Caustic Extraction Waste
Using Rotary Drum Vacuum Filter

	Test Number	
	1	2
Sample volume, gal	21	20
Alum added, gm/liter	1.5	1.5
Settling time, min	30	30
Volume filtered, gal	9	20
Drum speed, rpm	0.895	0.895
Vacuum, in. Hg	21	21
Filter area, sq ft	3.4	3.4
Filter aid cake thickness, in.	0.5	0.5
Filtration time, min	15	35
Volume filtered, gal/rev	0.67	0.64
Volume filtered, gal/sq ft, min	0.176	0.168

Sample Calculations

Calculations employed in this investigation are presented in this section.

Preparation of Acid for pH Titration. The volume of 12 normal acid needed to prepare 500 milliliters of 0.05 normal acid for use in pH titration of the caustic waste was determined by the following equation:

$$V' \times N' = V'' \times N''$$

where:

V' volume of concentration acid, ml

N' normality of concentrated acid

V'' volume of acid used for titration, ml

N'' normality of acid used for titration

$$V' \times 12 = 500 \times 0.05$$

$$V' = 2.08 \text{ ml}$$

Preparation of Alum Solution. The alum solution used in coagulation tests was prepared by dissolving 100 grams of $\text{Al}_2(\text{SO}_4)_3$ in 500 milliliters of boiling distilled water and then diluting the solution to 1000 milliliters. One milliliter of this solution will contain 0.1 gram aluminum sulfate.

IV. DISCUSSION

An analysis and discussion of the results obtained from this investigation are included in this section together with recommendations for future work and a summary of the limitations controlling the investigation.

Discussion of Results

The discussion of the results obtained from this investigation has been divided into the following three sections: (1) spectrophotometric studies, (2) activated carbon treatment, and (3) alum coagulation.

Spectrophotometric Studies. After selection of transmittance as the method of color measurement for this investigation, the effects upon transmittance of wavelength, waste dilution, and pH of waste were determined.

Wavelength Effect. As shown in Table II, page 37, and Figure 3, page 38, the transmittance of the caustic extraction waste increases from one to 99 per cent as wavelength was increased from 550 to 1000 millimicrons. From the curve in

Figure 3, page 38, the wavelength of 580 millimicrons was chosen to be used in analysis of all test samples for color reduction. This wavelength was selected because it would permit maximum utilization of the spectrophotometer sensitivity.

Waste Dilution Effect. It is shown in Table III, page 39, that by reducing the waste concentration from 100 to 0.99 volume per cent with distilled water, the transmittance was increased from 7.0 to 99.0 per cent. Intermediate values of concentration and corresponding transmittance readings are plotted in Figure 4, page 40. This curve may be helpful in estimating the effect that caustic extraction waste will have on the stream or river into which it is disposed. By knowing the stream flow rate, an approximate transmittance or color content value of the stream after waste addition can be determined.

pH Effect. The caustic extraction as it is discharged from the bleaching plant usually varies in pH value from 10.5 to 11.5. Table IV, page 41, and Figure 5, page 42, show the effect of pH on the transmittance of waste having an initial pH

value of 11.4. The transmittance of this particular sample was increased from 11.7 to 31.0 per cent by lowering the pH from 11.4 to 3.0.

Activated Carbon Treatment. From Table V, page 43, it is seen that treatment of the caustic extraction waste with NUCHAR CEE-N activated carbon resulted in no appreciable increase in waste transmittance. Carbon treatment at pH values of 3, 6, and 7 actually resulted in a lowering of the waste transmittance. It is possible that this lowering of transmittance was probably caused by elevation of the pH value of the waste by the adsorption of hydrogen ions from the waste solution.

Alum Coagulation. Alum coagulation of the caustic and filtration of the resulting sludge will be discussed under the following headings: determination of alum dosage, effect of pH and temperature on transmittance and sludge settling, sand filtration, and vacuum filtration.

Determination of Alum Dosage. As shown in Table VI, page 44, it was possible to increase the transmittance of the caustic waste from 37 to over 90 per cent by alum coagulation at

pH of 6. Samples 1 and 2, alum dosage of 0.2 gram per liter diluted waste, and sample 3, alum dosage of 0.3 gram per liter undiluted waste, resulted in a decrease in waste transmittance. It was observed in these samples that the floc particles formed by coagulation failed to settle properly, thus leaving suspended matter in the liquid which permitted less light to pass through the treated sample than passed through untreated waste. In an attempt to prevent this situation from occurring in treatment of undiluted waste, it was decided to use an alum dosage of 1.5 grams per liter for treatment of undiluted waste. A dosage of 1.5 grams per liter of undiluted waste corresponds to a dosage of 0.5 gram per liter of diluted waste.

Effect of pH and Temperature on Transmittance and Sludge Settling. Samples 1 through 14 in Table VII, page 46, show the effect of varying pH on transmittance and sludge settling. Although there was no significant difference in transmittance of 1000-milliliter samples treated at pH values of 6, 7, 8, 9, and 10, there was a

difference in sludge volume after permitting the samples to settle for 30 minutes. The volume occupied by the sludge varied from 300 milliliters at treatment pH of 6 to 850 milliliters at treatment pH of 10. It is desirable to treat the waste under conditions to obtain maximum transmittance and minimum sludge volume after a reasonable settling time.

The waste as it is discharged from the bleaching plant is at a temperature of approximately 61 °C. Alum coagulation at this temperature gives a transmittance of approximately 90 per cent and a sludge volume of 500 milliliters after settling for 30 minutes. The floc particles coagulated at this elevated temperature did not appear to be as large as those particles formed at 25 °C. It is believed that floc particle size varies inversely with pH of waste and treatment temperature.

Sand Filtration. Sand filtration of the sludge from alum coagulated caustic waste as shown in Table VIII, page 47, does not appear to have significant value as a means of liquid-solid separation. The throughput of 320

milliliters in 90 minutes obtained in this experiment is equivalent to a filtering rate of approximately 0.74 gallon per square foot per hour.

Figure 7, page 48, shows that after the first 10 minutes of filtration, there is no appreciable increase in rate of filtration, and the curve follows approximately the equation of a hyperbola.

Vacuum Filtration. Vacuum filtration of alum coagulated sludge samples through filter aid beds produced erratic filtration rate data. From the data of these tests, Table IX, page 49, it can be seen, for example, that the time required to filter 400 milliliters varied from 2.12 to 6.4 minutes. The variation in filter rates from 0.02 to 0.65 gallon per square foot per minute for these tests is not reasonable, but it can be partially explained in two ways. First, since the tests were performed on different days, there may exist uncontrollable conditions which have large effects on floc particle size. Second, the filter aid beds used could have been of different density even though the three beds were all 0.75-inch thick.

The data obtained from rotary drum vacuum filtration of the alum coagulated sludge are presented in Table X, page 50. Even though the entire volume of sample 2 was filtered, comparable filter rates of 0.176 and 0.168 gallon per square foot per minute, respectively, were obtained for the two samples. It is a greater possibility that the precoats used in these two tests were more uniform than the filter beds employed in the first three vacuum filtration tests. The increase in filter rate of the drum tests over the fixed bed tests may be attributed to a reduction from 0.75 to 0.5 inch in filter aid thickness.

Recommendations

It has been proven by this investigation that the color content of the caustic extraction waste from a sulfate pulp process can be reduced by coagulation. The following recommendations are made for projects designed to refine the coagulation process.

Coagulating Aids. It is recommended that a 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.

Coagulation Procedure. An investigation should be made concerning the recycling of a portion of the sludge particles into the untreated waste for floc seeding purposes during the coagulation procedure.

Vacuum Filtration. It is recommended that additional tests be conducted to evaluate a precoated rotary drum filter as a method for dewatering the sludge produced by coagulation. The constant removal of the sludge cake from the precoat during filtration should also be investigated.

Centrifuging of Sludge. It is recommended that a Bird centrifuge be investigated as a means of concentrating the sludge formed by coagulation.

Limitations

This investigation of caustic extraction waste color removal was conducted under the following limitations:

Caustic Extraction Waste. The caustic extraction waste employed in this investigation was obtained from the sulfate pulp process of the West Virginia Pulp and Paper Mill located at Covington, Virginia.

Activated Carbon Treatment. Treatment with NUCHAR CEE-N activated carbon was accomplished at the following conditions:

- (1) temperature of 25 °C
- (2) pH values of waste ranging from 3 to 11.4
- (3) carbon content of 0.1 and 0.3 gram per 100 milliliters of waste
- (4) stirring times of 1, 3, 5, 10, 15, and 30 minutes.

Aluminum Sulfate Treatment. Coagulation tests on the caustic extraction waste were performed under the following conditions:

- (1) temperatures of 25, 60, 61, and 62 °C
- (2) pH values of waste of 6, 7, 8, 9, and 10

- (3) alum additions of 0.6, 0.9, 1.2, and 1.5 grams alum per liter of undiluted waste
- (4) stirring time of 5 minutes at 75 revolutions per minute followed by 25 minutes at 45 revolutions per minute.

Vacuum Filtration. The alum coagulated sludge was filtered through an 11-square inch filter aid bed, 0.75-inch thick, at 25 °C under vacuum of 22 inches of mercury. Filtration employing a filter aid precoated drum was accomplished at 25 °C under vacuum of 21 inches of mercury and a drum speed of 0.895 revolution per minute.

V. CONCLUSIONS

The removal of color from the caustic extraction waste of the West Virginia Pulp and Paper Mill of Covington, Virginia, was investigated using NUCHAR CEE-N activated carbon and aluminum sulfate. This experimental work led to the following conclusions:

1. NUCHAR CEE-N activated carbon treatment at temperature of 25 °C, pH values of waste ranging from 3 to 11.4, carbon content of 0.1 and 0.3 gram per 100 milliliters of waste, and stirring times of 1, 3, 5, 10, 15, and 30 minutes will not remove a significant amount of color from the caustic extraction waste.

2. Ninety per cent of the color present in the caustic extraction waste at pH value of 6 can be removed by alum coagulation using 1.5 grams alum per liter of waste at 25 °C and stirring time of 5 minutes at 75 revolutions per minute and 25 minutes at 45 revolutions per minute.

VI. SUMMARY

The purpose of this investigation was to evaluate the use of NUCHAR activated carbon and aluminum sulfate as agents for removing a significant amount of color from the caustic extraction waste of a sulfate pulp process.

After a thorough search of the related literature was completed, experimental tests were conducted using activated carbon and aluminum sulfate. Fourteen tests employing activated carbon were made at 25 °C, pH values of waste ranging from 3 to 11.4, carbon content of 0.1 and 0.3 gram per 100 milliliters of waste, and stirring times of 1, 3, 5, 10, 15, and 30 minutes.

Treatment of the waste with aluminum sulfate was conducted at temperatures of 25, 60, 61, and 62 °C, pH values of waste of 6, 7, 8, 9, and 10, and alum additions of 0.6, 0.0, 1.2, and 1.5 grams alum per liter of undiluted waste. Stirring time for these treatments was 5 minutes at 75 revolutions per minute and 25 minutes at 45 revolutions per minute. Filtration of the sludge from alum coagulation of the caustic waste was performed through a sand bed and by vacuum

through filter aid. Filtration through filter aid indicates a greater possibility of development into a workable process.

It was concluded from this investigation that NUCHAR CEE-N activated carbon will not remove a significant amount of color from the caustic waste at the above conditions, but alum coagulation of the waste at pH of 6, temperature of 25 °C. alum dosage of 1.5 gram per liter of waste, and stirring of 5 minutes and 25 minutes at 75 and 45 revolutions per minute, respectively, will decrease the color content of the waste approximately 90 per cent.

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