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The Effect of Improved Brownstock Washing on Bleach Plant Effluent Quality

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THE EFFECT OF IMPROVED BROWNSTOCK WASHING ON BLEACH PLANT EFFLUENT QUALITY

BY

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ABSTRACT

The objective of this thesis was to quantitatively determine the effects of reduced brownstock washer carryover on bleach plant effluent quality with respect to BOD and Color. More specifically; if efforts are made to reduce brownstock washer carryover by "X" pounds of BOD and Color, how many pounds of BOD and Color will be removed from the bleach plant sewer?

Very little work has been done in this area.

The laboratory procedure involved extensive washing of hardwood pulp and subsequent re-introduction of weak black liquor to simulate carryover. Black liquor was added as pounds Salt Cake loss per ton pulp. The pulp was then bleached by Chlorination - Extraction, varying the Chlorine charge to obtain a 2.5 Kappa Number. The resulting bleaching effluent (combined) was analyzed for BOD_5, Color, and Total Organic Carbon (TOC).

CONCLUSIONS

1. The data found in this study is not necessarily predictive in industrial applications, however, the procedure outlined should generate excellent predictive data for any pulp mill.
2. For a particular system, using the procedure outlined, BOD and Color sewered at the bleach plant can be predicted by Salt Cake loss at the washers.
3. For a particular system, using the procedure outlined, effluent treatment and chemical cost savings resulting from improved brownstock washing can be determined.
4. Data generated from this and further study can be used in a dynamic simulation computer program (GEMS for example) to help determine mass balances in a washing - bleaching system.

KEYWORDS: BOD, Color, Sodium Sulfate, Bleaching

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INTRODUCTION

Because of rising costs and greater restrictions on wastewater treatment in the pulp and paper industry, it is becoming necessary to evaluate in-plant processes with regards to minimizing Biochemical Oxygen Demand (BOD) and color loading to the waste stream. To this end, this thesis will deal with what happends to the BOD and color of organic compounds, carried forward from brownstock washers, when subjected to bleaching.

Work done in this area is very limited. Potlacth Corporation investigated this topic in a mill wide study at their Lewiston, Idaho mill. Results were inconclusive due to the complexities of full scale studies. (6). In similar work, Lescot found that 95% of the BOD and 60% of the color contained in the brownstock washer carryover is carried into the bleach plant sewer. (1).

The focus of the laboratory work will be to quantitatively determine the effect of reduced brownstock washer carryover on bleach plant effluent quality with respect to BOD and color. More specifically; if efforts are made to reduce brownstock washer carryover by "X" pounds of BOD and color, how many pounds of BOD and color will be removed from the bleach plant sewer.

THEORETICAL DISCUSSION

In order to treat this topic fully, it will be necessary to understand brownstock washing more completely. The objective of brownstock washing is to recover as much cooking chemical as possible with a minimum dilution and at the same time deliver as clean a pulp as possible to the bleach plant. (10).

The result of incomplete brownstock washing is black liquor carryover, which in itself has detrimental effects on bleaching efficiency and bleaching effluent quality. (7). For our purposes black liquor carryover may be divided into the organic fraction (as measured by BOD and color) and the inorganic fraction (as measured by Sodium).

Analyzing BOD and color losses from brownstock washer systems is not as precise or reproducible as Sodium loss analysis due to the complexities of organic compounds. As with Sodium, a portion of the total BOD and color tend to be "bound" to the pulp mat either by adsorption or lack of solubility. Overall, the factors which bind BOD and color to pulp fibers, affecting transfer rates, are less understood than those affecting Sodium. (2,4,5,6) .

Because of these differences, literature suggests that it is generally not possible to predict BOD and color removal efficiencies from similar data on Sodium removal. (2,4,5). However, further studies show that for a given pulp the Sodium/BOD and Sodium/color relationships are linear. (4,6,16). It should be noted that these relationships hold only for a given pulp. Factors affecting the relationship include wood species, cooking variations, and Kappa Number of the resultant pulp. (2).

Understanding BOD and color carryover from brownstock washing systems is important in that increased organic loading to the bleach plant will increase bleaching chemical consumption and bleach plant effluent loading. (8).

Effluents from the bleach plant are a major contributer of BOD and color to the entire pulp mill waste stream. Several factors influence the strength of bleach plant effluents. These include: Kappa Number of the incoming pulp, organic loading to the first bleaching stage, amount of chemical on pulp, and various effects caused by different bleaching methods and sequences.

It should be noted first, that about 80% of the total BOD and about 95% of the total color in bleaching effluents results from the first two conventional bleaching stages (Chlorination - Extraction). (3). Therefore adequate consideration must be given to these stages and their respective effluents.

Generally reactions of Chlorine with wood pulps are not well understood with respect to lignin removal and carbohydrate degradation. This is due mainly to the fact that lignin is an amphorus high molecular wieght polymer whose exact structure is not known. (11).

As a result of lignin complexities, the reaction of Chlorine with lignin is similarly complex. Depolymerization of lignin by Chlorine may result from two types of reactions: (1) electrophilic side chain displacement, and (2) oxidative breakage of aryl ether bonds and decomposition of the aromatic nuclei. (12). In the former, 50 to 60% of the Chlorine is consumed rapidly. The latter proceeds slowly and accounts for the remainder of the Chlorine consumed. (12).

Voss and Alfthan have shown that Kappa Number of the incoming pulp has a significant effect on the bleaching effluent. (3,9). A linear relationship exists; with an increase in Kappa Number there is a corresponding increase in BOD and color of the bleaching effluent. Alfthan explains this phenomenon:

> Simlutaneously with the delignification, carbohydrate degradation takes place. The dissolved carbohydrates are biochemically easily degradrable while the dissolved lignin is considered to be relativily stable to biochemical degradation. The change in BOD_7 of the bleach plant effluent for different Kappa Nunbers of the unbleached pulp should therefore rather be explained by carbohydrate than by lignin dissolution. (3).

Kappa #

The addition of Chlorine Dioxide simultaneously with Chloine tends to counteract carbohydrate degradation while delignification is not markedly affected. (12). Alfthan shows that when 6% of the total Chlorine charge is added as Chlorine Dioxide, a 10 to 20% reduction in bleaching effluent BOD can be realized. Effluent color is also reduced 5 to 10% by the addition of Chlorine Dioxide. Alfthan explains color reduction by Chlorine Dioxide addition by cleavage of aromatic bonds and subsequent formation of muconic and other aliphatic acids instead of highly colored chloroquinones. (3).

A discrepency is shown by Voss in work on Chlorine

Dioxide substitution for Chlorine. Both softwood and hardwood pulps were bleached substituting Chlorine Dioxide for Chlorine from 0 to 100%. Results showed an increase in BOD loadings in the resultant effluents in all cases. Voss admits the unexpected results, but does not have a satisfactory explaination. (9).

As mentioned eariler, some products resulting from Chlorination side chain substitution are excellent substrates for oxidation to highly colored quinones. (11). Voss showed that combined C-E stage effluent contained maximum color at around 100% of the Chlorine demand of the pulp. Combined C-E stage effluent color was significantly less at Chlorine charges above and below the 100% Chlorine demand of the pulp. (9).

In Alkaline Extraction extensive lignin dissolution takes place. About 70% of the substituted Chlorine is removed as Chlorine by the alkali. With this dissolution of lignin, highly colored chromophoric and quinone groups are liberated into solution causing the highly colored Extraction stage effluent. (12).

The effect of dissolved organic matter on bleaching efficiency and bleaching effluent quality has been studied in great detail by Great Lakes Forest Products in their Closed Cycle bleach plant in Thunder Bay Ontario. (7,8). It was found that chemical consumption in the first bleaching stage (D - C) was linearly dependent upon the concentration of dissolved organic matter to the bleach plant. Increased organic loading to the bleach plant resulted in increased loading of BOD and color to the bleach plant sewer.

In summary, previous portions of this paper have shown not only a need for further study in this area, but also the complexities involved in the analysis of black liquor carry-over and bleaching mechanisms. In an unpublished NCASI Technical Bulletin dealing with this topic, it is stated that "The paucity of this information suggests a need for more extensive study in this area.".

It is hoped that through the following experimental plan further insite will be gained in quantitatively determining the effects of improved brownstock washing on bleach plant effluent quality. Results of this study may allow for a better understanding of the effects of brownstock washing carryover on bleaching effluent quality and, through cost analysis, justify improved brownstock washing.

EXPERMENTAL DESIGN

In order to meet the objective of this thesis the experimental design must involve bleaching of a pulp with a known amount of carryover from the brownstock washing system.

Pulp will be obtained at the last brownstock washer from S. D. Warren in Muskegon Michigan. It will be washed more extensively in the lab to remove all but the bound constituents. To accent the effect of carryover on the bleach plant effluent, hardwood pulp will be used. Literature suggests that hardwood pulp will contain less bound sodium, BOD, and color than softwood pulp.

Weak black liquor, obtained from the washer filtrate line at S. D. Warren will be added back to the pulp to simulate carryover. The weak black liquor will be analyzed for Salt Cake concentration and added back to the pulp at 4 different concentrations as pounds Salt Cake loss per ton pulp.

The resulting mixture will be bleached by Chlorination - Extraction only. Literature indicates that the vast majority of BOD and color sewered at the bleach plant results from these two stages. The chlorine charge will be varied to obtain a 2.5 Kappa Number (S. D. Warren's target value for C - E Kappa Number) for all carryover concentrations.

The resulting bleaching effluent (C - E combined) will be analyzed for BOD, color, and Total Organic Carbon (TOC).

With the generated data, plots of BOD, color, and TOC in the effluent vs. carryover loading as pounds Salt Cake loss per ton pulp will be made. Also, BOD, color, and TOC of the black liquor will be determined and plots of mass of BOD, color, and TOC in the bleach plant effluent vs. mass of BOD, color, and TOC added before bleaching will be made.

EXPERMENTAL PROCEDURE

A list of Chemicals and Equipment used during this procedure may be found in Appendix 1.

Pulp Washing

Hardwood pulp was washed extensively in the laboratory by dilution of about two pounds of pulp in 55 gallons of water and subsequent filtering through a cloth bag. This procedure was repeated four times. The pulp was then stored by refrigeration at 25% consistency for testing.

Carryover Concentration Determination

Weak black liquor was analyzed for Sodium ion concentration by the use of an Orion Sodium Ion Electrode. The resultant Sodium concentration was converted to Salt Cake concentration in mass of Salt Cake per volume of black liquor. See Appendix 2.

30 grams of pulp (oven dry basis) were to be bleached, thus the correct volume of black liquor needed to add to the pulp could be determined as pounds Salt Cake per ton pulp. Concentrations to be used were 0, 20, 40, and 60 pounds Salt Cake per ton pulp. These concentrations result in a net loss of Salt Cake from the Kraft recovery cycle, thus typical units will be pounds Salt Cake loss per ton pulp.

Bleaching

30 grams of pulp (oven dry basis) were bleached using the following procedure:

Bleaching Procedures:

1st Stage: Chlorination

2 batches of pulp will be used. Each should be 15 g OD.

_____% Cl_2 on OD pulp, room temperature, __50__ minutes, 2% consistency, (750 ml for each batch)

Disintegrate 15 g OD pulp in 400 - 500 ml of tap water. Add Cl_2 water and enough tap water to make a total volume of 750 ml. Mix this in a Waring blender for 1 minute. Pour the mixture into a 2 liter beaker. Repeat the procedure with the second batch as quickly as possible. Pour the second batch into the same beaker. (The beaker should now contain 30 g OD pulp and a total volume of 1500 ml.) Allow the mixture to stand for __50__ minutes under the hood covered with a watch glass. At the end of time, our into an empty Buchner filter and drain. Save about 200 ml of liquid for pH and residual liquor tests. Wash the pulp with 0.5 liter of HOT distilled water

2nd Stage: Caustic Extraction

2 batches of pulp will be used. Each should be 15 g OD.

__4__% NaOH on OD pulp, boiling point, __60__ minutes, 3% consistency, (500 ml for each batch)

Split the above pad in half. ~~Use hot water to heat the blender jar.~~ Quickly, rough weigh each pad and determine the amount of water in the pad. Disintegrate the first half in the Waring blender with the desired ammount of NaOH and boiling water. Pour this into the 2 liter beaker. Repeat with the second batch. (The beaker should contain 30 g OD pulp and 1 liter of hot water.) Place the beaker on the hot plate. Keep the slurry just below the boiling point. Stir occasionally. After __60__ minutes at the boiling point, drain the pulp on a Buchner funnel. Wash with 0.5 liters of hot water. Do not save the filtrate. Save approximately $\frac{1}{4}$ of the pad for Kappa number tests.

Initial Chlorine charge was determined by the following procedure:

Test of Chlorine Water

Pipet 25.0 ml of chlorine water into a 500 ml flask with 200 ml of distilled water and 10 ml of 1 N KI. Chlorine water should be pipeted quickly and carefully to avoid losing any of the dissolved chlorine. Titrate with 0.2 N $Na_2S_2O_3$ to a starch end point.

_____ ml 0.2 N $Na_2S_2O_3$ x 0.285 = _____ g/l Cl_2

Residual Chlorine was determined by the following procedure:

Analysis of Residual Bleach Liquors:

Use a 100 ml graduated cylinder to measure 100 ml of residual liquor into a 500 ml flask with 100 ml of distilled water, 5 ml of 4 N H_2SO_4, and 10 ml of 1 N KI. Titrate with 0.2 N $Na_2S_2O_3$ to a starch end point. (It will require only a few ml or maybe none at all.)

_____ ml 0.2 N $Na_2S_2O_3$ x 0.071 = _____ g/l residual bleach

The amount of 10 g/l NaOH to add to each extraction stage was determined by the following procedure:

Caustic Extraction Stage

Initial Liquor

$$\underline{15}\text{ g OD pulp} \times \frac{\underline{4}\ \%\ \text{NaOH on pulp}}{100} \times \frac{1000}{10\ \text{g/l NaOH}} = \underline{60}\ \text{ml NaOH for each batch}$$

Kappa Number of the C - E pulp was determined by the procedure located in Appendix 3.

If the Kappa Number of the C - E pulp was not within the range of 2.4 to 2.6 the procedure was repeated, varying the chlorine charge to move the C - E Kappa Number within the stated range.

It should be noted that the repeatability of the TAPPI Kappa Number procedure T-236 is 3.8% at Kappa Numbers near 2.5.

All carryover concentrations were bleached in duplicates to assure repeatability.

Control Groups

Two different control groups were run. The zero pound Salt Cake loss per ton pulp concentrations were one set of controls. The second set of controls were obtained by running the bleaching procedure with 20 and 60 pounds Salt Cake loss per ton pulp but adding no bleaching chemical. This control indicates the BOD and color and TOC extracted by the bleaching method and not by the bleaching chemical. A zero pound Salt Cake loss per ton pulp should also be run.

Bleaching Effluent Analysis

The bleaching effluent, C - E effluents combined, was analyzed for BOD, color, and TOC.

BOD

BOD_5 was measured for all effluents and the black liquor by the procedure in Standard Methods. pH was adjusted and residual chlorine was neutralized by the BOD pre-treatment procedure in Standard Methods.

Color

Color was determined for all effluents and black liquor by the Platinum - Cobalt method. The procedure was supplied by NCASI and is widely used throughout industry.

TOC

Total Organic Carbon was determined on a high temperature oxidation unit used by the NCASI Midwest Regional Center.

Bound Sodium

Bound Sodium was determined by an Acid Extraction procedure developed by NCASI and used widely. It should be noted that the extract must be analyzed for Sodium by use of an Atomic Absorption unit as the ionic strength of the extract is too high for analysis of Sodium by use of a Sodium probe.

RESULTS

Black liquor analysis and data generated from bleaching runs and effluent quality tests are presented on the following page.

Further data on each bleaching run is located in Appendix 4, with a sample calculation sheet located in Appendix 5. Results of the no chemical bleaching runs are located in Appendix 6.

All generated data was used to determine the objective except the data on the no bleaching chemical runs. This is due to an insufficient number of control runs (no bleaching chemical) to accurately determine the effect of the bleaching method on the pulp - carryover mixture.

RUN NUMBER	CARRY-OVER CONC. AS: lb Na_2SO_4 Loss/ton Pulp	% Cl_2 ON PULP	KAPPA NUMBER	% Cl_2 CONSUMED	BOD (lb/ton)	COLOR (lb/ton)	TOTAL ORGANIC CARBON (lb/ton)
2	0	3.50	2.58	97.76	13.69	105.2	28.77
9	0	3.50	2.39	95.53	15.96	96.83	30.12
7	20	4.70	2.44	98.90	18.28	227.0	38.29
10	20	4.70	2.42	96.67	18.40	162.6	38.26
8	40	5.85	2.40	98.00	27.31	298.7	55.12
11	40	5.85	2.55	97.33	28.34	277.7	52.81
6	60	7.00	2.51	99.26	32.85	402.7	61.11
12	60	7.00	2.60	99.44	36.83	410.2	62.61

BLACK LIQUOR ANALYSIS

	mg/l	lb/gal.
SALT CAKE CONC. —	95,057	0.7926
BOD CONC. —	37,099	0.3092
COLOR CONC. —	253,570	2.1139
TOC CONC. —	68,350	0.5700

SALT CAKE BOUND TO PULP = 1.110 $\frac{\text{lb } Na_2SO_4}{\text{ton Pulp}}$

DISCUSSION OF RESULTS

It should be noted first that the results of this thesis are not directly applicable to industrial processes. However, similar work on a specific industrial brownstock washing and bleaching system should yield similarly accurate data applicable to that system.

All plots obtained in this work were very linear. Included on each plot are "R" values and the equation of the line shown. These were obtained using a linear regression computer program.

Although it was not within the scope of this thesis, a plot of chlorine charge to obtain a 2.5 Kappa Number vs. Salt Cake loss per ton pulp is included in Appendix 7. This is of some importance as at an increased chlorine charge increased carbohydrate degredation takes place. This increased carbohydrate degradation may cause increased BOD. It should be noted that the cause of increased BOD, color, and TOC is probably the result of both increased chlorine charge and increased carryover loading. This thesis does not, and was not intended to, differentiate between the effect of each mechanism on bleach plant effluent quality.

Plots of effluent BOD, color, and TOC are located in Appendix 8a, b, c. From the slope of each line it can be seen that an increase of one pound of salt Cake loss results in an increase of 0.35 pounds BOD, 5.05 pounds color, and 0.56 pounds of TOC.

As mentioned earlier, Salt Cake was added as black liquor.

With the previous analysis of black liquor, plots were made of pounds per ton pulp of BOD, color, and TOC in the bleach plant effluent (sewered) vs. pounds per ton pulp of BOD, color, and TOC added before bleaching. These plots are located in Appendix 9a, b, c.

From the slope of the BOD plot it can be seen that an increase of one pound per ton pulp BOD to the bleach plant results in 0.88 pounds per ton pulp BOD in the bleach plant sewer. This value agrees well with what Lescot (1) found; 0.95 pounds BOD sewered for each pound BOD added.

From the slope of the TOC plot, it can be seen that an increase of one pound per ton pulp TOC to the bleach plant results in 0.78 pounds per ton pulp TOC to the bleach plant sewer. This is also expected, as for this work the BOD - TOC correlation was very good; "R"= 0.983 (plot not shown).

From the slope of the color plot it can be seen that a one pound per ton pulp increase in color to the bleach plant results in a 1.87 pound per ton pulp color increase in the bleach plant sewer. This is an unexpected result, as Lescot (1) found that only 60% of the color to the bleach plant was seen in the sewer. The reason for my result may be that the oxidative effect of bleaching changes the colored components of the black liquor to forms which exert more color than in their origional state. This is an excellent topic for further research as the benifits of removing one pound of color in brownstock washing could result in 1.87 pounds color removal in the bleach plant sewer.

A brief discussion of the no bleaching chemical control group should be presented here. As mentioned earlier, the control group consisted of running the bleaching procedure with 20 and 60 pounds Salt Cake loss per ton pulp but adding no bleaching chemical. This may be termed an extraction to determine the effect of the bleaching procedure on the pulp and carryover. In order to obtain accurate results, at least three extractions would have to have been made, one with no carryover added. With these results, a correlation could have been made with the other control group of zero pounds Salt Cake loss per ton pulp bleached to a 2.5 Kappa Number. Since 3 were not done, the data was not used.

ECONOMICS

Previous to a study of this type a pulp mill could only determine savings resulting from improved brownstock washing by savings in Salt Cake make-up and possibly by reduced chlorine consumption. By completing work of the type dicussed in this thesis a mill could also determine added cost savings due to reduced BOD in the bleach plant effluent. Reduced color is an added benifit if environmental regulations dictate strict color standards.

Although the data presented in this thesis is not necessarly applicable to industry, the following is an example of cost savings resulting from improved brownstock washing reducing Salt Cake loss by 5 pounds per ton pulp. Assume a 1000 ton per day pulp mill. Using current costs of Salt

Cake, Chlorine, and of processing BOD a savings of $350,000 per year could be realized. Of course, this savings would have to be weighted against the cost of decreasing Salt Cake loss by 5 pounds per ton pulp by improving brownstock washing. The cost savings analysis may be seen in Appendix 10.

CONCLUSIONS

1. The data found in this study is not necessarily predictive in industrial applications, however, the procedure outlined should generate excellent predictive data for any kraft pulp mill.
2. For a particular system, using the procedure outlined, BOD and color sewered at the bleach plant can be predicted by Salt Cake loss at the brownstock washers.
3. For a particular system, using the procedure outlined, effluent treatment and chemical cost savings resulting from improved brownstock washing can be determined.
4. Data generated from this and further study can be used in a dynamic simulation computer program (GEMS for example) to help determine mass balances in a washing - bleaching system.

RECOMMENDATIONS

Because of the lack of information in this area, much further research should be completed. First, this procedure should be tested in an industrial application to confirm its validity. Using the procedure outlined, a study of the behavior of softwood pulp is needed as it behaves much differently than hardwood during washing and bleaching. A study of the effect of partial chlorine dioxide in the first bleaching stage would also be of interest as it has been shown that chlorine dioxide may reduce BOD in the bleach plant sewer. Similarly, the effect of use of condensates in brownstock washer shower water would be of interest as these condensates often carry a high BOD load.

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APPENDIX 1

EQUIPMENT NEEDED

BLEACHING - CHLORINATION

4 2-liter beakers

large Buchner Funnel and Filter Pads

Graduate Cylinders: 100, 250, 1000 ml

Watch Glass for 2-liter beaker

BLEACHING —EXTRACTION

Thermomiter

Hot Plates

CHEMICAL ANALYSIS

50 ml Burret

Graduate Cylinders: 100, 1000 ml

Magnetic stirrer and bar

Timer

1 2-liter Beaker

Pipets: 10, 25, ml

CHEMICALS NEEDED FOR BLEACHING AND CHEMICAL ANALYSIS

Chlorine Water: (not stable) - 350 ml Chlorox Bleach diluted to 3000 ml. Adjust pH to 1.5 with HCl. 55-60 ml will be needed.

Sodium Hydroxide: at 10 g/l

Sodium Thiosulfate: at 0.20 Normal

Acetone: Solvent grade

Sulfuric Acid: at 4.0 Normal

Potassium Permanginate: at 0.10 Normal

Potassium Iodide: at 1.0 Normal

Starch Solution

BOD Dilution water: by Standard Methods Procedure

Platinum - Cobalt Standard

APPENDIX 2

CARRYOVER CONCENTRATION DETERMINATION

From analysis with the Orion Sodium ion electrode the Black Liquor was determined to be: 1.325 M in Na^+

Therefore, $1.325\ M\ Na^+ \times \frac{1\ Na_2SO_4}{2\ Na^+} \times M.W.\ Na_2SO_4\ (142)$ -

Salt Cake Concentration = $\frac{94.075\ g\ Na_2SO_4}{\text{Liter Black Liquor}}$

For 20 lb Na_2SO_4 / ton pulp: $\frac{20\ lb\ Na_2SO_4}{2000\ lb\ pulp} = 0.01\ \frac{lb\ Na_2SO_4}{lb\ pulp}$

$= 0.01\ \frac{g\ Na_2SO_4}{g\ pulp} \times \frac{30g\ pulp}{\text{bleaching batch}} \times \frac{\text{Liter Black Liquor}}{94.075\ g\ Na_2SO_4}$

= 0.003189 liters Black Liquor / Bleaching Batch

By similar calculations:

For 40 lb Na_2SO_4 / ton pulp: 0.006379 $\frac{\text{liters Black Liquor}}{\text{Bleaching Batch}}$

For 60 lb Na_2SO_4 / ton pulp: 0.009568 $\frac{\text{Liters Black Liquor}}{\text{Bleaching Batch}}$

The black liquor was diluted to 10% and added as ml.

APPENDIX 3

Kappa Number Determination:

For more details on this procedure see T 236 os-76.

Pulp Preparation

Dry Pulp: Weigh 5 grams of dry pulp, slurry in a Waring Blender with water, drain on a Buchner funnel, and process as wet pulp

Wet Pulp: Slurry 5 to 6 grams of pulp (OD basis, equivalent to about 50 grams of wet pulp) with 200 to 300 ml of acetone in a Waring Blender. Drain on a small Buchner funnel.
Pour an additional 100 ml of acetone through the pad.
Dry the pad in an oven at 105°C until dry (about 15 minutes).

Weigh on an analytical balance to the nearest 0.001 gram.
1 - 2 grams for unbleached pulps (see instructor)
3 - 5 grams for second stage bleached pulps (see instructor)

Test Procedure

Measure 800 ml of distilled water at 25°C.
Disintegrate the weighed acetone dried pulp with about 500 ml of this water in a Waring Blender.
Pour the slurry into a 2 liter beaker and use an additional 200 ml of the 800 ml of water to rinse the blender into the beaker.
Add a magnetic spin bar and place the beaker on a Magmix stirrer. Adjust the vortex to a depth of about 1 inch.
Obtain 100.0 ml of 4 N H_2SO_4 in a beaker. Pour this into the pulp slurry.
Obtain 100.0 ml of 0.1 N $KMnO_4$ in a beaker. Pour this into the beaker with the pulp slurry. Start the timer immediately. Use the remaining water to rinse the $KMnO_4$ beaker.
After 10.0 minutes, add 20 ml of KI solution to stop the reaction.
Titrate with 0.2 N $Na_2S_2O_3$ to a pale yellow color. Add a small ammount of starch solution and continue titrating to a colorless solution. This endpoint is very sharp.

Run a blank as above but without the pulp. Do not wait 10 minutes before adding the KI. You may find it helpful to run the blank before the test. It will give you a better feel for the procedure.

Calculations

Pulp will pick up about 2% moisture while you are weighing it. This has been built into the calculation.

$$\text{Uncorrected Kappa Number} = \frac{(\text{Blank ml of thio} - \text{Test ml of thio}) \times (2)}{\text{Dry weight of pulp} \times (0.98)}$$

← we titrate w/ .2 N instead of .1N

Corrected Kappa Number = Uncorrected Number x "p"

← 2% moisture pick up

The Kappa number test is designed as the number of ml of 0.1 N potassium permanganate solution consumed per gram of moisture free pulp. The results need to be corrected for the equivalent of

50% consumption of the permanganate by the test specimen. This correction (p) is obtained from the following table.

Table I

Factor "p" to correct for different percentages of permanganate used in the Kappa Number test.

% consumed in test = c = (Blank ml - Test ml) x 2

c	0	1	2	3	4	5	6	7	8	9
20	0.937	0.939	0.941	0.943	0.945	0.947	0.949	0.952	0.954	0.955
30	0.958	0.960	0.962	0.964	0.966	0.968	0.970	0.973	0.975	0.977
40	0.979	0.981	0.983	0.985	0.987	0.989	0.991	0.994	0.996	0.998
50	1.000	1.002	1.004	1.006	1.009	1.011	1.013	1.015	1.017	1.019
60	1.022	1.024	1.026	1.028	1.030	1.033	1.035	1.037	1.039	1.042
70	1.044	1.046	1.048	1.050	1.052	1.055	1.057	1.059	1.061	1.064
80	1.066	1.068	1.070	1.072	1.074	1.077	1.079	1.081	1.083	1.086
90	1.088	1.090	1.092	1.094						

APPENDIX 4

RUN # 2 DATE 3/7/84 TIME 10:30 A

CARRYOVER CONCENTRATION 0 lb Na_2SO_4/ton pulp --- 0 g Na_2SO_4/30 g pulp

TOTAL GRAMS OVEN DRY PULP 30 , NUMBER OF BATCHES 2

CHLORINATION

% Cl_2 on pulp	3.5 %
Temperature	25 °C
Time at temp.	50 min.
% Consistency	2 %
pH	2.2 pH
g/l Residual Cl_2	0.0157 g/l
% Cl_2 consumed	97.76 %
% Residual based on pulp	0.0785 %
% Residual based on carryover	0 %

EXTRACTION

% NaOH on pulp	4.0 %
Temperature	95 °C
Time at temp.	60 min.
% Consistency	3 %
C + E KAPPA NUMBER	2.58

EFFLUENT QUALITY

BOD_5	13.69 lb/ton pulp
Color	105.2 lb/ton pulp
Total Organic Carbon	28.77 lb/ton pulp

NOTES

RUN # 9 DATE 3/14/84 TIME 2:00 p

CARRYOVER CONCENTRATION 0 lb Na_2SO_4/ton pulp --- 0 g Na_2SO_4/30 g pulp

TOTAL GRAMS OVEN DRY PULP 30, NUMBER OF BATCHES 2

CHLORINATION

% Cl_2 on pulp	3.5 %
Temperature	25 °C
Time at temp.	50 min.
% Consistency	2 %
pH	<2 pH
g/l Residual Cl_2	0.03126 g/l
% Cl_2 consumed	95.53 %
% Residual based on pulp	0.1563 %
% Residual based on carryover	0 %

EXTRACTION

% NaOH on pulp	4 %
Temperature	95 °C
Time at temp.	60 min.
% Consistency	3 %
C + E KAPPA NUMBER	2.390

EFFLUENT QUALITY

BOD_5	15.96 lb/ton pulp
Color	96.83 lb/ton pulp
Total Organic Carbon	30.12 lb/ton pulp

NOTES

RUN # 7 DATE 3/8/84 TIME 11:00 A

CARRYOVER CONCENTRATION 20 lb Na_2SO_4/ton pulp - - - 0.30g Na_2SO_4/30g pulp

TOTAL GRAMS OVEN DRY PULP 30 , NUMBER OF BATCHES 2

CHLORINATION

% Cl_2 on pulp	4.7 %
Temperature	25 °C
Time at temp.	50 min.
% Consistency	2 %
pH	< 2 pH
g/l Residual Cl_2	0.0104 g/l
% Cl_2 consumed	98.90 %
% Residual based on pulp	0.0519 %
% Residual based on carryover	5.190 %

EXTRACTION

% NaOH on pulp	4 %
Temperature	95 °C
Time at temp.	60 min.
% Consistency	3 %

C + E KAPPA NUMBER - - - 2.439

EFFLUENT QUALITY

BOD_5	18.28 lb/ton pulp
Color	227.0 lb/ton pulp
Total Organic Carbon	38.29 lb/ton pulp

NOTES

RUN # 10 DATE 3/17/84 TIME 10:30 A

CARRYOVER CONCENTRATION 20 lb Na_2SO_4/ton pulp - - - 0.30 g Na_2SO_4/30 g pulp

TOTAL GRAMS OVEN DRY PULP 30 , NUMBER OF BATCHES 2

CHLORINATION

% Cl_2 on pulp - - - - - - - - - - - - - - - - 4.70 %

Temperature - - - - - - - - - - - - - - - - - 25 °C

Time at temp. - - - - - - - - - - - - - - - - 50 min.

% Consistency - - - - - - - - - - - - - - - - 2 %

pH - <2 pH

g/1 Residual Cl_2 - - - - - - - - - - - - - 0.03126 g/1

% Cl_2 consumed - - - - - - - - - - - - - - - 96.67 %

% Residual based on pulp - - - - - - - - - - - 0.1563 %

% Residual based on carryover - - - - - - - - - 15.63 %

EXTRACTION

% NaOH on pulp - - - - - - - - - - - - - - - - 4.0 %

Temperature - - - - - - - - - - - - - - - - - 95 °C

Time at temp. - - - - - - - - - - - - - - - - 60 min.

% Consistency - - - - - - - - - - - - - - - - 3 %

C + E KAPPA NUMBER - - - - - - - - - - - - - - 2.419

EFFLUENT QUALITY

BOD_5 - 18.40 lb/ton pulp

Color - 162.6 lb/ton pulp

Total Organic Carbon - - - - - - - - - - - - - 38.26 lb/ton pulp

NOTES

RUN # 8 DATE 3/14/84 TIME 1:30 A

CARRYOVER CONCENTRATION 40 lb Na_2SO_4/ton pulp - - - 0.60g Na_2SO_4/30g pulp

TOTAL GRAMS OVEN DRY PULP 30 , NUMBER OF BATCHES 2

CHLORINATION

% Cl_2 on pulp	5.85 %
Temperature	25 °C
Time at temp.	50 min.
% Consistency	2 %
pH	<2 pH
g/l Residual Cl_2	0.02342g/l
% Cl_2 consumed	98.00 %
% Residual based on pulp	0.1171 %
% Residual based on carryover	3.903 %

EXTRACTION

% NaOH on pulp	4.0 %
Temperature	95 °C
Time at temp.	60 min.
% Consistency	3 %
C + E KAPPA NUMBER	2.400

EFFLUENT QUALITY

BOD_5	27.31 lb/ton pulp
Color	298.7 lb/ton pulp
Total Organic Carbon	55.12 lb/ton pulp

NOTES

RUN # 11 DATE 3/17/84 TIME 11:00 A

CARRYOVER CONCENTRATION 40 lb Na_2SO_4/ton pulp --- 0.60g Na_2SO_4/30g pulp

TOTAL GRAMS OVEN DRY PULP 30 , NUMBER OF BATCHES 2

CHLORINATION

% Cl_2 on pulp	5.85 %
Temperature	25 °C
Time at temp.	50 min.
% Consistency	2 %
pH	<2 pH
g/l Residual Cl_2	0.03124 g/l
% Cl_2 consumed	97.33 %
% Residual based on pulp	0.1562 %
% Residual based on carryover	7.810 %

EXTRACTION

% NaOH on pulp	4.0 %
Temperature	95 °C
Time at temp.	60 min.
% Consistency	3 %
C + E KAPPA NUMBER	2.552

EFFLUENT QUALITY

BOD_5	28.34 lb/ton pulp
Color	277.7 lb/ton pulp
Total Organic Carbon	52.81 lb/ton pulp

NOTES

RUN # 6 DATE 3/4/84 TIME 10:00 A

CARRYOVER CONCENTRATION 60 lb Na_2SO_4/ton pulp - - - 0.40g Na_2SO_4/30g pulp

TOTAL GRAMS OVEN DRY PULP 30 , NUMBER OF BATCHES 2

CHLORINATION

% Cl_2 on pulp	7.0 %
Temperature	25 °C
Time at temp.	50 min.
% Consistency	2 %
pH	< 2 pH
g/l Residual Cl_2	0.01038 g/l
% Cl_2 consumed	99.26 %
% Residual based on pulp	0.05190 %
% Residual based on carryover	2.300 %

EXTRACTION

% NaOH on pulp	4 %
Temperature	95 °C
Time at temp.	60 min.
% Consistency	3 %

C + E KAPPA NUMBER - - - 2.509

EFFLUENT QUALITY

BOD_5	32.85 lb/ton pulp
Color	402.7 lb/ton pulp
Total Organic Carbon	61.11 lb/ton pulp

NOTES

RUN # 12 DATE 3/17/84 TIME 3:30 p

CARRYOVER CONCENTRATION 60 lb Na_2SO_4/ton pulp - - - 0.90 g Na_2SO_4/30 g pulp

TOTAL GRAMS OVEN DRY PULP 30 , NUMBER OF BATCHES 2

CHLORINATION

% Cl_2 on pulp	7.0 %
Temperature	25 °C
Time at temp.	50 min.
% Consistency	2 %
pH	2.2 pH
g/l Residual Cl_2	0.00780 g/l
% Cl_2 consumed	99.44 %
% Residual based on pulp	0.0390 %
% Residual based on carryover	1.300 %

EXTRACTION

% NaOH on pulp	4 %
Temperature	95 °C
Time at temp.	60 min.
% Consistency	3 %

C + E KAPPA NUMBER - - - 2.600

EFFLUENT QUALITY

BOD_5	36.83 lb/ton pulp
Color	410.2 lb/ton pulp
Total Organic Carbon	62.61 lb/ton pulp

NOTES

APPENDIX 5

Calculations Sheet

Run # ________ Time ________

Initial Liquor

______ ml 0.2 N $Na_2S_2O_3$ X .285 = ______ g/l Cl_2

$$\underline{15}\text{ g OD pulp} \times \frac{\_\_\_\%\ Cl_2 \text{ on pulp}}{100} \times \frac{1000}{\_\_\_\text{ g/l } Cl_2} = \_\_\_\text{ ml } \frac{Cl_2 \text{ Water}}{\text{Batch}}$$

Residual Liquor

______ ml 0.2 N Na_2SO_4 X 0.071 X ______ Factor = ______ g/l Residual Cl_2

$$\frac{\_\_\_\text{ g/l residual } Cl_2}{1000} \times \frac{\_\_\_\text{ ml total Liquid}}{30\text{g OD Pulp}} \times 100 = \_\_\_\ \%\text{ residual } Cl_2 \text{ based on pulp}$$

$$\frac{\_\_\_\%\text{ Orig. } Cl_2 \text{ on pulp} - \_\_\_\%\text{ res. } Cl_2 \text{ on pulp}}{\_\_\_\%\text{ original } Cl_2 \text{ on pulp}} \times 100 = \_\_\_\ \%\ Cl_2 \text{ Consumed}$$

$$\frac{\_\_\_\text{ g/l residual } Cl_2}{1000} \times \frac{\_\_\_\text{ ml total Liquid}}{\_\_\_\text{ g } Na_2SO_4 \text{ added}} \times 100 = \_\_\_\ \%\text{ residual } Cl_2 \text{ based on carryover}$$

Extraction Liquor

$$\underline{15}\text{ g OD Pulp} \times \frac{\_\_\_\%\ NaOH \text{ on pulp}}{100} \times \frac{1000}{10\text{ g/l } NaOH} = \_\_\_\text{ ml } \frac{NaOH \text{ water}}{\text{Batch}}$$

Kappa Number

$$\frac{(\_\_\_\text{ ml } Na_2S_2O_3 \text{ Blank} - \_\_\_\text{ ml } Na_2S_2O_3 \text{ Test}) \times 2}{\_\_\_\text{ g Dry weight pulp} \times .98} = \_\_\_\text{ Uncorrected Kappa}$$

C = (______ Blank − ______ Test) × 2 = ______ → "p" = ______

Corrected Kappa = ______ Uncorrected X ______ "p" = ______

APPENDIX 6

RUN # 13 DATE 3/21/84 TIME 11:00

CARRYOVER CONCENTRATION 20 lb Na_2SO_4/ton pulp - - - 0.30 g Na_2SO_4/30 g pulp

TOTAL GRAMS OVEN DRY PULP 30 , NUMBER OF BATCHES 2

CHLORINATION

% Cl_2 on pulp	0.0 %
Temperature	25 °C
Time at temp.	50 min.
% Consistency	2 %
pH	— pH
g/l Residual Cl_2	— g/l
% Cl_2 consumed	— %
% Residual based on pulp	— %
% Residual based on carryover	— %

EXTRACTION

% NaOH on pulp	0.0 %
Temperature	95 °C
Time at temp.	60 min.
% Consistency	— %
C + E KAPPA NUMBER	—

EFFLUENT QUALITY

BOD_5	11.58 lb/ton pulp
Color	84.70 lb/ton pulp
Total Organic Carbon	21.62 lb/ton pulp

NOTES

RUN # 14 DATE 3/21/84 TIME 11:15 A

CARRYOVER CONCENTRATION 60 lb Na_2SO_4/ton pulp - - - 0.90 g Na_2SO_4/30 g pulp

TOTAL GRAMS OVEN DRY PULP 30 , NUMBER OF BATCHES 2

CHLORINATION

% Cl_2 on pulp	0.0 %
Temperature	25 °C
Time at temp.	50 min.
% Consistency	2 %
pH	— pH
g/l Residual Cl_2	— g/l
% Cl_2 consumed	— %
% Residual based on pulp	— %
% Residual based on carryover	— %

EXTRACTION

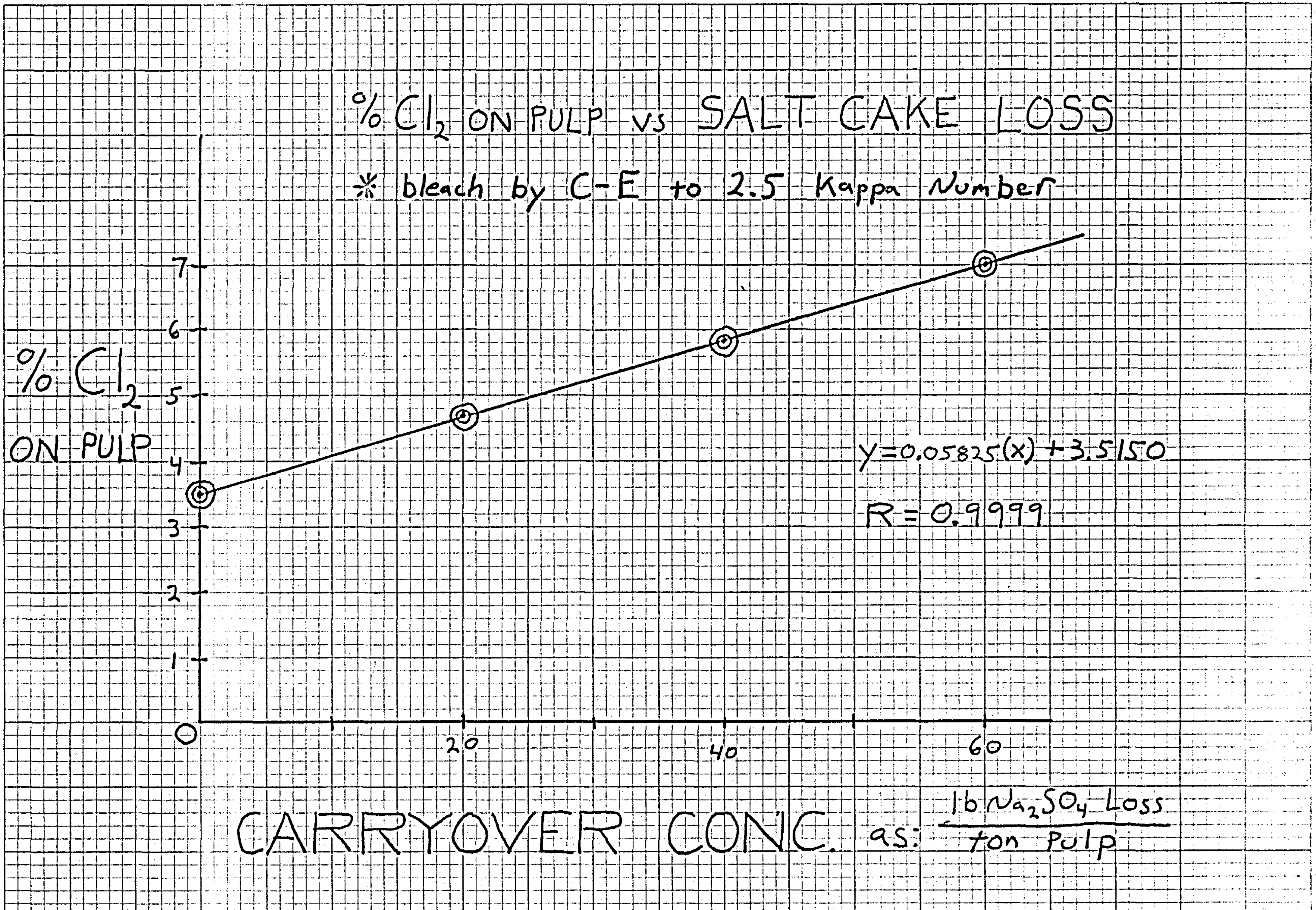
% NaOH on pulp	0.0 %
Temperature	95 °C
Time at temp.	60 min.
% Consistency	3 %
C + E KAPPA NUMBER	—

EFFLUENT QUALITY

BOD_5	28.44 lb/ton pulp
Color	218.40 lb/ton pulp
Total Organic Carbon	48.28 lb/ton pulp

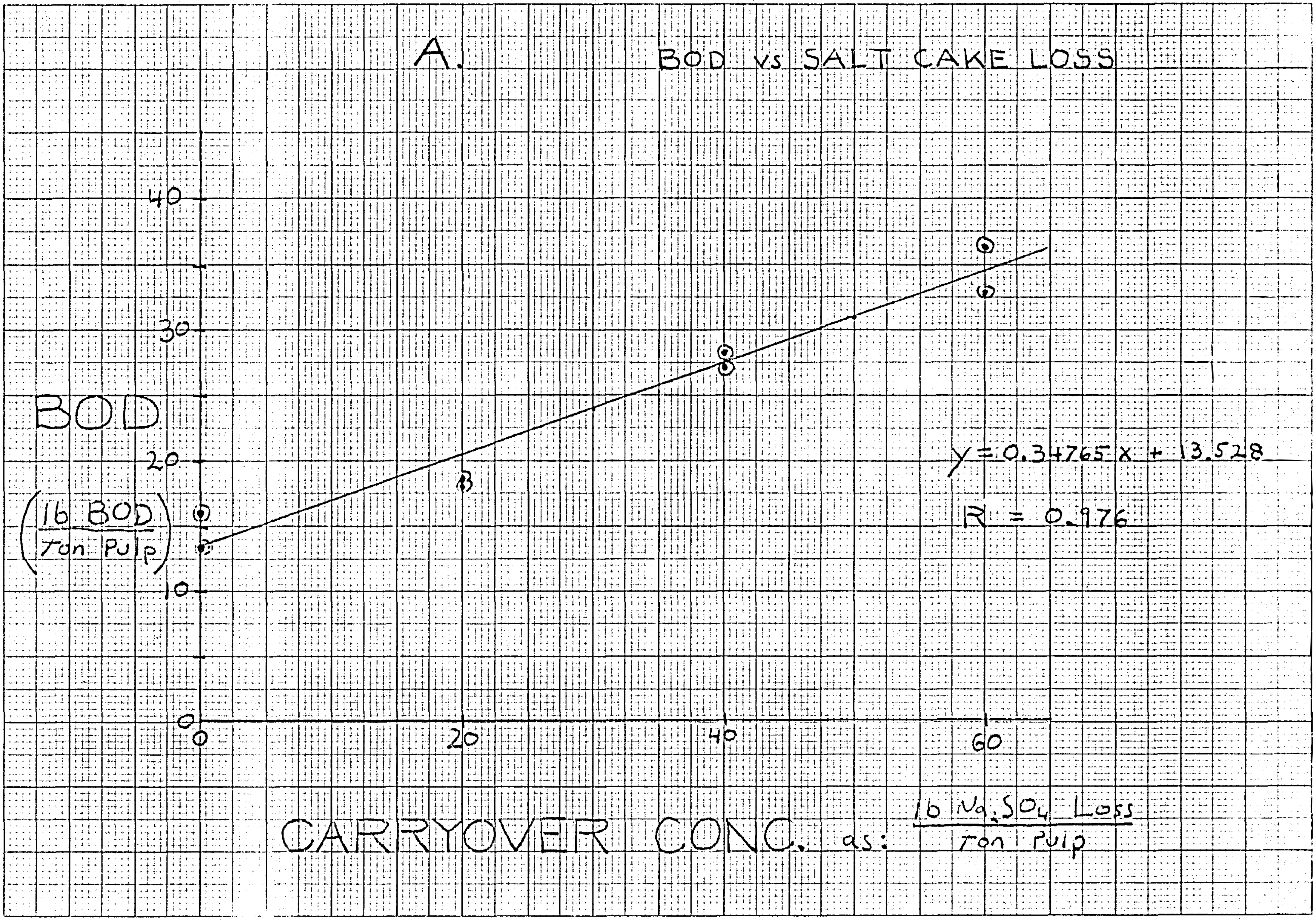
NOTES

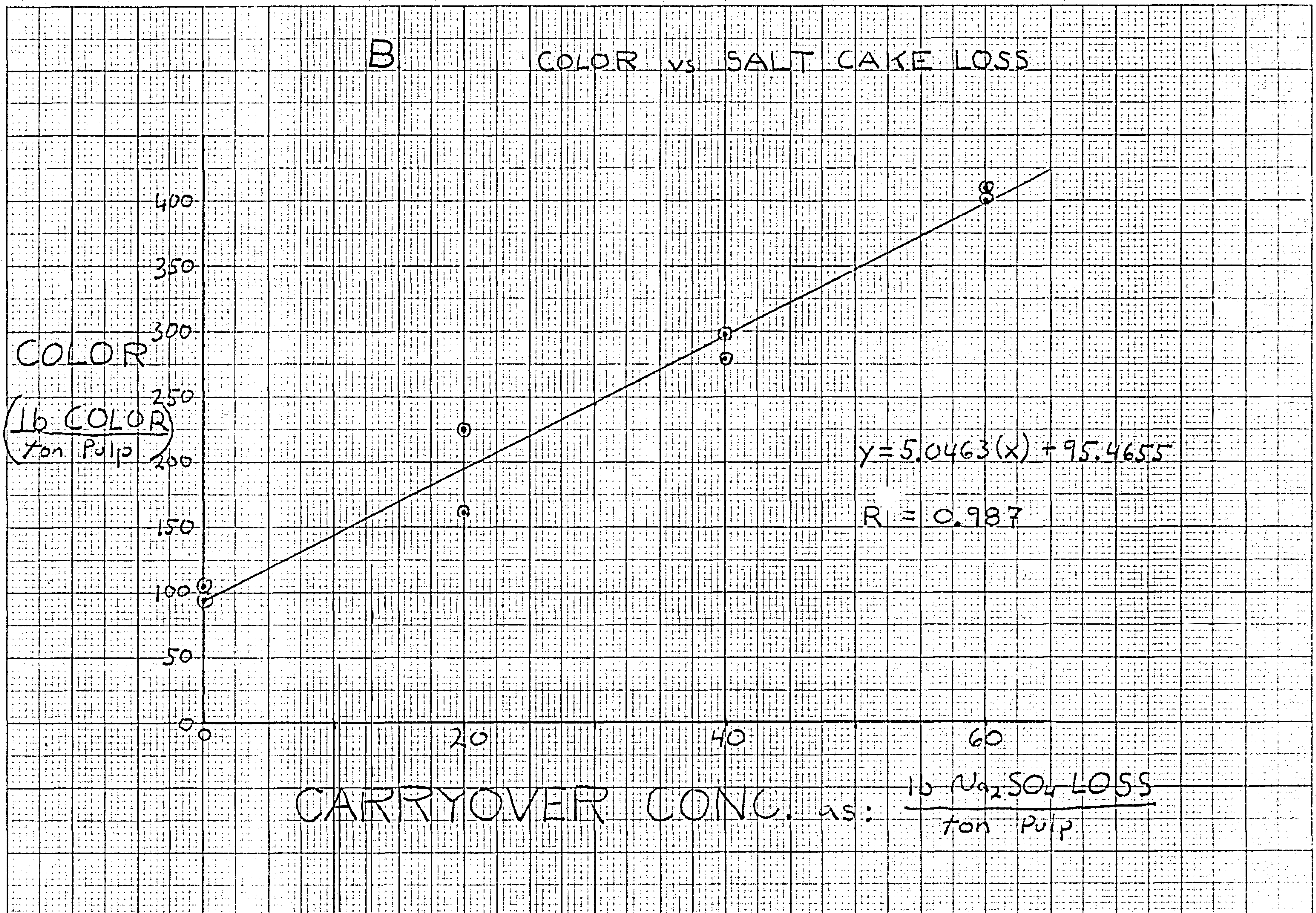
APPENDIX 7

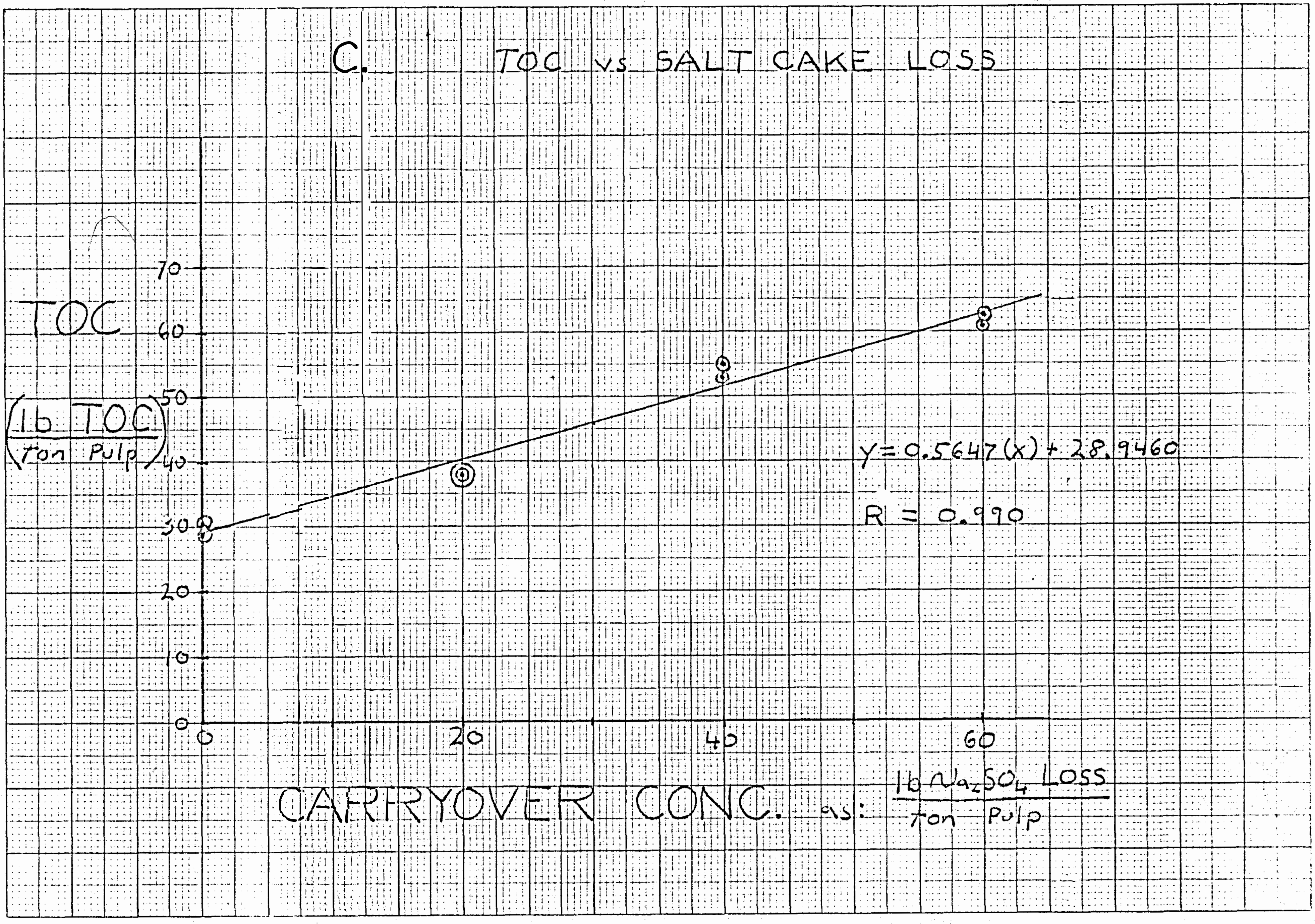


% Cl2 ON PULP vs SALT CAKE LOSS
* bleach by C-E to 2.5 Kappa Number
% Cl2 ON PULP
y=0.05825(x)+3.5150
R = 0.9999
0
1
2
3
4
5
6
7
20
40
60
CARRYOVER CONC. as: lb Na2SO4 Loss / ton Pulp

APPENDIX 8

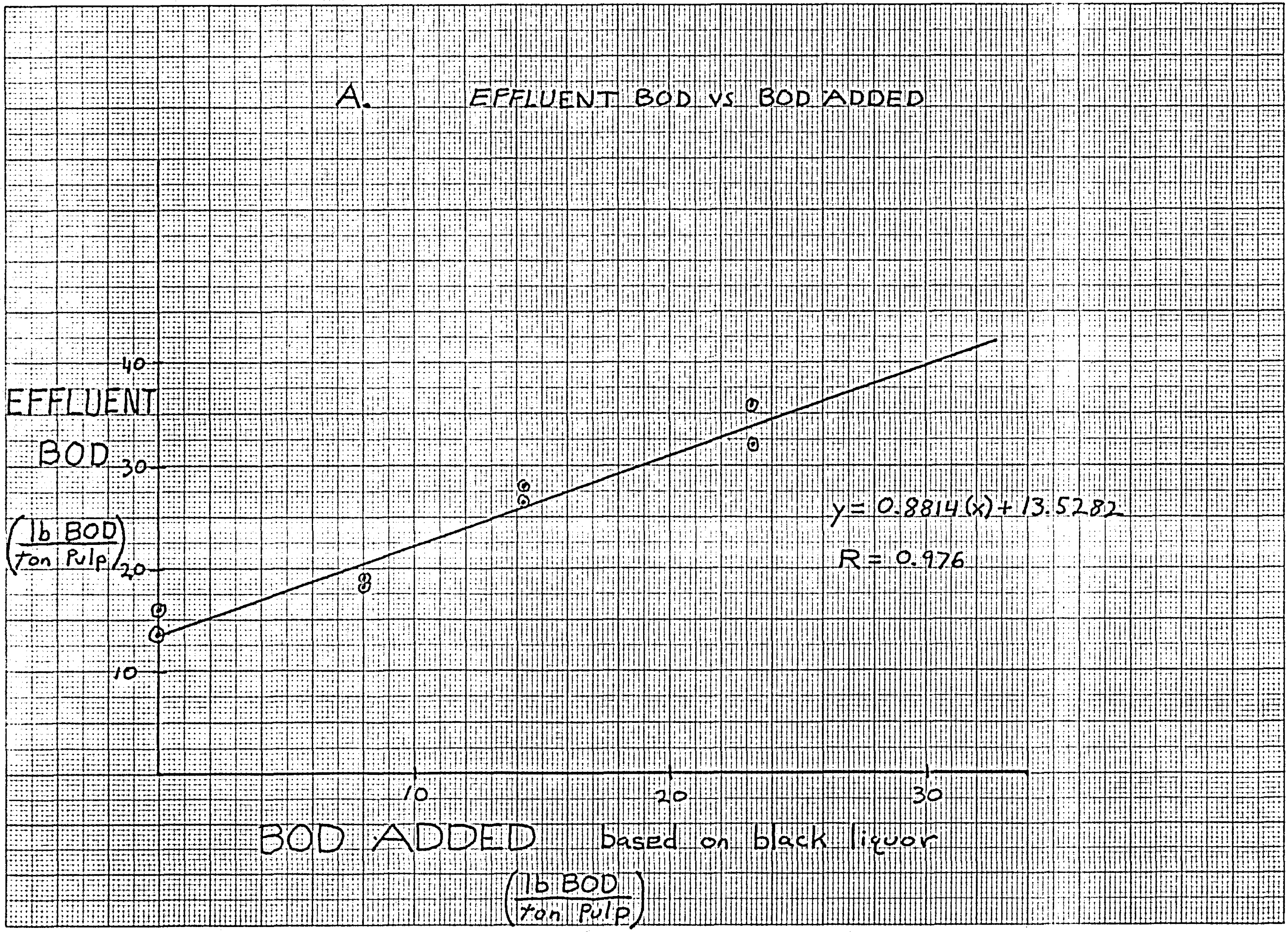

A.
BOD vs SALT CAKE LOSS
BOD
(lb BOD / Ton Pulp)
40
30
20
10
0
0
20
40
60
y = 0.34765 x + 13.528
R = 0.976
CARRYOVER CONC. as: lb Na2SO4 Loss / Ton Pulp


B
COLOR vs SALT CAKE LOSS
COLOR
(lb COLOR / ton Pulp)
400
350
300
250
200
150
100
50
0
0
20
40
60
y = 5.0463(x) + 95.4655
R = 0.987
CARRYOVER CONC. as: lb Na2SO4 LOSS / ton Pulp

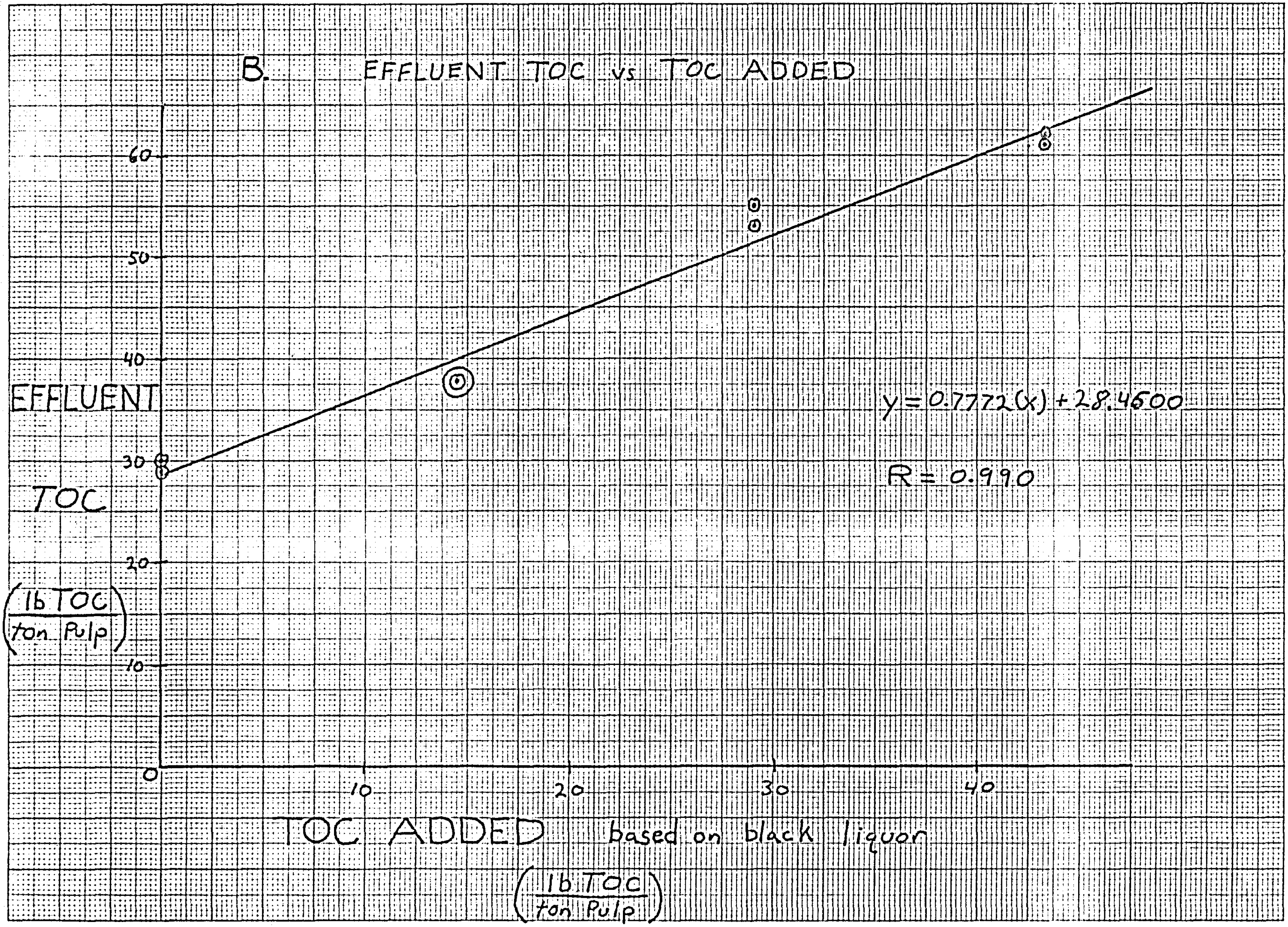


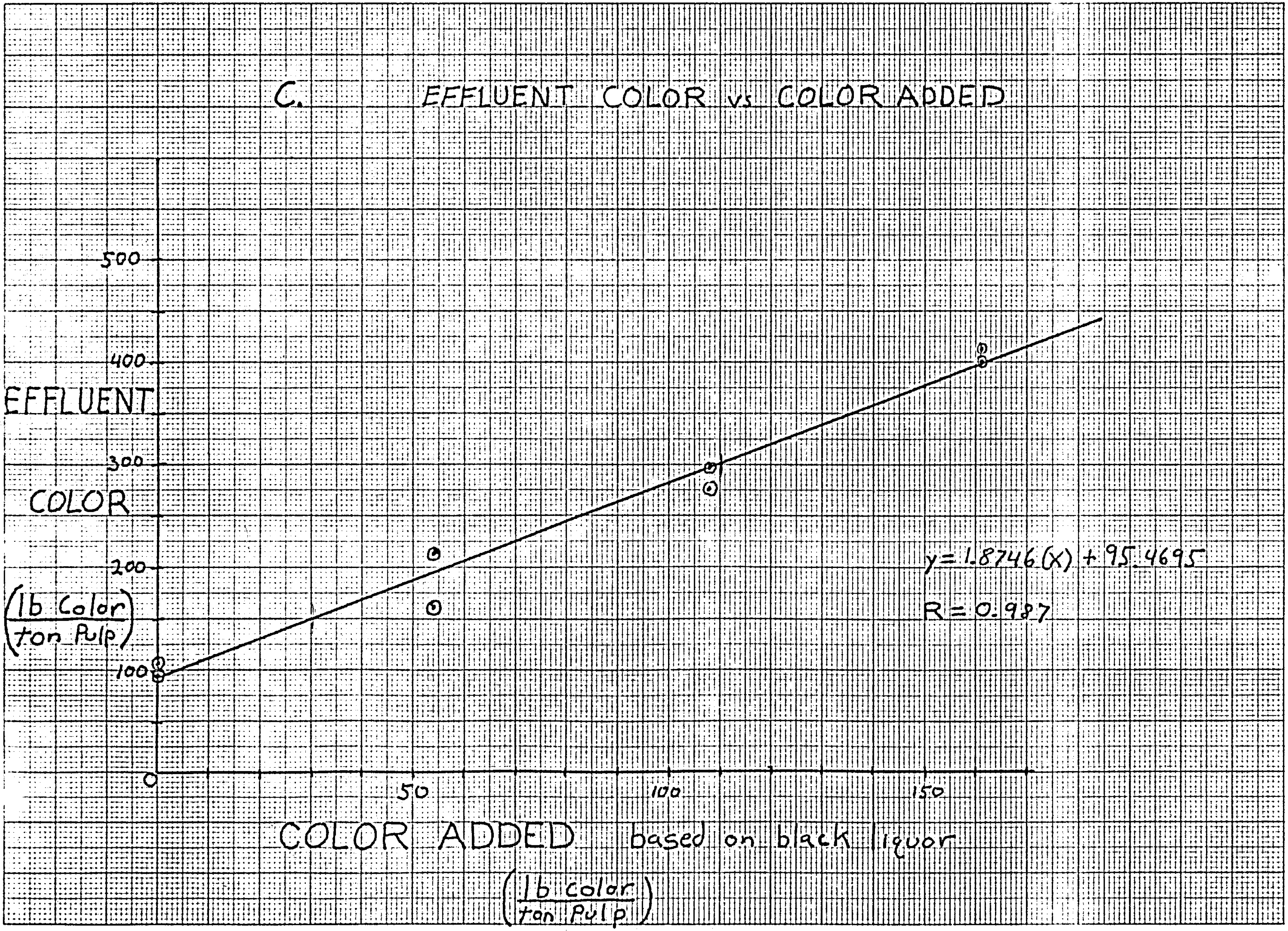
C.
TOC vs SALT CAKE LOSS
TOC
(lb TOC / ton Pulp)
0
10
20
30
40
50
60
70
0
20
40
60
Y = 0.5647(x) + 28.9460
R = 0.990
CARRYOVER CONC. as: lb Na2SO4 LOSS / ton Pulp

APPENDIX 9



A. EFFLUENT BOD VS BOD ADDED
EFFLUENT BOD (lb BOD / ton Pulp)
40
30
20
10
y = 0.8814 (x) + 13.5282
R = 0.976
10
20
30
BOD ADDED based on black liquor (lb BOD / ton Pulp)


B. EFFLUENT TOC vs TOC ADDED
EFFLUENT TOC
(lb TOC / ton Pulp)
0
10
20
30
40
50
60
y = 0.7772(x) + 28.4600
R = 0.990
TOC ADDED based on black liquor
(lb TOC / ton Pulp)



C. EFFLUENT COLOR vs COLOR ADDED
500
400
300
200
100
0
50
100
150
EFFLUENT COLOR (lb Color / ton Pulp)
y = 1.8746 (x) + 95.4695
R = 0.987
COLOR ADDED based on black liquor
(lb color / ton Pulp)

APPENDIX 10

COST ANALYSIS

REDUCING SALT CAKE LOSS BY 5 lb/TON PULP
1000 TON/DAY KRAFT PULP MILL

	REDUCTION - FROM SLOPE OF APPLICABLE CURVE.		
* SALT CAKE @ $\frac{\$70}{ton}$ →	$\frac{5\ lb}{ton}$	$\times \frac{1000\ ton}{day} \times \frac{365\ day}{year} \times \frac{\$70}{2000\ lb}$ →	63,875
* CHLORINE @ $\frac{\$150}{ton}$ →	0.291 % on Pulp	$\times \frac{2000\ lb}{ton} \times \frac{1000\ ton}{day} \times \frac{365\ day}{year} \times \frac{\$150}{2000\ lb}$ →	159,322
* BOD @ $\frac{\$0.20}{lb\ BOD}$ →	$\frac{1.738\ lb\ BOD}{ton\ pulp}$	$\times \frac{1000\ ton}{day} \times \frac{365\ day}{year} \times \frac{\$0.20}{lb\ BOD}$ →	126,874

TOTAL SAVINGS = 350,071 $/year

* SALT CAKE and CHLORINE Prices from PAPER TRADE JOURNAL 1984 - BUYERS GUIDE. BOD Cost from NCASI