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A Study of Bleach Effluents from Oxidative Extraction

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A Study of Bleach Effluents from Oxidative Extraction

PAPR 473

Senior Engineering Problem 2

by

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Advisor: Dr. Aravamuthan

Date: April 19, 1990

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Introduction

During the 1970's oxygen delignification was primarily undertaken before the bleaching stages in a pulp mill. However, towards the end of the 1970's further research was done to promote the use of oxygen as a decoloring agent within the bleaching stages. This was warranted because oxygen delignification was known to promote decreased chemical consumption, mainly chlorine. The process that was developed came to be known as oxidative extraction. This process has become very popular due to the fact that it is easier to install and operate than the conventional oxygen delignification system. Some other advantages that this process offers are its applicability to all pulps and the reduction in the number of bleaching stages in some instances.

Oxidative extraction involves the addition of oxygen to an alkaline pulp stream following a C-stage washing but ahead of the first extraction stage in a bleaching sequence. The oxygen acts to further delignify the pulp which in turn reduces the demand for bleaching chemicals in the following stage or stages. One major advantage of the decreased usage of chemicals is the improvement of the effluent quality from the bleaching sequences.

My project involves the Kraft cooking of a typical species of a hardwood common to Michigan. The pulp was cooked to a low and high kappa number, then each Kappa number pulp bleached to a common kappa number. The bleaching stages include a chlorine-chlorine dioxide stage (Cd) followed by an oxidative extraction (Eo) or extraction (E) stage. The effluents from this stage was then tested for COD, color, pH, chlorides, and total solids.

Literature Review and Analysis

Advantages of Oxidative Extraction

The fact that the oxidative extraction process saves on chemical usage has been well documented. In a Swedish study it was reported that a savings of 6.5 to 8.5 lb ClO₂/Bladt with the addition of 8 lb O₂/Bladt in a conventional five stage bleaching sequence at the Ostrand mill, Sweden could be accomplished (1). Skookumchucks pulp mill in British Columbia has also seen a reduction of bleaching chemicals, but only of the order of 4 lb/adt ClO₂ (1). Another study also showed that the addition of oxygen before the first extraction stage in a bleaching sequence of eucalyptus sulphate pulp reduced the total chlorine usage that would be required to reach a final brightness (2).

Another major advantage of oxidative extraction is that it can reduce the number of bleaching steps. In the Norrsundet Broks mill north of Stockholm, Sweden, they have obtained Kraft pulps bleached to high brightness in only three bleaching stages, where 5 or 6 were normally used (4). This was made possible by the improvement of the overall bleaching efficiency by the introduction of the oxygen-alkali extraction techniques.

One other advantage of oxidative extraction is its color reduction of the effluents. Traditional Kraft bleach plants in the past have had an objectional dark color in terms of its effluents (5). One mill employing the Eo technique has experienced an effluent color reduction of 25% from the combined (C+Eo) bleaching stages (1). This is very important due to the fact that most conventional secondary wastewater treatment plants can not treat colored

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materials (5). Some procedures that have been used to treat colored effluents include heavy metal ion coagulation, ion-exchange resins, treatment with fly ash, and recently by variations in the traditional bleaching procedures. Some examples of these variations include using large amounts of ClO_2 in the C-stage, hypochlorite in the first extraction stages effluent (14), and as discussed previously oxygen delignification.

Some of the major characteristics of the effluents such as BOD, COD, pH, chlorides, and total solids have not totally been evaluated in terms of the implementation of an oxidative extraction stage in a bleaching sequence. Since E_o allows for the reduction of bleaching stages, it reduces chemical and water usage (8). Many mills and laboratory tests have also confirmed that oxygen pre-delignification stages reduces combined bleach plant effluent BOD (8).

Another study conducted by Bugajer and Danilas (2) evaluated filtrates from the E and E_o stages of a sulphate eucalyptus pulp. They looked at COD, color, pH, chlorides, and total solids. In this experiment a commercial eucalyptus sulphate pulp, with a kappa number of 17.5 and a viscosity of 55.4 mPa.s was bleached with the addition of an E_o and E-Peroxide stage to CHH, CED, and CEDED bleaching stages. The E_o stage was carried out in a rotary pressurized stainless steel vessel. The air from the reactor containing the pulp and alkaline solution was substituted by oxygen up to a partial pressure of .2 mPa. They compared the E, E_p , and E_o stages in terms of physical and optical properties of the bleached pulps, brightness related to chlorine charge, chemical costs, and

effluent properties. In terms of the Eo stages effluent properties they found a significant decrease in solids and pH, along with a slight decrease in color. They did, however, report a slight increase in chlorides and color. However, they did not look at more than one kappa number and they varied the chemical charge in the subsequent stages to obtain the target brightness. Which would not specifically show how the implementation of an Eo stage affects the effluents characteristics.

How the Oxygen reacts with Lignin under an Alkaline Medium

When the pulp is in an alkaline medium and is treated with oxygen, the desirable reactions are those involving lignin and residual lignin fractions in the pulp. When reacting with oxygen the above fractions go through a considerable breakdown. The reactions of oxygen with lignin mainly takes place in four steps. These include (a) alkali-induced reactions (b) the formation of hydroperoxide anions (c) the reactions of hydroperoxide (d) an alkaline-oxidative degradation of the primary reaction products from hydroperoxide intermediates (7).

Background Information on my Experimental Set-Up

I plan using a hardwood species common to Michigan, quaking aspen. Quaking aspen is located throughout the United States and Canada, in Michigan it is located throughout the upper and lower peninsula and is a major pulpwood species (6).

With the above species I plan on Kraft cooking to a low and a high kappa number. I plan on using 40 as my high value with 15 as my low value. The choosing of 15 as the low Kappa number is based on a research project involving the feasibility of medium

consistency oxygen delignification, from which oxidative extraction evolved. The research was conducted in Sweden on a pilot plant which produced approximately 10 ton/day (9). In their project they started with pulp at a Kappa number of 30, and upon varying the retention times and temperatures reduced the Kappa number to 15. In another project, conducted at International Paper Co. corporate research center, they investigated opportunities for in-plant reduction of pollutants through process changes, and used 15 as their low Kappa number value (10). The basis of choosing 30 as the high kappa number also comes from the project evaluating the feasibility of medium consistency oxygen delignification (9).

In terms of the bleaching stages that I plan using, the kraft pulp will run through a chlorine/chlorine dioxide stage (Cd) followed by the oxidative extraction stage (Eo) or an Extraction stage. My implementing these stages into my experiment comes from several experiments involving the use of oxidative extraction in short sequence bleaching, and from data obtained from mills that have incorporated the (Eo) stage. Another study conducted on two pulp samples, one hardwood and one softwood, experimented in using a Cd-Eo-D sequence in place of a Cd-E-D sequence. They found that the Cd-Eo-D sequence obtained higher % ISO brightness levels per percent ClO₂ charge on the pulp (8). Also, in a mill located in Nackawic, New Brunswick an (Eo) was stage added to an existing Cd-E-D-E-D sequence ahead of the first extraction stage. The result was a significant chemical and energy savings as well as a substantial increase in the mill's bleaching capacity. The process did not affect the pulp strength characteristics, and the estimated payback

period for the system was just over four months (11). Based on these previous successes of using the initial sequences of Cd-Eo, I will use the same initial sequences for my experiment. One must keep in mind that the bleaching sequences must be well suited to the pulp quality requirements.

The chemical charges, times, temperatures, and consistencies for each of my bleaching sequences comes from the laboratory experiment done on the pulps from two Canadian mills (8). They used a chemical charge of .22 x kappa as total available chlorine, with a chlorine dioxide charge of .1% as ClO₂ on the pulp, for the Cd stage. For this stage they used a consistency of 3.5% and a retention time of 6 minutes at 50 degrees Celsius. I will also duplicate their conditions for the oxidative extraction part of the experiment. They used a thermostatically heated pressurized vessel with slow continuous agitation. I will duplicate this in the M/K digester. The consistency of the pulp at this stage was 10% and the retention time was 40 minutes at a temperature of 70 degree Celsius. The pressure used in their vessel was .14 MPa. They obtained excellent results under these conditions. Another experiment conducted by Gunna Carre in Sundsvall, Sweden also conducted the oxygen extraction stage in stainless steel autoclaves with approximately the same oxygen gauge pressure as the previous example of .15 MPa (12). In terms of the extraction stage the conditions from the Schleinkofer experiment will be used (8). They used a consistency of 10%, a retention time of 60 minutes with a temperature of 70 degree Celsius and a chemical charge of 1.0% on the O.D. pulp.

I will be using a 2 % consistency pulp for the actual oxidative extraction stage. This is considered a low consistency pulp suspension. The main reason for the use of a low-consistency pulp suspension is to ensure good oxygen distribution and minute bubble size as the liquor recirculates within the M/K digester (3). In industry whenever an oxidative extraction stage is implemented upflow towers are fine, but with downflow towers a preretention tube must be added to provide adequate oxygen contact time and to avoid channeling (3). The Eo stage vessel will also be under a constant specified pressure and temperature.

Past Data on Effluent analysis

The implementation of the oxidative extraction stage into a bleaching sequence has improved the quality of effluents in some cases. In the study conducted by Schleinkofer (8), he mentioned that oxygen pre-delignification stages reduced combined bleach plant BOD by 50% and color by 65-70%. However, no effluent data were evaluated in terms of the addition of the Eo stage. In another mentioned earlier, Bugajer and Danilas evaluated the filtrates of a sulphate eucalyptus pulp from the Eo bleaching stages (2). They noted a slight reduction in color, pH and total solids. These studies are important because they lay the foundation for my experiment.

Characteristics of the Effluents(13)

COD

Chemical oxygen demand is one of the most widely used parameters used when testing effluents today. The chemical oxygen demand is used as a measure of the organic matter content of a sample

that is susceptible to oxidation by a strong chemical oxidant. COD can also be related empirically to BOD, organic carbon, or organic matter. This test is also useful for monitoring and control after correlation has been established. A high COD value is considered to be 1000 mg/L, a medium value is around 500 mg/L, and a low COD value is around 250 mg/L (13). COD is generally higher than BOD because more compounds can be chemically oxidized than can be biologically oxidized.

Color

Color is a very important parameter to characterize an effluent due to the fact that the public can easily tell if an effluent is colored. Standard secondary treatment plants usually can not remove colored materials in the wastewater unless other expensive treatment methods are implemented.

pH

The pH of an effluent is very important in terms of cost. This is because before an effluent is discharged it must be near the neutral pH range. Thus the farther away the pH is from the neutral range the more caustic or acid it will take to return the pH to its desired range.

Chlorides

Chlorides are an important factor in wastewater since conventional methods of waste treatment do not remove chlorides to any significant extent. Therefore, it will be important to know if the Eo stage results in the reduction of chlorides. A high value for chlorides is around 100 mg/L, while a medium value is around 50 mg/L, and a low value is around 30 mg/L (13).

Total Solids

Total solids content of a wastewater is defined as all the matter that remains upon evaporation at 100-103 degree Celsius. This is important to know in that a wastewater is often classified by solids. A strong wastewater contains 1200 mg/L, a medium waste has 720 mg/L, while a weak waste has 350 mg/L (13).

Problem Statement

It is well known that the oxidative extraction stage accounts for a reduction of chlorine usage in traditional bleaching sequences (8). It has also been documented that when less chlorine is applied a decrease in the pollution of the effluent is achieved (15).

One study conducted did compare the effluent properties of the Eo and E stages. I plan on running the same type of study but with a new variable. The new variable that I plan to implement is the comparison of effluent properties of high and low kappa number pulps. For my experiment I will pulp aspen chips to a low and high kappa number, then bleach each of these pulps in a two stage bleaching sequence with and without oxygen injection to the extraction stage to a constant kappa number.

In doing so this will enable me to first compare the effluent properties between the Cd-E and Cd-Eo bleaching filtrates when starting the bleaching at a low and high kappa number. Secondly it will allow me to compare how the effluent properties differ between the low and high kappa number values themselves.

Experimental

In terms of the experimental schematic for this experiment I initially started out with kraft cooking of quaking aspen chips to a low and high kappa number and examined its effluent properties in terms of the implementation of the oxidative extraction stage.

As stated I used a hardwood species, quaking aspen, in my experiment. This species was then kraft cooked in the laboratory M&K digester. The quaking aspen chips were cooked to a low and high kappa number, 40 for the high value and 16 for the low value. An active alkali concentration value of 20% based on oven dry wood was held constant for all cooks with 25% Sulfidity, and a 5:1 liquor to wood ratio (see Appendix I). The cooking time for the 16 kappa number pulp was 45 min. at 170 C, and the cooking time for the 40 kappa pulp was 50 min. at 155 C. Two separate cooks were done at each of these conditions yielding 866.5 g. at a 54.1% yield for the 40 kappa number pulp and 727.8 g at a 45.5% yield for the 16 kappa number pulp. The kappa number determination procedure was done according to Tappi standard T 236 os-76 and the chemicals used to run kappa number was prepared according to Tappi standard T 610 om-87 "Preparation of indicators and standard solutions".

The pulp produced was then bleached, using 50 grams oven dry pulp, in the laboratory to a final kappa number of 3.5 for the low kappa number pulp and 13.5 for the high kappa number pulp. (see Appendix II for bleach chemical make up and conditions) The first stage consisted of a Cd(chlorine-chlorine dioxide) stage. Which took place in a plastic bag submerged in a water bath. The time of bleaching was for 6 minutes at 50 degrees Celsius, with

a consistency of 3.5%. Chlorine was charged at a rate of .25 x kappa number, with a chlorine dioxide charge of .3% based on oven dry pulp, for both high and low kappa numbers. This pulp was then transferred back to the M&K digester for the oxidative extraction part of the experiment. The pulp was then diluted to a consistency of 2.0 % in order to allow the oxygen to be dissolved into the recirculating liquor and thus come into contact with the fibers. It was my original intent to run the Eo stage at 10 %, however, this was not feasible if the M&K digester was to be used. The bleaching time in this stage was approximately 30 minutes at 70 degrees Celsius with an oxygen partial pressure of 30 psi(g) inside the vessel. An oxygen tank was attached to the relief valve on the M/K digester for this purpose. An equal amount of the pulp was also subjected to an extraction stage at the same temperature, consistency and chemical concentration of 3.0 % based on oven dry pulp, while submerged in a temperature controlled water bath. All bleaching stages were run in duplicate and a trial and error procedure was used to achieve equal kappa numbers for the high and low kappa number bleached pulps.

The filtrates from the Eo and E stages were then analyzed in terms of its effluent qualities. The tests that were done on the effluents included COD, total solids, color, chlorides, and pH.

Color was done according to Standard Methods (Platinum-Cobalt Procedure) (see Appendix III for details). It should be noted here that Standard Methods is governed by the American Public Health Association. Once a calibration curve was prepared using known

diluted samples of the Platinum-Cobalt standard, absorbance values could be converted to color units directly off the calibration curve (see appendix IV for graph). Chlorides was done according to Standard Methods Argentometric Method #407 A. For chlorides 30 % hydrogen peroxide solution was added to the sample in order to block the interference of any sulfide, sulfite, or thiosulfate ions that may have been present. Without the addition of the peroxide solution a color change during titration could not be seen. Total Dissolved Solids was done according to Standard Methods #209 B. COD was done according to Standard Methods Closed Reflux, Titrimetric Method #508 B. Lastly pH was determined by a standard laboratory pH meter.

Results and Discussion

The effluent from the oxidative extraction part of my experiment has yielded some very interesting and intriguing results. Table no. 1 shows the effluent testing results for both the low and high kappa number pulps, while table no. 2 shows the variance of testing for the values listed on table no. 1. As table no. 2 shows many of the runs have a testing variance of 0 for tests such as pH, and color, which is excellent, while effluent tests such as solids, COD, and chlorides have the larger variances in most instances. This larger testing variance can be attributed to the nature of the tests themselves. Chlorides for instance calls for determination of a color change by titration. Often during testing this color change was hard to pinpoint. COD was also determined by titration, in this case a micro-buret was used, from which the drops were sometimes big enough to overshoot the endpoint. These types of testing problems were often common as some of the testing variances indicate.

The data from table no. 1 was then averaged for each run and then put into the form of bar graphs. The variances between each of the runs are listed on table no. 3 along with the means, T values, and confidence level. The variances and confidence levels are also written on each individual figure for convenience.

The effluent test results for pH for both the low and high kappa number pulp is shown on figure 1. For the low kappa number pulp the confidence level is very high, 0.98. Which means that there should be a statistical difference between the Cd-E and Cd-Eo filtrates. This, however, I feel is not very significant

Table 1: Effluent Testing Results

Low Kappa Number Pulp

		pH	Color ppm	COD mgO ₂ /l	Chlorides mg Cl/L	Solids %
<u>Cd-E</u>						
Run #1	(a)	11.80	364	147.11	60.83	.0840
	(b)	-	364	131.21	60.83	.0816
Run #2	(a)	11.75	596	174.94	70.19	.0900
	(b)	-	588	178.92	70.19	.0896

Cd-Eo

Run #1	(a)	11.85	516	159.04	60.83	.0912
	(b)	-	500	163.02	51.47	.0892
Run #2	(a)	11.85	924	167.00	51.47	.0896
	(b)	-	920	163.02	46.79	.0860

High kappa Number PulpCd-E

Run #1	(a)	9.95	4000	-	215.25	.1528
	(b)	-	4000	1065.57	196.53	.1460
Run #2	(a)	10.35	4000	1081.47	187.18	.1556
	(b)	-	4000	1086.77	196.53	.1560

Cd-Eo

Run #1	(a)	7.50	3150	1134.49	224.61	.1700
			3150	1176.90	224.61	.1676
Run #2	(a)	9.15	2700	1028.46	177.82	.1512
	(b)	-	2700	1017.86	187.18	.1512

Table 2: Variance of Effluent Tests for Each Run
Two tests were run on each sample

		Low Kappa Pulp Cd-E	Cd-Eo	High Kappa Pulp Cd-E	Cd-Eo
pH	Run #1	0	0	0	0
	Run #2	0	0	0	0
Color	Run #1	0	128	0	0
	Run #2	32	8	0	0
COD	Run #1	128	8	-	899
	Run #2	8	8	14	56
Chlorides	Run #1	0	50	175	0
	Run #2	0	8	44	44
Solids	Run #1	2.9×10^{-6}	2.0×10^{-6}	2.3×10^{-5}	2.9×10^{-6}
	Run #2	8.0×10^{-8}	6.5×10^{-6}	2.8×10^{-4}	0

Table 3: Student's "t" Distribution Values

$$\text{Degree's of Freedom} = n_1 + n_2 - 2 = 4 + 4 - 2 = 6$$

Low Kappa Number Pulp

	variance Between Runs 1 & 2	Mean	T values	Confidence Level
<u>pH</u>				
Cd-E	.0008	11.78	-	-
Cd-Eo	0	11.85	-	-
Conclusion	-	-	3.5	+0.98
<u>Color</u> (ppm, color units)				
Cd-E	25,992	478	-	-
Cd-Eo	85,698	715	-	-
Conclusion	-	-	1.42	Not Significant
<u>COD</u> (mg O ₂ /L)				
Cd-E	713	158	-	-
Cd-Eo	8	163	-	-
Conclusion	-	-	0.07	Not Significant
<u>Chlorides</u> (mg Cl/L)				
Cd-E	44	66	-	-
Cd-Eo	25	53	-	-
Conclusion	-	-	3.11	+0.95
<u>Solids</u> (percent)				
Cd-E	2.45×10^{-5}	.086	-	-
Cd-Eo	2.83×10^{-6}	.089	-	-
Conclusion	-	-	1.15	Not Significant

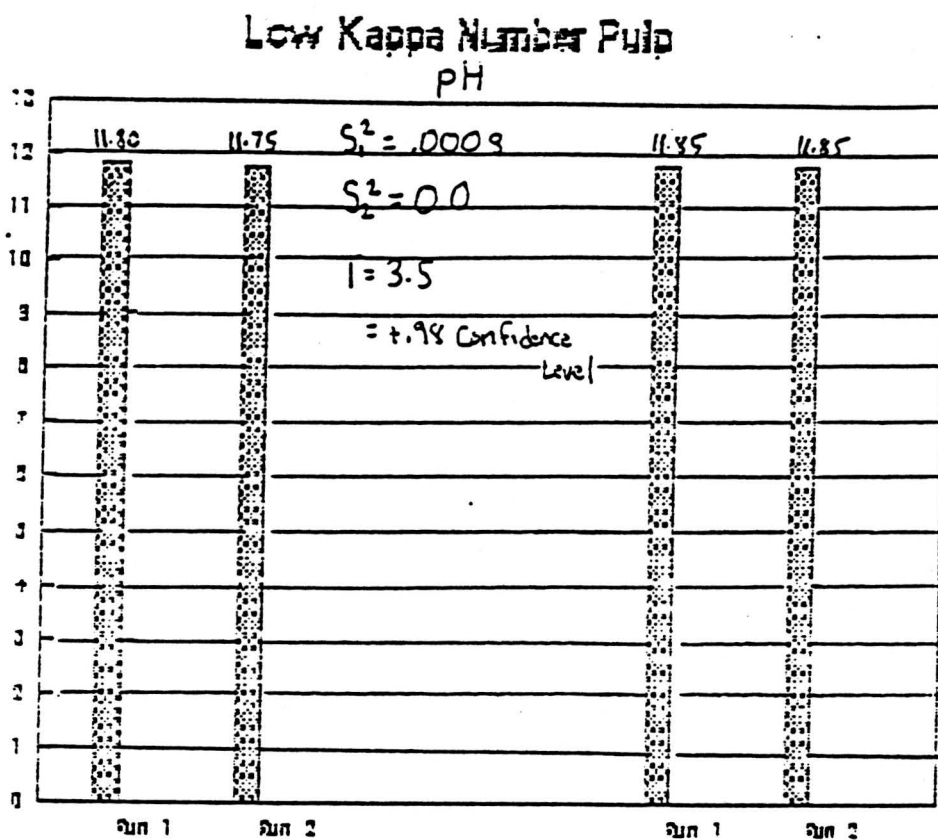
Table 3 (cont.): Student's "t" Distribution Values

Degree's of Freedom = $n_1 + n_2 - 2 = 4 + 4 - 2 = 6$ High Kappa Number Pulp

	variance Between Runs 1 & 2	Mean	T values	Confidence Level
<u>pH</u>				
Cd-E	0.08	10.15	-	-
Cd-Eo	1.35	8.33	-	-
Conclusion	-	-	2.15	+0.90
<u>Color</u> (ppm, color units)				
Cd-E	0	4000	-	-
Cd-Eo	101,250	2925	-	-
Conclusion	-	-	6.76	+0.99
<u>COD</u> (mg O ₂ /L)				
Cd-E	172	1075	-	-
Cd-Eo	8,783	1089	-	-
Conclusion	-	-	0.31	Not Significant
<u>Chlorides</u> (mg Cl/L)				
Cd-E	883	199	-	-
Cd-Eo	98	204	-	-
Conclusion	-	-	0.29	Not Significant
<u>Sulfas</u> (percent)				
Cd-E	2.05×10^{-5}	.153	-	-
Cd-Eo	1.55×10^{-4}	.160	-	-
Conclusion	-	-	1.12	Not Significant

Fig. 1

pH

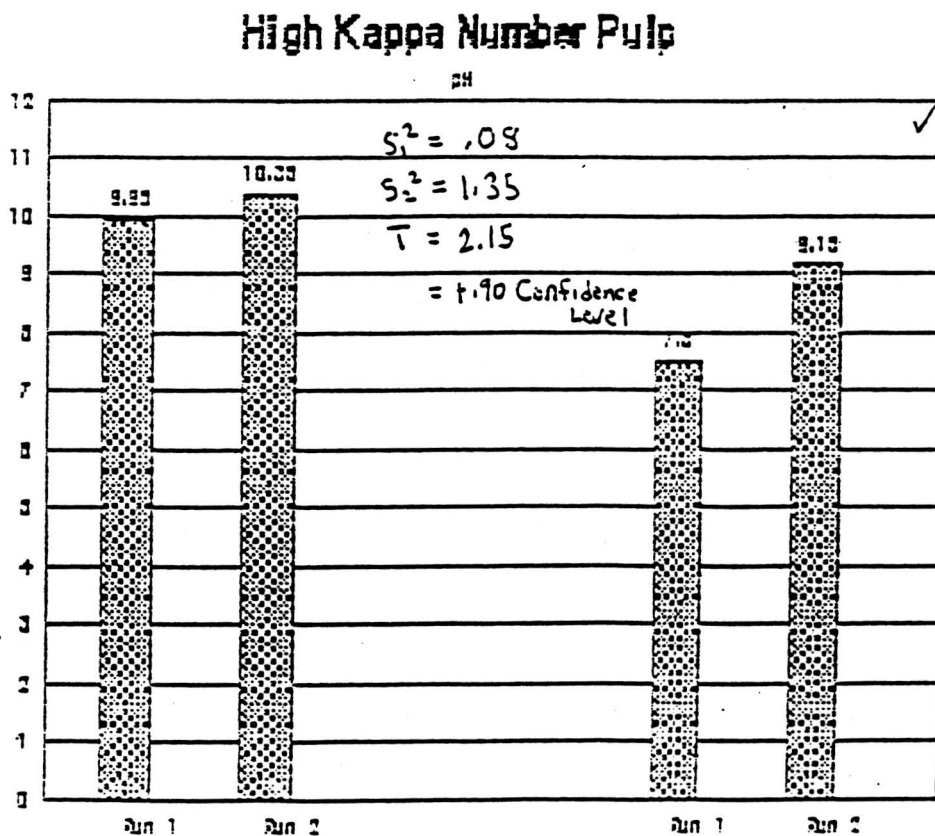


Cd-E

VS

Cd-Eo

pH



Cd-E

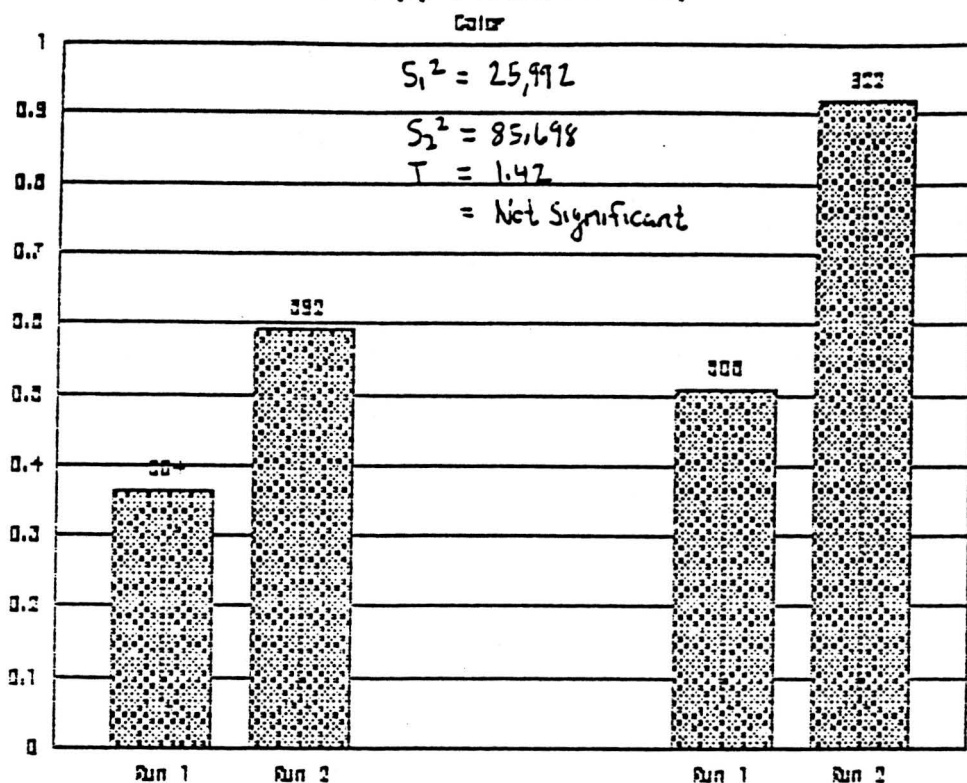
VS

Cd-Eo

Fig. 2

ppm, thousands

Low Kappa Number Pulp

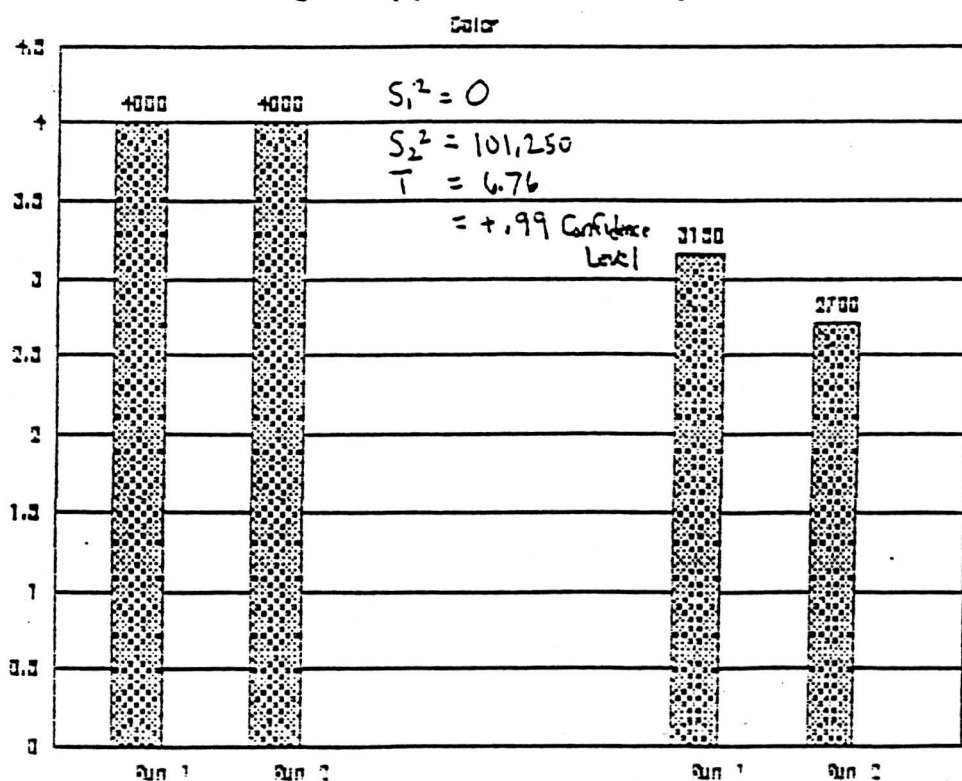


Cd-E

VS

Cd-E₀

High Kappa Number Pulp



ppm, thousands

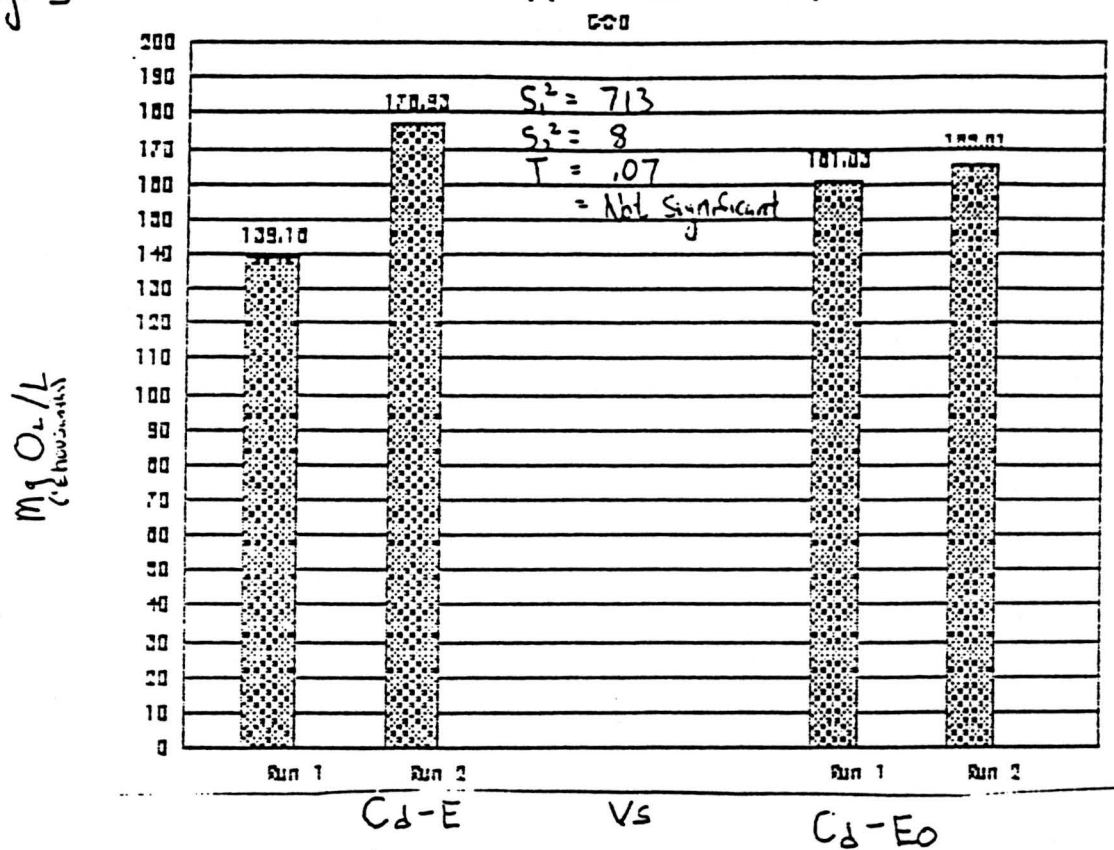
Cd-E

VS

Cd-E₀

Fig. 3

Low Kappa Number Pulp



High Kappa Number Pulp

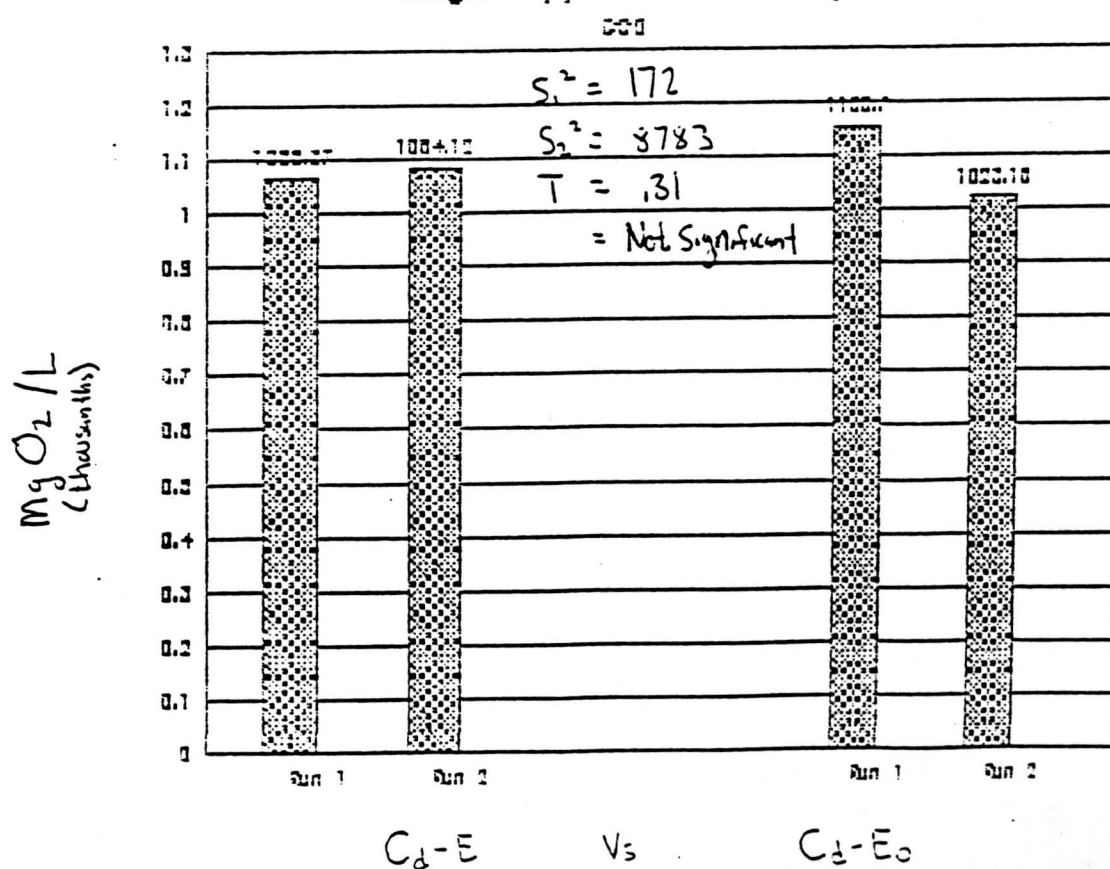
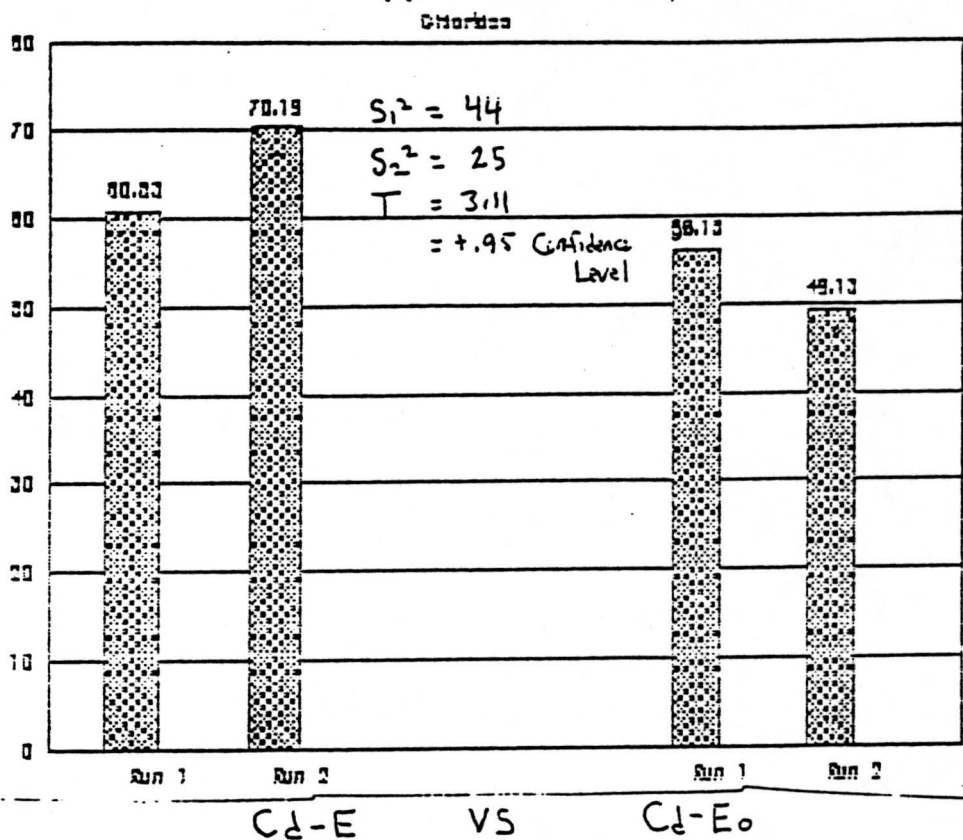


Fig. 4

mg Cl⁻/L

Low Kappa Number Pulp



High Kappa Number Pulp

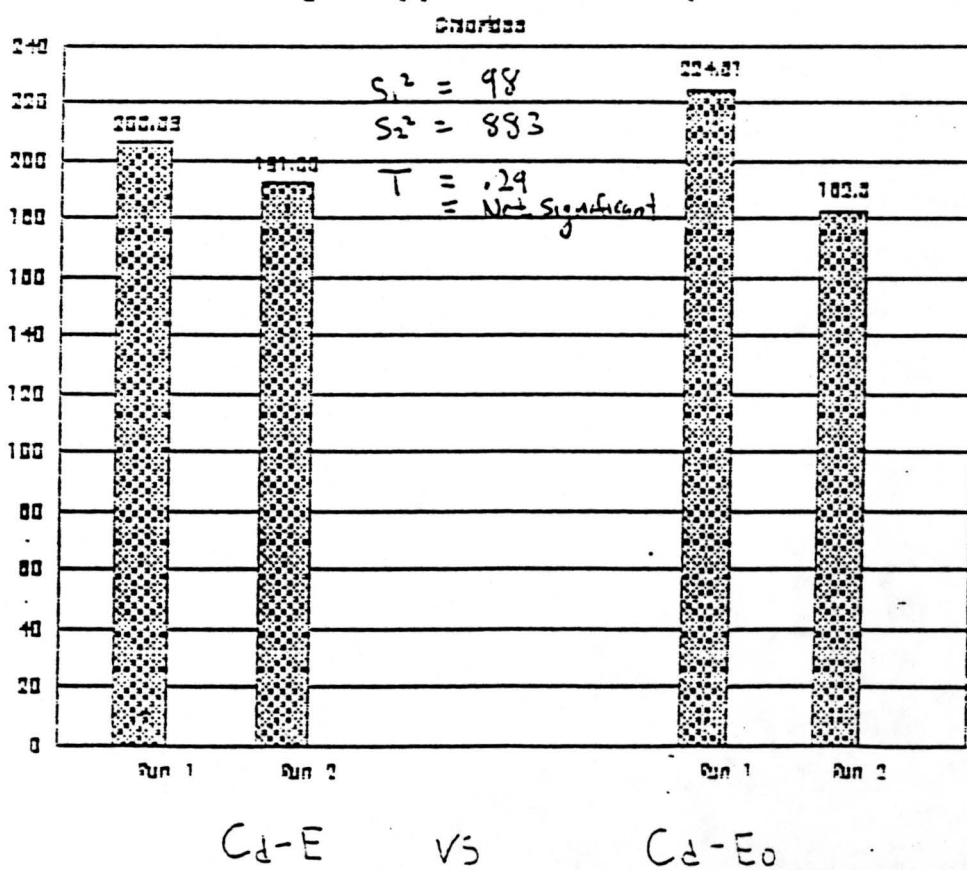
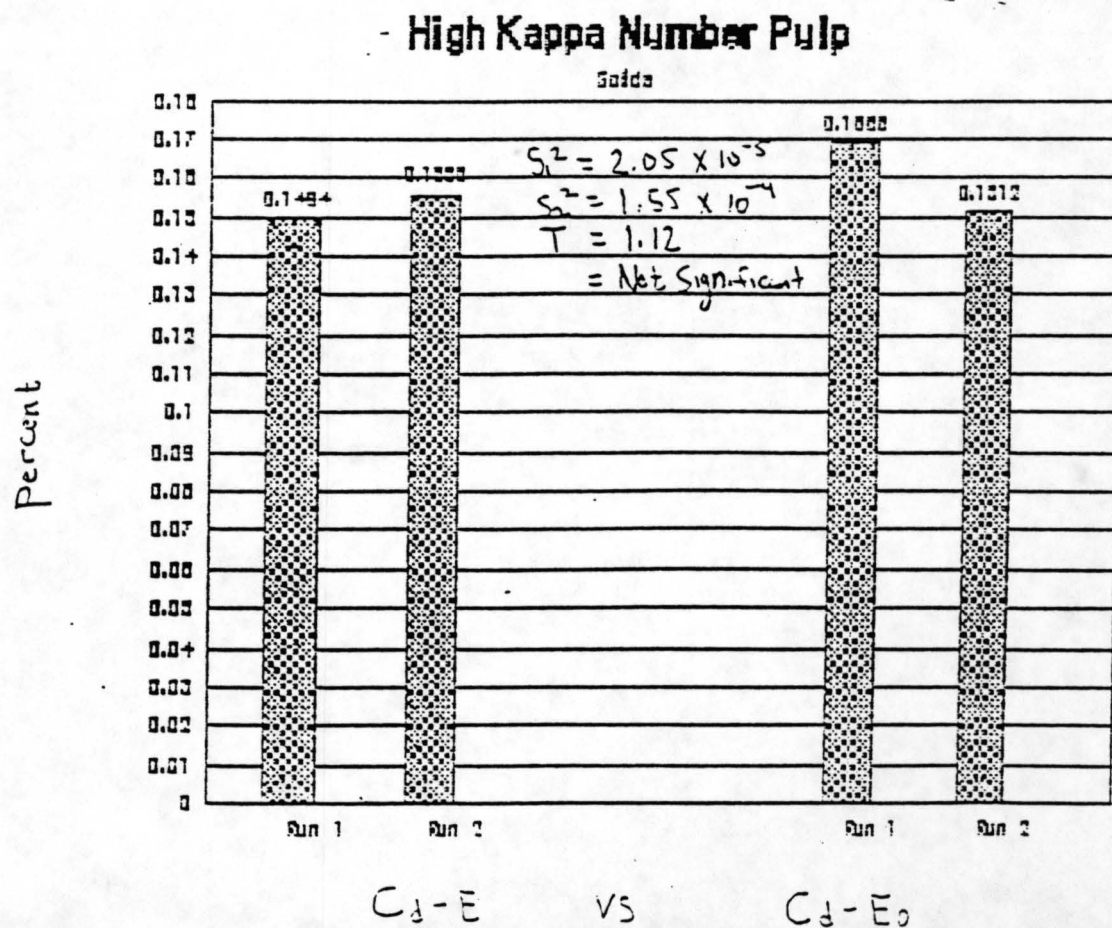
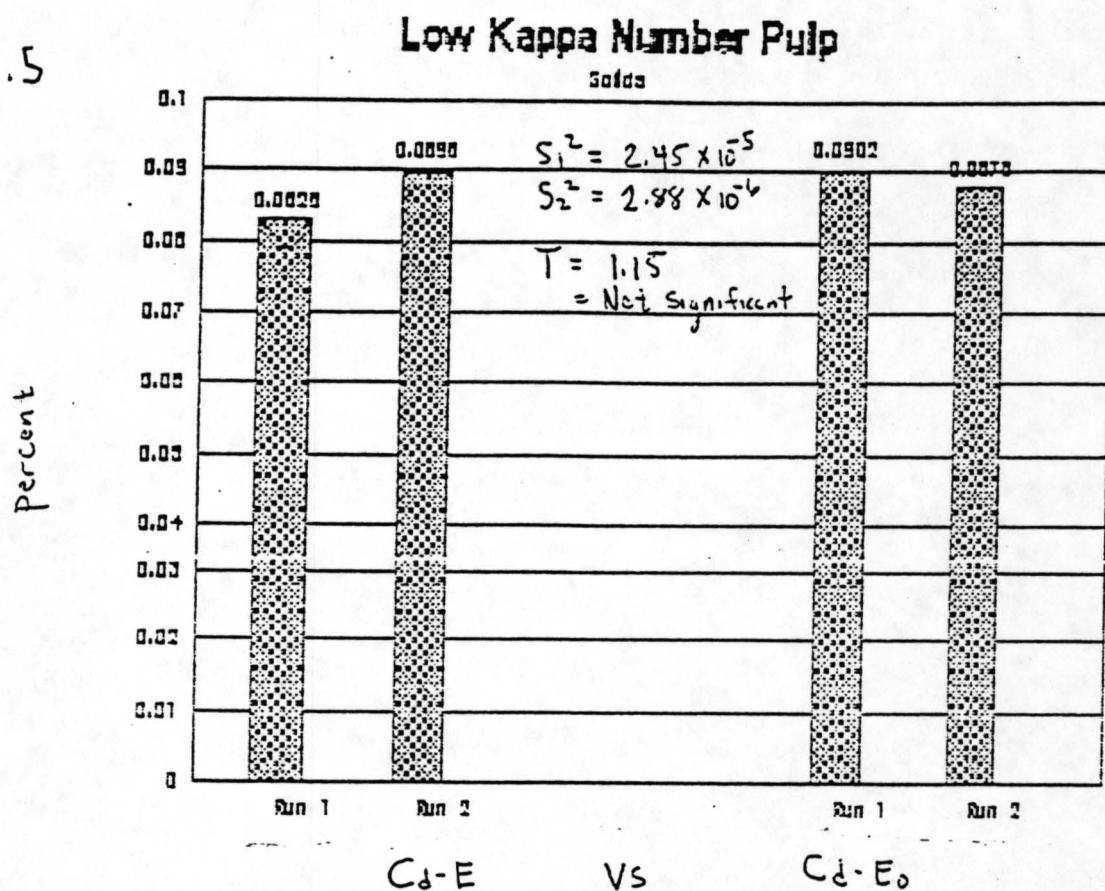
mg Cl⁻/L

Fig. 5



as the maximum difference in pH between the Cd-E and Cd-Eo pulps is 0.1. The high kappa number pulp also has very good confidence level, .90, when comparing the Cd-E to Cd-Eo filtrates pH. In this case the Cd-Eo bleached pulp has a significantly lower pH. This I believe is due to the fact that the oxygen reacts with the lignin during the Eo stage. This reaction in turn makes for acidic conditions which of course lowers the pH. I feel that the reason why there was not such a trend in the low kappa pulp was because there just was not the amount of lignin available for the oxygen to react with, as the starting kappa number for the low kappa pulp was only 15 compared to the starting kappa number of 40 for the high kappa pulp.

The effluent test results for color is shown in figure 2. For the low kappa number pulp a T value of 1.42 was calculated, which when viewed on the Student's T Distribution chart at 6 degrees of freedom proves not to be significant. However, the high kappa number pulp does show a .99 confidence level on the Student's T chart, which means the result of the Cd-Eo filtrate being less colored than the Cd-E filtrate is quite significant. Again like pH I believe the reason for this has to do with the amount of lignin present in the high kappa number pulp. The lignin liberated from the fibers in the Eo stage is getting bleached, while the low kappa pulp just does not have enough lignin being liberated into the filtrate to show any significant results in terms of color.

The effluent test results for COD is shown on figure 3. For the low kappa number pulp there is no significant statistical difference between the Cd-E and Cd-Eo pulp. This I believe is

due to the fact that both the Cd-E and Cd-Eo pulps were bleached to the same kappa numbers. Therefore, the same amount of solid material would be liberated from each type of pulp, which would not be affected by any oxygen injection during the Eo stage. The same type of reasoning also relates to the high kappa number pulp. As this pulp also shows no significant statistical difference in the COD values.

The effluent test results of chlorides is shown on figure 4. For the low kappa number pulp a Student's T value of a .95 confidence level was shown. This of course means that there is a significant statistical difference between the Cd-E and Cd-Eo pulps. Chlorides usually show trends in how severe an effluent is. This means that an effluent with more chlorides is stronger in terms of its effluent properties. This is very interesting that the Cd-Eo pulp should reveal fewer chlorides than the Cd-E pulp while not showing any improvements in COD and as I will later show, Percent Solids. The only reason that I can give for this result is that in order to reach a final kappa number in the bleached pulp the Cd-Eo stage only required 25 min. of bleaching time while the Cd-E sequence required 30 minutes. Thus, I believe this extra 5 minutes of bleaching for the Cd-E pulp was enough to increase the chlorides beyond that of the Cd-Eo pulp, while not showing any effect on solids or COD. The high kappa number pulp on the other hand did not show any significant statistical difference for chlorides between the Cd-E and Cd-Eo sequences. This may be due to the fact that the filtrates of the high kappa pulps are very strong when compared to the low kappa pulps, which

may mean any additional chloride addition from an extra 5 minutes or bleaching is insignificant when compared to the amount already in the filtrate.

The last figure, figure 5, shows the results of the Percent Solids in the filtrates. For both the low and high kappa number pulps there is no statistical difference between the Cd-E and Cd-Eo sequences. This is because both high and low kappa numbers were bleached to a constant kappa number. Thus, the amount of solid material in the filtrate should be essentially the same.

Conclusions.

My data suggests that the Cd-Eo stage gives several advantages to the filtrate when compared to the Cd-E stage at the same chemical addition rates. Also the characteristics of the filtrate changes depending on whether the pulp bleached is started at a high or low kappa number.

It was found that there was no differences in pH between the Cd-E and Cd-Eo sequences of the low kappa number pulp, basically theorized to be due to the relatively low amount of lignin present. However a lower pH was obtained for the high kappa number pulp Cd-Eo sequence probably due to the reaction between the oxygen and lignin acidifying the filtrate. It was also determined that no significant differences for COD and Solids was noticed between the Cd-E and Cd-Eo sequences for both the high and low kappa number pulps. This could be attributed to the fact that both high and low kappa pulps were bleached to a constant kappa number meaning an equal amount of solid material would exist in the filtrates regardless of any oxygen addition. It was also found that the

high kappa pulp showed a decrease in the color of its Cd-Eo sequence filtrate. This probably could be attributed to the fact that that large amount of solid material present in the filtrate of the high kappa number pulp was bleached by the oxygen during the Eo stage, thus giving decreased color values. The low kappa pulp did not show any significant color differences, probably due to the low amount of solid material in the filtrate available to be bleached by the oxygen. Lastly, a significant decrease in the amount of chlorides in the Cd-Eo filtrate for the low kappa pulp was noticed. This is attributed to the fact that the bleaching time for the Eo stage was 5 minutes less than the E stage to reach the same kappa number. The high kappa pulp did not show any significant differences in chlorides. This I feel was due to the fact that the filtrate for both Cd-E and Cd-Eo sequences at the high kappa number was very strong as filtrates go, thus the 5 minutes difference in bleaching time was not enough to affect the overall chloride concentration of the filtrate.

Suggestions for Future Study

This thesis has yielded some results which I believe can be built upon. I looked at a low and high kappa number pulp, perhaps other kappa numbers should be evaluated in the same manner. The other kappa numbers could include 35, 30, 25, and 20. This would enable one to see if the observed trends extends over these kappa numbers. Another area that I feel could be further investigated would be the reactions involved in the lowering of pH of the filtrate for the high kappa number pulp.

Appendix I
Pulping Conditions and Results

Moisture Content of Chips: 46.0%

Active Alkali: 25%

Sulfidity: 25%

Liquor to wood Ratio: 5:1

Grams O.D. chips/digester 800

Low Kappa Pulp: 170 F with 45 min. at max. temp.

High Kappa Pulp: 155 F with 50 min. at max. temp.

Results of Cook

High Kappa Pulp: 40 @ 54.1% yield

Low Kappa Pulp: 16 @ 45.5% yield

Appendix II

Bleaching Conditions and Final Kappa Numbers

<u>Stage</u>	<u>Consistency</u>	<u>Temperature</u>	<u>Time</u>	<u>% Chemical</u>
Cd (16 Kappa)	3.5 %	50 C	6 min.	3.7 % Cl ₂ 0.3 % ClO ₂
Cd (40 Kappa)	3.5 %	50 C	6 min.	9.7 % Cl ₂ 0.3 % ClO ₂
E (16 Kappa)	2.0 %	70 C	35 min.	3.0 % NaOH
E (40 Kappa)	2.0 %	70 C	30 min.	3.0 % NaOH
Eo (16 Kappa)	2.0 %	70 C	30 min.	3.0 % NaOH
Eo (40 Kappa)	2.0%	70 C	25 min.	3.0 % NaOH

Note - For all Eo stages pressure inside vessel was 30 psi(g)
 - Magnesium Sulfate was added to All Eo stages at .1 % on oven dry pulp

Final Kappa Numbers

Low Kappa Pulp

Cd-E Run #1 - 3.8
 Run #2 - 3.5

Cd-Eo Run #1 - 3.4
 Run #2 - 3.6

High Kappa Pulp

Cd-E Run #1 - 14.5
 Run #2 - 15.5

Cd-Eo Run #1 - 12.0
 Run #2 - 13.4

Appendix III

COLOR PROCEDURE

Compiled August 1977

Method Reference: Standard Methods (Platinum-Cobalt Procedure) or NCASI Technical Bulletin Spectrophotometric Method

Special Considerations: The pH of the sample and the care taken in the filtration step are very important.

Procedure Summary:

Preparation of Standards

Dilute 2.5, 5.0, 10.0, 15.0, 20.0, and 25.0 ml stock color standard with distilled water to 50 ml in stoppered volumetric flasks. This will give solutions with color values of 25, 50, 100, 150, 200, and 250 respectively.

Preparing a Calibration Curve

1. Set spectrophotometer to 465 ^{nanometers} ~~mμ~~.
2. Zero machine with distilled water using a matched set of cells.*
3. Run the standards through the machine and record absorbance readings.
4. Construct a curve on regular graph paper (color units vs. absorbance).
5. Draw the best possible straight line.

Preparation of Sample

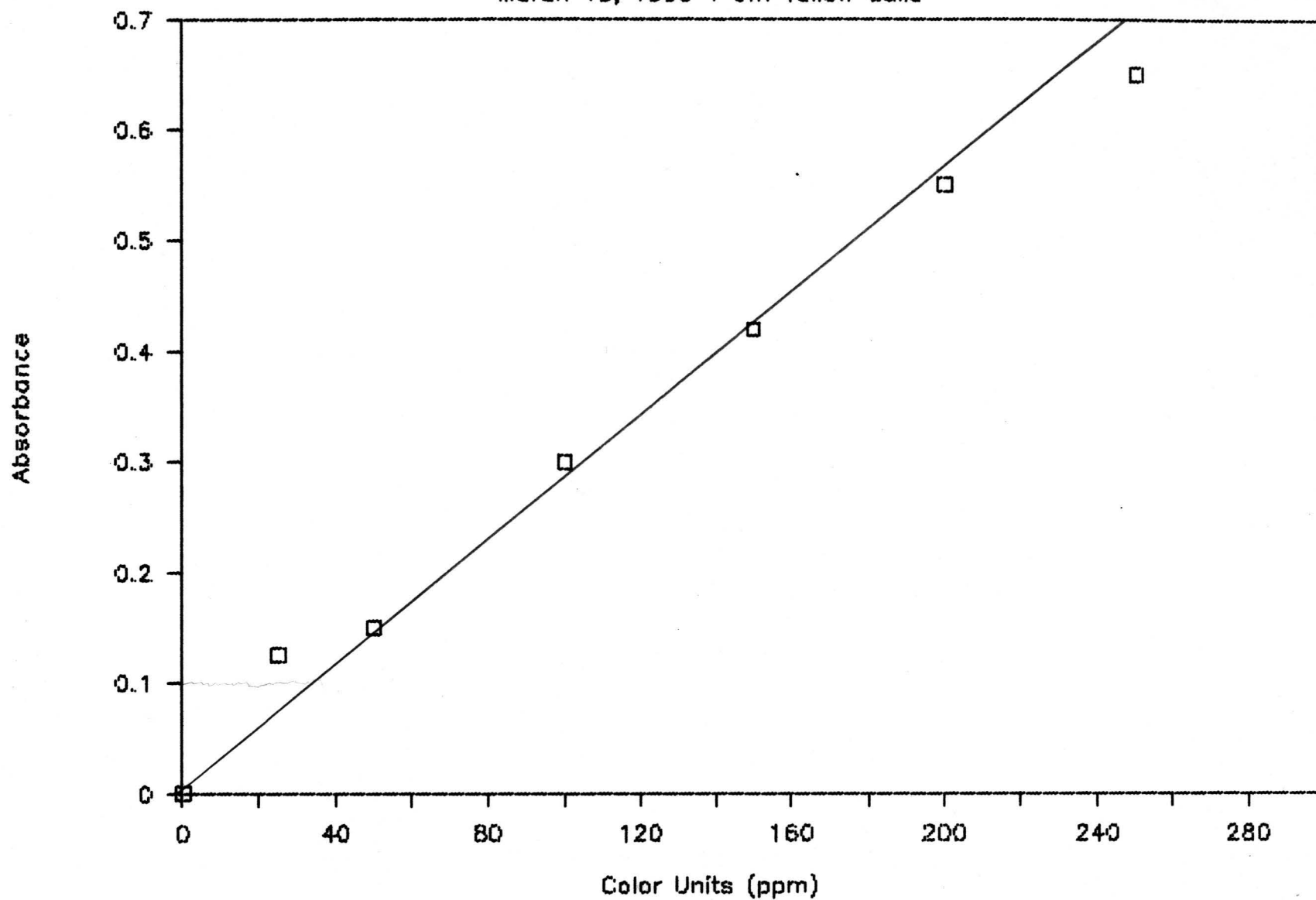
1. Adjust the pH of a 200 ml sample to 7.6 with the aid of a pH meter and HCl and NaOH solutions. (If the sample volume is changed more than 1% by the additions, the sample should be discarded and the procedure started again with stronger acid and base solutions.)

2. Sample should be filtered with a .8 ^{micron} ~~mm~~ membrane filter that has been rinsed with distilled water. (No more than 30 ml sample should be filtered through any one filter paper. Severe clogging should be avoided.)
3. Machine should be re-zeroed with distilled water.
4. Run 3 different portions of the sample filtrate in matched cells and record the absorbance.*
5. The color units can then be read directly off the graph or a linear regression may be run on the computer to derive the color value.

* Any spectrophotometric analysis should be carried out with a matched set of absorption cells. The proper method of filling cells is to rinse the cell with sample, discard that sample and then fill the cell again. The cell is then wiped dry with a Kimwipe or soft towel before insertion into the machine.

Color Calibration Curve

March 13, 1990 1 cm Yellow Cells



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