

AN ABSTRACT OF THE THESIS OF

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Title: INVESTIGATION OF THE FUNDAMENTALS OF FLUORESCENT BEHAVIOR

OF KRAFT-ANTHRAQUINONE PULPING LIQUORS

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The kraft and kraft-anthraquinone pulping processes were used for pulping Douglas-fir chips at 170°C, 180°C and 190°C temperatures. Anthraquinone was added to the pulping liquor at two levels, 0.1% and 0.2% based on wood, to study its effect on pulp delignification at the three temperatures. The fluorescent behaviors of kraft and kraft anthraquinone liquors were related to pulping times, Kappa numbers, and yields.

The beneficial effects of anthraquinone decreased as the pulping temperatures increased. Anthraquinone showed the least improvement at 190°C (0% change in yield, -10 points change in Kappa number), while its best effect was shown at 170°C pulping temperature (.6% change in yield, -33 points change in Kappa number), all values relative to kraft cooks at these temperatures. These results suggest that at 190°C, anthraquinone did not stabilize the carbohydrates of the pulp nor the dissolved lignins in the pulping liquor.

The fluorescent intensity of the pulping liquor at 170°C was increased by the addition of anthraquinone; but at 190°C pulping temperature, anthraquinone did not show any significant effect on this property. These results suggest that, at 170°C pulping temperature, addition of anthraquinone increased the amount of lignin in the pulping liquor, but at 190°C anthraquinone probably did not prevent the condensation of the dissolved lignin. This was also suggested by the decrease in fluorescent factors with the pulping time.

The redox potentials of the pulping liquor increased as the sulfidity increased, but, at temperatures beyond 170°C they decreased with pulping time. The redox potentials of the pulping liquor could indicate the reduction capacity of the pulping liquor during the pulping time.

Investigation of the Fundamentals of Fluorescent Behavior
of Kraft-Anthraquinone Pulping Liquors

by

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INVESTIGATION OF THE FUNDAMENTALS OF FLUORESCENT BEHAVIOR OF KRAFT-ANTHRAQUINONE PULPING LIQUORS

INTRODUCTION

Cellulose, in the form of fiber, is the basic raw material for papermaking, and wood is the most important source of cellulose (fiber) in paper manufacturing. However, fibers can be obtained from other materials such as straws and sugar cane.

The constituents of wood can be divided in two groups: carbohydrates and non-carbohydrates. The first group is composed mostly of cellulose and hemi-cellulose. In the second group are included lignin, resins and fats, lignin being the largest component of this group. During chemical pulping, part of the non-carbohydrate material is dissolved, and later it is removed by washing. Then the fibers can be easily separated from each other. During cooking, the chemicals react not only with lignin, but also with carbohydrates, even though cellulose is the most resistant to chemical attack. (This means that part of the fibers are dissolved along with lignin.) This fact shows the inefficiency of current pulping processes, and is created in part by our lack of understanding of the delignification reactions that occur during the pulping process.

Today, the delignification of wood is being measured by analysis of pulp, which is difficult to remove from the digester during the cooking cycle. This means that the analysis of the pulp is not performed until the end of the cook. Under these circumstances we are not able to detect the degree of delignification of wood during the

cooking time. Part of this problem can be resolved through the analysis of lignin in pulping liquor, since, during a cook, pulping liquor can be easily removed from the digester. Once lignin in the liquor has been measured during a cook, correlations can be made between lignin in the liquor, cooking conditions (time, temperature, and chemicals charge), Kappa number, and total yield.

When lignin is excited with ultraviolet light it has the property of fluorescence, allowing detection at very low concentrations. By using this property of lignin it has been possible to measure the lignin in effluent streams. In the last few years, fluorescence has been used for measuring lignin in black liquor. The purpose of this research project was to detect lignin in the liquor by fluorometry during the cooking process.

For a long time, the kraft pulping process has been the system most used in the pulp and paper industry. Its popularity has been due to the high yield and good quality of pulp obtained by this process. However, a new product has been recently introduced that is making an impact on the pulp and paper industry. This product (anthraquinone AQ) added to the kraft pulping liquor in very small quantities reportedly improves the efficiency of delignification. In the present project we wished to study the effect of AQ on the fluorescent properties of kraft liquor.

The objectives of this thesis were:

1. To study the fluorescence of Douglas-fir kraft liquors as a function of pulping time, temperature, and chemical composition of pulping liquor.

2. To relate the fluorescence of these liquors to other pulping responses such as oxidation-reduction potential, liquor pH, and chemical content of the liquor.
3. To study the effect of the additive anthraquinone on the fluorescent behavior of kraft liquor.

LITERATURE REVIEW

I. The Kraft AQ and AHQ Pulping Process

1. Yield and Kappa Number

The addition of AQ to kraft cook liquor produces a marked increase in total yield at a given kappa number (1). The increase of total yield can be explained by an increase in the delignification rate and in the stability of carbohydrates (2, 3). Cooking time and chemical charge can be also reduced by AQ pulping. An increase in total yield is reflected by the optimization of these variables. Holton (4) reports that the pulp kappa number can be reduced 15 units under constant cooking conditions by adding AQ to the liquor. He also found that at constant kappa number, effective alkali demand was reduced by 1.5% and yield was increased by 2-3%. Blain (5) agrees with Holton's findings by reproducing some of his results. In a full mill trial, the AQ additive shows better results than in laboratory trials. This increase was probably due to better recirculation of pulping liquor in the digester of the mill (4).

2. Stabilization of Carbohydrates

The stabilization of carbohydrates during AQ pulping is due to the formation of aldonic acid end group (2, 3). Analysis of pulp from a kraft AQ pulping process showed that the contents of glucomannan and xylan were considerably higher than in a conventional kraft pulp (2). During a cook, carbohydrates react with AQ which is reduced to the correspondent anthrahydroquinone (AHQ). During

carbohydrate oxidation, the aldehydic end group changes to a carboxylic end group (6).

3. Redox Catalysis

The AQ additive is a catalyst for oxidation-reduction reactions where AQ is reduced to AHQ by carbohydrates, while lignin is reduced (dissolved) by the AHQ which is oxidized back to AQ (6). In order to reduce AQ to AHQ, one reducing end group loses one electron which is gained by AHQ, and the carbohydrates are protected from further degradation (7, 10) by conversion of the aldehyde end group to a carboxyl end group.

4. Redox Potentials

The redox potentials of kraft pulping liquor are strongly negative. This negativity is probably due to the presence of reducing solutions which originate during pulping (5). However, redox potentials can be correlated with the rate of delignification (8). The negativity of redox potential in the black liquor can be increased by 60 mV when AQ is added to soda-pulping liquor during a cook (9). In agreement with the theory that electrons from carbohydrates represent an important resource for delignification in AQ pulping, the solubility of lignin was accelerated when small quantities of glucose were added to the AQ pulping liquor (7).

5. Pollution Control

The ability of AQ to increase pulping rates and improve yields can be one approach for lowering sulfidity, and thus the contamination

of the air by sulphur compounds from kraft mills can be reduced (5). Also, at lower kappa numbers, the chemical charge for the bleaching of pulp can be reduced and simultaneously reduce the water pollution load from the bleach plant.

6. Pulp Quality

At a given kappa number, the quality of AQ pulp is improved because such pulp is produced under less severe conditions of temperature and chemicals (1). Thus, properties such as pulping uniformity and the brightness and strength of the paper can be improved (11).

II. Fluorescence

1. Definition

Fluorescence is the emission of light during 10^{-12} seconds from a molecule or atom which has absorbed light (12).

2. Light and the Excited State

Light is a form of electromagnetic radiation or energy that is characterized by frequency (f), wavelength (λ) and velocity (c). Such characteristics are related by the following formula:

$$f = \frac{c}{\lambda} \quad \text{Equation 1}$$

The fluorescent substances absorb all or part of light in discrete energy units called quanta. One electron absorbs a quantum of energy (15) when it is shifted from one energy level to a higher one (19). The following equation represents the energy of a quantum

$$E = hf = h \frac{c}{\lambda}$$

Equation 2

where h = Plank's constant and f = frequency (15).

3. Equilibrium Excited State

The absorption of a quantum of light by a molecule is nearly instantaneous (10^{-15} seconds) producing an excited state. While this excited state persists for 10^{-8} seconds (19), the molecules are deactivated, and under these conditions they return to the lowest vibrational level (equilibrium excited state EES) by losing some energy. From this level (EES) the electron returns to the ground state (15) by losing energy which is detected as fluorescence. In Equation 2, the wavelength increases when the energy (E) decreases, given that h and c are constant. This explains the fact that wavelength of emitted light (fluorescence) is longer than that of the absorbed light (12).

4. Fluorescence and Chemical Structure

Most aliphatic compounds do not fluoresce because their electrons are bound very tightly. Therefore, the high energy required for excitation of these compounds produces the disruption of molecular bonding (16). However, aliphatic aldehydes and ketones can fluoresce. In the aromatic compounds, the fluorescence is more intense when the molecule has a rigid and planar structure (20). The nonrigid molecules are very sensitive to the environment, especially to the temperature (16). Condensation or cross linking of lignin can lower the fluorescent intensity, but may not change the peak frequency

of emission (20). However, the fluorescence increases when an OH^- group is a substituent in the aromatic compound, but it decreases when the SH^- group is a substituent. Regarding the HSO_3^- group, it does not show any effect on fluorescence (15, 16). The roles of these groups are very important when lignin is being dissolved by the pulping processes, especially the soda, kraft and sulfite processes (21). In the fluorescence analysis of lignin, it was found that the intensity of fluorescence decreases when the molecular weight of lignin was increased (17, 19).

5. Quenching Reactions

Fluorescence quenching is an interaction of the fluorescent molecule with its solvent, or with other solutes, in such a manner as to lower the efficiency of the fluorescence process (17, 19). This means that the fluorescent compound will exhibit less fluorescence when it is in the presence of the quenching substances. The following equations represent the absorption of light, fluorescence, and quenching reactions:



where M is the fluorescent compound, hf energy and Q the quenching molecule. Equation 3 represents the light absorption, Equation 4 the fluorescence, and Equation 5 the quenching reaction (15, 16).

6. The Environmental Effects

Many authors (14, 19) have discussed the effects on fluorescence of temperature, solvents, concentration, other solutes, and pH. According to C. Wade (8) and Christman and Minear (17) the fluorescence is pH dependent and decreases with increasing temperature. Moreover, the fluorescent intensity of lignin is a linear function of lignin concentrations at low concentrations (around 1:10,000). Bublitz and Meng (14) found that the wavelength of emitted light has a direct relation to the pH. However, sometimes it is difficult to predict the effect of such facts because they can interfere by many ways. Sometimes a pure solvent does not show any fluorescence itself; however, it can be a quencher in the fluorescence process.

EXPERIMENTAL PROCEDURE

1. Sample Preparation

In order to accomplish the present research project, samples of Douglas-fir chips were pulped by the kraft pulping process. The chips were conditioned at room temperature for one week until the moisture content of such chips reached equilibrium. Then, the chips were screened on a Williamson chip screen (a round hole screen) for five minutes. The fractions retained on the 3/8" and 5/8" diameter hole screens were separated from the remainder for pulping. These fractions were stored in plastic bags at room temperature and at the same time, their moisture contents were determined. Bark, rot, and knots were removed from the chips before pulping.

2. Wood Analysis

The chip samples were ground in a Wiley mill using a 50-mesh screen in accordance with TAPPI Standard T-11 os-74. The alcohol-benzene solubility was determined on the wood meal in accordance with TAPPI Standards T 204. The Klason lignin content was determined by TAPPI Standard T 222 os-74.

3. Pulping Procedure

A series of cooks was performed in the 50 grams oven dry wood bombs digesters which are heated by using an electric tape. Four different cooking times, three levels of AQ, and three cooking temperatures were the conditions under which the cooks were performed.

The chemical charges and liquor to wood ratios were constants for all cooks.

The active alkali and sulfidity were measured by TAPPI Standard T 624 os-68.

TABLE 1. KRAFT PULPING CONDITIONS FOR BOMB DIGESTERS

Active alkali, as Na_2O	22.8 gpl in white liquor 16.0% on o.d. wood
Sulfidity	20%
Liquor to wood ratio	7:1
Time to temperature	45 minutes
Times at temperature	60, 90, and 120 minutes
Maximum temperatures	170°C, 180°C, and 190°C
AQ concentrations	0.0, 0.1, and 0.2% on o.d. wood

After each cook, the bombs were quickly cooled. As soon as the bombs were opened, samples of black liquor were rapidly tested for redox potentials in order to avoid oxidation of the pulping liquor. The samples of black liquor were also tested for optical density in a Beckman Model ACTA III spectrophotometer. The fluorescence was analyzed by using an Aminco-Bowman spectrofluorimeter and a filter fluorimeter (Turner Model 111).

4. Pulping Liquor Testing

In order to determine the redox potentials, pH's and fluorescences in the pulping liquor during cooking time, chips were pulped in a circulating digester (one kg. wood capacity) which was heated

electrically. While a pump was circulating the pulping liquor, samples of black liquor were taken every ten minutes during cooking time. These samples were analyzed for the properties already mentioned, including absorption and emission analysis.

TABLE 2. KRAFT PULPING CONDITIONS FOR THE CIRCULATING DIGESTER

Active alkali (as Na_2O)	12% and 16% on o.d. wood
Sulfidity	10% and 20%
Liquor to wood ratio	7:1
Time to temperature	60 minutes
Time at temperature	4 hours
Final temperatures	170°C, 180°C and 190°C

In the circulating digester, eight cooks were made in total; while in the bombs 48 cooks were performed.

All black liquor samples were stored under refrigeration before they were tested for optical density and fluorescence.

The samples of pulping waste liquor tested for fluorescence in the Turner 111 filter fluorometer were diluted 10,000 times. The solvent was sodium hydroxide 0.1 N (this solution was prepared with distilled water). However, the samples that were tested for fluorescence in the Aminco spectrophotofluorometer were diluted 5000 times in a solution of 0.1 N sodium hydroxide prepared with double distilled water. In both cases, ten microliters of pulping waste liquor were directly diluted in 50 ml and 100 ml of 0.1 N sodium

hydroxide in order to give dilution ratios of 1:5,000 and 1:10,000 respectively.

5. Pulping Testing

The amount of lignin present in the pulp was determined by performing the kappa number analysis on the pulp, according to TAPPI Standard T-236. In both bomb and circulating digester cooks, the yields were determined as total yield. This means that the pulps were not screened and therefore, the rejects were included in the pulp.

6. Spectral Conditions

In order to obtain the wavelength corresponding to the maximum optical density, samples of pulping waste liquor were tested for percent transmission using a Beckman double beam UV absorption spectrophotometer.

TABLE 3.

<u>Absorption Conditions</u>	<u>Beckman UV Absorption Spectrophotometer</u>
Wavelength range	250 nm to 350 nm
Scan speed	1 nm/sec.
Span	1.0
Chart expansion	25 nm/inch
Dilution ratios	1:1000 and 1:5000

Once the absorption peak for lignin was obtained and identified, the instrument was manually controlled for finding the wavelength of light corresponding to the highest point on the absorption peak. Light of this wavelength was used for excitation in the Aminco

spectrofluorometer when the fluorescence analysis of lignin was performed with this instrument. A solution of quinine sulfate was used as reference compound.

TABLE 4.

<u>Spectral Conditions</u>	<u>Aminco-Bowman Spectrofluorometer</u>
Excitation wavelength	285 nm
Emission wavelength	350 nm to 460 nm
Dilution ratios	1:1000 and 1:5,000
Excitation slit	Minimum
Emission slit	Minimum
Photomultiplier turret	5
Multiplier	.003
Sensitivity	40
Recorder:	
input	5 mV
speed	5 cm/min.

A Turner 111 filter fluorometer was also used for measuring fluorescence. This instrument automatically subtracts the fluorescence intensity of the solvent from that of the sample. The excitation and emission wavelengths are controlled by using optical filters.

TABLE 5.

<u>Spectral Conditions</u>	<u>Turner Model 111 Fluorometer</u>
Excitation bandwidth	9.5 nm
Excitation wavelength	280 nm
Emission bandwidth	35 nm
Emission wavelength	430 nm
Fluorescent intensity	10x
Dilution ratio	1:5000

For excitation, a Turner lamp #110-855 was used for providing a range of wavelengths from 270 nm to 350 nm. A 440 nm cut off emission filter from Dittit Optics, Inc., with an effective transmission range of 400 to 435 nm, was used in this study.

7. Redox Potentials

Samples of pulping waste liquors were tested for redox potentials in a digital pH meter (Orion 601A) using Fisher electrodes Cat. 13-639-51(SCE) and 13-639-115(PE). The saturated calomel electrode was used as a reference electrode.

8. Statistical Analysis

The principle of analysis of co-variance was applied to the data to study the response of a correlation between two parameters to a variation in a third parameter. Only linear correlations were tested. Two hypotheses were tested:

1. There were no statistically significant differences between the slopes of the linear regression lines.
2. If the first hypothesis is true, then there is no statistically significant difference between the adjusted means.
If both hypotheses are true, all the linear correlations belong to a single population. If either is not true, then the linear correlations are functions of the third parameter.

RESULTS AND DISCUSSION

I. Pulping Results

A. Bombs

1. Yield versus pulping time

Several studies have shown that the addition of anthraquinone AQ to the kraft pulping liquor affects mainly the Kappa numbers of the pulp while the pulp yields are slightly increased. Figures 1a and b show that pulp yield decreased with increased pulping time as expected. For a given pulping time, the pulp yield was increased when either 0.1% AQ or 0.2% AQ was added to the pulping liquor at 170°C or 180°C pulping temperatures respectively. However, Figure 1c shows that at 190°C, the addition of AQ to the pulping liquor had negative effects; for a given pulping time, the yield was lower because of the addition of AQ. In summary, regarding yields, the best pulping conditions were 0.1% AQ (as an additive in the pulping liquor) and 170°C temperature.

2. Kappa number - pulping time relationship

As expected the Kappa numbers (lignin contents of the pulps) decreased when pulping times increased (Figures 2a, b and c). The effect of AQ was not the same for three temperatures. It is interesting to see that the amount of added AQ is not linearly proportional to the change in Kappa numbers of the three temperatures. This means that the addition of AQ to the pulping liquor is only

Figure 1. Fluorescent intensity and fluorescent factor versus pulping time.

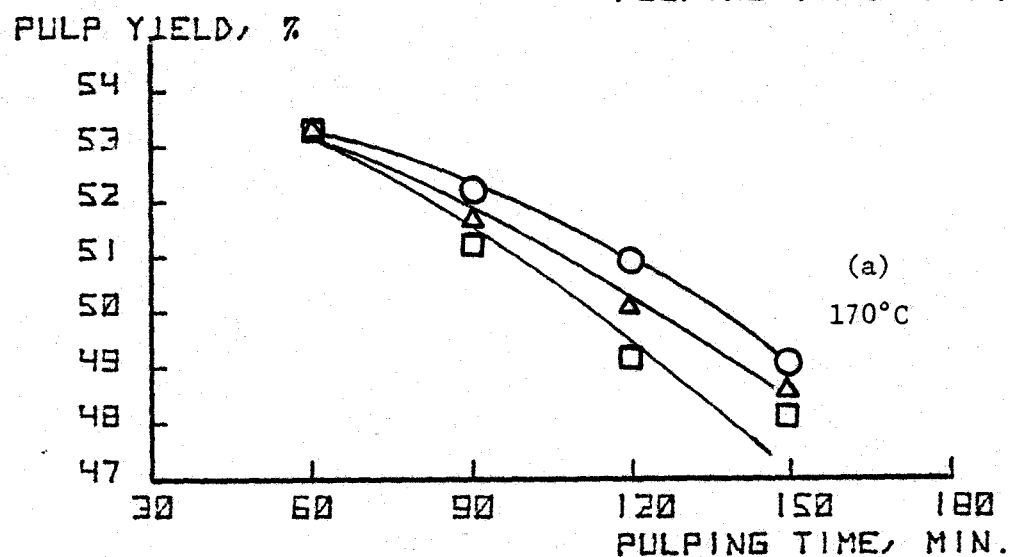
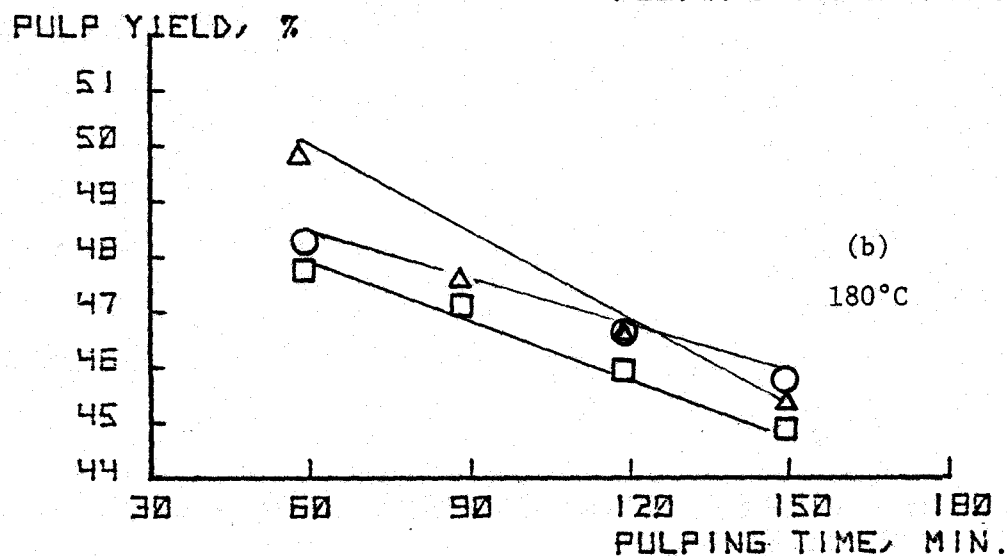
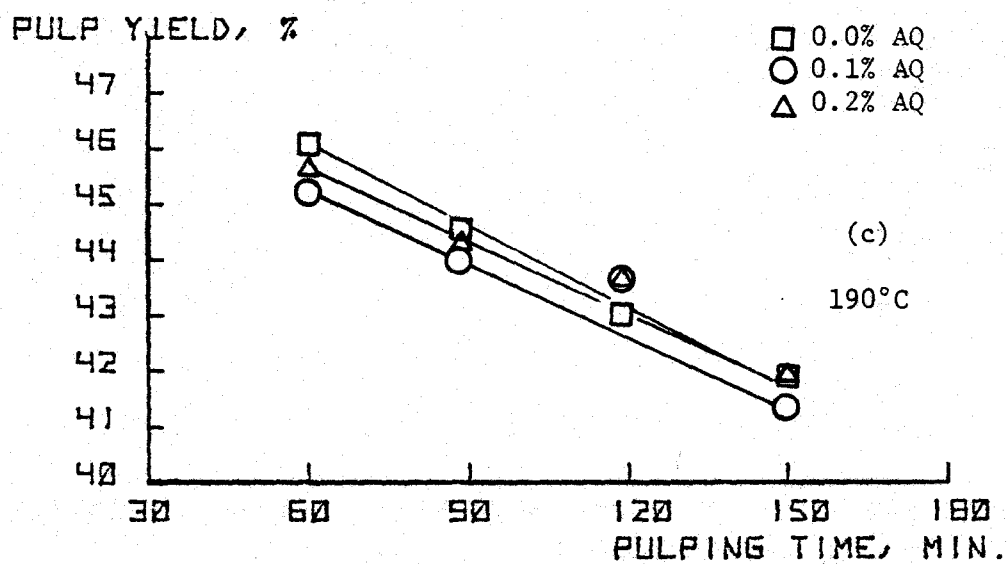
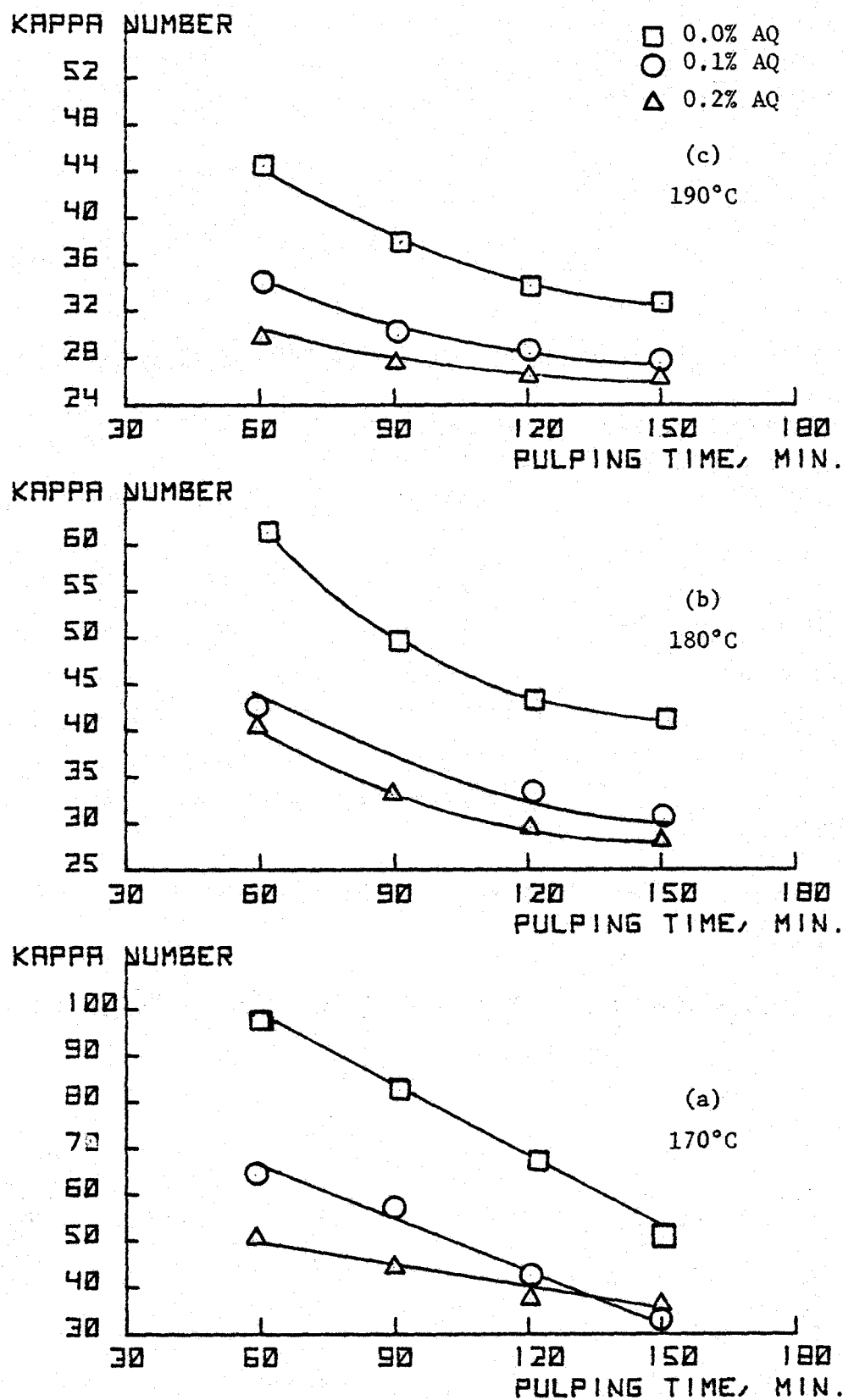


Figure 2. Kappa number versus pulping time.



effective up to certain levels of concentration. Figures 2a, b and c suggest that proportionally greater benefits are obtained by adding 0.1% AQ than by adding 0.2% AQ to the pulping liquor.

3. Pulp yield - Kappa number relationship

Figures 3a, b and c show the results of a set of cooks performed in bomb digesters. The AQ concentration and temperature both had marked influences on the pulp yields and Kappa numbers. The yields were positively correlated to the Kappa numbers. The yield-Kappa number relation is more linear at 170°C than at the 180°C and 190°C pulping temperatures. The addition of AQ showed a positive effect on the Kappa numbers and yields. For example, at a given yield, the Kappa number decreased several units by the addition of AQ to the pulping liquor. According to the theory proposed by several authors (1-6), the beneficial effect of AQ on pulping is probably due to the stabilization of carbohydrates by oxidation of reducing end groups to an alkali-stable configuration. In addition, the amount of lignin dissolved in the pulping liquor increases when AQ is present in the liquor. It seems that the role of AQ in pulping is similar to that of a redox catalyst: reduce (dissolve) the lignin and oxidize (stabilize) the carbohydrates.

B. Circulating Digester

1. Yield - Kappa number relationship

In order to measure the fluorescent intensity and redox potentials during pulping time several cooks were performed at

different temperatures and chemical charges, keeping the pulping time constant. The results of these cooks are shown in Figure 4. By statistical analysis it was found that the relationship between yields and Kappa numbers can be represented by the following equation: $\text{Yield} = -6.65 + 1.16 \text{ Kappa number}$, with a coefficient of determination (r^2) equal to 0.99.

The effect of AQ in the delignification of pulp was studied at three different temperatures and two levels of concentration. These results are shown in Figure 5, which compares the differences in pulp yields against the differences in Kappa numbers between kraft cooks (0.0% AQ) and kraft AQ cooks (0.1% and 0.2% AQ). Figure 5 shows that AQ produces better delignification of pulp at 170°C pulping temperature than at 180° or 190°C. At this temperature the Kappa number was lowered 33 units by the addition of AQ, while at 180°C and 190°C the AQ addition lowered the Kappa numbers only 15 and 10 units respectively. In proportion to the amount of AQ added to the pulping liquor, better results were obtained at 0.1% AQ addition for the three pulping temperatures. The addition of AQ showed negative effect on yield at 190°C. However, the pulp yield was increased by the AQ addition at 170°C and 180°C pulping temperatures.

II. Fluorescent Characteristics of Kraft AQ Pulping Liquor

Fluorescent intensity was calculated by the following formula for the Turner 111 filter fluorometer:

$$F = \frac{L \times D}{S \times 1000}$$

Figure 4. Pulp yield versus Kappa number.

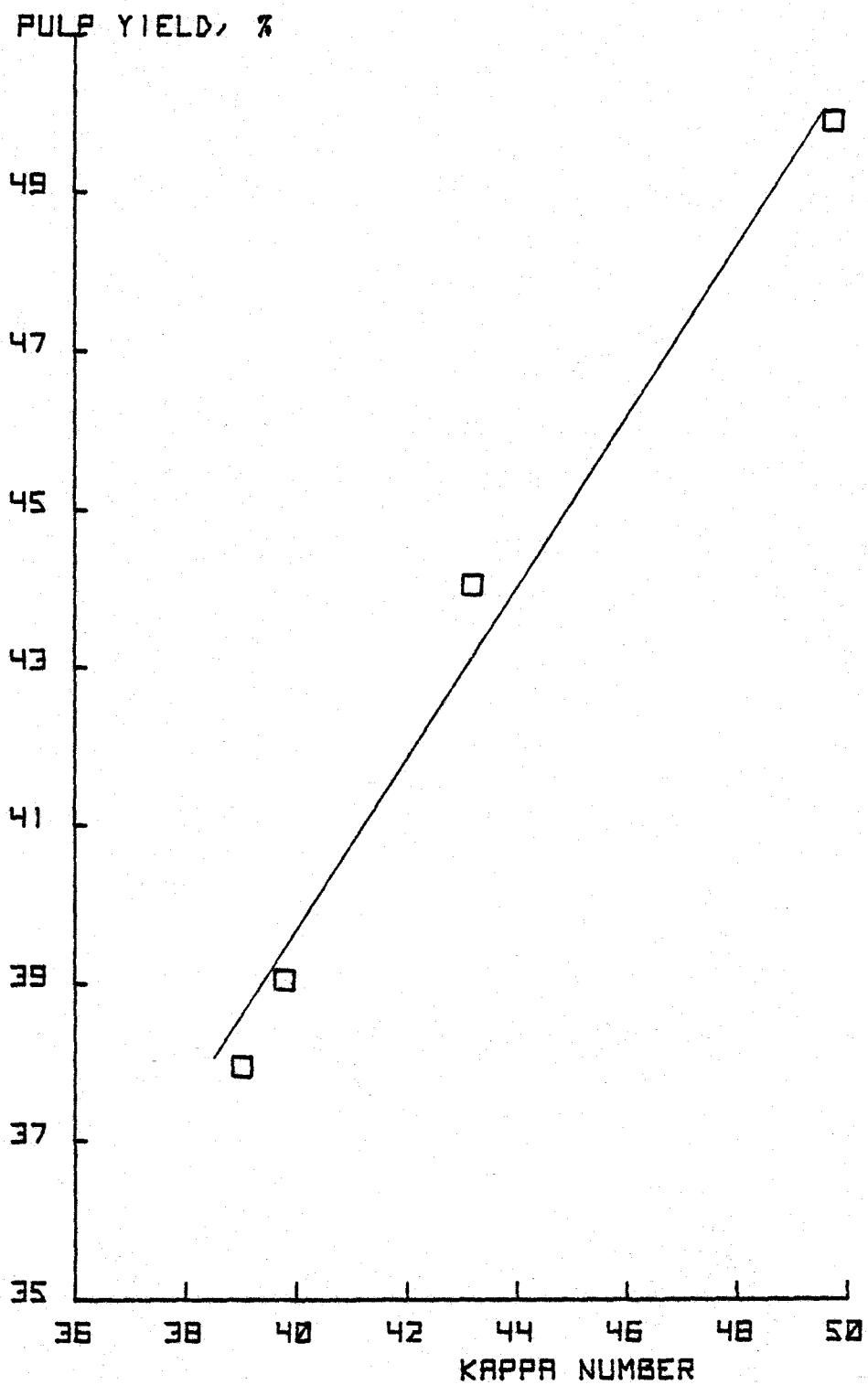
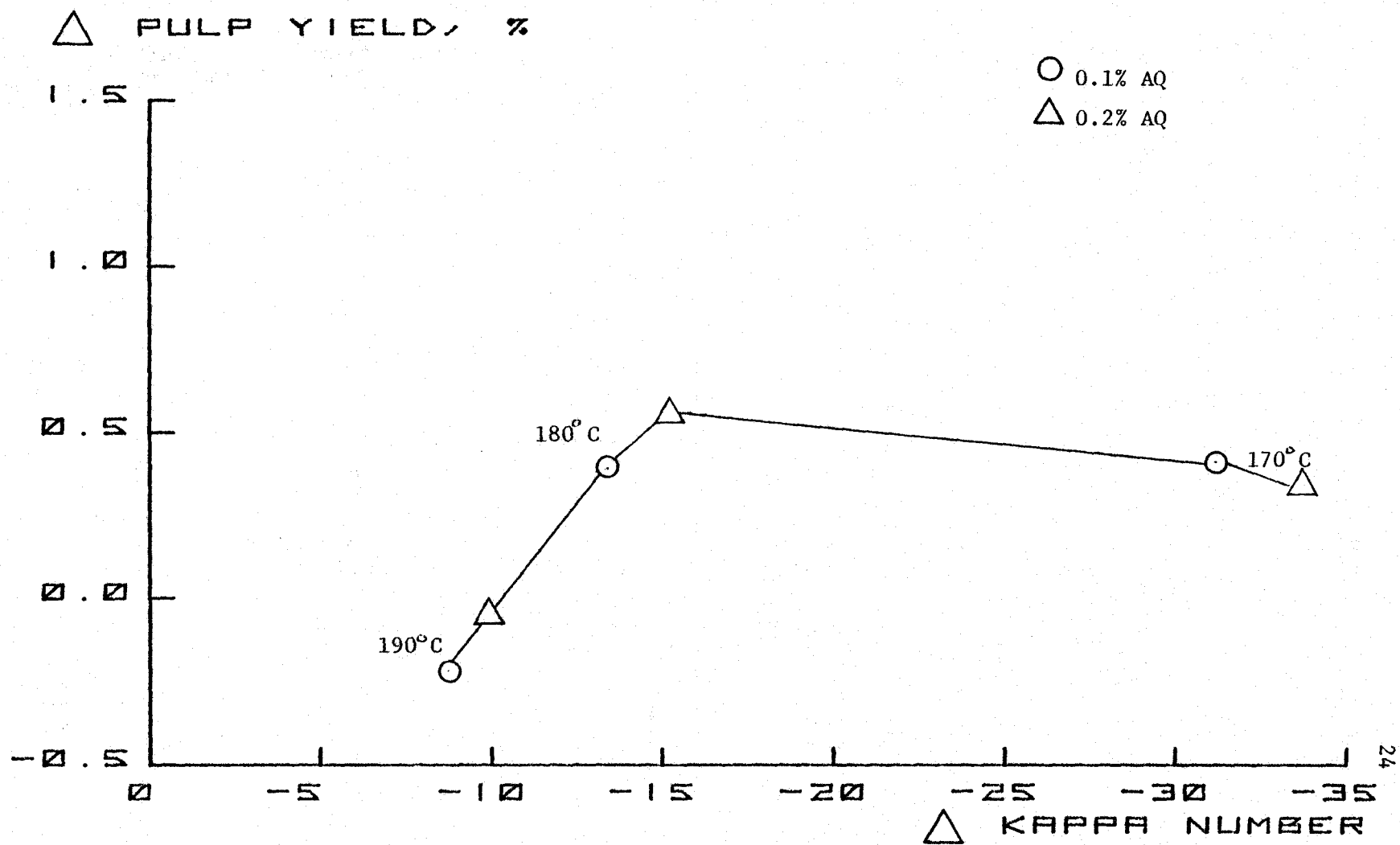


Figure 5. Effect of AQ on Kappa number and pulp yield.



where

F = Fluorescent intensity

D = Dilution of the sample

S = Sensitivity setting

When fluorescent intensities were measured on the Aminco Bowman spectrophotofluorometer, the heights of the peaks of the trace were taken as values of the fluorescent intensities.

The fluorescent factor is equal to the fluorescent intensity divided by the amount of lignin in the pulping waste liquor (parts per million) in the sample. The amount of lignin in the pulping waste liquor was calculated by using the following formula:

$$\text{Lignin concentration, (gpk)} = \frac{10L - 0.015KY}{1 - .01Y + R}$$

where:

L = Klason lignin (%)

K = Kappa number

Y = Pulp yield (%)

R = Liquor to wood ratio

The expression, .015K, is an estimation of the percent Klason lignin in pulp and is generally accepted as a reasonable approximation of this value for full chemical pulps.

A. Bombs

1. Fluorescent intensity and fluorescent factor versus pulping time

Figure 6. Fluorescent intensity and fluorescent factor versus pulping time at 170°C.

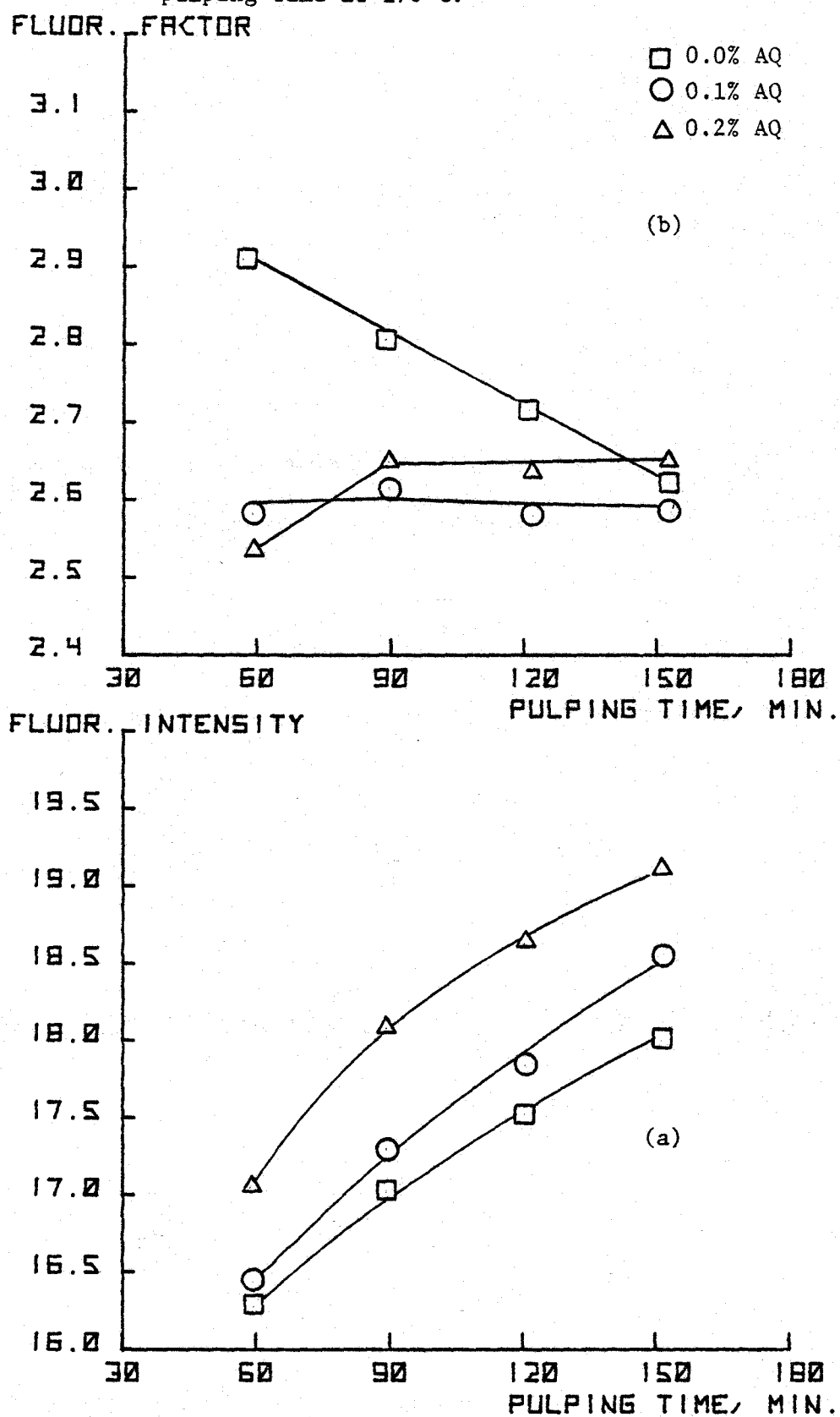
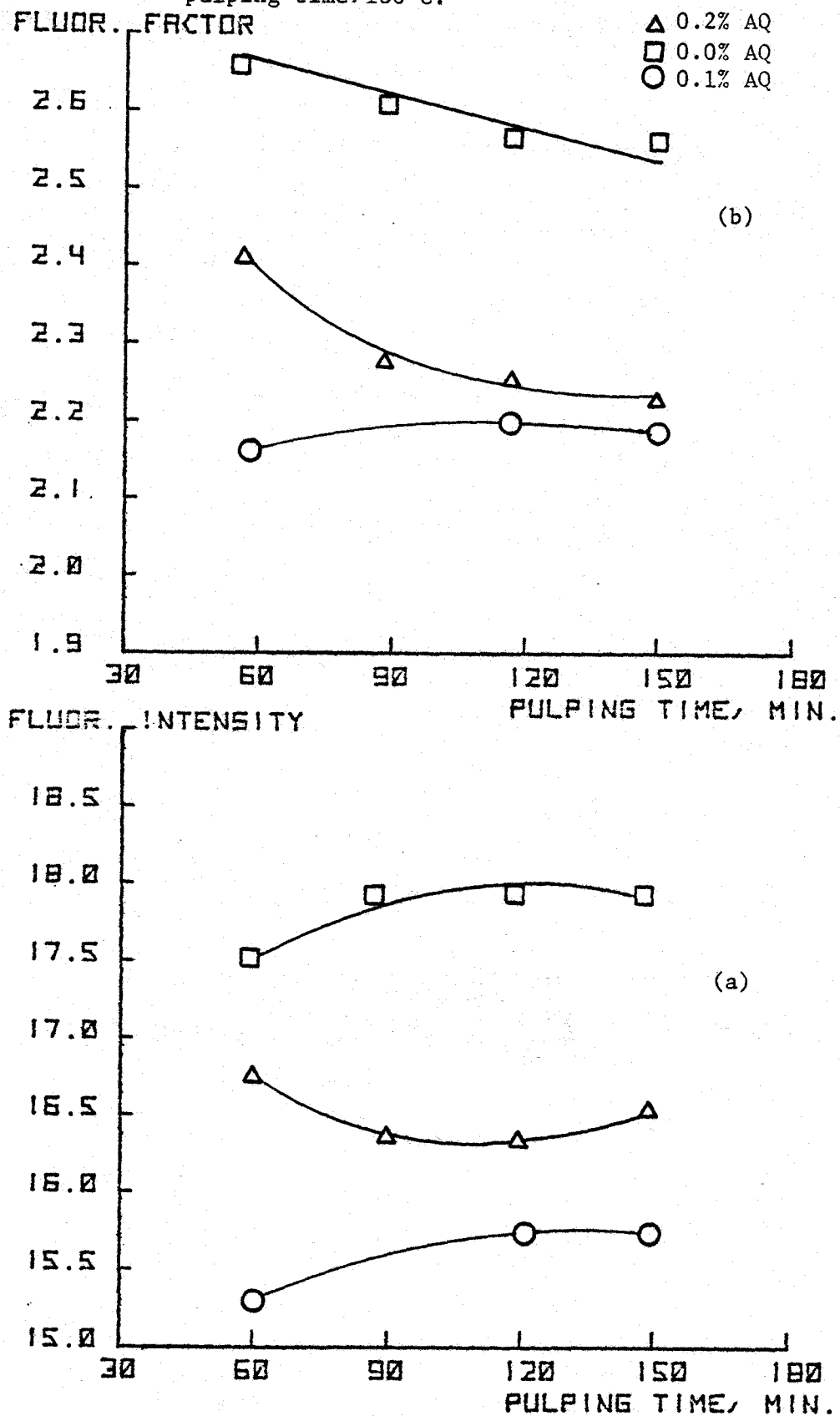


Figure 7. Fluorescent intensity and fluorescent factor versus pulping time. 180°C.



a. 170°C

The fluorescent intensities and pulping times are positively related (Figure 6a), and the AQ showed a consistent effect on the fluorescent intensity - pulping time relationship. In other words, the fluorescent intensity not only increased with an increase in pulping time but also because of an increase of AQ in the pulping liquor. Figure 6 suggests that the fluorescent factor of lignin was stabilized by the addition of AQ. However, the fluorescent factor of lignin in the kraft liquor was decreasing during pulping. The AQ probably keeps the lignin fragments in dispersion, permitting them to move and resonate freely. In other words, at 170°C, the atomic excitation of the lignin compounds by a certain amount of light (energy) is higher when the AQ is added to the pulping liquor. On the other hand, such excitation tends to decrease during the cook when AQ is not present in the pulping liquor.

It has been proven (Table 7) that AQ increases delignification in pulp, producing an increase of lignin in the pulping waste liquor. Figure 6a shows that the fluorescent intensity of pulping waste liquor was increased when AQ was added to the pulping. In other words, the increase of lignin in the pulping waste liquor due to the AQ addition was detected by fluorescence. At 170°C, Figures 6a and 6b show that changes in lignin concentration can be correlated with fluorescent intensity. In addition, the quantum efficiency can be estimated by the fluorescent factor. This is important because the changes of fluorescent factor during pulping time can indicate some change in the molecular structure of lignin

TABLE 6. PULPING DATA 170°C (BOMBS)

Cook No.	Time Min.	AQ %	Lignin in Pulp, Gms	Lignin in B.L. GPK*	F** L
1	60	0.0	3.54	29.75	1.97
2	90	0.0	3.10	30.85	1.99
3	120	0.0	3.19	33.21	1.91
4	150	0.0	1.74	34.35	1.90
5	30	0.1	4.37	27.61	2.35
6	60	0.1	2.87	31.52	2.11
7	90	0.1	2.18	33.3	1.97
8	120	0.1	1.70	34.5	1.96
9	60	0.2	2.24	33.15	1.66
10	90	0.2	1.93	33.9	1.80
11	120	0.2	1.54	34.93	1.82
12	130	0.2	1.40	35.23	1.89

* Grams of lignin per kilogram of black liquor

** Fluorescent intensity per parts per million of lignin

TABLE 7. PULPING DATA AT 180°C (BOMBS)

Cook No.	Time Min.	AQ %	Lignin in Pulp, Gms	Lignin in B.L. GPK*	$\frac{L^{**}}{F}$
1	60	0.0	2.27	32.96	2.66
2	90	0.0	1.77	34.26	2.63
3	120	0.0	1.49	34.94	2.57
4	150	0.0	1.5	34.86	2.57
5	60	0.1	1.54	34.91	2.18
6	90	0.1	--	--	--
7	120	0.1	1.15	35.87	2.19
8	150	0.1	1.06	36.08	2.18
9	60	0.2	1.6	34.8	2.40
10	90	0.2	1.2	35.79	2.29
11	120	0.2	1.02	36.04	2.27
12	150	0.2	1.00	36.21	2.25

* Grams of lignin per kilogram of black liquor

** Fluorescent intensity per parts per million of lignin

TABLE 8. PULPING DATA AT 190°C (BOMBS)

Cook No.	Time Min.	AQ* %	Lignin in Pulp, Gms	Lignin in B.L. GPK**	F*** L
1	60	0.0	1.55	34.77	2.60
2	90	0.0	1.28	34.41	2.54
3	120	0.0	1.12	35.78	2.48
4	150	0.0	1.06	35.88	2.45
5	60	0.1	1.14	35.83	2.51
6	90	0.1	0.98	36.17	2.52
7	120	0.1	0.89	36.40	2.48
8	150	0.1	0.85	36.41	2.43
9	60	0.2	1.04	36.11	2.56
10	90	0.2	0.91	36.38	2.51
11	120	0.2	0.86	36.48	2.50
12	150	0.2	0.82	36.52	2.47

* Anthraquinone

** Grams of lignin per kilogram of black liquor

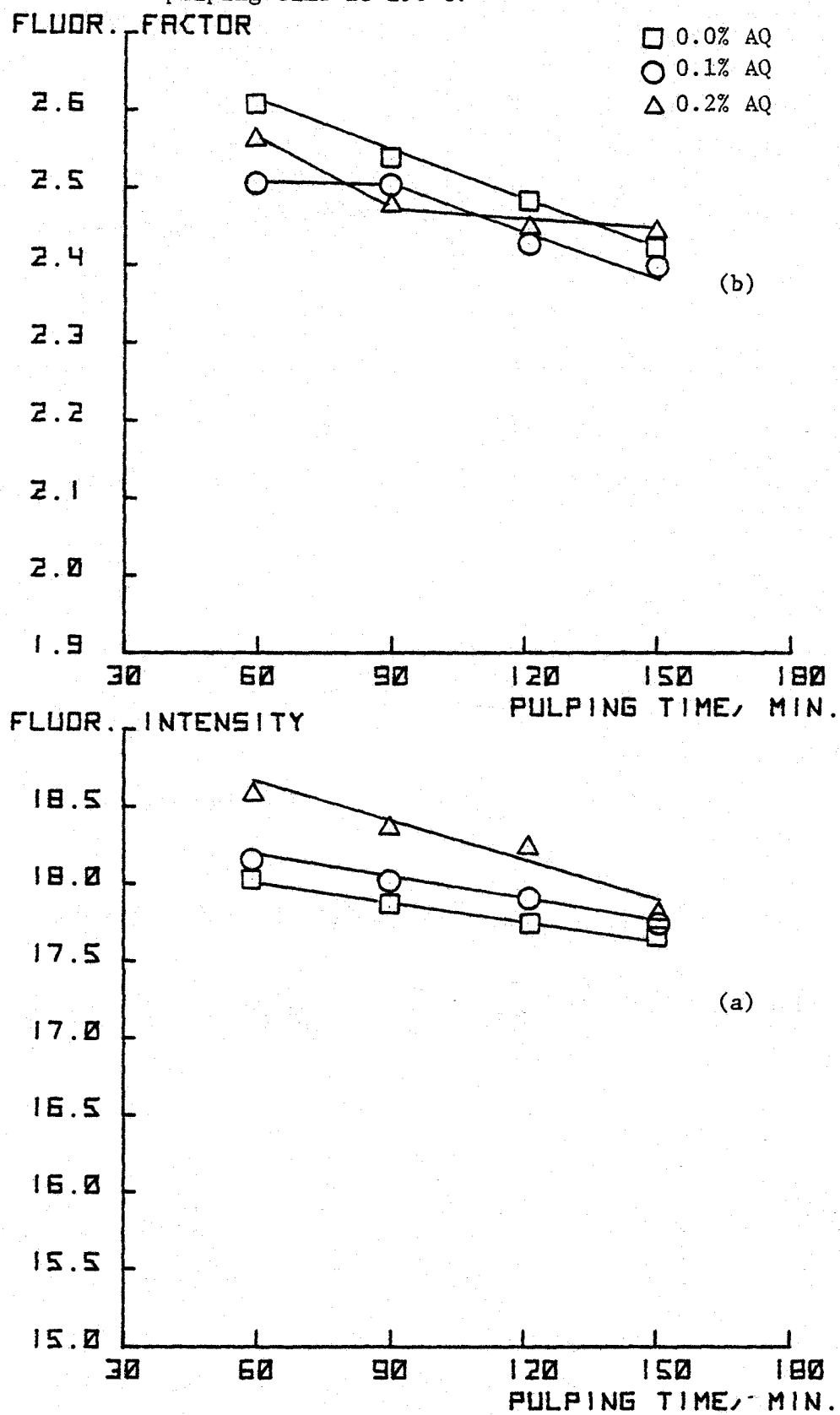
*** Fluorescent intensity per parts per million of lignin

such as an increase in molecular weight (condensation) as suggested by Figure 6a. The positive effect of AQ in the stabilization of fluorescent factor is reflected in Figure 4 where the AQ showed its best effect at 170°C pulping temperature.

b. 180°C temperature. Fluorescent intensity versus time

Figure 7a shows that, during the cook, the fluorescent intensity of pulping waste liquor with 0.2% added AQ did not increase. The fluorescent intensity at 0.1% AQ addition showed a small increase while the fluorescent intensity of the kraft liquor did not show a clear increase with pulping time. By comparing the set of cooks, Figure 7b shows that AQ lowered the fluorescent factor of lignin. However, the fluorescent factor was practically stable at 0.1% AQ while at 0.0% AQ and 0.2% AQ the fluorescent factor was decreasing during the cook. Both Figures 7a and 7b show that at this temperature the AQ loses some of its beneficial effect on the delignification of pulp. The fact that the 0.2% AQ addition decreases the fluorescent factor leads to the conclusion that lignin fragments in solution started forming bigger lignin compounds by condensation even though AQ was present in the pulping liquor. For example, the fluorescent factor at 0.0% AQ and 0.2% are negatively correlated with pulping time while the fluorescent factor at 0.1% shows no changes with pulping time. Such results indicate that at 180°C the AQ still shows a positive effect when it is added to the pulping liquor at very low concentrations, that is, not beyond 0.1%. Furthermore, the fluorescent factors of the kraft waste liquors

Figure 8. Fluorescent intensity and fluorescent factor versus pulping time at 190°C.

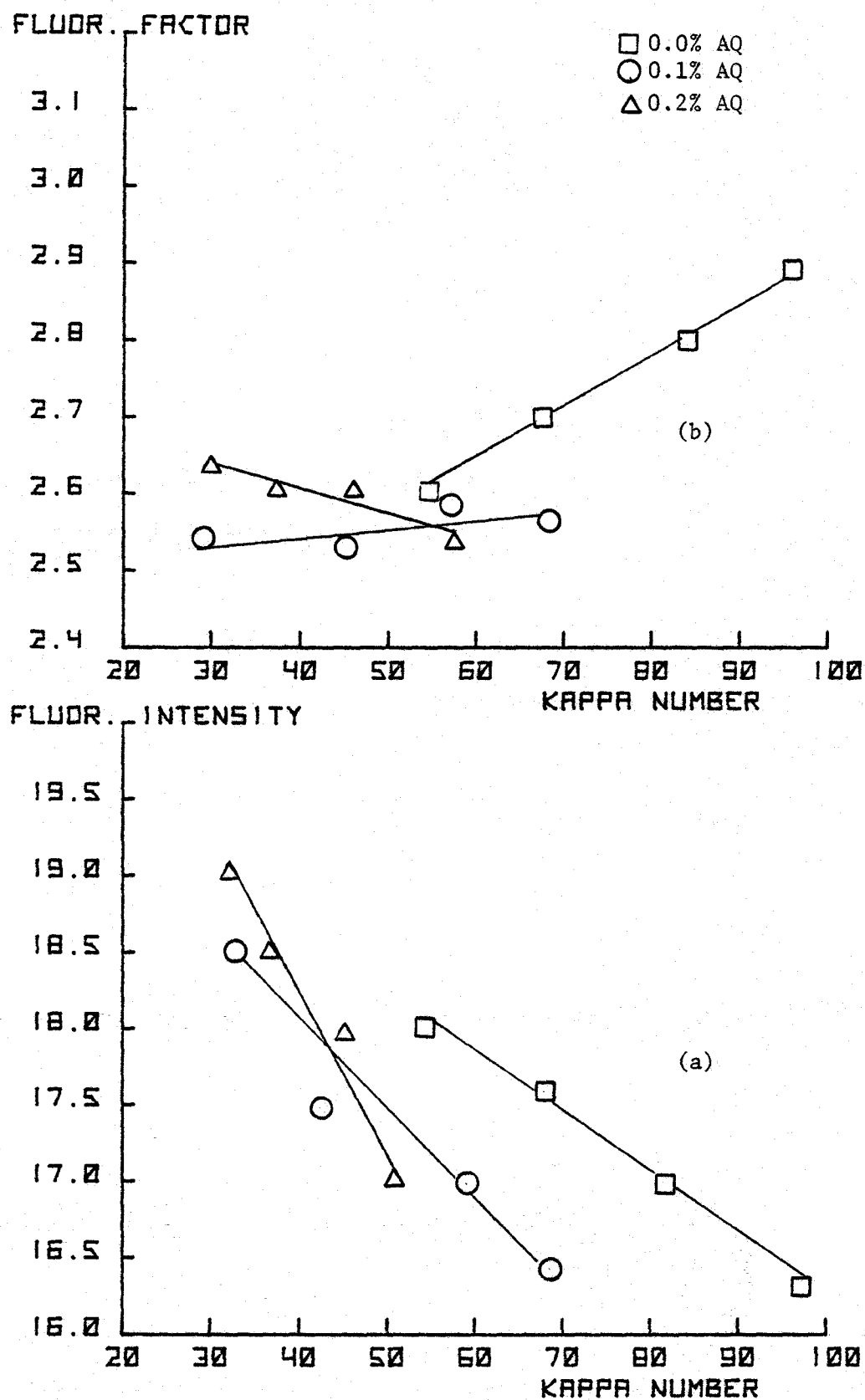


show possible condensation of lignin. The conclusion stated above is based on the fact that the fluorescent intensity per unit weight of lignin is decreasing with the pulping time.

c. 190°C temperature

All fluorescent intensities of pulping liquors decreased with time when the cooks were performed at a temperature of 190°C (Figure 8a). However, for each set, the values of fluorescent intensity had small range. This behavior is caused by the small increases of lignin in the pulping waste liquors during the cooks. Table 8 shows that not only grams of lignin per kilogram of pulping waste liquor (gpk) increase very little during pulping, but also from one set to another, the increase of lignin concentration was small. Therefore, the changes in fluorescent intensity from one set to another set of cooks were very small. At this temperature the fluorescent factors for all cooks decreased during the pulping periods (Figure 8b). These results strongly suggest some chemical changes in the dissolved lignin compounds because the fluorescent intensity was decreasing in spite of the fact that the lignin concentration in the pulping waste liquor was increasing. Many authors (25-26) accept the possibility of some condensation of lignin when wood is pulped at high temperatures. Both Figures 8a and 8b indicate that AQ added to the pulping liquor did not show any positive effect in the delignification of the pulp at 190°C. These results agree with the results of Figure 4 which showed that AQ at 190°C did not increase the yield nor the delignification of

Figure 9. Fluorescent intensity and fluorescent factor versus Kappa number at 170°C.



the pulp. This behavior suggests that AQ did not hold the lignin compounds (or fragments) in dispersion in the pulping liquor at this temperature. The results of Figure 8b verify this point, since the fluorescent factors decrease with pulping time even though the AQ was present in two of the pulping liquors. In a few words, at 190°C the AQ did not avoid the condensation of lignin fragments.

2. Fluorescent intensity - Kappa number relationship

a. 170°C

Figure 9 shows that Kappa numbers and fluorescent intensities are negatively correlated to each other because the fluorescent intensity increases as the amount of lignin in the pulping liquor increases and the lignin content of the pulp decreases. With respect to Kappa numbers, the fluorescent intensity decreased when AQ was added to the pulping liquor. The addition of AQ to pulping liquor affected the fluorescent intensity - Kappa numbers relationship by increasing the slope of lines at 0.1 and 0.2% AQ.

b. 180°C

Figure 10a indicates that the fluorescent intensity increases in inverse proportion to the Kappa number when wood is pulped by the kraft process and at 0.1% AQ addition. However, because of the small range of Kappa numbers at 0.1% and 0.2% AQ addition, the fluorescent intensity behavior with regard to Kappa number is unclear. Figure 10b shows that AQ had a positive effect on stabilizing the fluorescent factor at 0.1% addition.

Figure 10. Fluorescent intensity and fluorescent factor versus Kappa number at 180°C.

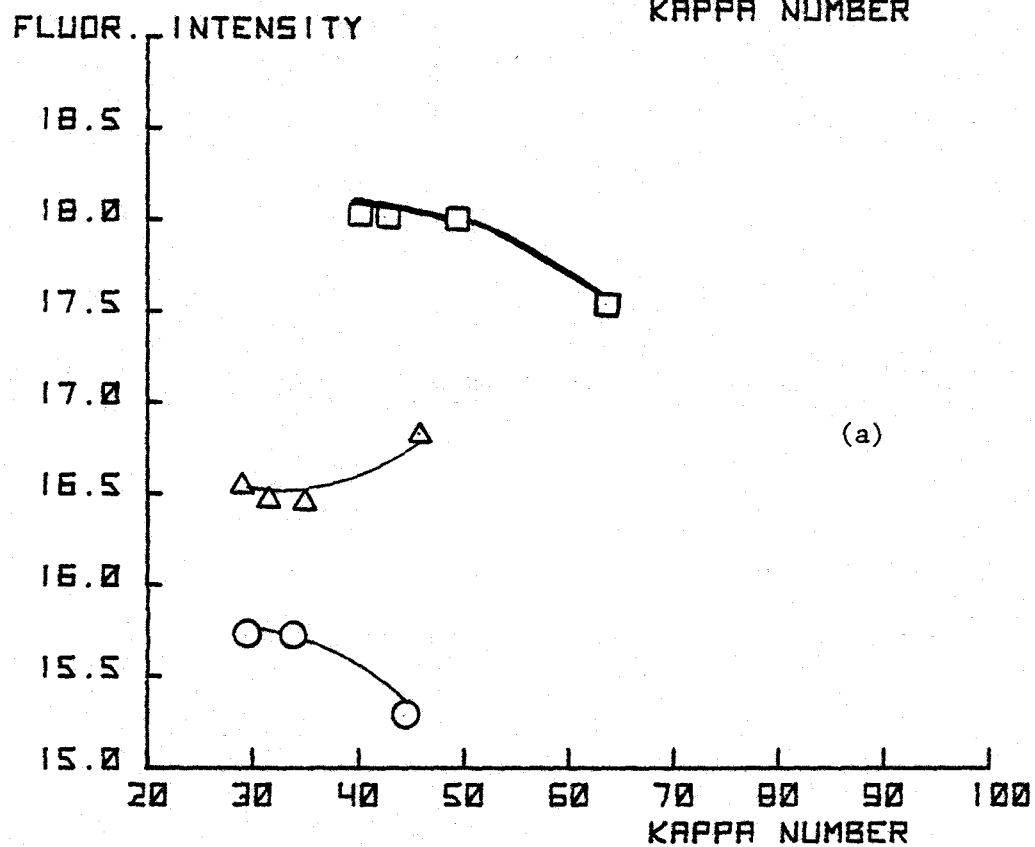
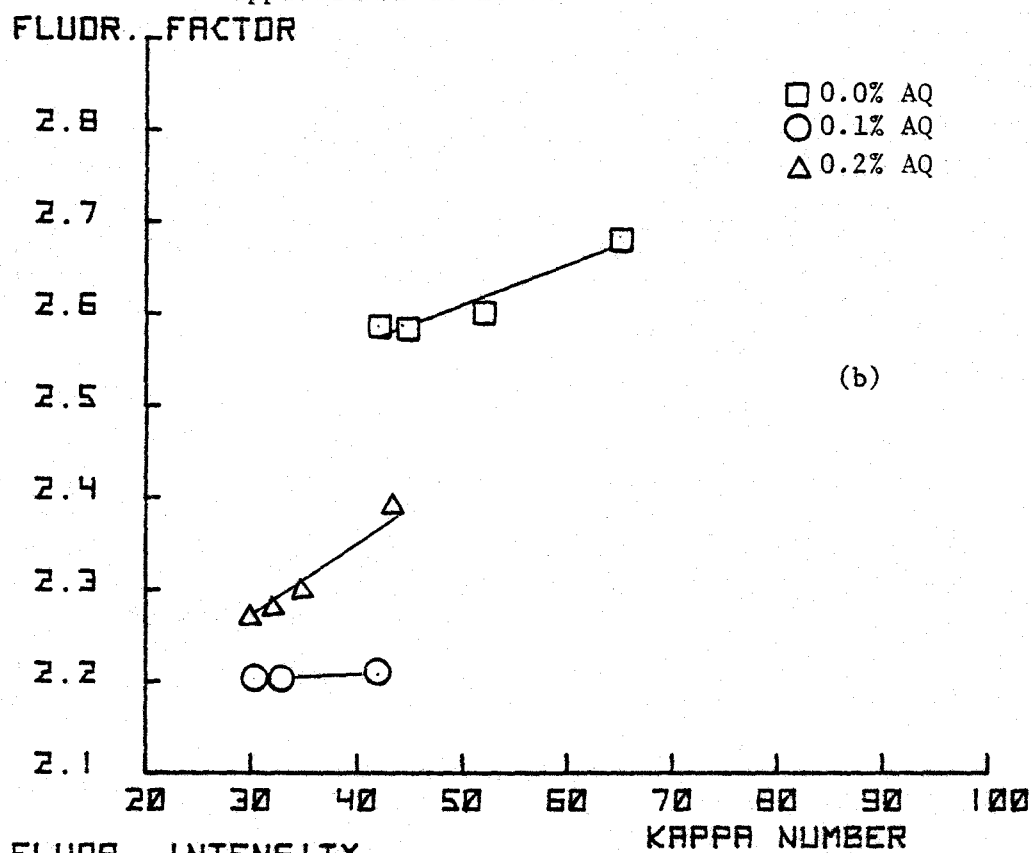
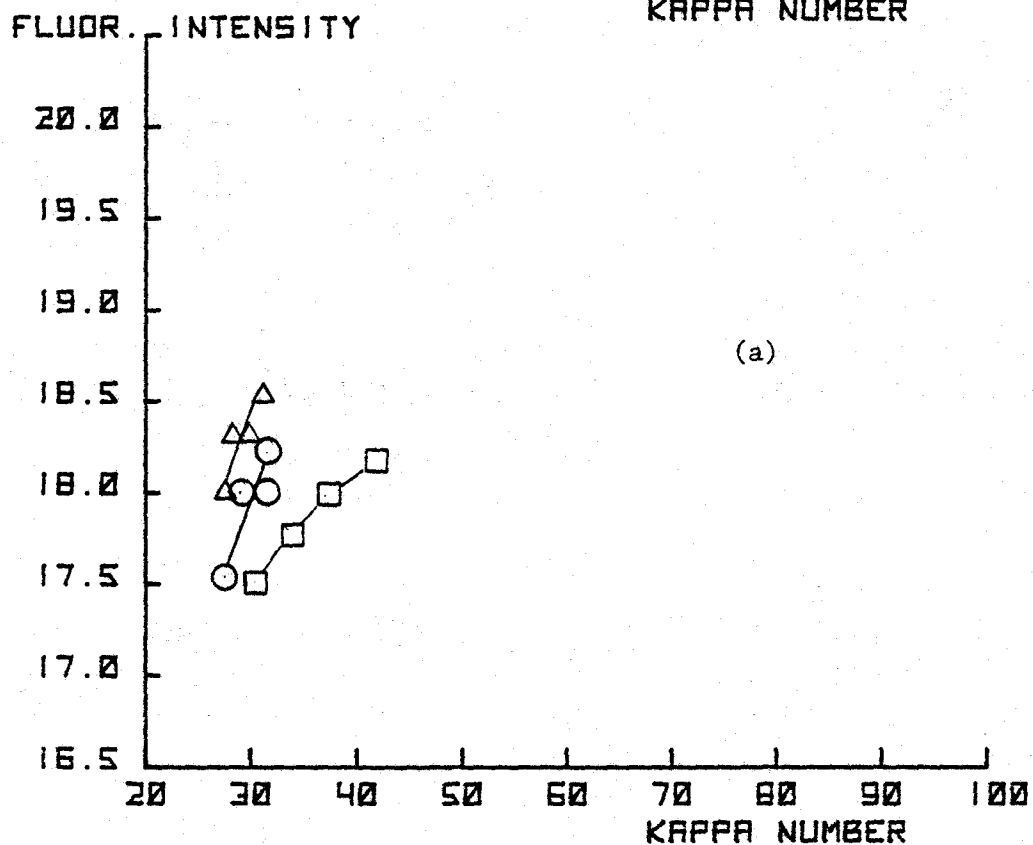
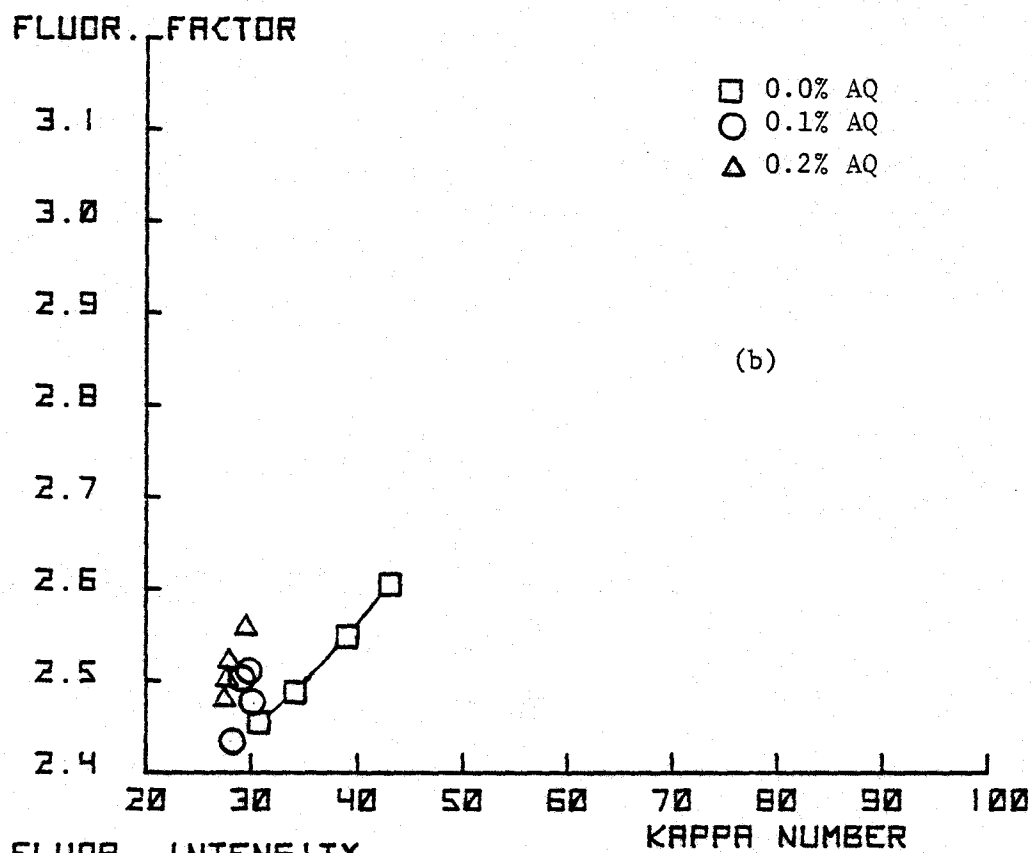


Figure 11. Fluorescent intensity and fluorescent factor versus Kappa number at 190°C.



c. 190°C

Figure 11a indicates that the fluorescent intensity was increased by addition of AQ at 190°C. However, the tendency of the fluorescent intensity to decrease during pulping was increased by the AQ. The fluorescent factors, however, were not stabilized by the AQ (Figure 11b). These results suggest some change in the dissolved lignin fragments because the fluorescent intensity of the pulping waste liquor was positively correlated to the Kappa number in spite of the fact that the amount of lignin in the pulping liquor increased during the cooks (see Table 8).

The relationships of fluorescent intensity and fluorescent factor with pulping time, pulp yield and Kappa number are very consistent at the three temperatures (170°C, 180°C, 190°C). Therefore, the explanation of the fluorescent behavior of the lignin is similar with regard to pulping times, pulp yields, and Kappa numbers.

3. Fluorescent intensity and fluorescent factor versus pulp yield

Fluorescence is a property which is exhibited by certain chemical compounds. The presence or amount of such compounds as lignin in solution can be detected or measured by measuring the fluorescence of the solution, which increases in direct relationship to the concentration of the fluorescing compound. This relationship is shown in Figure 12a where the fluorescent intensity *F* increases as the pulp yield decreases. This behavior can be

Figure 12. Fluorescent intensity and fluorescent factor versus pulp yield at 170°C.

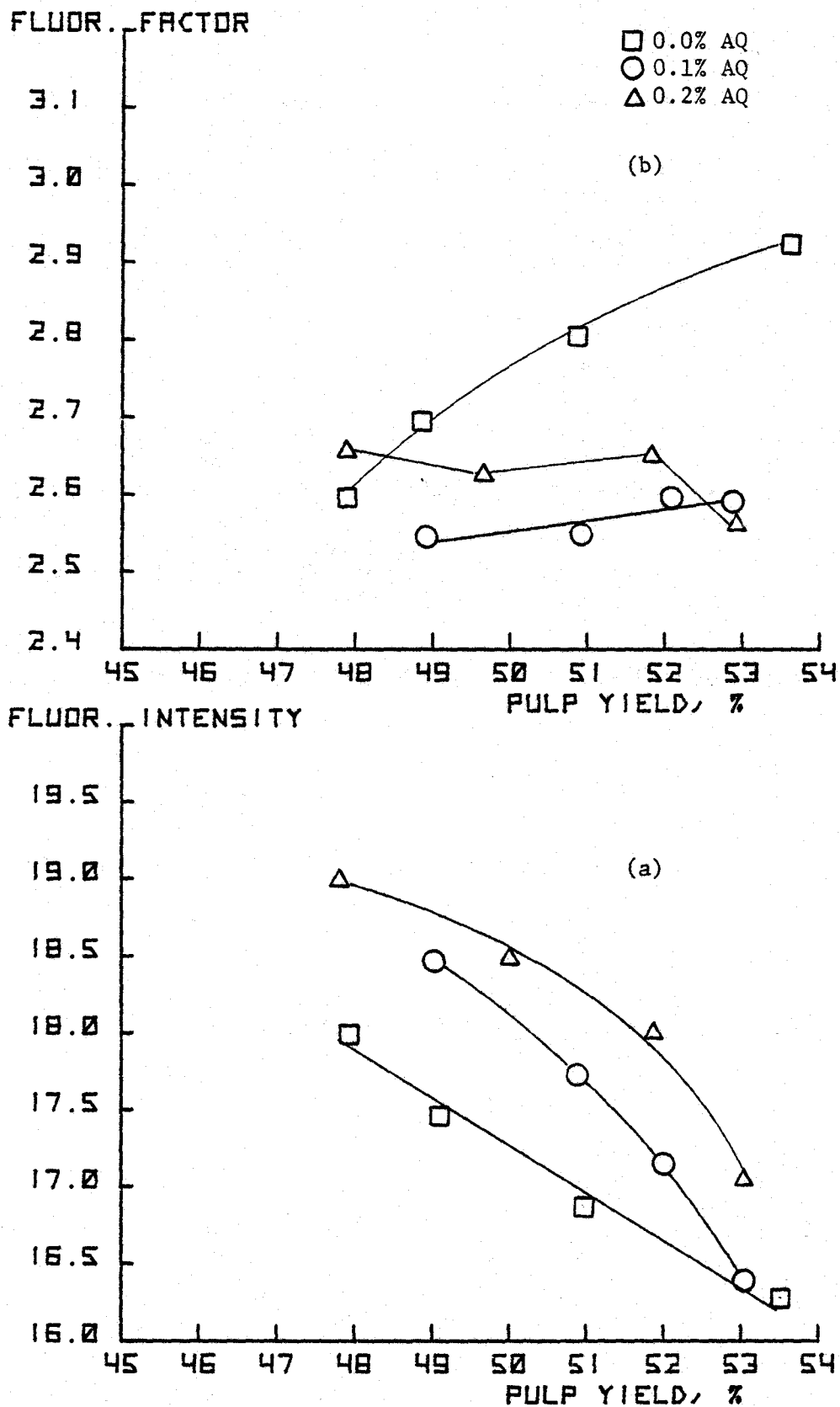
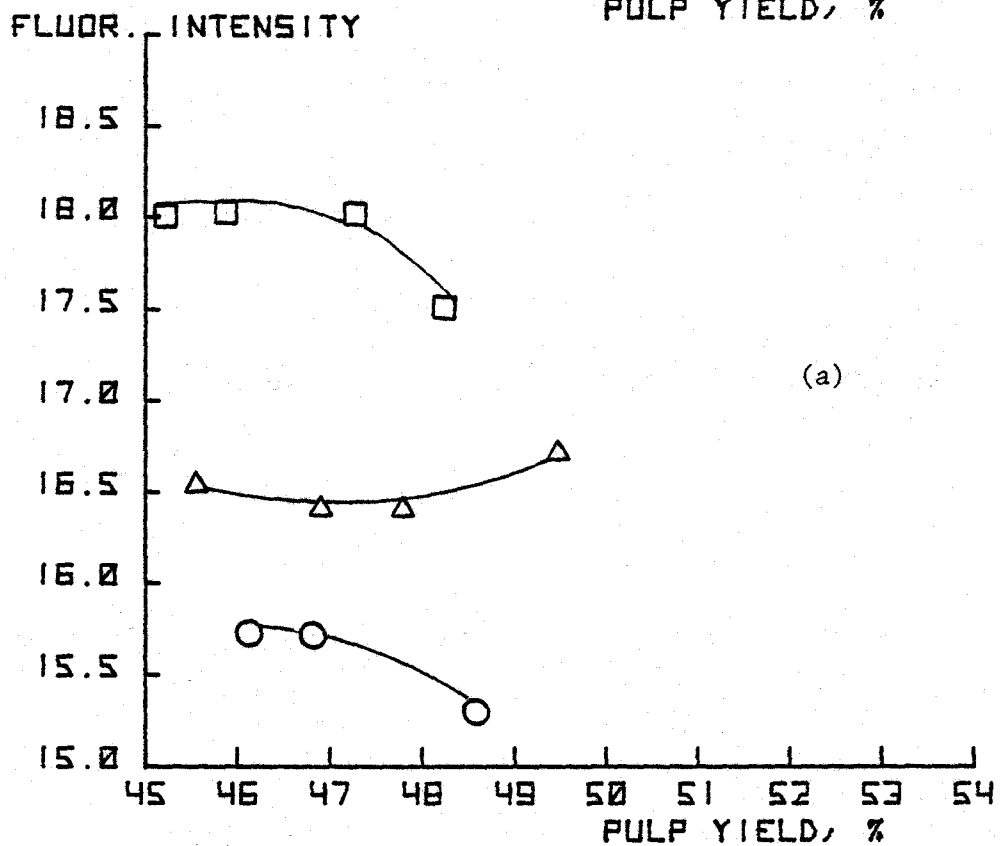
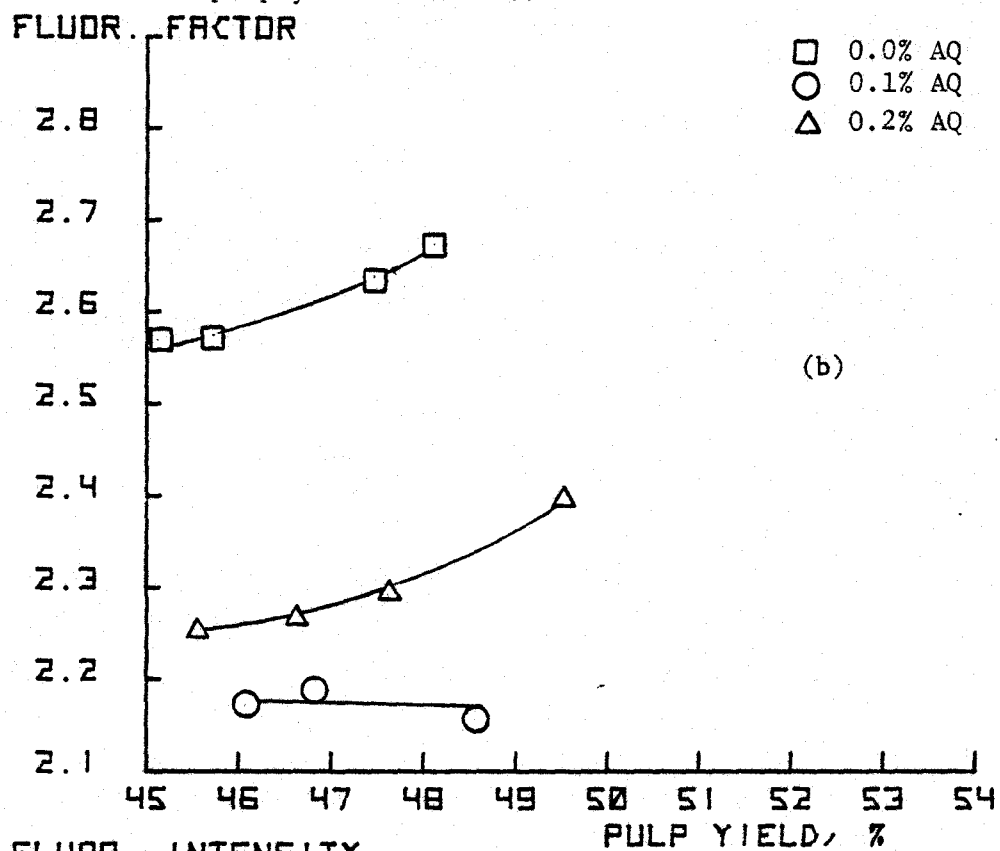


Figure 13. Fluorescent intensity and fluorescent factor versus pulp yield at 180°C.



explained by the fact that almost always the lignin concentration in the pulping liquor increases when the yield decreases as the cook progresses.

a. 170°C temperature

The results of three sets of cooks performed at this temperature are shown in Figures 12a and 12b. The fluorescent intensity varies inversely with the yield, and the AQ showed a positive effect on the fluorescent intensity values. Figure 12b shows that the fluorescent intensity per unit weight of lignin was higher at high yields for kraft cooks. However, because of the increase in fluorescent intensity caused by the AQ, the fluorescent factor was approximately constant at the different pulp yields for the 0.1% and 0.2% AQ cooks. These findings suggest that fluorescence can be a tool for estimating the yield during the cooking time.

b. 180°C temperature

Figures 7a and 13b show a marked effect of AQ on F and FF at 180°C. For the waste liquors from the 0.2% AQ cooks, there was no change in F with a change in yield; however, the fluorescence of liquors with 0.1% AQ decreased when the pulp yield was increasing (Figure 13a). The FF (Figure 13b) of waste liquors at 0.2% AQ increased at low concentrations of lignin (or at higher yield). These results indicate that 0.2% AQ changed the lignin compounds in such a way that they did not show any increase in the fluorescent intensity even though the lignin concentration in the black liquor was increased.

c. 190°C temperature

The results shown in Figure 14a indicate that the fluorescent intensities of the pulping waste liquors decreased even though the amount of lignin was probably increasing. The lignin concentration in the waste liquors varies inversely with the yield; therefore, the variation of fluorescent intensities of the pulping liquors was opposed to the expected. Figure 14b indicates that AQ did not show any improvement in delignification of the pulp. The fluorescent factors (Figure 14b) decreased in direct relation to the yields even though AQ was added to the pulping liquor.

II. Analysis of Covariance

A. Pulping

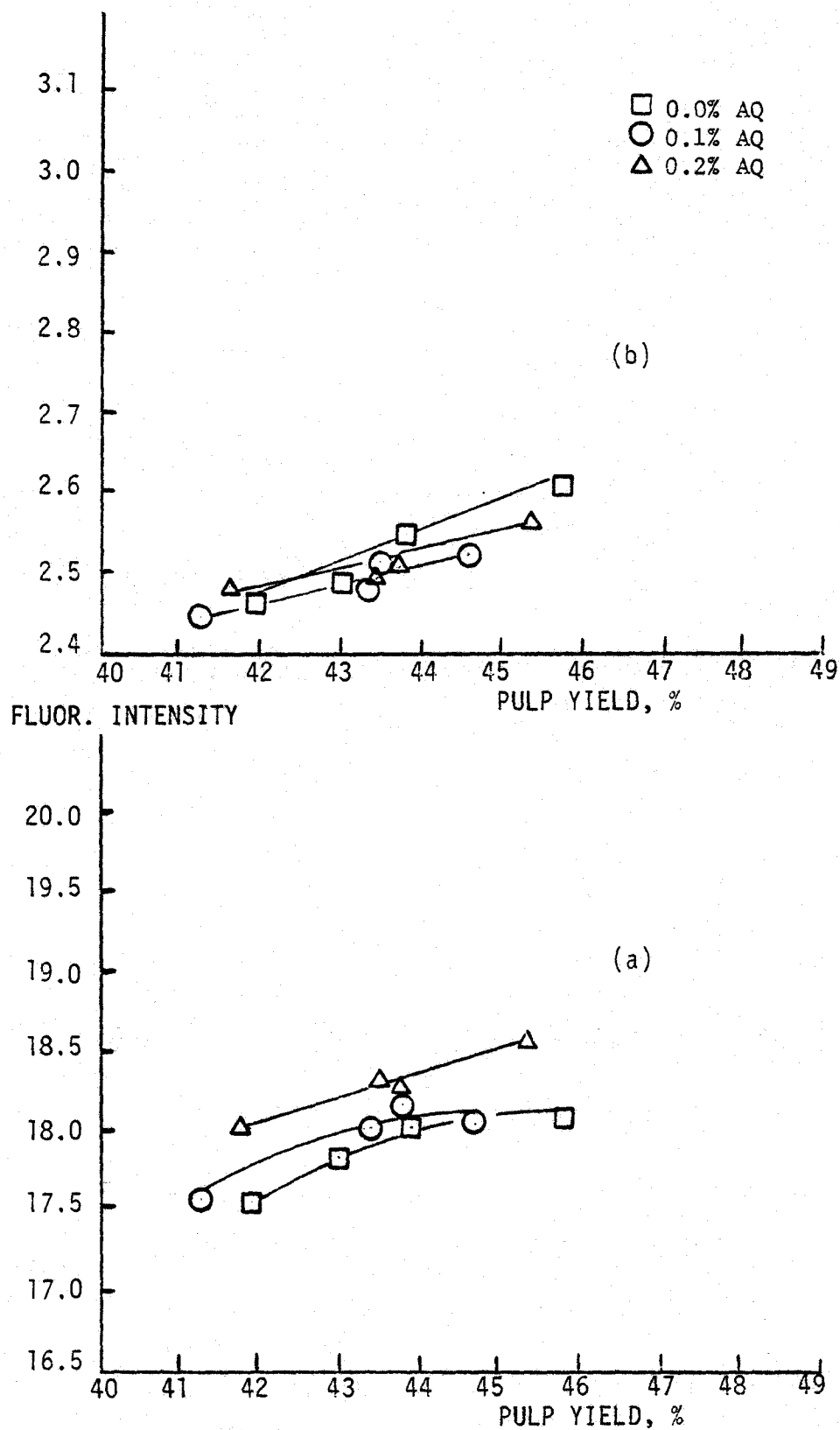
1. Kappa numbers vs pulping time (Table 9)

There were good linear correlations between Kappa numbers and pulping times for the kraft and kraft AQ cooks. The minimum r^2 was 0.84 at a level of statistical significance $\geq 99\%$. The slopes of the linear regression lines within each set of cooks showed less difference than the difference between the means.

2. Pulp yield vs pulping time (Table 9)

The analysis showed that the lowest r^2 was .94 at the 99.9% level of significance. This means that there is a good correlation between pulp yields and pulping time. In addition, the slopes and the means of the lines for the three temperatures are different.

Fig. 14 Fluorescent intensity and fluorescent factor
FLUOR. FACTOR versus Kappa number at 190 C



3. Pulp yield vs Kappa numbers (Table 9)

At 170°C, the slopes and the means of the lines are different. The lowest value of r^2 is 0.98 at a level of statistical significance $\geq 99\%$. Therefore there is a very good correlation between yields and Kappa number. Moreover, the lines have different slopes. At 180°C the kraft AQ cooks showed better yield-Kappa number relationships ($r^2 > .91$) than the kraft cook. The lines have different means; this means that they are different populations. At 190°C the yield-Kappa number relationship was excellent for the kraft cooks ($r^2 = .98$), while for the kraft AQ cooks it was lower. However, the means of the lines were different.

B. Fluorescent Intensity versus Pulping Time (TABLE 9)

1. 170°C

The analysis shows that the lines have different slopes. In addition, the linear correlation between fluorescent intensity and pulping time was excellent given that the lowest value of r^2 was equal to .96 for both kraft and kraft AQ cooks.

2. 180°C

The slopes of lines are different. Also, the correlation between fluorescent intensity and pulping time was good ($r^2 = 0.90$) for kraft and kraft AQ (0.1% AQ) cooks. However, the linear regression line for the kraft AQ cook (0.2% AQ) did not fit at all ($r^2 = .06$).

3. 190°C

These results showed that the fluorescent intensity and pulping time of the kraft and kraft AQ (0.1% AQ) cooks have poor linear correlation; but the kraft AQ cook (0.2% AQ) showed good linear correlation. The lines have different slopes.

C. Fluorescent Intensity vs Kappa Number (Table 9)

1. 170°C

The analysis of covariance showed that the lines have different slopes, meaning that they represent different populations. There was a good linear relationship between fluorescent intensity and Kappa number for the kraft and kraft AQ cooks. The lowest r^2 is equal to 0.95 with a level of statistical significance of 95%. The lines have slightly different slopes.

2. 180°C

These results show that the means of the lines are different. The kraft and kraft AQ (0.1% AQ) cooks show a good linear relationship between fluorescent intensity and Kappa number, but for the kraft AQ cook (0.2% AQ), the linear relationship was very poor.

3. 190°C

The means of the lines are different. A non-linear relationship between fluorescent intensity and Kappa number was shown for the kraft AQ (0.1% AQ), but, a linear relationship was found in the kraft cooks.

D. Fluorescent Intensity versus Pulp Yield (Table 9)

1. 170°C

The data shows that the means of the linear are different, but the slopes are the same. Since the r^2 for the kraft and kraft AQ cooks are very high, the correlation (linear) between fluorescent intensity and pulp yield is very high. The lowest level of statistical significance is equal to 99%.

2. 180°C

The kraft AQ (0.1%) cooks was the only set that showed linear relationship ($r^2 = .91$). The lines represent different populations (different means).

3. 190°C

These results show that there was good linear relationship between fluorescent intensity and Kappa numbers for the kraft and kraft (0.2%) cooks. The means of the three sets of cooks are different.

TABLE 9. STATISTICAL DATA FROM KRAFT ANTHRAQUINONE PULPING.

Fig. No.	Temper- ature	% AQ	r^2	F Values		Adjusted Means
				Regr.	Slopes	
<u>Kappa Numbers Versus Pulping Time</u>						
1	170°C	0.0	.99	1803***	42***	64***
		0.1	.99	297***		
		0.2	.98	147**		
1	180°C	0.0	.88	15*	1.6	25***
		0.1	.93	28*		
		0.2	.84	10*		
	190°C	0.0	.93	28*	90***	432***
		0.1	.87	13*		
		0.2	.84	10*		
<u>Pulp Yield Versus Pulping Time</u>						
2	170°C	0.0	.99	531***	745***	29***
		0.1	.97	81**		
		0.2	.99	861***		
	180°C	0.0	.97	93***	24***	42***
		0.1	.99	231***		
		0.2	.98	113**		
	190°C	0.0	.97	80**	118***	608***
		0.1	.94	35**		
		0.2	.97	75**		
<u>Pulp Yield Versus Kappa Number</u>						
3	170°C	0.0	.99	1171***	29***	82***
		0.1	.98	151**		
		0.2	.99	353***		

TABLE 9 (continued)

Fig. No.	Temper- ature	% AQ	r^2	F Values		Adjusted Means
				Regr.	Slopes	
<u>Pulp Yield Versus Kappa Number (continued)</u>						
3	180°C	0.0	.80	7	29***	82***
		0.1	.97	71**		
		0.2	.92	21*		
	190°C	0.0	.98	96.0**	1.8	9.2*
		0.1	.75	6.0		
		0.2	.85	11.0		
<u>Fluorescent Intensity Versus Pulping Time</u>						
6	170°C	0.0	.99	261***	1955***	143***
		0.1	.99	256***		
		0.2	.96	56**		
7	180°C	0.0	.90	18*	70***	328***
		0.1	.90	18*		
		0.2	.06	0.1		
8	190°C	0.0	.60	3	159***	936***
		0.1	.47	1		
		0.2	.90	18*		
<u>Fluorescent Intensity Versus Kappa Number</u>						
9	170°C	0.0	.98	175**	9.5*	7.4*
		0.1	.97	90**		
		0.2	.95	40**		
10	180°C	0.0	.86	12*	7*	115***
		0.1	.92	25*		
		0.2	.36	1		

TABLE 9 (continued)

Fig. No.	Temper- ature	% AQ	r^2	F Values		
				Regr.	Slopes	Adjusted Means
<u>Fluorescent Intensity Versus Kappa Number (continued)</u>						
11	190°C	0.0	.85	11*	.6	11**
		0.1	.16	0.4		
		0.2	.77	6		
12	170°C	0.0	.99	220***	2.6	29***
		0.1	.97	80**		
		0.2	.96	43**		
13	180°C	0.0	.46	1.7	3	119***
		0.1	.92	25.0*		
		0.2	.12	0.2		
14	190°C	0.0	.91	21*	.3	12.5**
		0.1	.46	1		
		0.2	.97	68**		

*** F test 99.9% level of significance

** F Test 99.0% level of significance

* F test 95.0% level of significance

B. Circulating Digester

1. Fluorescent intensity versus pulping time

Figure 15 shows the fluorescent intensities of the pulping liquor samples taken every fifteen minutes from the beginning to the end of the cooks (five hours total pulping time). The fluorescent analyses were made by using the Turner 111 filter fluorometer. Cooks A, B and C (lines A, B and C) were pulped with the same amount of chemicals but at different temperatures (170°C, 180°C and 190°C). Figure 15 shows that the highest temperature corresponds to the highest fluorescent intensities (line C) while the lowest fluorescent intensities corresponds to the lowest temperature (line A). So far, the fluorescent intensity has increased when the temperature increases. Figure 15 shows also the effect of amount of chemicals on the fluorescent intensities of the pulping liquors. For example, cook C and cook D were pulped at the same temperature, but with different amount of chemicals (cook C - 16%, cook D - 12% T.A.). Kleinert (23, 24) states that the sulfidity of the pulping liquor plays an important role in the delignification of wood in the kraft process. He says that the lignin compounds are stabilized by the sulfide (SH^-) which avoids condensation of the lignin fragments due to free radical recombination. In other words, the sulfidity has a positive effect in the delignification of the wood. This effect is also shown in cook D and cook E. They were pulped at the same temperature and total alkali but with different sulfidities. Comparing these two cooks, the highest fluorescent intensities correspond to the cook with

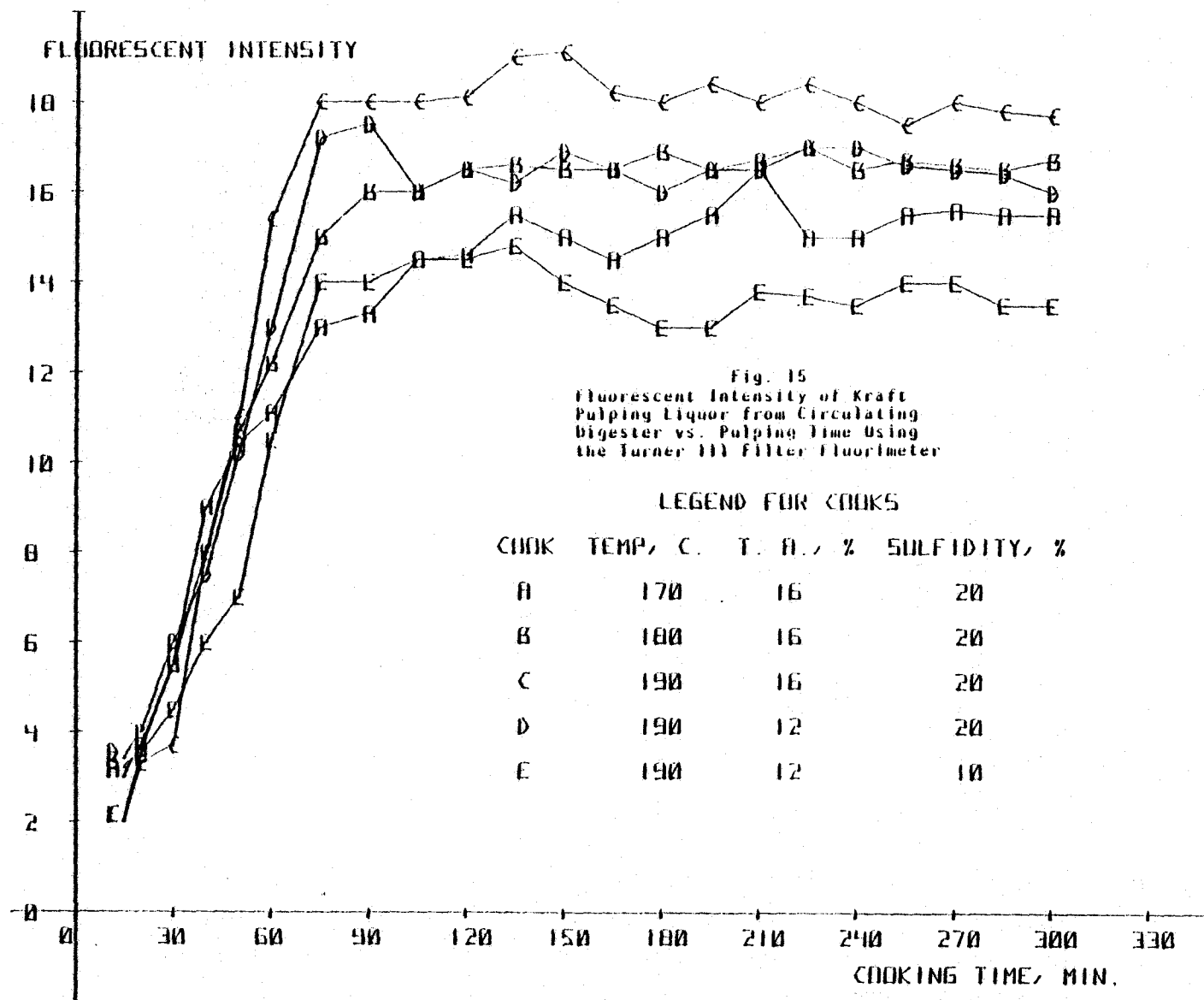
the highest sulfidity (cook D) while the lowest fluorescent intensities correspond to the cook with the lowest sulfidity (cook E). This behavior in the fluorescent intensities of the pulping liquors from cook D and cook E could be caused by the recondensation of the lignin and/or poor delignification of the pulp in the cook E. In summary, the fluorescent intensities of the pulping liquors increase with increases in temperature (cooks A, B and C), the amount of chemicals, and the sulfidity of the kraft pulping liquor.

B. Circulating Digester

1. Fluorescent intensity versus pulping time
2. Analysis of pulping liquor in the Aminco spectrophotofluorometer

There are some differences between the Aminco-Bowman spectrophotofluorometer and the Turner 111 filter fluorometer. In the Aminco instrument, the wavelengths and bandwidths of the excitation and emission radiation are selected by using monochromators while the Turner 111 has only one wavelength for excitation light (280 nm) and one wavelength for emission light (430 nm) selected by suitable filters.

Two more cooks were performed in the circulating digester, and samples of pulping liquor were periodically taken from the digester during the pulping process. These samples were analyzed in the spectrophotofluorometer in order to measure the fluorescent intensity of lignin in the pulping liquor. The diluting solvent of



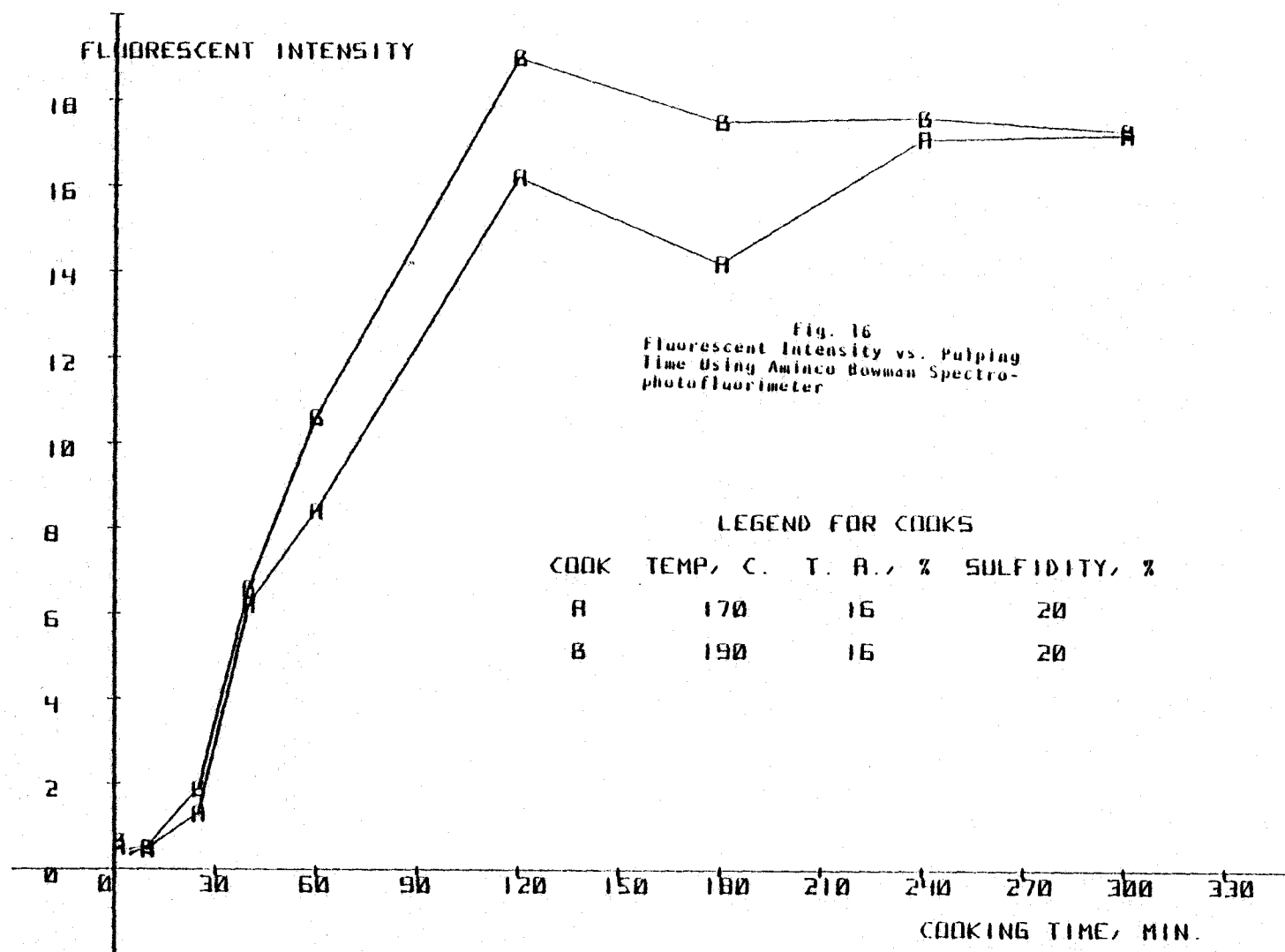
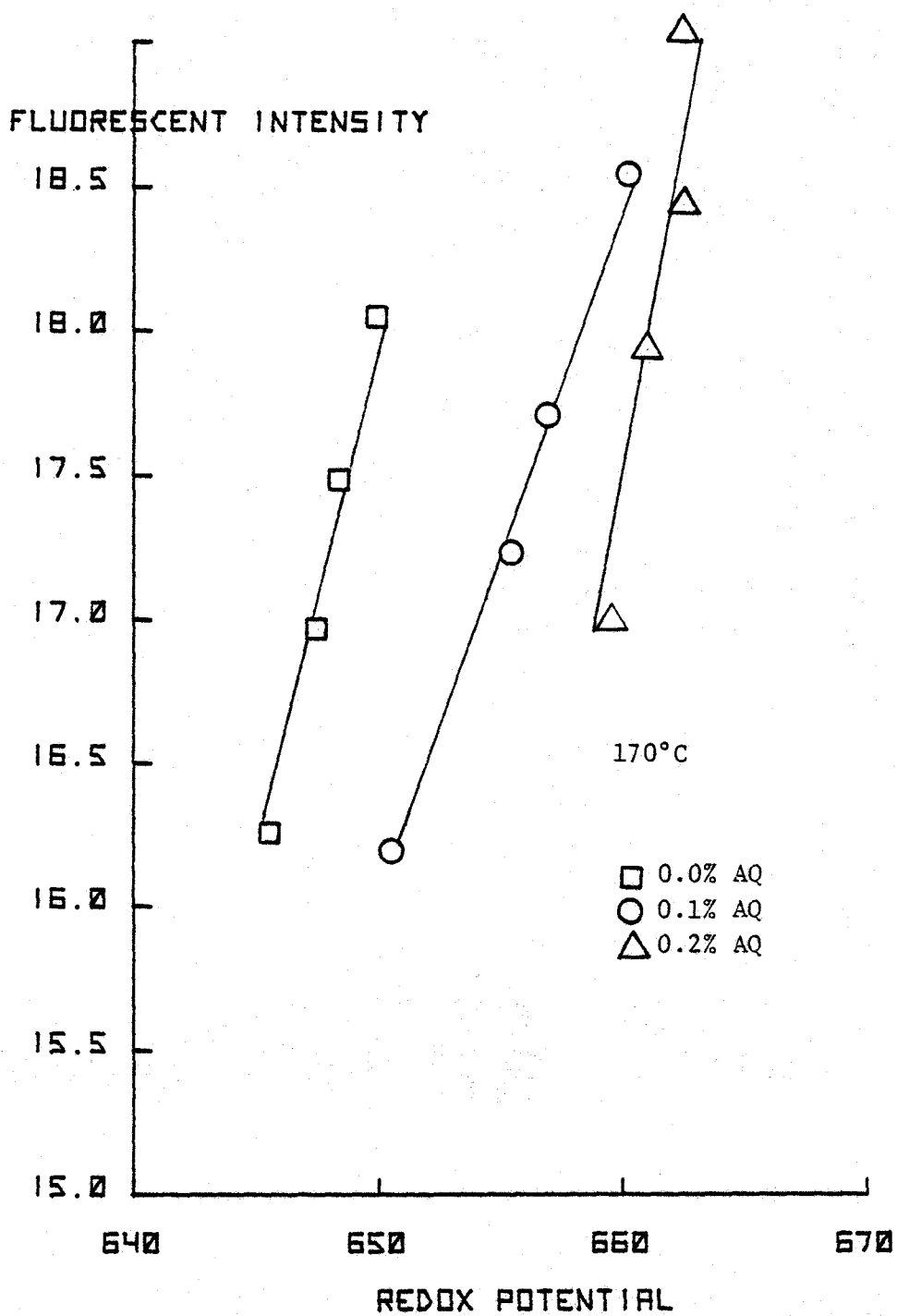


Figure 17. Fluorescent intensity redox potentials.

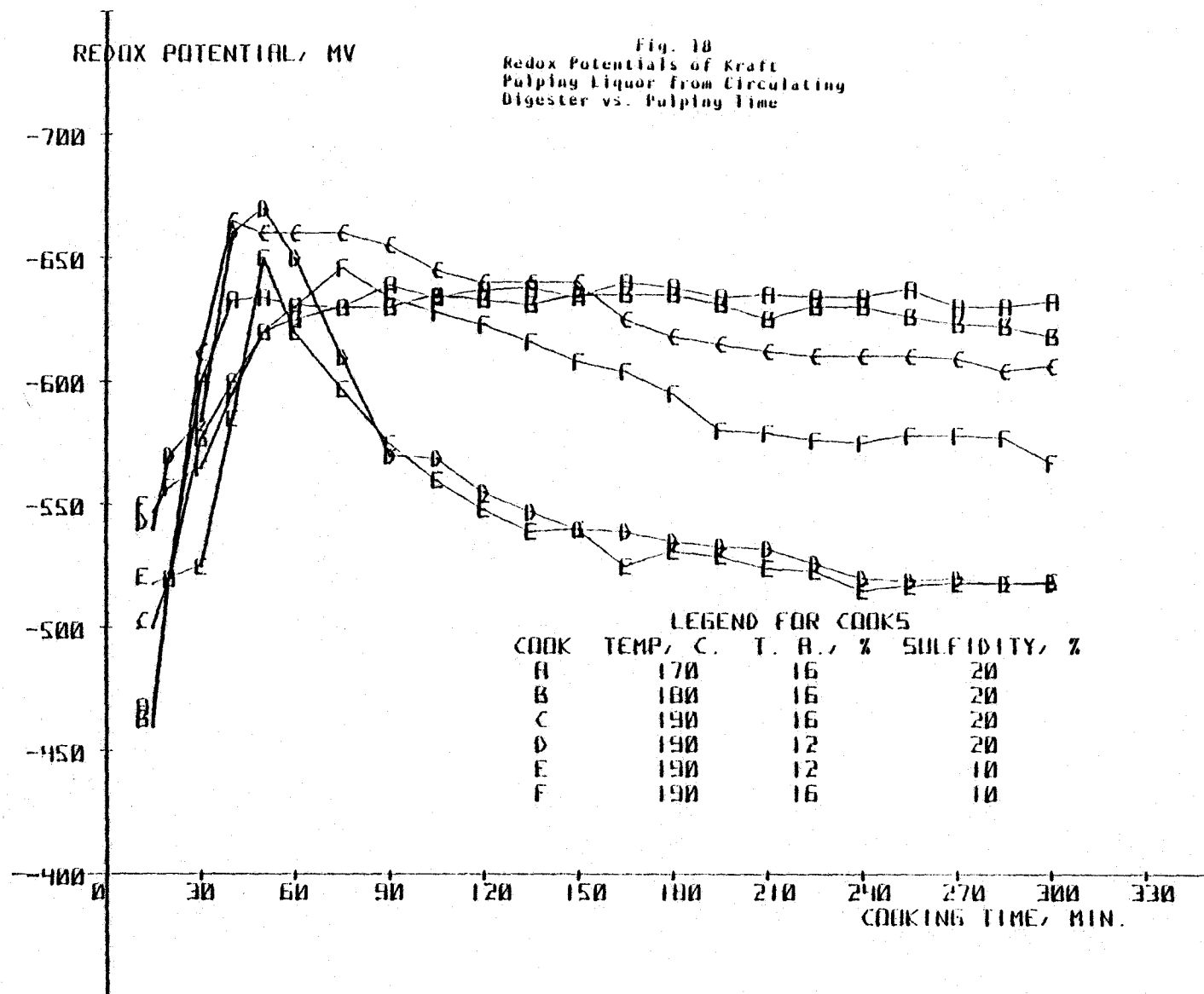


the sample was prepared with double distilled water. The results of this experiment are shown in Figure 16. In general, these results agree with the results obtained from the Turner 111 fluorometer. In both instruments the fluorescent intensity of lignin increases faster during the first 90 minutes than during the rest of the cook. In fact, after two hours of pulping time at 190°C, the fluorescent intensity starts decreasing when the pulping temperature is 190°C. Figure 16 shows also that higher temperatures increase the fluorescence of waste liquor; thus, the fluorescent intensity is higher at 190°C than at 170°C pulping temperature. It is probably that the lignin compounds (or fragments) suffer some alteration at high temperatures such as condensation.

A. Bombs

1. Fluorescent intensity versus redox potentials

The values of redox potentials, fluorescent intensities of pulping waste liquors are shown in Figure 17. The fluorescent intensity increases in direct proportion to the redox potentials in the three sets of cooks (see Figure 17). At a given value of fluorescent intensity the redox potentials increased when the AQ was added to the pulping liquor. These results indicate that AQ increases the reduction capacity of pulping liquor showing a better effect at 0.2% of concentration.



B. Circulating Digesters

1. Redox potentials versus pulping time

At the beginning of kraft cooks, the pulping chemicals ($\text{NaOH} + \text{Na}_2\text{S}$) attack both lignin and carbohydrates, but the ratio of lignin to carbohydrates removed is larger at the beginning than at the end of the cooks. This ratio is also affected by the amount of chemicals, and the pulping temperature.

Figure 18 shows the effect of temperature and chemical charge and composition on the pulping liquor redox potential. The lines A, B, and C show the effect of temperature on the redox potential when the amounts of chemicals were kept constant. The results indicate that the pulping liquor was more reducing at 170°C , but less reducing at 180°C and 190°C pulping temperatures. The importance of sulfidity in the kraft pulping liquor is indicated by cooks C and D which were pulped at the same temperature and chemical charge, but had different sulfidities (ratio of Na_2S to NaOH). That is the reason by which the pulping liquor D (line D) is less reducing than liquor C (line C). Regarding delignification of pulp, it is known that increased sulfidity (up to certain levels) can make the pulping liquor more effective for dissolving lignin (29). The cooks E and F have the lowest redox potentials because they have the smallest amount of chemicals in the pulping liquors. For the first 40 minutes of pulping time, the redox potentials for all of the 190°C cooks are the same (except cook D); however, ten minutes later the redox potential of cook F falls

drastically to its lowest value. Ten minutes later the cook E redox potential (line E) goes down to the second lowest position in the graph. The explanation of these results can be given by the role of chemicals (NaOH and Na_2S) during the kraft pulping process. In the beginning of the cook, sodium hydroxide (NaOH) is the compound that reacts with the lignin and carbohydrates. When the NaOH concentration decreases, sodium sulfide (Na_2S) is hydrolyzed to sodium hydrogen sulfide (NaHS) plus sodium hydroxide (NaOH) which in part replenishes the NaOH consumed at the beginning of the cook. Therefore, if the amount of sodium hydroxide (NaOH) in the pulping liquor is small (as in cook E and cook F), the delignification efficiency of the pulping liquor (redox potential) would tend to decrease during the pulping time. Regarding the sulfidities (Na_2S) of cooks E and F, the explanation of the results is the same given for cooks C and D.

SUMMARY

Pulping Results

At the 170°C and 180°C pulping temperatures the yields were increased by the addition of AQ; while at 190°C AQ did not show any effect. The addition of AQ had lowered the positive effect on Kappa numbers at the 170°C and 180°C pulping temperatures. However, there is not a linear relationship between the amount of added AQ and the changes in yields and Kappa numbers, and 0.1% AQ is nearly as beneficial as 0.2% AQ. AQ showed better effect on Kappa number than on pulp yield. It seems that the beneficial effect of AQ is due to its catalytic action: it reduces (dissolves) lignin and oxidizes (stabilizes) carbohydrates.

Fluorescent Intensities and Fluorescent Factors of Pulping Liquors

At the 170°C pulping temperature, the fluorescent intensity of the pulping liquor was increased by the addition of AQ. At 180°C, AQ showed little effect on the fluorescent intensity of the pulping liquor, while at 190°C it did not show any effect on either the fluorescent intensity or the fluorescent factor of the pulping liquors. For the three temperatures, the fluorescent factor of the kraft pulping liquors decreased during the cooks. These results suggest some molecular change in the dissolved lignin compounds such as condensation, which is a re-combination of the lignin fragments into larger molecules. However, at 170°C, the fluorescent factor of the kraft AQ pulping liquor was stabilized by the addition of AQ.

From one set of cooks to another, the beneficial effect of AQ in the delignification of the pulp decreased as the temperature increased. For a given set of cooks, the increase of the lignin concentration in the liquor from the beginning to the end of the set was very small and the difference was smallest at 190°C. This was one of the reasons for small changes in fluorescent intensities of the pulping liquor at high temperatures.

Regarding fluorescent intensities of the pulping liquors versus Kappa numbers of the pulps, they were negatively correlated when the pulping temperature was 170°C, but positively correlated at 190°C. A similar effect was seen with the fluorescent factors. At 170°C, the fluorescent factor of the kraft liquor increased in direct proportion to the Kappa numbers, but was almost constant for the kraft AQ pulping liquor. However, at 190°C, the fluorescent factors of the kraft and kraft AQ pulping liquors increased in direct relation to the Kappa numbers. These results indicate that at 190°C, the fluorescent intensities and fluorescent factors of the pulping liquor decreased even though the absolute amounts of lignin in the pulping liquors increased as the yield decreased. This behavior was also observed in the fluorescent factors of the kraft pulping liquors at 170°C and 180°C pulping temperature. Therefore, it can be assumed that condensation of lignin was present at 170°C but it accelerated at 190°C.

The relationships of the fluorescent intensities and fluorescent factors versus pulp yields were similar to those observed for Kappa numbers.

Samples of pulping liquor from the circulating digester were taken for analyzing the fluorescent intensity and redox potential. The fluorescent intensities were analyzed in both the Turner 111 filter fluorometer and the Aminco-Bowman spectrophotofluorometer. The fluorescent intensity of the liquor increased when the pulping temperature, amount of chemicals, or sulfidity was increased. In the beginning of the cook, the fluorescent intensities of the liquors were larger than those obtained later during the cook. It is well known that the delignification rate during the cook is higher in the beginning of the cook than during the rest of the cook. This fact could explain the fast increases in fluorescent intensity in the beginning of the cook. The redox potentials of the pulping liquor increased in direct proportion to the sulfidities of the liquors. These results indicate that the sulfidity increases the reduction capacity of the pulping liquor producing better delignification (reduction) of the pulp.

CONCLUSIONS

1. AQ showed a better effect on delignification of wood at 170°C than at 180°C or 190°C pulping temperature.
2. 0.1% AQ addition showed a proportionately better effect on the delignification of wood than 0.2% AQ addition to pulping liquor.
3. For all temperatures, AQ showed a proportionately better effect on Kappa number than on pulp yield.
4. The fluorescent intensities of kraft pulping waste liquors increase with increases in pulping temperature, amount of chemicals, and sulfidity of the white liquor.
5. During kraft pulping, the fluorescent intensity of the liquor increases rapidly in the early stages, and then remains constant or decreases slightly after about one hour of cooking time.
6. During a kraft cook the fluorescent factor decreases with pulping time, indicating some molecular change in the dissolved lignin in the pulping liquor.
7. At 170°C pulping temperature, the fluorescent intensities for all cooks increased with pulping time, while at 190°C the fluorescent intensities decreased with pulping time.
8. At 170°C pulping temperature, AQ stabilizes the fluorescent factors, probably by keeping the lignin fragments in dispersion permitting them to move and resonate freely.
9. The redox potentials increased with the sulfidity and with the amount of chemicals in the pulping liquor, but decreased with higher pulping temperatures.

10. The fluorescent intensities and redox potentials increased when AQ was added to the pulping liquor at 170°C pulping temperature.
11. In general, the behavior of the fluorescent intensities of kraft pulping liquor determined by using the Aminco-Bowman spectrophotofluorometer is similar to that observed by using the Turner 111 filter fluorometer.
12. At 170°C, the statistical analysis indicates good linear correlations between the independent pulping parameters and the dependent pulp properties, but at 180°C and 190°C, the correlations are less significant.

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APPENDIX

APPENDIX

TABLE 1. PULPING DATA AT 170°C

Cook No.	Time Min.	AQ %	Kappa Number	Yield %	Fluorescent Intensity	Redox Potentials
1	60	0.0	98.0	53.4	16.3	645
2	90	0.0	84.3	51.6	17.0	648
3	120	0.0	68.1	49.5	17.5	649
4	150	0.0	54.3	48.0	18.0	652
5	60	0.1	68.6	53.4	16.4	652
6	90	0.1	58.7	52.3	17.2	656
7	120	0.1	44.0	51.0	17.7	657
8	150	0.1	30.0	48.9	18.5	659
9	60	0.2	52.9	53.5	17.0	658
10	90	0.2	46.3	52.0	18.0	660
11	120	0.2	36.6	50.1	18.5	661
12	150	0.2	31.6	48.6	19.0	660

APPENDIX

TABLE 2. PULPING DATA AT 180°C.

Cook No.	Time Min.	AQ %	Kappa No.	Yield %	pH	R.P.	Fluorescent Intensity
1	60	0.0	62.8	48.2	13.00	667	17.5
2	90	0.0	49.8	47.6	12.94	667	18.0
3	120	0.0	43.0	46.2	12.81	667	18.0
4	150	0.0	41.5	45.1	12.58	653	18.0
5	60	0.1	42.5	48.4	13.0	678	15.2
6	90	0.1	--	--	--	--	--
7	120	0.1	32.9	46.8	12.97	675	15.7
8	150	0.1	30.7	46.2	12.95	662	15.7
9	60	0.2	43.2	49.6	13.07	677	16.7
10	90	0.2	33.5	47.8	13.02	673	16.4
11	120	0.2	31.1	46.9	12.86	658	16.4
12	150	0.2	29.3	45.6	12.70	652	16.6

APPENDIX

TABLE 3. PULPING DATA AT 190°C.

Cook No.	Time Min.	AQ %	Kappa No.	Yield %	pH	R.P.	Fluorescent Intensity
1	60	0.0	44.9	46.0	12.92	636	18.1
2	90	0.0	38.7	44.1	12.64	630	18.0
3	120	0.0	34.8	43.1	12.37	625	17.8
4	150	0.0	33.2	42.0	11.85	615	17.6
5	60	0.1	33.4	45.4	12.81	636	18.0
6	90	0.1	30.0	43.8	12.58	634	18.2
7	120	0.1	27.5	43.4	12.29	633	18.0
8	150	0.1	27.5	41.4	11.69	620	17.7
9	60	0.2	30.3	45.6	12.61	630	18.5
10	90	0.2	27.6	44.0	12.40	624	18.25
11	120	0.2	26.3	43.4	11.97	610	18.25
12	150	0.2	26.2	42.0	11.46	604	18.0

APPENDIX

TABLE 4. PULPING DATA OF CIRCULATING DIGESTER AT 180°C and T.A. = 16%, S = 20%.

Sample Number	Time Min.	Redox Potentials	Fluorescent Intensity	pH
1	10	460	3.2	13.20
2	20	520	3.6	13.20
3	30	577	5.5	12.95
4	40	600	8.0	12.76
5	50	620	10.7	12.68
6	60	625	12.2	12.60
7	75	630	15.0	12.50
8	90	630	16.0	12.38
9	105	635	16.0	12.42
10	120	633	16.5	12.40
11	135	631	16.6	12.32
12	150	635	16.5	12.18
13	165	635	16.5	12.31
14	180	635	16.9	12.20
15	195	631	16.5	12.22
16	210	625	16.7	12.18
17	225	630	17.0	12.10
18	240	630	16.5	11.80
19	255	626	16.7	11.60
20	270	623	16.6	11.55
21	285	622	16.5	11.53
22	300	618	16.7	11.40

APPENDIX

TABLE 5. PULPING DATA OF CIRCULATING DIGESTER AT 170°C;
T.A. = 16%, S = 20%.

Sample Number	Time Min.	Redox Potentials	Fluorescent Intensity	pH
2	10	465	3.0	12.96
3	20	520	3.7	12.84
4	30	600	5.5	12.82
5	40	633	9.0	12.80
6	50	634	10.4	12.40
7	75	631	11.1	12.70
8	90	630	13.0	12.42
9	105	639	13.3	12.23
10	120	634	14.5	12.00
11	135	637	14.6	11.79
12	150	638	15.5	11.78
13	165	634	15.0	11.61
14	180	640	14.5	11.64
15	195	638	15.0	11.62
16	210	634	15.5	11.50
17	225	635	16.5	11.53
18	240	634	15.0	11.30
19	255	634	15.5	11.27
20	270	637	15.6	11.23
21	285	630	15.5	11.26
22	300	630	15.5	11.21

APPENDIX

TABLE 6. PULPING DATA OF CIRCULATING DIGESTER AT 190°C,
T.A. = 16% and S = 20%.

Sample Number	Time Min.	Redox Potentials	Fluorescent Intensity	pH
1	10	500	2.0	13.10
2	20	520	2.6	13.02
3	30	612	5.5	12.91
4	40	665	8.0	12.85
5	50	660	10.7	12.75
6	60	660	12.2	12.67
7	75	660	15.0	12.66
8	90	655	16.0	12.37
9	105	645	16.0	12.00
10	120	640	16.5	11.97
11	135	640	16.6	11.80
12	150	640	16.5	11.82
13	165	625	16.5	11.75
14	180	618	16.9	11.61
15	195	615	16.5	11.60
16	210	612	16.7	11.55
17	225	610	17.0	11.42
18	240	610	16.5	11.25
19	255	610	16.7	11.01
20	270	609	16.6	10.89
21	285	604	16.5	10.58
22	300	606	16.2	10.60

APPENDIX

TABLE 7. PULPING DATA CIRCULATING DIGESTER AT 190°C,
T.A. = 12% and S = 20%.

Sample Number	Time Min.	Redox Potentials	Fluorescent Intensity	pH
1	10	540	3.4	13.20
2	20	570	4.0	13.20
3	30	584	6.0	13.12
4	40	660	7.5	13.05
5	50	670	10.2	13.84
6	60	650	13.0	12.51
7	75	610	17.2	10.73
8	90	570	17.5	10.21
9	105	569	16.0	9.80
10	120	555	16.5	9.73
11	135	547	16.2	9.63
12	150	540	16.9	9.53
13	165	539	16.5	9.47
14	180	535	16.0	9.43
15	195	533	16.5	9.33
16	210	532	16.5	9.26
17	225	526	17.0	9.22
18	240	520	17.0	9.20
19	255	519	16.5	9.18
20	270	520	16.5	9.15
21	285	518	16.4	9.10
22	300	518	16.0	9.05

APPENDIX

TABLE 8. PULPING DATA OF CIRCULATING DIGESTER AT 190°C,
T.A. = 12% and S = 10%.

Sample Number	Time Min.	Redox Potentials	Fluorescent Intensity	pH
1	10	---	---	---
2	20	520	3.5	13.32
3	30	525	4.5	13.28
4	40	585	6.0	13.24
5	50	650	7.0	12.93
6	60	620	10.5	12.44
7	75	597	14.0	11.53
8	90	575	14.0	10.71
9	105	560	14.5	10.33
10	120	548	14.5	10.25
11	135	539	14.8	10.15
12	150	540	14.0	10.01
13	165	525	13.5	9.98
14	180	531	13.0	9.97
15	195	529	13.0	9.96
16	210	524	13.8	9.90
17	225	523	13.7	9.84
18	240	515	13.5	9.78
19	255	517	14.0	9.75
20	270	518	14.0	9.71
21	285	518	13.5	9.68
22	300	519	13.5	---

APPENDIX

TABLE 9. PULPING DATA OF CIRCULATING DIGESTER AT 190°C,
T.A. = 16%, and S = 10%.

Sample Number	Time Min.	Redox Potentials	Fluorescent Intensity	pH
1	10	547	1.0	13.55
2	20	557	3.5	13.47
3	30	565	7.5	13.47
4	40	595	8.1	13.38
5	50	620	9.2	13.30
6	60	630	15.2	13.13
7	75	646	18.0	12.97
8	90	634	18.5	12.76
9	105	628	18.7	12.53
10	120	623	18.5	12.24
11	135	616	18.7	12.00
12	150	608	18.5	11.73
13	165	604	18.5	11.63
14	180	595	18.5	11.44
15	195	580	18.2	11.35
16	210	579	18.7	11.26
17	225	576	18.5	11.16
18	240	575	18.5	11.08
19	255	578	18.5	11.03
20	270	578	18.1	10.96
21	285	577	18.0	10.90
22	300	567	18.5	10.71

