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The Influence of the Bleaching Medium on Caustic Extraction Efficiency (I):
The Role of Fiber Swelling

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THE INFLUENCE OF THE BLEACHING MEDIUM ON CAUSTIC EXTRACTION EFFICIENCY (I): THE ROLE OF FIBER SWELLING

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ABSTRACT

In the alkaline extraction of softwood kraft pulp, delignification was inhibited when the bleaching medium contained >50% (v/v) ethanol. The observed effect was initially attributed to lignin fragment entrapment caused by fiber de-swelling. Caustic extractions were performed with various media at a given fiber swollen volume to test the hypothesis. Extractions conducted with ethanol and aqueous BaCl₂ solutions showed similar levels of delignification; however, extractions performed with aqueous NaCl solutions yielded conflicting results. Estimates of the effective diffusion coefficients did not differ appreciably among the media investigated. Further analyses indicated that the average lignin fragment diameter is smaller than the reduced average pore width. These results suggested that other factors are responsible for the decreased extent of delignification in ethanol-water and aqueous BaCl₂ media.

INTRODUCTION

The early stages in a bleaching sequence are primarily designed to selectively remove the residual lignin remaining after pulping while preserving carbohydrate integrity. Usually, the first stage, such as (DC), D and Z, modifies and fragments the residual lignin [1]. A significant portion of the altered lignin, up to 80% [2-4], is removed in the subsequent E or (EO) stage. Successful brownstock bleaching is dependent upon the optimization of lignin removal in *both* the oxidative and extraction stages.

A potential method for enhancing lignin dissolution during bleaching might be to substitute a portion of the bleaching liquor with a water-miscible organic solvent such as an alcohol. Pulping processes such as Alcell®, Organocell, and ASAM often employ 15 to 70% alcohol in the cooking liquor [5-7]. Recent studies indicated that substantial amounts of residual lignin can be removed from Alcell® brownstocks if an aqueous ethanol medium is used instead of water [8,9]. It is believed that the alcohol-water medium used in these processes facilitates lignin removal from the fiber through the improved solvation of lignin fragments [9]. Significant improvements in ozone bleaching selectivity have been reported when the bleaching medium consisted of an organic solvent-water solution (e.g., alcohol-water) in-

stead of water [10-13]. However, these studies have not examined the use of an organic solvent-water medium in a subsequent extraction stage or in multiple stages for enhancing delignification during bleaching.

We are investigating “organosolv bleaching” with the DE delignification sequence using an ethanol-water medium [14]. Our studies have yielded several interesting observations on chlorine dioxide bleaching and subsequent caustic extraction; the results from the former investigation will be reported in a later article. This paper examines the influence of an ethanol-water medium on caustic extraction, and examines the postulate that the observed effects are due to lignin transport limitations and fiber de-swelling.

ALKALINE EXTRACTIONS IN ETHANOL-WATER MEDIA

Preliminary investigations conducted with an ethanol-based organosolv DE bleaching sequence afforded some unanticipated results concerning the alkaline extraction stage (Fig. 1) [14]. Adjusting the extraction from an aqueous to a 50% (v/v) ethanol-water medium caused a small increase in the post-extraction kappa number. There was a sharp increase in the kappa number as the ethanol concentration was increased from 50 to 85% in the extraction medium; afterwards, the post-extraction kappa reached a plateau value of ~16 at high ethanol concentrations ($\geq 85\%$). The delignification results differ from what might be expected based on the results reported for ethanol-water washing of organosolv pulps [8,9]. One possible explanation is decreased fiber de-swelling in ethanol-water media.

THE INFLUENCE OF FIBER SWELLING ON LIGNIN TRANSPORT

Proposed Hypothesis

Earlier reports have suggested that a limiting factor in delignification during bleaching is the hindrance of lignin fragment diffusion out of the fiber wall [2,3]. The fiber wall itself is a porous composite material composed of an intricate network of voids and channels [15,16]. These pores and channels allow for both water and reagents to penetrate within the fiber wall. The size of the pores can also control the size of the molecular fragments diffusion from the wall's interior into the bulk solution. Several investigations have shown a correlation between the removed lignin fragment size and the pore size during delignification [16-18]. Fiber de-swelling can cause the pores to contract and impede the transport of lignin fragments that would have otherwise diffused out of a swollen fiber.

In general, most water-miscible organic solvents are poor swelling agents for cellulosic materials [19]. Similar observations have been made for polysaccharide gels in alcohol-

water solutions [20-23]. Ni and van Heiningen [24] recently measured the swelling of Al-cell® pulp fibers in various water-ethanol solutions; fibers soaked in 100% ethanol showed a 20% reduction in swollen volume compared to water-soaked fibers. Fiber de-swelling in organic solvents, such as ethanol, is due to unfavorable solvent-carbohydrate polymer segment unit interactions [20,21,24,25]. Thus, the decreased extraction delignification observed with ethanol-water media could be caused by entrapment of lignin fragments brought about by decreased fiber swelling.

Testing the Hypothesis

Fiber distention can also be manipulated by its polyelectric gel properties [20-22,25], as has been demonstrated by Grignon and Scallan [26]. Donnan theory states that when a gel with attached ionizable groups (e.g., carboxyl groups) is placed in an ionic solution, an exchange of mobile ions occurs between the gel and the bulk solution. However, the attached ionizable groups result in a concentration gradient of mobile ions between the gel's interstitial fluid and the bulk solution. The gel swells due to the influx of water into the gel matrix in order to equilibrate the ion concentration imbalance.

Lindström and Carlsson [27] have reported a 20% reduction in unbleached kraft fiber swelling in various inorganic salt solutions. Multivalent cationic salts were observed to cause more de-swelling than monovalent cationic salts at a given molar concentration. Besides the Donnan effect, the multivalent cations may be associating with multiple anionic groups (e.g., carboxylic anions) and shield the negative repulsive charges inside the gel, thus, causing the gel to de-swell [27].

If fiber de-swelling, with the associated lignin fragment entrapment, is the principal mechanism for the decreased alkaline extraction efficiency in ethanol-water media, then other fiber de-swelling media should also cause a similar effect. To test the hypothesis, we extracted D-stage treated pulps with two aqueous salt solutions: BaCl₂ and NaCl. The divalent cationic salt, BaCl₂, was chosen to ensure a significant amount of de-swelling over a wide concentration range, and is one of the few multivalent cationic salts that is appreciably soluble under alkaline conditions [28].

Measurement of the effective lignin fragment diffusion coefficient can also provide some insights into whether decreased fiber distention is impeding delignification. Decreases in the fiber pore sizes, according to Favis [17,18], should cause a large reduction in the effective diffusion coefficient of lignin. Estimates of lignin diffusion coefficients (D) for our alkaline extraction media were calculated using Favis' porous plate diffusion model [17,18]:

$$\bar{\gamma}(t) = \frac{C_L(t) - C_L(\infty)}{C_L(0) - C_L(\infty)} = 2 \sum_{n=0}^{\infty} \left(\frac{2(-1)^n}{(2n+1)\pi} \right)^2 e^{-\frac{(2n+1)^2 \pi^2 \tau}{4}} \quad (1)$$

where τ is the dimensionless Fourier number (Dt/ℓ^2); ℓ is one-half the fiber wall thickness; and $\bar{\gamma}(t)$ is the ratio of the remaining leachable lignin at time t to the total amount of leachable lignin within the fiber. Tabulated values of $\bar{\gamma}$ versus τ have been given by Favis [17]. The effective diffusion coefficients in selected de-swelling media can thus be compared to the aqueous case to determine if de-swelling is affecting lignin fragment transport.

EXTRACTION DELIGNIFICATION AND FIBER SWELLING

Alkaline extraction experiments were conducted with various aqueous BaCl_2 solutions (Fig. 2). The addition of BaCl_2 retarded lignin removal from the pulps as indicated in the post-extraction kappa numbers; the extent increased greatly above 0.0025 M BaCl_2 . This delignification profile for caustic extraction is similar to the profile obtained with ethanol-water media (Fig. 1).

Fiber swelling measurements were made on a DE bleached pulps to see if the two different media yielded the same distention level. Table I reports the swelling levels measured with the selected media using the modified centrifugal technique of Abson [29]. Fiber swelling under alkaline extraction conditions (~ 12.6 pH) was decreased by $\sim 12\%$ for both absolute ethanol and 0.01 M BaCl_2 versus water. The presence of alkali slightly inhibited fiber swelling in ethanol and BaCl_2 . Alkali extractions performed with 100% ethanol and 0.01 M BaCl_2 yielded similar extracted kappa numbers at the same level of fiber swelling.

Fiber swelling measurements were also performed on DE pulps soaked in NaCl solutions (Table I). A 0.40 M NaCl solution matched the same distention level observed with the 0.01 M BaCl_2 solution. However, caustic extractions performed with the 0.40 M NaCl medium did not limit delignification to the same levels observed with the other two de-swelling media. The alkaline leaching study of Li and MacLeod noted similar influences on brownstock delignification with aqueous NaCl and BaCl_2 media [28].

An alkaline extraction was performed with an air-dried, D-stage treated pulp. The fiber swelling level of the air-dried pulp decreased by $\sim 26\%$ as compared to the never-dried pulp in water (Table I). The post-extraction lignin concentration for the air-dried pulp was much lower than that observed for extractions utilizing 0.01 M BaCl_2 or absolute ethanol as the medium, even though the air-dried pulp showed a lower level of swelling. These results, coupled with the NaCl results, do not support fiber de-swelling as the major mechanism

causing the decreased delignification when either ethanol-water or BaCl₂ solutions are used as the extraction medium.

DETERMINATION OF EFFECTIVE DIFFUSION COEFFICIENTS

The final phase of this experimental program determined the effective diffusion coefficient (D) of the lignin fragments during caustic extraction in selected de-swelling media. Low consistency (0.5%) alkaline extractions were performed at 1 and 12 h with a D-stage treated pulp (Table II); afterwards, the micro-kappa numbers were measured and served as representation of the average lignin concentration ($C_L(t)$) within the fiber [16]. The pre-extraction kappa, 19.5, was used for $C_L(0)$, and the 12-h post-extraction in the various media were used for $C_L(\infty)$ in Equation (1).

Low consistency extraction values for water and 75% ethanol were similar to those observed during the medium consistency extractions (Fig. 1 and Table II). The pulps from a 0.01 M BaCl₂ extraction at 1 h had a lower kappa number than its corresponding 10% consistency extraction (Fig. 2 and Table II). The 12-h extraction with absolute ethanol resulted in an exit kappa higher than its initial kappa. Apparently, there are some reactions occurring that is increasing the amount of oxidizable material in the fiber over the long reaction time. Reactions, such as methylglucuronic acid conversion to hexenuronic acids [30] and/or quinone condensations [31] may be occurring at the extended reaction times; the resulting structures may consume more KMnO₄ than the original structures, and thus, cause a higher kappa number. An effective lignin diffusion coefficient could not be calculated for the absolute ethanol case due to the increase in the post-extraction kappa at extended reaction times (i.e., $C_L(\infty) > C_L(0)$ and Equation (1) is invalid).

The values of D for the remaining media were calculated based on the tabulated values of $\bar{\gamma}$ and τ (i.e., Dt/ℓ^2) from Equation (1) [17] at 1 h, and the average fiber wall thickness of 5 μm ($\ell = 2.5 \mu\text{m}$) [17,18,28]. The D values for each of the three media (Table II) were similar to the lignin diffusion coefficients reported by Li and MacLeod for alkaline leaching of kraft brownstocks ($\sim 8.8 \times 10^{-12} \text{ cm}^2/\text{s}$ at 60°C) [28]. However, the determined values of D were all of the same order of magnitude. If pore size was limiting delignification, then the diffusion coefficients for the de-swelling media should have been much smaller than for water, i.e., at least an order of magnitude smaller [17,18]. Again, these experimental results suggest that pore shrinkage, due to de-swelling, is not the primary inhibiting mechanism for lignin removal during caustic extraction with either ethanol-water solution or BaCl₂ solutions.

EXPLANATIONS FOR OBSERVED RESULTS

The failure of fiber de-swelling to account for the decreased extraction delignification efficiencies in ethanol-water and BaCl₂ solutions could be related to the lignin fragment sizes being smaller in comparison to the fiber pore sizes. The diameter of a lignin fragment (d_l) can be estimated if a spherical conformation for a fragment is assumed:

$$d_l = \left(\frac{6M_w v}{\pi N_A} \right)^{1/3} \quad (2)$$

where M_w is the molecular weight; v is the specific volume of the fragment; and N_A is Avogadro's number [16]. Several investigations have approximated v to be 0.714 to 0.870 cm³/g [16-18,32]. Schwantes [33,34] has reported molecular weights (M_w) ranging from 500 to 20,000 for lignin fragments in an extraction effluent from a softwood kraft pulp subjected to a D(EO) sequence. A lignin fragment diameter range of 1.0 to 3.8 nm was calculated utilizing Equation (2) based on the values of v and M_w from the literature. Schwantes [33,34] noted that ~65% of the leachable lignin in the extraction stage had an $M_w < 1000$; thus, most of the fragments have a $d_l < 1.4$ nm.

Ahlgren, et al. [16] have reported that the weight average pore width for an 80% delignified (~40 kappa) softwood kraft pulp is ~6.0 nm. Favis [17] has observed that an 80% delignified pulp had a pore size range of 1 to 10 nm and a median pore width of 3.6 nm; a similar range and median for pore sizes has been shown earlier by Stone and Scallan [15]. Pugliese and McDonough [35] have shown that a CE bleaching sequence has negligible effects on the pore size distribution for a softwood kraft pulp with an unbleached kappa number of ~40. The above reported sizes and ranges for pores were taken to be representative for our softwood kraft pulp in this study.

Thus, the fiber pore sizes given in the literature [15-17,35] are larger than the sizes of the oxidized lignin fragments from an extraction stage. Favis [17,18] reported that a 10% reduction in fiber swelling (similar to the swelling level observed in ethanol and 0.01 M BaCl₂) corresponded to a 3.5% reduction in pore diameter. Such a small reduction in the pore's diameter is going to have negligible effects on the transport of lignin fragments from the fiber wall.

A possible explanation for the observed decrease in delignification efficiency during alkali extraction in ethanol or BaCl₂ media is the solubility of the oxidized fragments. Kraft lignin solutions are known to coagulate and precipitate out of solution when multivalent ca-

tions, such as Ba^{+2} , are added [29,36]. A later publication [14,37] will examine the applicability of this hypothesis to alkline extraction in aqueous ethanol and BaCl_2 media.

CONCLUSIONS

High concentrations of ethanol (>50%) or BaCl_2 ($\geq 0.0025 \text{ M}$) severely retarded delignification during caustic extraction of a chlorine dioxide treated pulp. Both media showed a reduction in fiber swelling of up to 12% compared to an aqueous alkali solution. Sodium chloride solutions at a concentration chosen to cause a 12% reduction in fiber swelling did not significantly impede delignification. Furthermore, the effective diffusion coefficient for oxidized lignin fragments did not differ appreciably among the various media examined ($\sim 10^{-11} \text{ cm}^2/\text{s}$ at 60°C).

Fiber de-swelling and subsequent lignin entrapment appeared to play a minor role in alkline extraction delignification with ethanol-water and BaCl_2 solutions. The size of the lignin fragments was estimated to be smaller than the size of the pores. The small change in pore width associated with a 12% reduction in swelling cannot be the major reason for the lower delignification efficiency observed with high concentrations of ethanol or BaCl_2 in the extraction stage. Other phenomenological constraints, such as lignin fragment solubility, could be affecting delignification during alkali extraction.

EXPERIMENTAL PROCEDURES

Pulp Bleaching

A conventional softwood kraft pulp (southern pine) with a kappa number of 29.3 was used throughout this study. The pulp was obtained from a mill and was produced at these conditions: 17.5% AA (on o.d. wood as Na_2O), 31.3% sulfidity, liquor:wood of 3:1 L/kg, 45 minutes to 167°C , and an H-factor adjusted to a target kappa of 30 and a yield of 48%. Prior to chlorine dioxide treatment, the pulp was washed with warm, deionized water using a Büchner funnel until the filtrate was clear; afterwards, the pulp was pressed to ~25% consistency and stored in a cold room (at $\sim 4^\circ\text{C}$) until needed.

Chlorine dioxide bleaches were performed on the washed pulp at the given conditions: 1.79% ClO_2 on o.d. pulp (0.16 kappa factor), 3.0% consistency, initial pH of 4.2 prior to ClO_2 addition, 45°C , and 30 minutes reaction time. A 1 M HCl solution was used to acidify the pulp. After the ClO_2 treatment, the pulp was washed with copious amounts of deionized water until the filtrate was clear. The resulting treatment yielded a pulp with a kappa number of 19.5 ± 0.3 , and a bleach filtrate with a 2.4 pH and no residual ClO_2 .

Medium consistency extractions were performed on 5 to 10 g samples of the ClO₂ treated pulp. Prior to extraction, the pulp was soaked at room temperature in the appropriate medium for 2 h (at 4% consistency and pH ~5), drained, and pressed to ~40% consistency. General extraction conditions were as follows: 2.58% NaOH on o.d. pulp (0.55 caustic multiple), 10% consistency, 60°C, and 60 minutes reaction time. Extractions were performed in Kapak/Scotchpack heat-sealable pouches. Afterwards, the pulp was emptied into a Büchner funnel and washed with ~130 mL/o.d. g of pulp of the corresponding medium (without alkali). The pulp was then pressed to ~25% consistency and placed into cold storage until micro-kappa number measurements were made (TAPPI Useful Method UM-246).

Fiber Swelling Measurements

Fiber swelling measurements were performed on an aqueous, never-dried DE bleached pulp with an 8.5 kappa number produced at the conditions given earlier. Approximately 5 o.d. g of this pulp were washed with the swelling medium of interest and drained to ~25% consistency; afterwards, the pulp was diluted to 0.5% consistency with the medium and allowed to soak for 12 h. Fiber pads of various basis weights were produced by draining the various volumes of the pulp slurry onto a Millipore® filter funnel. Fiber swelling measurements were performed on the above fiber pads according to Abson's modification [29] to the water retention value test (WRV, TAPPI Useful Method UM-256). Measurements are reported in terms of cm³/o.d. g pulp; ethanol retention values were adjusted to the corresponding WRV based on the specific gravity of ethanol (0.785).

Estimations of Effective Diffusion Coefficients

Effective lignin diffusion coefficient experiments were performed in a 1 L reagent bottle equipped with laboratory mixer and stopper, and at 60°C. Approximately 5 o.d. g of the D-stage treated pulp were washed with the appropriate medium and drained; afterwards, the pulp was placed in the bottle and diluted to 0.5% consistency with the medium. The amount of NaOH dissolved in the medium corresponded to the same concentration level as the 10% consistency extraction stage (~0.071 M). At the end of the extraction period (1 or 12 h), the pulp was separated from the extraction effluent, pressed to 25% consistency, and placed into cold storage until micro-kappa number measurements could be made.

NOMENCLATURE

Bleaching stages

| | |
|------|---|
| C | chlorine stage |
| D | chlorine dioxide stage |
| (DC) | chlorine dioxide with chlorine addition stage |
| E | caustic extraction stage |
| (EO) | oxygen reinforced extraction stage |
| Z | ozone stage |

Equations

| | |
|-------------------|---|
| $C_L(t)$ | average lignin concentration in the fiber at time t , (denoted by kappa number) |
| D | effective diffusion coefficient, (cm ² /s) |
| d_l | diameter of lignin fragment, (nm) |
| $\bar{\gamma}(t)$ | Ratio of removable lignin at time t to total amount of removable lignin |
| ℓ | one-half average fiber wall thickness, (cm) |
| M_w | Molecular weight of lignin fragment, (daltons) |
| N_A | Avogadro's number, (dimensionless) |
| v | specific volume of lignin, (cm ³ /g) |
| τ | Fourier Number, (Dt/ℓ^2) |
| t | time, (s) |

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FIGURE CAPTIONS

Figure 1. Effect of ethanol concentration on alkaline extraction delignification efficiency.

Figure 2. Effect of BaCl₂ concentration on alkaline extraction delignification efficiency.

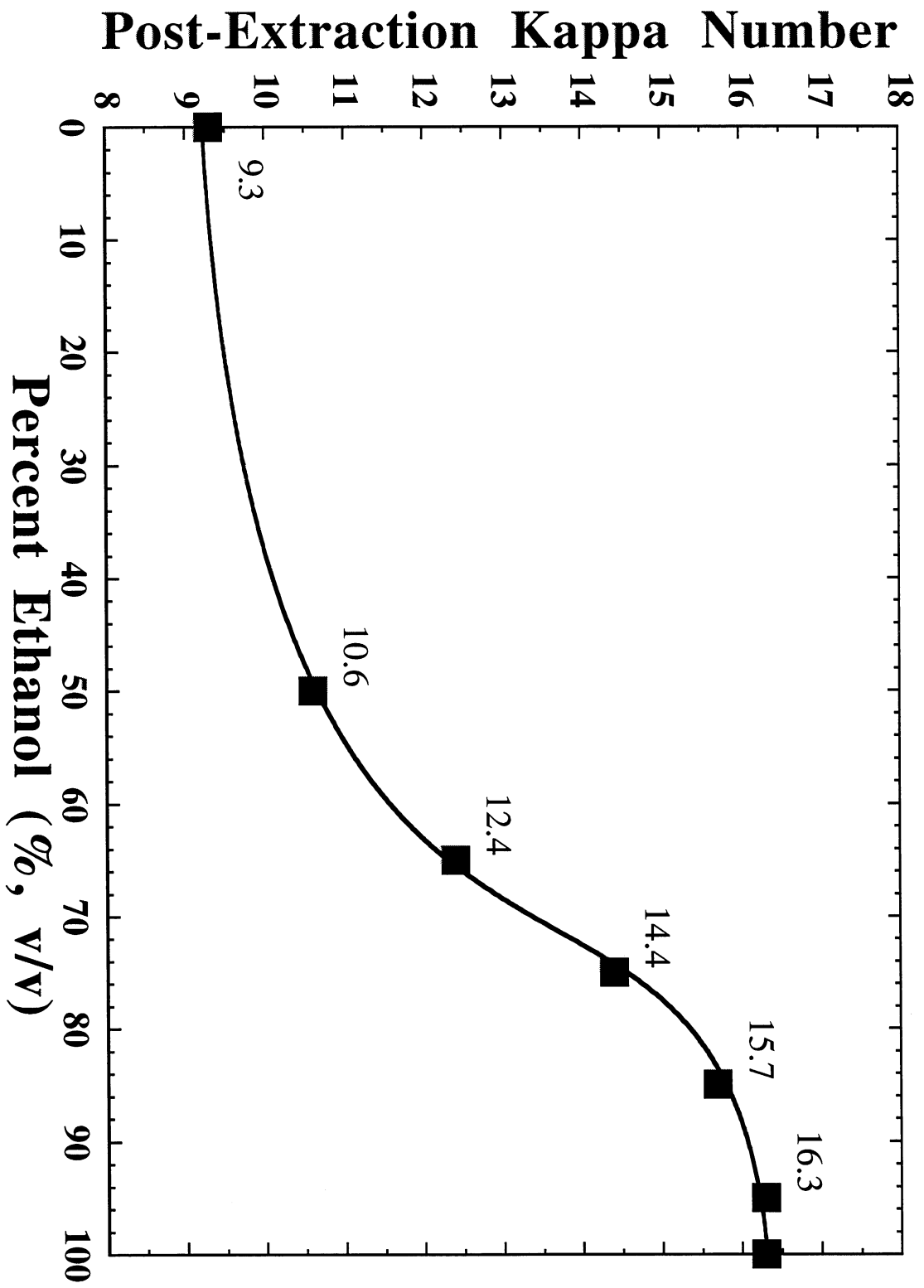


FIGURE 1

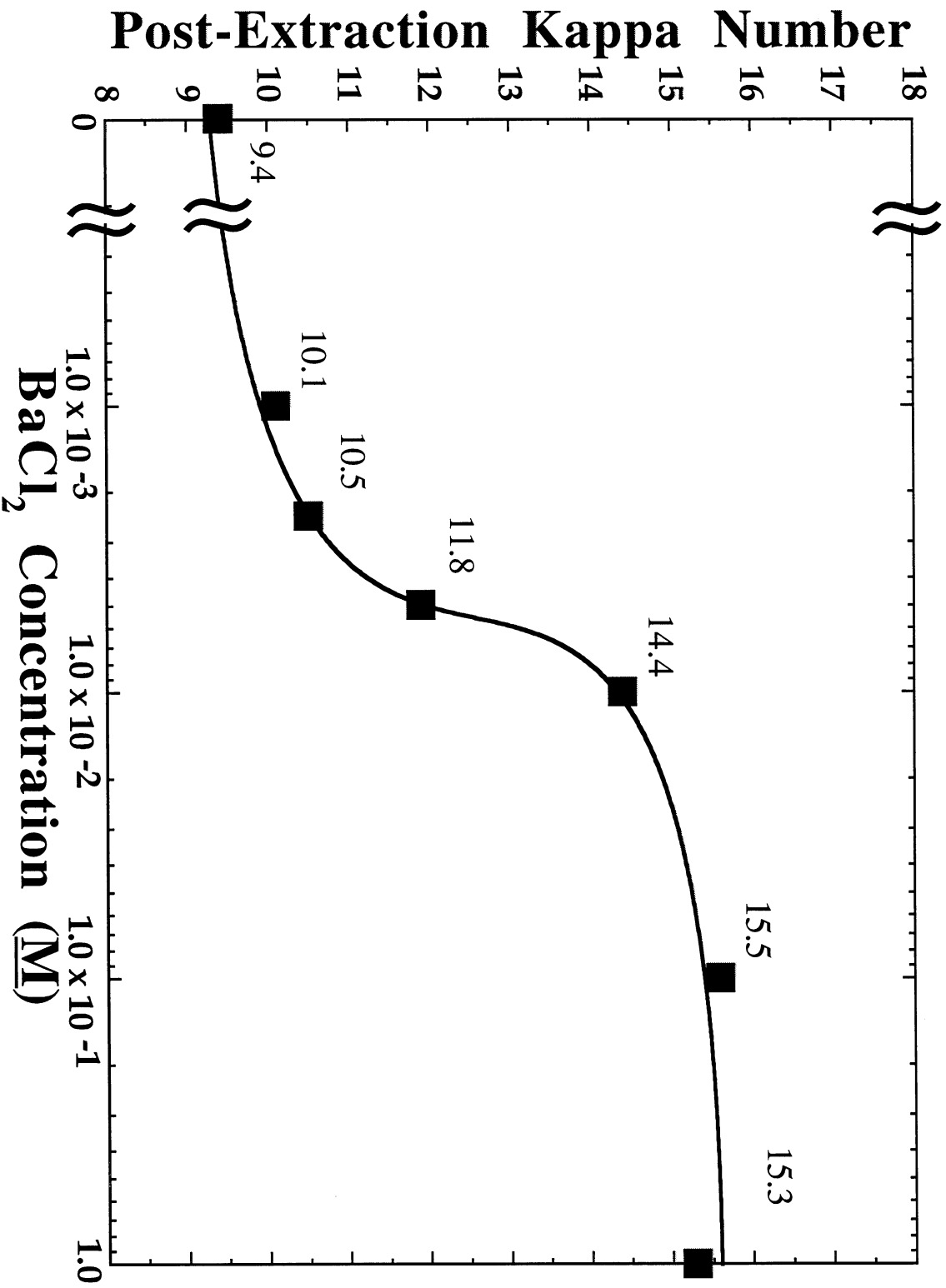


FIGURE 2

Table I. Influence of the fiber swelling level on alkaline extraction delignification.

| Treatment | Fiber Swelling Level (cm ³ /g o.d. pulp) ^{a,b} | | Post-Extraction Kappa Number ^c |
|---|---|-----------------------------------|--|
| | Neutral Conditions (pH ~8) | Alkaline conditions (pH ~12.6) | |
| Water (100%) medium | 1.91±0.07 | 1.87±0.07 | 9.2 |
| Ethanol (100%) medium | 1.81±0.08 | 1.65±0.04 | 16.3 |
| 0.01 M BaCl ₂ medium | 1.72±0.08 | 1.64±0.05 | 14.4 |
| 0.04 M NaCl medium | 1.77±0.02 | 1.81±0.06 | - ^d |
| 0.40 M NaCl medium | - ^d | 1.70±0.03 | 10.9 |
| Air-dried pulp ^e ; water (100%) medium | - ^d | 1.38±0.03 | 11.3 |

^a Swelling measurements performed on an aqueous DE bleached pulp with post-extraction kappa 8.5.

^b ± Values are the observed standard deviations of the modified centrifugal technique [29] in the various media.

^c Extraction performed on an aqueous D-stage treated pulp (pre-extraction kappa 19.5).

^d Value was not determined.

^e Swelling measurements performed on an air-dried DE bleached pulp with post-extraction kappa 8.5; E-stage performed on an air-dried D-stage treated pulp (pre-extraction kappa 19.5).

Table II. Estimation of effective diffusion coefficient (D) of lignin fragments during low consistency (0.50%) alkaline extraction in various media of an aqueous D-stage bleached pulp ($C_L(0) = 19.5$).

| Medium | Post-Extraction Kappa Number | | $\bar{r}(t)$ | Estimation of D^a [Eq. (1)] | |
|--------------------------|------------------------------|---------------------------------|----------------|----------------------------------|--------------------------|
| | After 1 h ($C_L(3600)$) | After 12 h ($C_L(\infty)$) | | τ | D (cm ² /s) |
| Water (100%) | 8.8 | 6.1 | 0.201 | 0.568 | 9.9×10^{-12} |
| Ethanol (100%) | 19.3 | 21.1 | - ^b | - ^b | - ^b |
| Ethanol (75%) | 14.5 | 10.9 | 0.419 | 0.270 | 4.7×10^{-12} |
| 0.01 M BaCl ₂ | 11.4 | 9.5 | 0.190 | 0.589 | 10×10^{-12} |

^a Effective diffusion coefficient calculated at 1-h extraction time ($\bar{r}(3600)$).

^b Value was not determined.

