Dissolution of Lignin from Kraft Pulp after Treatment with Nitrogen Oxides

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DISSOLUTION OF LIGNIN FROM KRAFT PULP AFTER TREATMENT WITH NITROGEN OXIDES

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ABSTRACT

Laboratory experiments show that pretreatment with NO_2 including heating and ripening at 5% consistency and 90°C for 3 hours in the presence of NO_3^- and H^+ led to a dissolution of approximately 50-60% of the lignin in unbleached kraft pulp. Only 5-15% were dissolved when the treatment was terminated after heating to 90°C. An extensive fragmentation of the lignin during the ripening explains the extensive delignification in acid medium.

Fractionated dissolution of the remaining lignin by alkaline extraction gave fractions with small variation in N-contents (2.9-3.4%) and hydrophilicity. The last fraction exhibited the highest sorption of water vapor. The delignification was related to the decrease in molecular size during the pretreatment and during the subsequent alkaline treatments.

INTRODUCTION

Laboratory experiments show that pretreatment of kraft pulp with NO_2 followed by oxygen bleaching permits the production of fully bleached pulp without application of elementary chlorine[1]. The most favor-

able results were obtained in the S3-process in which
the pulp after reacting with NO_2 was ripened at high
temperature and medium consistency in acid nitrate
solution simulating spent liquor from the pretreat-
ment[2,3]. The main purpose of this report is to
describe the effect of the ripening conditions on the
dissolution of lignin during the pretreatment and on
the properties of the lignin remaining in the pulp
after this stage.

EXPERIMENTAL

Pretreatments

Never-dried kraft pulp from softwood, mainly Pinus
sylvestris, produced in a Swedish pulp mill and a
laboratory pulp prepared by conventional cooking at
high sulfidity were washed carefully with distilled
water. Potentiometric titration showed that the pulps
slurried in 0.2 M NaCl consumed 1.3-1.8 mmol HCl per
100 g dry pulp before the pH dropped to 4.5.

The pretreatment according to the S3-method was,
if not otherwise stated, started at 27% consistency.
Air was removed by evacuation and introduction of
nitrogen before addition of NO_2 [43.5 mmol (2 g)
calculated per 100 g dry pulp] at 40°C. After 15 min
the diluent containing $NaNO_3$ in dilute nitric acid
was added so that a consistency of 5 or 8% was obtain-
ed. The amount of added $NaNO_3$ corresponded to 0.28
mol $NaNO_3$ per kg water in the final mixture. After
the dilution the suspension was heated to 90°C in 50
min.

In the experiments denoted rip. 0 the ripening was interrupted when this temperature was reached. In those denoted rip. 3 the ripening was continued for 3 hours at 90°C. The pretreatments were terminated by rapid cooling. In the experiments referred to in Table 1 oxygen was introduced to atmospheric pressure and the reactor shaken to dissolve the nitric acid formed by oxidation of produced NO. Due to superatmospheric pressure no oxygen was introduced after the other pretreatments. The spent liquors were removed by centrifugations. In the experiments in Table 1 the

Table 1. Consecutive alkaline extractions of an industrial kraft pulp (kappa number 33.2; viscosity 1156 dm^3/kg) subjected to pretreatment terminated after heating to 90° (rip.0) or ripening at 90°C for 180 min (rip. 3). Reactor with a volume of 2400 ml loaded with water-impregnated pulp corresponding to 90 g dry pulp. Diluent added to 5% consistency.

Extractions			Kappa number		Lignin[a],g		% N		Sorption[b],H2O		M_w(50)x10^{-3}	
Liquor	min	°C	rip.0	rip.3	rip.0	rip.3	rip.0	rip.3	rip.0	rip.3	rip.0	rip.3
Pretreatment at 12% consistency, 36.4 mmol HNO3 in the diluent												
NaHCO3	10	20	29.8	14.2	0.25	0.22	3.4	4.3	2.55	2.31	7.20	5.00
NaOH	5	20	26.4	11.7	0.41	0.37	3.0	3.8	2.76	2.81	5.95	5.64
NaOH	5	50	24.2	9.6	0.24	0.27	3.0	3.5	2.71	2.60	7.76	7.96
NaOH	30	106	18.5	5.4	0.69	0.54	2.9	3.2	3.23	2.92	7.62	8.33
Pretreatment at 12% consistency, 50.7 mmol HNO3 in the diluent												
NaHCO3	10	20	26.9	12.0	0.20	0.25	3.9	4.0	2.96	2.86	8.49	4.82
NaOH	5	20	24.0	8.9	0.38	0.34	3.1	3.5	2.64	2.65	6.18	5.44
NaOH	5	50	21.8	7.2	0.28	0.23	2.9	3.5	2.45	2.99	7.01	6.08
NaOH	30	106	15.7	4.1	0.81	0.39	3.0	-	3.54	3.36	8.66	6.76
Pretreatment at 27% consistency, 50.7 mmol HNO3 in the diluent												
NaHCO3	10	20		11.1		0.31		3.9		3.12		4.90
NaOH	5	20		7.8		0.38		4.0		3.32		6.22
NaOH	5	50		6.5		0.19		3.7		3.03		7.61
NaOH	30	106		3.8		0.26		3.6		3.23		9.25

a) Precipitated lignin, g per 100 g pulp.
b) Mol per 100 g precipitated lignin

pulp was slurried in distilled water, filtered off on
a Buchner funnel, washed and slurried repeatedly in
water. About 80 liters of water of 20°C were consumed
during washing of 90 g pulp for 60 min.

Alkaline Extracts

Consecutive alkaline extractions of the wet, pretreat-
ed pulps were carried out with 0.1 M $NaHCO_3$ in one
stage followed by 0.1 M NaOH at 20°, 50° and finally
at 106°C. The pulp consistency was 4%. After each ex-
traction stage the pulp was centrifuged under standar-
dized conditions to remove the main part of the
liquor. Samples of pulp withdrawn after each extrac-
tion were washed with water and kappa number and in-
trinsic viscosity determined according to SCAN.

　　　To precipitate lignin dissolved in the extraction
stages the liquors obtained by centrifugation were
acidified with 3 M hydrochloric acid to pH 2 at 20°.
The temperature was increased to 80°C in 20 min and
kept at this level for 40 min. A portion of the lignin
suspension was transferred to a glass filter and the
solution drained off without suction. The lignin was
dissolved in DMF and the solution applied for determi-
nation of the molecular size index by GPC. Drying of
the samples in air at room temperature led to an in-
crease in the observed index which for most samples
was between 50 and 100% [cf. ref.(4)].

　　　The precipitates were isolated from the remaining
suspension by centrifugation, decantation and drying
in air. These samples were used to determine the
sorption of water [4] over saturated NaCl-solution at
22°C. The samples were then dried at 106°C to obtain

the weight of dry precipitate. Nitrogen was determined
in the dried samples[4]. Acid hydrolysis and subse-
quent determination of the monosaccharides showed that
a small amount of saccharides (approximately 1.5%) was
present. The nitrolignin was dissolved upon washing
with water and the precipitates were therefore dried
in the presence of the produced sodium chloride. The
amounts of sodium chloride were about 20% of the
weight of the precipitate. The reported amount of lig-
nin was equal to the weight of the dried precipitate
minus the amounts of NaCl and saccharides. The nitro-
gen contents and the sorption of water were calculated
on the weight of lignin free from NaCl and saccharides.

GPC

The chromatographic columns and general conditions
were the same as described previously[4]. The alkaline
lignin solutions produced during oxygen bleaching
exhibited no sharp peak containing high molecular mass
material excluded effectively from the stationary
phase (Fig. 1). We therefore calculated the $M_w(50)$-
values defined as the relative molecular mass at the
eluent volume at which a perpendicular line divides
the area of the elution curve (absorbance at 280 nm
versus eluent volume) in two equal parts. The rela-
tionship between eluent volume and relative molecular
mass was determined by calibration[4].

UV-absorption

The absorbance of the spent pretreatment liquors
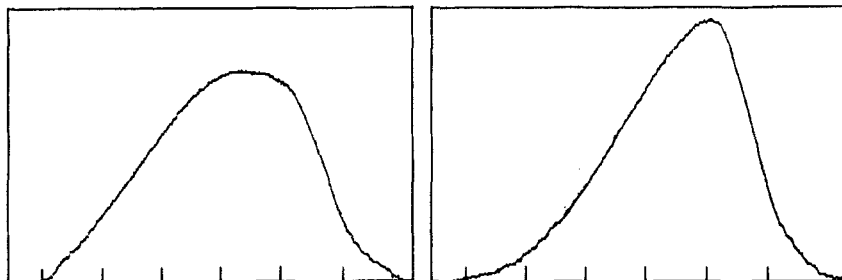was determined at 280 nm and pH 6.6 after dilution

FIGURE 1. Absorbance at 280 nm versus eluent volume
during GPC of lignin in spent liquors from O_2-bleaching.
Left diagram: initial spent liquor. Right diagram:
spent liquor wet-oxidized with O_2 for 70 min at 106°
and initial oxygen pressure of 0.12 MPa (determined at
22°C).

with an aqueous buffer. The reported values A280 were
calculated for the undiluted liquor on the assumption
that the absorbance was directly proportional to the
solute concentration. The $\triangle$-values according to
Aulin-Erdtman[5] were determined from $\triangle A_{305}/A_{280}$,
where $\triangle A_{305}$ is the difference in absorbance at
305 nm at pH 12.0 and at pH 6.6.

RESULTS AND DISCUSSION

Fractionated Dissolution of Lignin

In agreement with previous reports Table 1 shows
that ripening for 3 hours at 90°C (rip. 3) resulted in
much lower kappa numbers after extraction with $NaHCO_3$
solution than those obtained in the pretreatments ter-
minated when this temperature was reached (rip. 0). In

rip. 3 at an initial consistency of 12% and the
largest addition of HNO_3 the kappa number decreased
from 33.2 to 12.0 after the $NaHCO_3$-extraction. This
corresponds to a removal of approximately
$0.15x(33.2-12.0)=3.2$ g lignin from 100 g unbleached
pulp. The amount of precipitated lignin isolated from
the $NaHCO_3$-extract was only 0.25 g. Calculated on
the same basis, the dissolution during this pretreat-
ment, including the water-wash, amounted to 2.9 g.
Evidently, approximately 90% of the dissolved lignin
was removed already during the pretreatment in acid
medium and subsequent washing. Calculated as a per-
centage of the lignin in the unbleached pulp approxi-
mately 60% was dissolved in acid medium. Similar
results were obtained in the other pretreatments with
ripening for 3 hours.

The highest kappa number after the $NaHCO_3$-ex-
traction, 29.8, was obtained by the pretreatment with
the lowest addition of nitric acid with no ripening at
90°C. The removal of lignin calculated from the de-
crease in kappa number was only 0.5 g per 100 g pulp
and the isolated precipitate 0.25 g. Hence, only about
5% of the lignin in the pulp was removed during the
NO_2-treatment in acid medium. The increased amount
of HNO_3 in the diluent led to a detectable decrease
in kappa number without any increase in precipitable
lignin in the $NaHCO_3$-extract. Evidently, conditions
during the pretreatments which led to an improved
generation of NO_2 from HNO_3 gave rise to an in-
creased dissolution of lignin already during the pre-
treatment.

Accordingly, the UV-absorption at 280 nm of the
spent pretreatment liquors was much larger in the ex-

periments with ripening for 3 hours at 90°C than in
the parallel experiments terminated when this tempera-
ture was reached (Table 2).

A comparison was also made between the decrease in
kappa number during the treatments with NaOH and the
amounts of precipitable lignin recovered from the
NaOH-extracts. Appreciable errors can be involved in
both determinations. To decrease their effect we cal-
culated the cumulative changes during the three conse-
cutive extractions reported in Table 1. Under the
mildest conditions the calculated dissolution of
lignin in NaOH amounted to 0.15x(29.8-18.5) = 1.70 g
while the amount recovered in the three NaOH-extracts
was equal to 1.3 g. Calculations carried out for the
other treatments confirmed that the lignin dissolved
in NaOH was recovered in rather high yield by acidifi-
cation.

The nitrogen contents in the precipitated lignin
samples varied within a rather narrow range, from 2.9
to 4.3%. Interestingly, the change in the ripening
time at 90°C from 0 to 3 hours which led to a decrease
in kappa number after $NaHCO_3$ extraction by 52 and
55% respectively and an even larger decrease (71 and
74%, respectively) after the NaOH-treatment at 106°C
exerted a modest effect on the nitrogen contents in
the lignin fractions. Our results indicate that a very
large number of nitro groups in the lignin is not a
prerequisite for an effective delignification during
the alkaline stage following the NO_2-treatment.

After the pretreatments at 12% consistency the
highest nitrogen content was found in the lignin
samples extracted with $NaHCO_3$. The subsequent ex-
traction with NaOH for 5 min at 20°C led to signifi-

Table 2. UV-absorption of spent pretreatment liquor.
Absorbance at 280 nm, A280, multiplied by the volume
(V,dm^3) of spent liquor per 100 g dry untreated
pulp.

	A_{280} x V		A_{305}/A_{280}	
	rip.0	rip.3	rip.0	rip.3
12% consistency, 36.4 mol HNO$_3$	6.7	23.5	0.15	0.03
12% consistency, 50.7 mol HNO$_3$	7.9	23.0	0.14	0.07
27% consistency, 50.7 mol HNO$_3$	-	22.1	-	0.07

cantly lower N-contents in the precipitated lignin.
The consecutive extractions of the pulps at elevated
temperature yielded lignin samples whose nitrogen con-
tents were the same or slightly lower compared to that
isolated by NaOH-extraction at room temperature.

These results do not permit the conclusion that
the nitrolignin recovered in the last extraction
stages contained a lower number of nitrogen containing
groups already after the pretreatment. Instead a loss
of such groups during the alkaline extractions can be
anticipated both in the fiber phase and after dissolu-
tion of the lignin. Separate experiments (Table 3)
show that treatment in 0.1 M NaOH at 70°C of a nitra-
ted kraft lignin gave rise to a large loss of nitrogen
groups already after 10 min. An increased duration had
only a small effect. This indicates that the nitro
groups remaining in the lignin were virtually stable
during the prolonged treatment. Ion chromatography of
the solution after removal of precipitable lignin
showed that the major loss of nitrogen in the lignin
was accounted for as nitrate. The results are at
least in part explained by a saponification of nitric
acid esters[4].

Table 3. Treatment of 6 g nitrated Indulin A[a] in 300
ml 0.1 M NaOH at 70°C

Time min	Recovery[b] % of added	% N	Nitrate mol/100 g	Sorption, H_2O mol/100 g	Size index
0	–	3.16	–	0.638	0.229
10	86.7	2.45	0.033	1.004	0.097
30	89.2	2.41	0.042	1.115	0.081
90	84.9	2.40	0.043	1.072	0.073

a) Prepared by heating Indulin A with acid sodium nitrate
solution[10]. b) Precipitation as described under Experimental.

Likewise the ripening for 3 hours had little
effect on the sorption of water from air at constant
relative humidity by the lignin precipitated from the
alkaline extracts (Table 1). In the pretreatments at
an initial consistency of 12% the lignin from the last
NaOH-extract exhibited a higher water sorption, i.e.
was more hydrophilic than the lignin fractions dissol-
ved under milder extraction conditions. Evidently, the
more severe conditions required for dissolution of
this fraction can hardly be related to a low hydrophi-
licity.

Table 3 shows that hot alkali treatment of nitro-
lignin gives rise to an increased sorption of water.
Hence, the large water sorption of the lignin isolated
from the last fraction, obtained by treatment with 0.1
M NaOH at 106°C, can at least in part be attributed to
reactions during the extraction stage in the fiber
phase and in the dissolved nitrolignin.

Among groups which contribute to the hydrophilic
properties of the lignin are carboxylic groups and
phenolic hydroxyl groups. Carboxylic acid groups are
produced in the lignin during the pretreatment[4,6].

These groups can contribute to an increased dissolu-
tion of lignin in the pulp already during the treat-
ment in acid medium. On the other hand NO_2-treatment
results in a decreased number of phenolic hydroxyl
groups in the lignin[6]. Intensified pretreatment con-
ditions give rise to an increased loss of these
groups. Accordingly, Table 2 shows that the effect on
the absorbance at 305 nm, A_{305}, of an increased pH,
leading to formation of phenolate ions, was strongly
influenced by the intensity of the pretreatment. Hence
the ratio $\Delta A_{305}/A_{280}$ indicated that the ripening
at 90°C resulted in a decreased number of phenolic
hydroxyl groups.

  Our experiments indicate that the dissolution of
lignin during the pretreatment and the consecutive ex-
tractions was impeded neither by an insufficient
hydrophilicity of the lignin nor by a too low degree
of nitration. GPC of the spent pretreatment liquors
(Fig.2) showed that the relative molecular size of the
lignin fragments recorded at 280 nm was very low both
after treatments with and without ripening at 90°C.
These results together with the extensive delignifica-
tion during the ripening indicate that covalent link-
ages in the lignin which survived when the ripening
was omitted were cleaved and gave rise to small frag-
ments when the pretreatment included a ripening period
at 90°C. We conclude that this is a prerequisite for
the observed extensive delignification during the
ripening.

  It is noteworthy that the relative molecular size
decreased drastically during the alkali treatment at
70°C of the nitrated kraft lignin (Table 3). The rela-
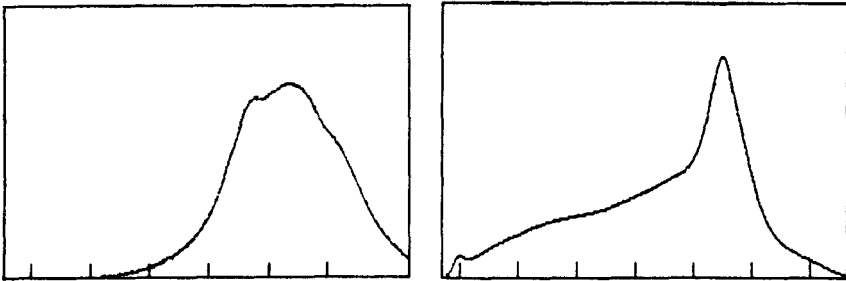tive molecular size distribution was changed markedly

FIGURE 2. Absorbance at 280 nm versus eluent volume
during GPC of pretreatment liquor. Left diagram: no
ripening at 90°C. Right diagram: ripening for 3 hours
at 90°C.

and already after 10 min the size index was much lower
than for the lignin samples isolated from the NO_2-
treated kraft pulp by alkaline extractions. The chro-
matograms in Fig. 3 show that the first peak which
contained lignin of high molecular mass, excluded com-
pletely from the stationary phase, decreased markedly
with increasing duration of the alkali treatment while
the relative amount of lignin of lower molecular mass
increased.

    Alkaline treatments of the nitrolignin remaining
in the pulp after the pretreatment will give rise to
similar fragmentation reactions. These will contribute
to a dissolution of lignin during the consecutive
alkaline extractions (Table 1). A delignification
under given extraction conditions will require that
the fragments are sufficiently small to permit their
dissolution and transfer from the fiber phase into the
external solution. Another requirement is that the
lignin fragments are not linked by stable bonds to
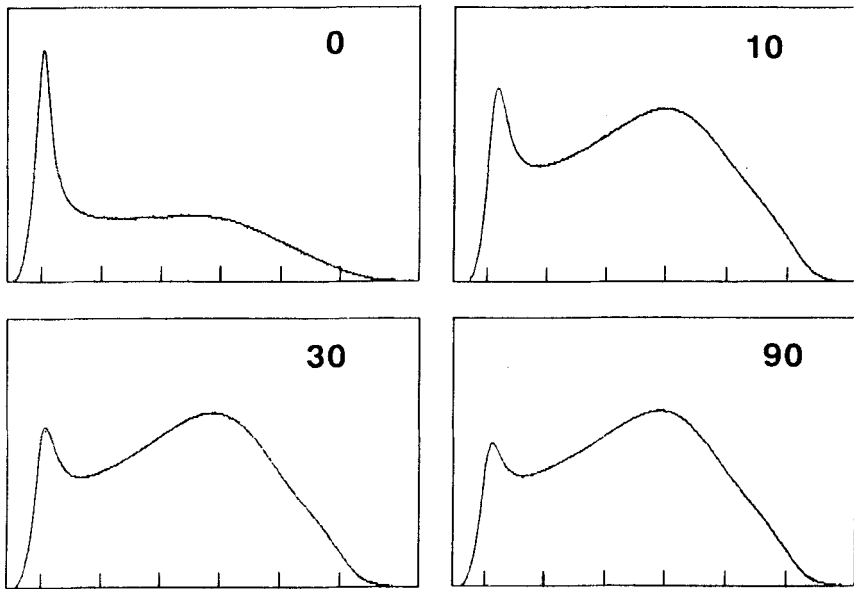insoluble material.

FIGURE 3. Absorbance at 280 nm versus eluent volume during GPC of nitrolignin treated with 0.1 M NaOH for 0 min (no alkali treatment), 10 min, 30 min and 90 min.

The amounts of lignin in the NaHCO$_3$-extracts calculated per 100 g pulp were very similar indepen- dent of the pretreatment conditions. This is remark- able since in the pulps ripened at 90°C for 3 hours about 50-60% of the lignin had been removed already before the NaHCO$_3$-extraction while only 5-15% had been removed from the other pulps. Likewise, the in- fluence of the pretreatment conditions on the dissolu- tion of lignin in the subsequent NaOH-extractions was modest.

Moreover, the conditions exerted only small effects on the relative molecular size of the lignin fractions obtained by the consecutive extractions in

alkaline media. It should be emphasized that nitro-
lignin contains both ester linkages and alkali-labile
linkages of higher alkali stability[4]. As observed by
Lindeberg and Walding β-arylether linkages in lignin
models[7] become alkali-labile by nitration. The
cleavage of both types of linkages results in a de-
crease in relative molecular size[4]. Hence, the $M_w(50)$-
values in Table 1 refer to lignin degraded by both
NO_2-treatment and subsequent alkaline treatments in
the fiber phase. Most likely some attack was obtained
also after the lignin was dissolved in the final stage
referred to in the table. The largest decrease in
relative molecular size can be anticipated for the
fraction extracted with 0.1 M NaOH at 106°C. It is
noteworthy that independent of the pretreatment condi-
tions this fraction exhibited a higher molecular
size than the preceding fractions extracted at 20°
after the same pretreatment. We conclude that an ex-
tensive depolymerization of the lignin was a prerequi-
site for an efficient dissolution of the lignin not
only during the pretreatment but also during subse-
quent alkaline extractions. From a practical point of
view it is important that the greatly improved delig-
nification as a result of the ripening at 90°C was
mainly due to the fragmentation and dissolution of
lignin already during the ripening.

Soaking at Low Temperature

The large conversion of lignin to acid-soluble
products during ripening at 90°C (Table 1) justified a
study of the effect of the duration of the soaking in

water on the kappa number of the pulp. For comparison
soakings were carried out in weakly alkaline solutions.

To simulate a carry-over of black liquor from a
pulp mill to the pretreatment an unbleached laboratory
pulp (kappa number 28.5; viscosity 1198 dm^3/kg) was
impregnated with 22.2 g black liquor per 100 g dry
pulp[8]. After NO_2-treatment according to the stan-
dard procedure ripening was carried out at 8% consis-
tency with an addition of 84.0 mmol HNO_3 in the
diluent, calculated per 100 g dry pulp. In Fig. 4 zero
time refers to pulp centrifuged after the pretreatment.

For the pulp ripened at 90°C for 3 hours (left
diagram) the kappa number after centrifugation was 28%
lower than the initial kappa number. After the pre-
treatment (rip. 0) interrupted when this temperature
was reached, the observed kappa number was somewhat
higher than that of the well-washed untreated pulp.
Evidently, the effects of the adhering liquor and pre-
cipitated lignin were larger than that of the dissolu-
tion of the lignin in the pulp. The results confirmed
that pretreatment conditions which gave rise to a
massive generation of NO_2 resulted in a large con-
version of the lignin to products soluble in aqueous
acid. An improved delignification during the pretreat-
ment corresponded to larger amounts of dissolved
material present in the pulp after the centrifugation.
Accordingly stirring of the centrifuged pulp ripened
for 3 hours in one 500-ml portion of water for 10 min
decreased the kappa number by 18% (calculated as a
percentage of that of the unbleached pulp). For the
other pulp (rip. 0) the decrease was only 3%. When the
pulps were stirred with 2 x 500 ml water during the
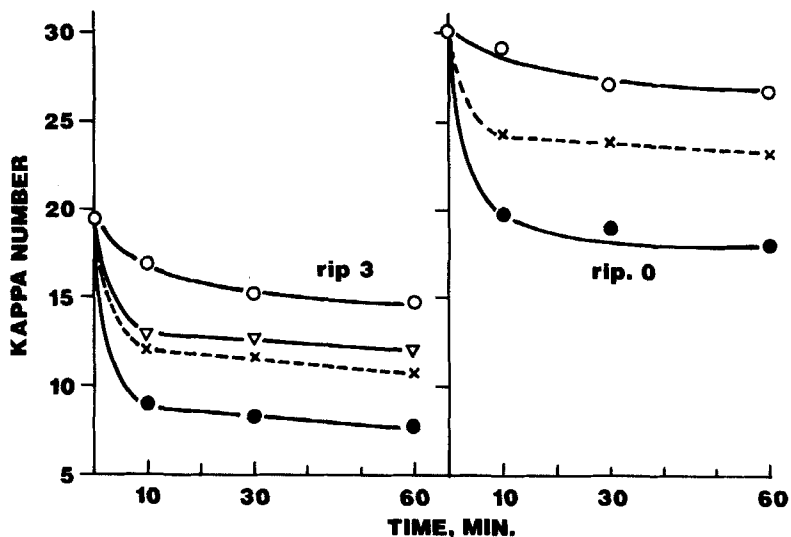period 10-60 min the additional decrease in kappa

FIGURE 4. Kappa number versus time of soaking at 22°C
of pretreated pulp corresponding to 5 g dry, un-
bleached pulp in 500 ml of various solutions replaced
by fresh solutions after 0, 10 and 30 min. ○ Water; ▽
0.1 M NaHCO$_3$, ✕ 0.2 M NaHCO$_3$, ● 0.1 M NaOH.

number was approximately 13 and 9%, respectively. The
slow decrease in kappa number after the first 10-min
soaking in water suggests that chemical lignin reac-
tions occurred in the suspension and had a large in-
fluence on the over-all dissolution rate of remaining
nitrolignin.

Previous investigations have shown that the visco-
sity of pretreated pulps subjected to washing with
water decreases significantly when the samples are
stored at room temperature[9]. This is a serious dis-
advantage with regard to the practical analytical
work. For this reason we have in most previous reports
employed rapid soaking in 0.2 M NaHCO$_3$ at 22°C be-

fore determination of both viscosity and kappa number of the pretreated pulps. The same method was used in the present work. It can be mentioned that the viscosities of the pulps subjected to one 10-min soaking in water and drying at room temperature were 922 and 1173 dm^3/kg, respectively, while the samples soaked in 0.2 M $NaHCO_3$ for 5 min and washed with water before drying, exhibited significantly higher viscosities (967 and 1218 dm^3/kg). The viscosity determinations were carried out 4 days after the pretreatment and soaking.

Fig. 4 shows that soaking in bicarbonate solutions at 22°C resulted in significantly lower kappa numbers than soaking in water. A decrease was obtained when the duration of the soaking was increased from 10 to 60 min. For the pulp ripened for 3 hours lower kappa numbers were obtained by soaking in 0.2 M than in 0.1 M $NaHCO_3$. For the pulp pretreated under milder conditions the difference was insignificant. For clarity the results with 0.1 M solution are not shown.

Soaking with 0.1 M NaOH under otherwise unchanged conditions resulted in a significantly improved delignification compared to that obtained with $NaHCO_3$. Again an increased soaking time resulted in a significant decrease in kappa number. The results suggest that the improved dissolution of the pretreated lignin in alkaline media achieved by an increased duration of the soaking depended on some chemical lignin reactions which occurred at ambient temperature.

Fig. 5 shows that an increased temperature from + 6°C to 32°C led to a markedly improved dissolution of lignin. Somewhat lower kappa numbers were obtained
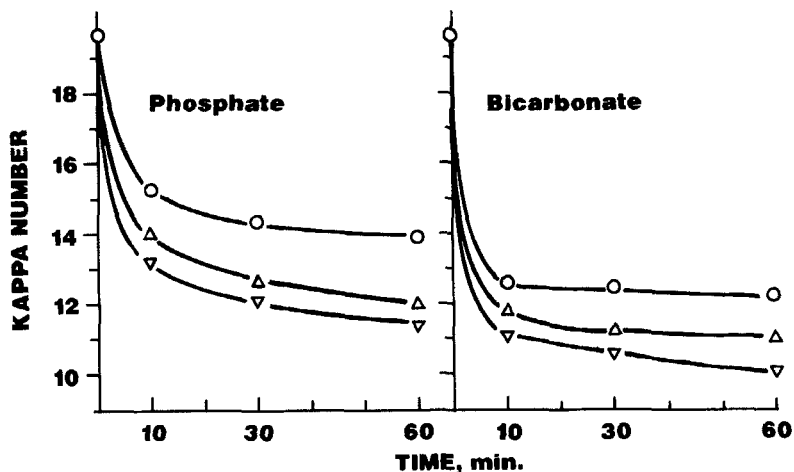
FIGURE 5. Kappa number versus time of soaking of pre-
treated pulp corresponding to 5 g dry, unbleached pulp
in 500 ml phosphate buffer (pH 6.6) or 0.2 M $NaHCO_3$.
Solutions replaced by fresh solutions after 0, 10 and
30 min. ○ 6°C; △ 19°C; ▽ 32°C.

Table 4. Soaking at 22°C and 1% consistency for
varying lengths of time in phosphate buffer or 0.2 M
$NaHCO_3$ of pretreated and subsequently water-washed
pulp[a].

Soaking time hours	Kappa number of soaked pulp		Absorbance[b] of solution, 280 nm	
	Phosphate	$NaHCO_3$	Phosphate	$NaHCO_3$
4	11.4	9.9	0.165	0.245
20	10.5	9.1	0.045	0.051
68	9.8	8.4	0.034	0.033

a) Pretreated pulp referred to in Fig. 5. Centrifuga-
   tion, washing twice with 500 g water per 5 g pulp
   and addition of 500 g of buffer or $NaHCO_3$-solution
   to the centrifuged pulp. Solutions replaced by
   fresh solutions after 4 and 20 h.

b) Calculated per liter solution obtained by soaking
   10 g pulp.

with 0.2 M sodium bicarbonate than with a phosphate
buffer of pH 6.6 (50 ml 0.1 M KH_2PO_4+16.4 ml 0.1 M
NaOH). A substantial dissolution of lignin occurred at
the highest temperature even after repeated soakings.
Determinations of kappa number of the pulps and the
UV-spectrum of the solution (Table 4) showed that the
dissolution of lignin continued when the soaking time
was increased from 20 to 68 hours. Again the bicarbo-
nate solution which exhibited a higher pH (8.6) gave
rise to a more effective delignification than the
phosphate buffer. These results support the conclusion
that the increased dissolution was related to a
cleavage of covalent lignin bonds.

ACKNOWLEDGEMENTS

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