A SUMMARY OF COMPLETED RESEARCH
AND
AN INTERPRETATION OF DATA LEADING TO AREAS
OF FUTURE RESEARCH IN THE USE OF OXYGEN
IN PULPING AND BLEACHING

An outline summarizing the information discussed with the members of Group Project 3092 at the final project meeting February 12, 1974.
A SUMMARY OF COMPLETED RESEARCH

AND

AN INTERPRETATION OF DATA LEADING TO AREAS
OF FUTURE RESEARCH IN THE USE OF OXYGEN
IN PULPING AND BLEACHING

An outline summarizing the information discussed with the members of Group Project 3092 at the final project meeting February 12, 1974.
INTRODUCTION

This outline is not a formal report in the sense of the two previous communications to the cooperators on October 5, 1973 and December 20, 1973. The large amount of data generated by the research in this project could be evaluated in many ways with different emphasis each time. The previous reports constituted a compilation of the facts gleaned and an interpretation of them in terms of the immediate project objectives. Thus it was possible to conclude that our attempts at bleaching kraft pulp were failures since the immediate objectives were not obtained. These same facts could be interpreted to indicate a possible way in which the objectives could be achieved. These trends and possibilities were alluded to in the reports but they were scattered and not encompassed in a single hypothetical concept.

It has been possible to devise a hypothesis concerning the role of oxygen and accessory chemicals in pulping and bleaching technology. These ideas have been supported by experimentation as far as has been possible in the limited time interval between December 20, 1973 and February 12, 1974. The format employed here is based entirely upon the slides and the comments used by the author at the final meeting and the reader will have to imagine himself at a podium and realize that many of the ideas presented here have not been developed as fully or as exhaustively as possible.

Norman S. Thompson
Senior Research Associate
Division of Materials
Engineering & Processes
1. Original proposal
2. Known facts of oxygen reactions
3. Reasons for measuring O2 consumption
4. Schematic diagram of oxygen bleaching equipment
5. The metal content of unbleached southern pine pulps
6. The reaction of K series pulps over 120 minutes
7. The reaction of K series pulps over 15 minutes (KA series)
8. Changes in the pH of the bleaching liquor
9. The relationship of rate of oxygen consumption and pH
10. The reaction of cotton linters with oxygen
11. Summary of kinetic data
12. Yield vs. time
13. Permanganate number vs. time
14. Viscosity vs. time
15. Zero-span vs. time
16. GE brightness vs. time
17. Summary of changes with time of bleaching
18. Permanganate number vs. viscosity
19. Factors influencing the initial behavior of pulps during oxygen bleaching
20. Zero-span vs. strength of alkali treatment
21. Zero-span vs. number of alkaline treatments
22. GE brightness vs. permanganate number
23. Yield vs. permanganate number
24. GE brightness vs. zero-span
25. GE brightness vs. viscosity
26. Types of reactions which occur during oxygen reactions
27. Changes in the physical nature of lignin
28. Condensation reactions during alkali pulping
29. Requirements for removal of lignin by oxygen
30. Sources of peroxide
31. Techniques for minimizing the effect of peroxide
32. Multistage - zero-span vs. time
33. Multistage - viscosity vs. time
34. Multistage - permanganate number vs. time
35. Multistage - brightness vs. time
36. Modification of lignin - outline
37. Comparison of K series treatments
38. A comparison of the effects of different bleaching agents
39. Brightness vs. zero-span
40. Brightness vs. zero-span - multistage
41. A comparison of pulp quality produced by different bleaching processes
42. The degradation of cellulose in oxygen and alkali
43. A schematic representation of pine lignin
44. Hypothetical changes in pulp quality caused by oxygen bleaching
45. Functional groups in typical lignin derivatives
1. The Research was initiated on July 27, 1972.

2. Its purpose was to gain a better understanding of the potential of oxygen as a bleaching agent in order that the use of more esoteric subsequent bleaching agents such as peroxide might be minimized.

3. The objectives are shown in their broadest details in slide 1:
   a) primary interest was in bleaching after the oxygen stage.
   b) no interest in the earlier stage.
   c) the parameters of significance to oxygen stage itself were thought to be important as they could affect the subsequent peroxide stages.

4. As it turned out, the whole sequence of pulping and bleaching involving oxygen is a carefully integrated sequence, more so than any other pulping and bleaching sequence.

5. Considerable research had already been carried out before we began our work. A summary of some of the available facts is shown on the next slide.

\[
\begin{array}{ccc}
\text{Oriamion} & \text{unbleached} & \text{CHED} \\
\text{Perm. No} & 20.5 & \text{Brightness} \\
\text{Z-
\text{Span}} & 13.3 & 86.5 \\
\text{Z-
\text{Span}} & 13.7 & \\
\end{array}
\]
WOOD

↓

PULPING AND FIBERIZING STAGE

↓

OXYGEN BLEACHING

↓

FINAL BLEACHING STAGES

{ AREA OF INTEREST OF PROJECT 3092
HALOGEN-FREE BLEACHING PROCESSES WOULD BE POSSIBLE IF TERMINAL PEROXIDE STAGES COMPATIBLE WITH EARLIER OXYGEN STAGE

PULP
1. Many of these facts may be classified according to their relationship to:
   delignification
   physical property
   versatility

2. The transition between bulk and residual delignification at about pH 10 suggests the importance of phenolate ion in the system although other mechanisms are possible.

3. Not listed in the slide is a classification called "miscellaneous" -- Here we would put:
   a) significance of peroxide to carbohydrate degradation.
   b) the seemingly low viscosity of oxygen bleached pulps without a corresponding yield loss.
   c) the lack of a simple relationship between pulp viscosity and many physical properties more generally, the surprising physical differences caused by the oxygen stage.

4. One major problem was to determine what properties of the bleach should be measured. Continuous monitoring would be ideal, but many properties obviously cannot be handled that way.

5. Kinetic significance was desired, even at the expense - at this stage of the investigation - of exact technological methodology.

6. The use of oxygen consumption data was therefore considered and the reasons for relying heavily on this index of reaction is given in the next slide.
KNOWN FACTS

1. TWO REACTIONS OCCUR, BULK DELIGNIFICATION AND RESIDUAL DELIGNIFICATION.
2. TRANSITION BETWEEN THEM OCCURS AT ABOUT pH 10.
3. BOTH ARE PSEUDO FIRST ORDER WITH RESPECT TO LIGNIN.
4. INITIAL REACTION DEPENDS ON [NaOH], [O₂], [L], [M], T, CONSISTENCY.

PHYSICAL PROPERTIES

1. RAPID INITIAL LOSS OF PROPERTY WITH [NaOH], T, [M].
2. MAGNESIUM SALTS PARTLY OVERCOME EFFECTS OF [M].
3. ACID WASH NOT QUITE AS EFFECTIVE.
4. STRENGTH INVERSELY RELATED TO LIGNIN CONTENT BEFORE O₂ STAGE.
5. O₂ DELIGNIFIED SODA PULP WEAKER THAN KRAFT.
6. SOME STRENGTH REGAIN ON SUBSEQUENT BLEACHING.
7. DEGRADATION RELATED TO PRESENCE OF PEROXIDE IN O₂ STAGE.

VERSATILITY

1. CAN BE USED BEFORE, AFTER OR INSTEAD OF CHLORINATION STAGE.
2. CHLORINE DIOXIDE IS EFFECTIVE SUBSEQUENT BLEACH.
1. The reasons on the slide are apparent and are:

2. The apparatus we used for this purpose was described in detail in the previous reports --

3. and is shown on the next slide:

4. Error on slide - 3A should read: where oxygen reaction can be unambiguous.
REASONS FOR MEASURING OXYGEN CONSUMPTION

1. EXPERIMENTAL PROCEDURES WELL ESTABLISHED.

2. CONTINUOUS MEASUREMENTS OF PRESSURE, TEMPERATURE.

3. CAN GET INITIAL REACTION RATES
   A. WHERE OXYGEN REACTION CAN BE SIGNIFICANT.
   B. WHERE MOST OF THE REACTION SEEMS TO OCCUR.

4. SENSITIVE METHOD FOR DETERMINING CHANGES IN THE REACTIVITY OF PULPS.
1. The bleaching equipment can be inspected in the laboratory where Hugh Corbett will describe the exact manipulations which are followed to give reproducible results.

2. This procedure must be adhered to rigidly because many opportunities for inconsistencies of operation are possible. These can yield different results on bleaching.

3. One of the important discoveries of this research (we feel) was the result of a variation in our experimental procedure. Without a knowledge of this change, our results would have been nonsensical.

4. The metal contents of our pulps were carefully determined and are shown in the next slide.
Ethylene Glycol Bath

Pressure Recorder
Temperature Recorder

Steam Inlet

Oxygen Inlet

N₂ Inlet

Reference Chamber

Fluffed Pulp

Teflon-Coated Thermocouple

Teflon Steam Purge Line

Teflon Line

2 Liter S.S. Parr Bomb

Heater
1. The metal analyses were determined by flame spectroscopy by our analytical group.

2. The most important metal analyses were those of the transition metal ions - Cu, Fe, Ti, V, while Cr, and Mn were present in only trace amounts.

3. The table gives an idea of how inefficient our washing procedures were: The original pulp provided by Champion picked up copper as a result of our washing. This was found to be derived from a single small brass component in an otherwise all stainless system to give the D and M-series of pulps. When this component was replaced by stainless, the K-series resulted which had much less contaminant.

4. In addition, other chemical analyses were carried out on the starting material.
   - cellulose
   - viscosity, dl/g
   - brightness
   - brightness reversion
   - carbonyl
   - zero-span

5. Typical oxygen consumption curves, using the K-series of pulps, is shown in the next slide.
THE METAL CONTENT OF UNBLEACHED SOUTHERN PINE PULPS

<table>
<thead>
<tr>
<th></th>
<th>Original Pulp</th>
<th>K-Series</th>
<th>M-Series</th>
<th>D-Series</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total ash</td>
<td>0.95</td>
<td>0.60</td>
<td>--</td>
<td>0.55</td>
</tr>
<tr>
<td>Ba, p.p.m.</td>
<td>18</td>
<td>2.2</td>
<td>2.2</td>
<td>1.7</td>
</tr>
<tr>
<td>Ca</td>
<td>2400</td>
<td>1700</td>
<td>1446</td>
<td>1500</td>
</tr>
<tr>
<td>Mg</td>
<td>660</td>
<td>670</td>
<td>464</td>
<td>440</td>
</tr>
<tr>
<td>Sr</td>
<td>--</td>
<td>--</td>
<td>12</td>
<td>--</td>
</tr>
<tr>
<td>Na</td>
<td>1000</td>
<td>68</td>
<td>115</td>
<td>85</td>
</tr>
<tr>
<td>B</td>
<td>0.8</td>
<td>--</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Al</td>
<td>130</td>
<td>58</td>
<td>20</td>
<td>64</td>
</tr>
<tr>
<td>Si</td>
<td>560</td>
<td>220</td>
<td>293</td>
<td>300</td>
</tr>
<tr>
<td>Pb</td>
<td>1.3</td>
<td>1.2</td>
<td>8.8</td>
<td>6.0</td>
</tr>
<tr>
<td>Cu</td>
<td>1.1</td>
<td>3.6</td>
<td>102</td>
<td>200</td>
</tr>
<tr>
<td>Fe</td>
<td>48</td>
<td>70</td>
<td>19</td>
<td>46</td>
</tr>
<tr>
<td>Ti</td>
<td>20</td>
<td>7.7</td>
<td>4.4</td>
<td>5.4</td>
</tr>
<tr>
<td>V</td>
<td>1.7</td>
<td>0.6</td>
<td>1.8</td>
<td>1.0</td>
</tr>
</tbody>
</table>
1. The observations include:
   a) continuous measurements of pressure by the Pace unit.
   b) recording gauge pressure every 5 minutes.
   c) continuous monitoring of temperatures - especially those inside the reactor, the bath, and the reference cell.

2. Raw data include the average of several bleaches at five minute intervals of both gauge and Pace measurements of oxygen consumption.

3. Calculations include:
   a) conversion of psig to grams O₂/100 g pulp.
   b) corrections for heat loss of apparatus.
   c) correction for temperature within reactor - which varies with pulp, alkalinity, and oxygen pressure.

<table>
<thead>
<tr>
<th>Series</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>D-series</td>
<td>121.5°C</td>
</tr>
<tr>
<td>M-series</td>
<td>117.5°C</td>
</tr>
<tr>
<td>K-series</td>
<td>108.5°C</td>
</tr>
</tbody>
</table>

4. The plots have kinetic significance up to 40 minutes reaction.

5. After that time our equivalent to the residual delignification reported by Chang and co-workers seems to occur.

6. Early stages were initially of interest because:
   a) the rapidity with which reaction seems to go.
   b) hopes of finding a difference in lignin and cellulose reactivities.

7. Modification of procedure was therefore required:
   a) heated oxygen before addition to reactor.
   b) changes in the air purging procedure.
   c) inadvertent lengthening of warming period of pulp from 15 to 30 minutes.

8. Results shown on the next slide:
- KB 6.6% alkali on pulp
- KD 3.3% alkali on pulp
- KP 1.7% alkali on pulp

![Graph showing reaction time vs. O2 consumption over pulp.](image-url)
1. No evidence of an induction period was evident in oxygen consumption. This differs from the behavior of pure cellulose under analogous conditions.

2. Use of initial reaction rates to indicate the behavior of oxygen during the bleach before the onset of side reactions is therefore justified.

3. Kinetic dependence on [NaOH] same as in previous experiment.

4. Assume all other relationships determined for the non-isothermal procedure are equally valid and initial reaction rates have significance.

5. The pH of the bleaches was measured with time. Since we did not have continuous monitoring of pH, measurements could only be taken after samples were removed for pulp analysis.

6. Data shown on next slide are for K-series.
The Reaction of Unbleached Kraft Pulp (Series K) with 130 psig Oxygen at 100°C and Different Alkali-to-Pulp Ratios Using Improved Kinetic Procedure
1. The rapid initial loss of pH occurs as a result of the warming or heating up period and can be attributed to:
   a) formation of phenolate ion.
   b) peeling reactions consuming some caustic.
   c) buffering action of organic acids/salts in the pulp.

2. Not shown are data for 15 minutes reaction at 3.3 and 1.7% alkali on pulp.


4. For K-series, inflection in $O_2$ consumption curve occurs at 40 minutes or at about a pH of 11. This may correspond to the pH at which the phenolate ion concentration becomes negligible and is a slightly higher value than that found by Chang et al at North Carolina State.

5. No rapid loss of pH occurs after the heat-up period.

6. Plots of the rate of consumption of $O_2$ vs. pH or [NaOH] should be straight lines if a pseudo first order dependence is occurring.

7. This plot is shown on the next slide.
CHANGES IN THE pH OF THE BLEACHING LIQUOR DURING
THE BLEACHING OF KRAFT PULP

<table>
<thead>
<tr>
<th>Time of Reaction, min.</th>
<th>Initial Percent of Alkali on Pulp</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (before heating to temp.), pH</td>
<td>~14</td>
</tr>
<tr>
<td>0 (after heating to temp.), pH</td>
<td>12.1</td>
</tr>
<tr>
<td>5, pH</td>
<td>11.9</td>
</tr>
<tr>
<td>15, pH</td>
<td>11.7</td>
</tr>
<tr>
<td>30, pH</td>
<td>11.2</td>
</tr>
<tr>
<td>60, pH</td>
<td>10.7</td>
</tr>
<tr>
<td>120, pH</td>
<td>9.9</td>
</tr>
</tbody>
</table>

*Reacted with 130 p.s.i. oxygen at 100°C. and 25% consistency.*
1. The K-series pulp reacts with oxygen in a manner dependent upon the pH of the system at that moment and does not depend upon the initial alkali charge nor upon the time of reaction.

2. This is shown by the smooth (almost linear?) curve at the top of the figure.

3. The D-series does not exhibit this relationship - suggesting the mechanism is different after the initial reactions.

4. This is in agreement with Sinkey's studies of the behavior of magnesium ion and transition metal ion on model substances in oxygen and alkali.

5. The observation also agrees with the effect of transition metal ion on the consumption of oxygen by the D-series of pulps during the initial stages of the reaction.

6. Formal kinetic analysis of the oxygen consumption data observed here is in complete agreement with this qualitative examination.

7. These relationships will be discussed after a brief look at the effect of no lignin on oxygen consumption in the next slide.
K-Series Initial Reaction of D-Series

Reactions of D-Series

Rate of Oxygen Consumption, g O₂/100 g pulp/min

The Relationship Between pH and Rate of Oxygen Consumption During the Oxygen Bleaching Stage
1. The study of the behavior of cotton during the conditions of oxygen bleaching has been studied by many investigators. Most have studied the properties of the cotton sample.

2. These studies show it is degraded at a slower rate than wood pulp and this rate depends upon contaminants such as lignin, hemicellulose, metal ions.

3. The consumption of oxygen under these conditions of reaction have not been studied, although it has been studied under milder alkali-aging conditions.

4. The results of our study of the "aging" of cellulose in alkali and oxygen at 100° C are shown on this slide:

5. Note
   a) small consumption of oxygen.
   b) induction effects.
   c) obviously complex kinetics.

6. We must conclude lignin has pronounced effect - as others have concluded by adding lignin to linters.

7. We also have added lignin to linters - the effect is identical to behavior of lignified pulp.

8. We have oxidized cellulose with chlorite - the carbonyl groups have no effect on properties although a slightly larger consumption of oxygen occurs.

9. The behavior of pulps which contain lignin during oxygen bleaching is summarized on the next slide.
The Reaction of Cotton Linters with Oxygen (130 psig) at 100°C at Different Alkalinites
1. The data and information confirm the importance of lignin as far as oxygen consumption is concerned.

2. The results may be summarized in kinetic terms as shown in items number 4 and 5.

3. This behavior is probably characteristic of one particular lignin.

4. Support comes from the observation that chlorite oxidized pulps do not exhibit this simple kinetic behavior.

5. This information does not tell much until it is compared with the kinetic behavior of other chemical and physical transformations associated with the consumption of oxygen by the pulp.

6. The next several slides show the variation in some of the chemical and physical properties of pulps which were isolated at different time intervals and analysed.
SUMMARY OF KINETIC DATA

1. RAPID INITIAL RATE OF OXYGEN CONSUMPTION DUE LIGNIN IN PULP – NO OBVIOUS INDUCTION PERIODS.

2. MAGNITUDE AND RATE OF OXYGEN CONSUMPTION VARIES AS AMOUNT AND TYPE OF LIGNIN IN PULP.

3. TRANSITION METAL ION INCREASES INITIAL RATES OF CONSUMPTION OF OXYGEN.

4. CONSUMPTION OF OXYGEN INITIALLY:

\[ \frac{dO_2}{dt} = a [NaOH]^1 [O_2]^1 [M]^1 \]

5. AT LATER STAGES OF THE BLEACH.

\[ \frac{dO_2}{dt} = a [NaOH]^1 [O_2]^0 [M]^0 \]
1. The next several slides show the variation of different pulp properties with time of bleaching of:
   
   a) D-series, 6.6% alkali on pulp. 
   b) D-series, 1.7% alkali on pulp. 
   c) K-series, 6.6% alkali on pulp. 

2. These limited sequences were chosen from many and demonstrate the type of results we obtained. 

3. The tests included:
   
   a) yield 
   b) permanganate number 
   c) viscosity 
   d) zero-span 
   e) GE brightness 

4. None exhibit simple kinetic relationships with the possible exception of brightness which can be manipulated by devious means to yield an apparent first order dependence. 

5. All but brightness drop very rapidly to values dependent upon the alkalinity and the transition metal ion content of the pulps. 

6. There seems to be no relationship between this drop and the transition from bulk to residual delignification or to the increase in liquor pH above 11.
The Change in Yield with Time During Oxygen Bleaching

- D-Series, 6.6% Alkali on Pulp
- D-Series, 1.7% Alkali on Pulp
- K-Series, 6.6% Alkali on Pulp
The Change in Permanganate Number with Time of Oxygen Bleaching
The Change in Viscosity with Time of Bleaching

- D-Series, 6.6% Alkali on Pulp
- D-Series, 1.7% Alkali on Pulp
- K-Series, 6.6% Alkali on Pulp
The Variation in Zero-Span Breaking Length with Time of Oxygen Bleaching
SLIDE 16

1. The behavior of brightness during bleaching in these experiments recalls the behavior reported by R. Marton (ESPRA) - bleaching continues after delignification has ceased even if the pH approaches neutrality.

2. This suggests that delignification and chromophore removal are not necessarily the same reactions.

3. Transition metal ion affects bleaching in a different manner than in its absence, i.e., it does not simply accelerate bleaching but seems to catalyze different chemical reactions.

4. The comparison of this results with those of the kinetic studies are summarized on the next slide.
The Change in Pulp Brightness with Time of Bleaching

- D-Series, 6.6% Alkali on Pulp
- D-Series, 1.7% Alkali on Pulp
- K-Series, 6.6% Alkali on Pulp
1. The slide is not complete; it should point out that the change from fast oxygen consumption to slow oxygen consumption at about pH 11 (40 minutes) does not coincide with the transition of the rapid degradation of property of the pulp to the slow rate of degradation. This change occurs in less than 15 minutes.

2. A similar behavior is exhibited at other alkalinity levels by other pulps and by other paper making properties such as tensile burst and tear as well.

3. The degradative reactions chiefly occur during the first few minutes of the bleach. All measures to prevent degradative action must therefore be available instantly and not be dependent upon diffusion, equilibria, and other conveniences.

4. The comparison of the relative rates of lignin removal compared to polysaccharide degradation gives a relationship which is relatively constant for the bleaching behavior of a given pulp. Such plots have often been used by Norrstrom and others to evaluate the effectiveness of an oxygen bleaching experiment.

5. The behavior of the M, K, and D-series of pulps, as well as the behavior of a commercially bleached pulp are compared by this method in the next slide.
SUMMARY

1. DATA CONFIRM KNOWN RAPID DECREASE OF PROPERTY WITH TIME.

2. INITIAL CHANGES ARE GREATEST.

3. NO SIMPLE KINETIC DESCRIPTION.

4. DATA CONFIRMS EFFECT OF ALKALINITY, PRESSURE, AND TRANSITION METAL IONS ALREADY KNOWN.

5. NO SIMPLE SOLUTION TO OPTIMIZATION OF OXYGEN PROCESSES.
1. Compared here are the relative bleaching efficiencies which occur during
the oxygen bleaching of the D, M, and K-series of pulps together with the
estimated performance of the same pulp during commercial bleaching.

2. Obviously most oxygen bleached pulps have been degraded to a greater extent
than have the commercially bleached pulp.

3. Only a few of the oxygen bleached pulps could be subsequently bleached to
have properties comparable to the commercial bleach. [SHOW]

4. And then only at great expense because of the high lignin contents.

5. The presence of transition metal ion shifts the delignification-degradation
relationship away from the ideal behavior.

6. For oxygen bleaching to succeed, the relationships plotted here must
proceed to the right of the hypothetical commercial bleaching relationship
shown in the diagram.

7. The oxygen bleaching process used by Chesapeake Corporation does not
attempt to do this type of delignification. The initial two stage D/C1
employed by them before the oxygen stage reduces the permanganate from
12-14 to about 3-5. Most of the work of delignification has already been
done by the chlorination stage. The final properties are here. [SHOW]

8. Instead it would be desirable to change the lignin so that it would react
readily with oxygen and not cause appreciable carbohydrate degradation.
[SHOW] In this manner, subsequent treatment would yield a pulp similar to
the Champion bleached pulp.

9. As mentioned previously, it was desired to adapt the reactor for a more
ideal type of "isothermal" operation - not only to investigate the initial
stages of the bleach but also to give a more defined and controlled short
term bleaching stage for use in multistage oxygen bleaching.

10. The lengthening of a warm-up period caused great changes in property
behavior and required a review of the conclusions reached earlier.

11. The major parameters we will be concerned with are shown in slide 19.
Effect of Oxygen Pressure on Pulp Viscosity

A Comparison of the Permanganate Number and Pulp Viscosity of Southern Pine Kraft Pulps Bleached with Oxygen
1. Three types of southern pine kraft pulp were employed which differ in their content of transition metal ion.

2. The K-series pulps were reacted with oxygen provided to the reactor at two temperatures; 20° and 100° C respectively.

3. The pulps reacted at 20° C were pretreated for 15 minutes, while the pulps reacted at 100° C were pretreated for 30 minutes.

4. After the steam purging stages, the zero-span tensile of the unbleached pulp was found to be reduced significantly.

5. As shown on the next slide, the decrease depended upon the alkalinity applied.
### TABLE III

FACTORS INFLUENCING THE INITIAL BEHAVIOR OF PULPS DURING OXYGEN BLEACHING

<table>
<thead>
<tr>
<th>Bleach Series</th>
<th>Transition Metal Ion Content, ppm</th>
<th>Temperature of Added Oxygen, °C</th>
<th>Time of Steam Purging, min</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>82</td>
<td>20</td>
<td>15</td>
</tr>
<tr>
<td>KA</td>
<td>82</td>
<td>100</td>
<td>30</td>
</tr>
<tr>
<td>M</td>
<td>127</td>
<td>20</td>
<td>15</td>
</tr>
<tr>
<td>D</td>
<td>252</td>
<td>20</td>
<td>15</td>
</tr>
</tbody>
</table>
1. This behavior occurs for sulfite pulps as well as for kraft pulps.

2. It occurs in mildly acidic solutions and so may be dependent upon many factors besides alkalinity.

3. The pulp is not stabilized by such treatment and the zero-span may be further reduced by additional treatments as shown on the next slide.
The Change in Zero-Span Tensile with the Strength of Alkali Used in the Oxygen Bleaching Stage
1. In this slide, two treatments with 3.3% alkali are just as harmful or even more so than a single 6.6% alkali to pulp treatment.

2. Number of treatments is therefore very critical as well as alkalinity.

3. Of all commercial bleaching processes, oxygen bleaching employs the greatest temperatures for the longest times and therefore this change in physical strength we have observed here must be a significant factor to consider in commercial oxygen bleaching installations.

4. This is demonstrated in the next slide which shows the longer pretreatment time causes changes in the relationships between delignification and chromophore removal. Lignin behavior as well as zero-span strength are affected by the treatments!
The Effect of the Number of Alkaline Pretreatments on Zero-Span Breaking Length of Kraft Pulp

- ○ 3.3% Alkali on Pulp (30 min Treatments)
- □ 6.6% Alkali on Pulp (30 min Treatments)
1. Lignin behavior as well as fiber strength are affected by the duration of the pretreatment since curves for K-series and KA-series do not coincide in this graph.

2. This change in lignin reactivity shows up when the plots of yield after bleaching vs. bleached permanganate are plotted.
The Change in GE Brightness with Permanganate Number

- 6.6% Alkali, 30 min Pretrmt.
- 3.3% Alkali, 30 min Pretrmt.
- 2-Stage, 30 min Pretrmt.
- K-Series, 15 min Pretrmt.
- M-Series, 15 min Pretrmt.
1. We feel the less satisfactory behavior of the D-series compared to the K-series in this plot is due to the excessive carbohydrate degradation catalyzed by transition metal ion.

2. On the other hand, the less satisfactory behavior of the KA-series has been attributed to delayed lignin removal rather than accelerated carbohydrate removal for reasons which will be discussed later.

3. Great changes are seen when the zero-span breaking length is compared with other properties such as lignin removal or pulp degradation.
THE RELATIONSHIP BETWEEN YIELD AND DELIGNIFICATION AFTER OXYGEN BLEACHING
1. The original zero-span tensile strength of the pulp has been diminished by pretreatment before oxygen bleaching. [SHOW]

2. After bleaching commences, the strength rapidly changes to a level at which a slower change occurs. [SHOW]

3. Transition metal ion catalyzes a greater change or loss of strength. This is probably due to the greater carbohydrate degradation. [SHOW]

4. Longer pretreatment results in similar, though not as marked behavior. This could be due either to changed carbohydrate degradation (affecting zero-span strength) or to a changed behavior of the zero-span strength independent of pulp viscosity.

5. This question can be resolved on the next slide (25).
1. The greater carbohydrate degradation to lignin or chromophore removal for M and D-series pulps is readily apparent in this slide.

2. There is no difference between lignin removal and carbohydrate degradation for the KA and K-series of pulps as both sets of points seem to fall on one continuous curve. This is an apparent anomaly in light of previous results but is not difficult to rationalize if one assumes the degradation products from lignin removal catalyze carbohydrate degradation.

3. It seems likely that there is some kind of change in the strength of the pulps induced by the treatment of the pulp before oxygen bleaching as well as the change in lignin reactivity.

4. This behavior brings to mind immediately the other reports of unusual behavior of the physical properties of pulps after oxygen bleaching and raises the possibility we may have chanced onto the origin of some of them.

5. The next slide summarized our results to this point.
The Change in XE Brightness and Pulp Viscosity with Oxygen Bleaching Conditions
1. At last we are beginning to get an idea of the degradations which occur during oxygen bleaching.

2. If we examine each of the major classifications of degradation in turn, perhaps we can find ways to overcome them.

3. Polysaccharide degradations are widely recognized as a source of difficulty and we feel they are principally related to lignin degradation. For now I would like to skip over them and reconsider them later.

4. The changes in physical properties we have just discussed are also lignin induced changes and will be discussed on the next few slides.

5. But first let us look at the sources of our troubles. The remaining degradations include the delignification reactions:
   a) oxidation of lignin and the resulting harmful by-products this causes.
   b) cleavage of phenolic nuclei and the production of solubilizing groups.
   c) polymerization reactions are probably very significant in oxygen bleaching.
   d) the solubilization of lignin may or may not be related to item b depending upon the significance of c.

6. The bleaching reactions are closely (but not entirely) dependent upon the delignification reactions. Bleaching is possible without lignin removal.

7. The recognition of the importance of peroxides in oxygen bleaching by various contemporary scientists is a major breakthrough. All aspects of peroxide chemistry that pertain to high temperature alkaline reactions is of significance to us. Unfortunately not much exists in the literature on this aspect of peroxide chemistry although the more stable and ideal reactions that occur in neutral and acid solutions have been exhaustively dealt with.

8. An examination of each of these factors tells us exactly what to do to develop oxygen bleaching or even oxygen pulping processes.

9. To begin with, I would like to support my contention that the loss of zero-span strength by fibers on heating in alkali is due to lignin-derived transformations.

10. Next slide.
TYPES OF DEGRADATIONS WHICH OCCUR DURING THE REACTION OF PULP WITH OXYGEN

1. POLYSACCHARIDE DEGRADATION — OXIDATION OF PYRANOSE RINGS
   CLEAVAGE OF GLYOSIDIC BONDS
   YIELD LOSS

2. LIGNIN-INDUCED CHANGES IN PHYSICAL PROPERTIES.

3. DELIGNIFICATION REACTIONS — OXIDATION OF LIGNIN
   CLEAVAGE OF PHENOLIC NUCLEI
   SOLUBILIZATION OF LIGNIN

4. BLEACHING REACTIONS —
   DESTRUCTION OF CHROMOPHORES
   REMOVAL OF METAL CONTAMINANTS

5. GENERATION OF PEROXIDES.
1. Lignin may affect the properties of pulps in two ways:
   a) by its physical behavior, hardens, softens, expands, spreads, etc.
   b) by its chemical behavior, becomes less susceptible to removal, more or less colored, etc.

   and probably does so by a combination of these.

2. According to David Goring* (PPRIC), lignin is plasticized when heated:
   a) plasticization temperature is lowered by water.
   b) plasticization temperature is lowered as the lignin is degraded. Thus spruce dioxane lignin has a lower PT than periodate lignin, and different kraft lignins of differing molecular weight have PT related to MW.
   c) lignins with a wide spread of molecular weights show a broad diffuse plasticization temperature.

3. This slide illustrates the behavior of a dioxane lignin.

4. Once plasticized, the lignin can bond sheets of paper.

5. The significance of this on paper properties as a result of groundwood preparation was considered by Goring.

6. The flow of lignin suggested by the slide can actually be seen in electron micrographs of lumen surfaces before and after heating to $120^\circ$ C.

7. Lignin can also undergo a variety of condensation reactions which will affect its subsequent chemical behavior. The next slide shows the type of condensation reaction to be expected.